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HEAT SENSITIVE REPRODUCTION SHEET METHOD OF
MAKING AND METHOD OF USING
Filed March 4, 1959

2,999,035

HEAT SENSITIVE COATING
OF FINE PARTICLES OF A
HEAVY METAL SALT OF
DITHIOCARBAMIC ACID IN
A BINDER.

FIG. 1

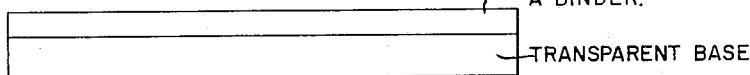


FIG. 2
REFLEX
PRINTING

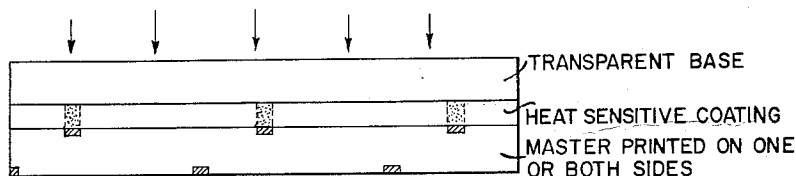


FIG. 3
CONTACT
PRINTING

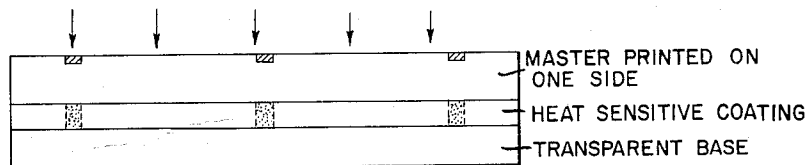


FIG. 4
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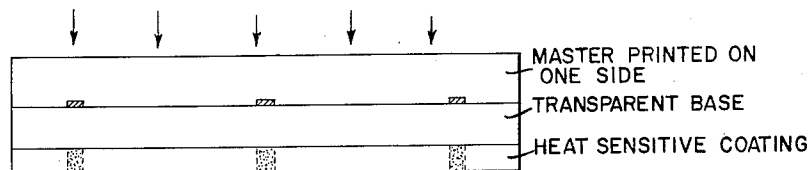


FIG. 5
CONTACT
PRINTING

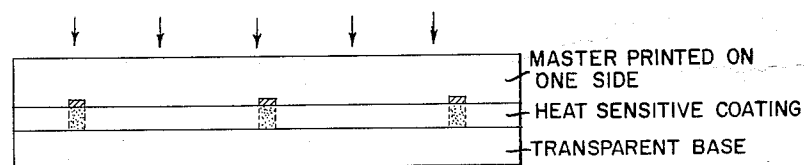


FIG. 6
CONTACT
PRINTING

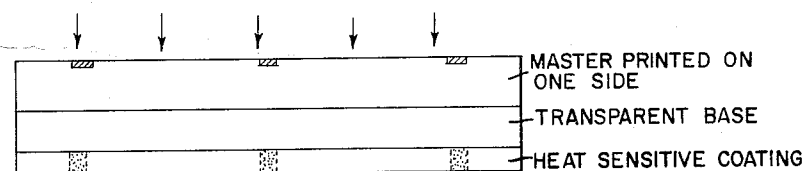
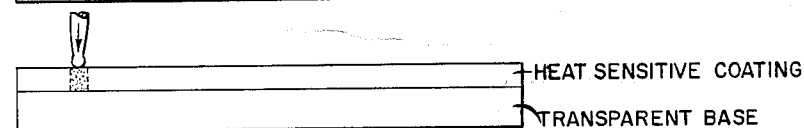


FIG. 7
HEATED
STYLUS
OR STAMP



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HEAT SENSITIVE REPRODUCTION SHEET, METHOD OF MAKING AND METHOD OF USING

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This invention relates to heat sensitive materials for the reproduction of documents and the like. More particularly, the invention relates to heat sensitive materials of the type coated with a substance which upon exposure to sufficient heat undergoes a chemical change which involves a color change.

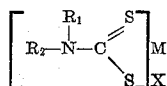
Heat sensitive materials for reproduction purposes are in use which are coated with a heat sensitive layer including two reactants which at normal room temperatures do not come into reactive relationship with each other, but upon the application of heat, at least one of the reactants and/or the binder fuses so that the reactants do react forming a colored reaction product.

The improved heat sensitive reproduction coatings of the present invention contain as the heat sensitive substance heavy metal salts of aminodithioformic acids (dithiocarbamic acids) in which the nitrogen atom is secondary or tertiary because of the presence of substituent univalent organic radicals which may form a ring with each other which may be substituted by an organic radical, such as lower alkyl, e.g. methyl, ethyl, propyl, or butyl radicals.

Heavy metal salts suitable for the heat sensitive substance according to the invention are, for example, salts of lead, mercury, tin, bismuth, cadmium, silver, thallium and bivalent iron. The compounds are colorless to pale yellow. Other heavy metal salts such as those of univalent copper, cobalt, and nickel are more deeply colored and therefore of less practical importance for application in the present invention.

The term "heavy metal" is used herein to relate to a metal (other than an alkali metal or alkaline earth metal of groups Ia and IIa, respectively) or metalloid element which forms adequately stable salts with an acid radical, and particularly with the N-substituted dithiocarbamic acid radicals, and belongs to the fourth or higher period of the periodic table (atomic number=19 upwards). Preferably, the heavy metals of the b-sub-groups or of the transition group (VIII) of the table having an atomic number of at least 26 and at most 83 and being in the lower valence state, e.g. from 1 to 3, are used.

The heat sensitive heavy metal salts of the N-substituted dithiocarbamic acids in question comprise such of the general formula



wherein:

R₁ stands for hydrogen or a lower alkyl radical,

R₂ stands for an organic residue, and

R₁ and R₂ may join to form a ring which may be substituted with a lower alkyl radical,

M stands for a heavy metal having an atomic number of at least 26 and at most 83 and belonging to the sub group b or the transition group VIII of the periodic table and having a valence state from 1 to 3, and

X stands for an integer equal to the valence of the heavy metal.

The above mentioned lower alkyl radicals are such as methyl, ethyl, propyl, butyl, isobutyl, pentyl radicals.

The said organic residues represented by R₂ comprise alkyl, aralkyl and aryl, which may be substituted by at least one carboxylic, carboxylic ester, alkoxy, or dithiocarbamic acid group.

The nitrogen atom of the dithiocarbamic acid may together with the residues R₁ and R₂ form a ring, such as a piperidine or pyrrolidine ring, which may be substituted by lower alkyl residues.

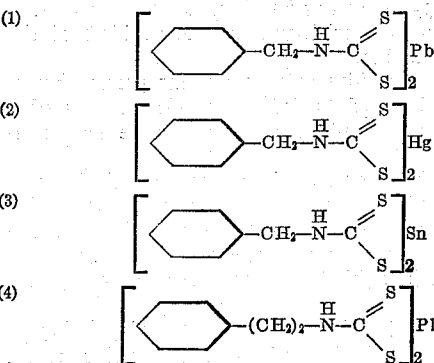
The preparation of dithiocarbamates suitable for the heat sensitive reproduction coatings provided by the invention is described in the literature. Those heavy metal salts of the dithiocarbamic acids that are not yet known are prepared in analogous manner to the dithiocarbamic acid salts for which instructions are already available. Generally, the preparation of the heat sensitive heavy metal salts of the dithiocarbamic acid in question can be prepared in organic solvents, in aqueous solution or in suspension. Two mols of the primary or secondary amine (which in the interest of a reduced reaction temperature are in solution) are permitted to react with one mol of carbon disulphide. After the reaction mixture has cooled, but before the salt (which is formed with the excess amine from the dithiocarbamic acid produced) has precipitated, a solution of a salt of the heavy metal in question is added, e.g. heavy metal chloride or acetate. The heavy metal salt of the dithiocarbamic acid is immediately precipitated. Alternatively, by the addition of alkali hydroxide or ammonia to the mixture of amine and carbon disulphide, the alkali or ammonium salts of the dithiocarbamic acids in question can first be formed and the heavy metal salt of the dithiocarbamate precipitated thereafter by the addition of a heavy metal salt in organic solvents or aqueous solution. The advantage of this latter method is that only one mol of the amine is needed, which is completely used up in the formation of the dithiocarbamic acid.

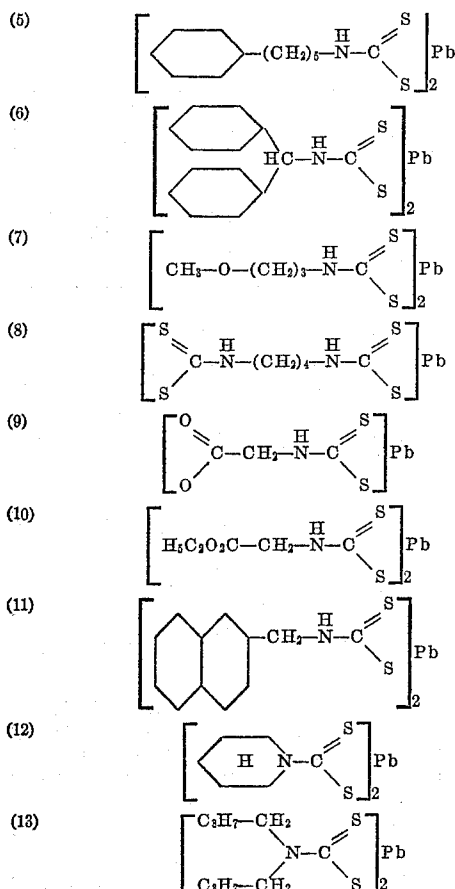
Formulae 1-13 are examples of dithiocarbamates useful in the present invention and are shown on the attached sheets.

The heavy metal salt of a dithiocarbamate is applied to a suitable base material in the form of a coating including a suitable binding agent which may be a cellulose derivative such as ethyl cellulose, methyl cellulose and cellulose acetate; a polyvinyl compound, such as polyvinyl butyral, polyvinyl carbazole, polyvinyl alcohol, or polyvinyl chloride and its copolymers, e.g. with polyvinyl acetate; a polyamide or a silicone resin.

Suitable base materials for the reproduction coatings of the present invention are sheets and films of transparent materials, e.g. glass, naturally transparent paper, cellulose hydrate film, transparent plastic film, such as those made of polyvinyl chloride, cellulose acetate, polyethylene terephthalate, and other substances in the form of films or sheets and capable of being permeated by light rays.

Alternative procedures by which images are produced by heat-action according to the invention are as follows:





(1) A reflex process, in which the material provided with the heat sensitive coating is placed with its coated side against the master or original to be copied, which may have printing or writing on one or both sides. Radiant heat is applied through the back of the heat sensitive material, for example by means of an infra-red lamp. The more intense the source of energy, the sharper is the image and the shorter the radiation time required. In the heat sensitive coating there is formed a direct, deeply colored mirror-image of the master which can be read correctly through the back of the transparent support.

(2) Masters with printing or typing on one side only can also be copied by the radiation of heat through the master when the latter is in contact with the heat sensitive reproduction coating and it is immaterial whether the heat sensitive reproduction coating has its back or its front in contact with the master.

The duration of heat action for the production of satisfactory heat images which will be sharp and rich in contrast cannot be generally specified. This must be established from case to case. It is dependent on a number of factors such as the type and intensity of the source of energy as well as its distance from the master, the type of base material and the composition of the heat sensitive coating.

(3) The heat sensitive materials of the present invention can also be used to form images by means of a heated stylus or a heated stamp applied to the heat sensitive coating.

The use of the invention will be more clearly brought out as illustrated in the accompanying drawing wherein:

FIG. 1 illustrates the heat sensitive material including a coating of fine particles of a heavy metal salt of dithiocarbamic acid in a binder supported on a transparent base.

FIG. 2 illustrates the reflex method of printing in which the heat rays indicated by arrows pass through the

transparent base and the heat sensitive coating and are reflected in differing proportion in accordance with the image on the surface of the master in contact with the heat sensitive coating regardless of whether the master is printed on one or both sides to produce the image on the heat sensitive material.

FIG. 3 illustrates contact printing with the heat sensitive coating of the material being in contact with the image free surface of the master.

FIG. 4 illustrates heat rays passing through a master printed on one side with such printed side of the master in contact with the transparent base and the heat sensitive coating on the opposite surface.

FIG. 5 illustrates contact printing with the master printed on one side and that side in contact with the heat sensitive coating and the heat rays passing through the master.

FIG. 6 illustrates the heat rays passing through the master which is printed on one side with such printed side adjacent the source of heat rays and the printing free side in contact with the transparent base and the heat sensitive coating on the opposite surface.

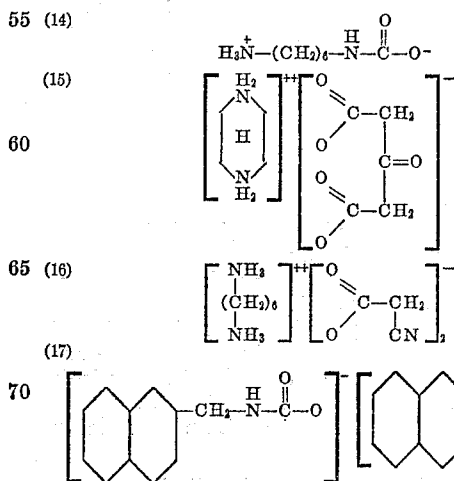
FIG. 7 illustrates forming images by means of a heated stylus or stamp in contact with the heat sensitive coating.

It has further been found that the heat sensitivity of the heavy metal salts of the dithiocarbamic acids according to the present invention can be improved by adding to the heat sensitive coating amine salts or ammonium salts of readily heat-decomposable acids, i.e. acids whose molecules are readily split or decomposed by the action of heat. Reproduction coatings modified in this way require less heat for the formation of the colored image. The practical significance of this is that the temperature at which color change takes place is lower than in the case of coatings containing the dithiocarbamates of heavy metals without any such amine salt or ammonium salt of an acid.

Amine salts and ammonium salts that have proved particularly suitable are those of carbonic acid, carbamic acid, trichloroacetic acid, and tribromoacetic acid, cyanoacetic acid, acetoacetic acid, acetone dicarboxylic acid, mono or dichloromalononic acid and mono or dibromomalononic acid. Acid amides such as acetamide and benzamide and also symmetrically substituted diarylguanidines, such as N,N' -diphenyl-guanidine and derivatives thereof substituted in the nucleus, can also be used for a similar purpose.

Free amines and guanidines with asymmetric or aliphatic substitution can also be used if the heat sensitive coating composition is to be used soon after its preparation.

A few compounds of the types referred to above are illustrated by Formulae 14-17.



The heavy metal salts of dithiocarbamic acids to be

used as heat sensitive substances as provided by the invention are stable at normal temperatures and are unaffected by exposure to sunlight. When applied to the base materials they form colorless or lightly colored coatings. Their heat decomposition products are deeply colored so that images rich in contrast are obtained.

The images obtained keep well. If they are required to be protected from any further influence of high temperatures, they can be subjected to a fixing process to convert the amine and ammonia salts of the readily heat-decomposable acids into heat-resistant salts. The images will then remain unaffected by temperatures up to over 150° C. It has been discovered that the fixing can be effected by an acid treatment. In general it is sufficient for a coating which has been subjected to heat to form an image to be exposed to the fumes of volatile acids. Examples of suitable acids are hydrochloric acid, acetic acid and formic acid. Fixing is also effected if one of the acids mentioned is rubbed or sprayed on the coated side of the finished heat copy. After drying, the copy is resistant to the effect of heat within the limits mentioned above.

Examples

1. Lead benzyldithiocarbamate (Formula 1) is prepared by dissolving 53.3 g. of benzyl amine in 700 cc. of methanol and adding with stirring 19 g. of carbon disulphide. When the reaction temperature has fallen again to normal, 48 g. of lead acetate dissolved in 100 cc. of water are stirred into the reaction mixture at about 25-30° C. The lead benzyldithiocarbamate precipitates, is separated by suction, washed consecutively with water, methanol and ether and dried in the air. 80 g. of pure white substance are obtained. The product decomposes with black coloration if it is placed for one second on a plate (melting bed) heated to 211° C.

100 g. of the lead benzyldithiocarbamate are suspended in 500 cc. of methylene chloride and ground for two hours in a ball mill. 250 cc. of a 5% solution of ethyl cellulose in methylene chloride are then mixed into the suspension to form suspension A.

200 g. of 1,6-diaminohexane are dissolved in 500 cc. of methanol and with external cooling, carbon dioxide is fed in until precipitation ceases. The precipitated product is 1,6-diaminohexane carbamate corresponding to Formula 14. It is filtered by suction and washed with methylene chloride and is then pure white. After this product has been dried in the air, 100 g. are finely milled in a colloid mill with 500 cc. of methylene chloride and the suspension is mixed with 100 cc. of a 5% solution of ethyl cellulose in methylene chloride to form suspension B.

Suspensions A and B are then thoroughly mixed together. The mixture is applied to naturally transparent paper and dried in moderate heat.

For the production of a heat image the coated transparent paper is placed with its coated side against the master to be copied, e.g. a sheet printed on both sides, and subjected to the action of a powerful infra-red lamp in such manner that the radiation passes through the non-coated side of the heat-sensitive reproduction paper. The heat is heavily absorbed in the printed parts of the master to raise the temperature in the heat sensitive coating adjacent thereto which sets off the decomposition reaction in the parts of the heat sensitive coating in contact with the printing. Direct mirror-image reproductions of the master are obtained in brown black, which can be read as correct images through the back of the transparent paper.

So that the copy obtained may be made resistant to further heat action, it is placed in a fume chamber over strong acetic acid at room temperature for three hours. The copy thus obtained is now heat-resistant up to about 150° C. and shows no alteration even after prolonged storage.

(2) Lead-N-(ω -phenyl-n-pentyl)-dithiocarbamate corresponding to Formula 5, which is prepared from ω -phen-

yl-n-pentylamine in analogous manner to the lead benzyldithiocarbamate described in Example 1, is practically colorless and decomposes within a second to form black coloration if it is placed on a plate (melting bed) heated to 134° C. 100 g. of this product are finely milled (for three days) in a ball mill in 500 cc. of carbon tetrachloride and then mixed with an equally finely divided suspension of 30 g. of acetamide in 250 cc. of carbon tetrachloride. 250 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride are added to the suspension and the mixture is thoroughly mixed. The mass obtained is applied to the side of a cellulose hydrate foil that has been provided with a water-resistant coating and is then dried. By the copying process described in Example 1, dark brown images are obtained.

(3) For the preparation of lead-N-(carbethoxymethyl)-dithiocarbamate corresponding to Formula 10, 14 g. of glycolcollethylester hydrochloride are dissolved in a mixture of 50 cc. of methanol and 5 cc. of water and to this mixture a solution of 4 g. of sodium hydroxide in 10 cc. of water is slowly added at +10° C. 7.6 g. of carbon disulphide are then added with thorough cooling and mixing and the reaction mixture is left to stand for an hour during which it is occasionally shaken. The carbon disulphide will then go into solution and the solution will become neutral. The liquid is filtered off from the common salt that precipitates and cooled to +10° C. 100 cc. of a normal aqueous solution of lead acetate are added with thorough stirring. The colorless lead salt of N-carbethoxymethyl-dithiocarbamic acid precipitates immediately. It is separated by suction, filtering suspended in acetone, again separated by suction, washed in ether and dried in the air. The colorless substance melts with decomposition (black coloration) if placed for one second on a plate (melting bed) heated to 195° C.

5.6 g. of the lead dithiocarbamate obtained are finely ground in 50 cc. of methylene chloride in a ball mill and the suspension is mixed with a suspension of 4 g. of the benzylamine salt of cyanoacetic acid in 50 cc. of methylene chloride similarly prepared in a ball mill. To this mixture 60 cc. of a 5% solution of cellulose acetate (2½ acetate) containing 52 to 56 percent of acetic acid in methylene chloride are added. The resultant product is thoroughly mixed and applied in a thin layer by means of a spray gun to a cellulose acetate film. The coating is then dried. With this reproduction material violet-brown images are obtained by the process described in Example 1.

(4) Lead benzhydryl-dithiocarbamate corresponding to Formula 6 is obtained if 183 g. of benzhydrylamine are dissolved in 200 cc. of concentrated methanolic ammonia and 200 cc. of ether and 60 cc. of carbon disulphide are added under reflux with cooling by ice. The ammonium salt of benzhydryl dithiocarbamic acid is formed. A little more ether is then added to the reaction mixture to complete precipitation and the precipitate is separated by suction filtration and washed with ether.

The ammonium salt is dissolved in 1000 cc. of methanol and the resultant solution is run into 1000 cc. of normal aqueous lead acetate solution containing additionally 60 g. of glacial acetic acid, cooling being maintained by the addition of pieces of ice. The precipitated lead salt is separated by suction filtration, suspended in methanol and again separated by suction. It is then suspended in ether, again separated by suction and washed with ether. The pure white product is dried in the air. The substance decomposes within a second with black coloration if put on a metal plate (melting bed) heated to 212° C.

7.2 g. of lead benzhydryl dithiocarbamate are finely ground in a ball mill with 50 cc. of carbon tetrachloride. Suspension A is thus obtained.

8.4 g. of N,N'-diphenylguanidine are finely ground in a ball mill in 100 cc. of carbon tetrachloride to produce Suspension B.

Suspensions A and B are mixed and to the mixture are

added 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride, 40 cc. of a solution of 0.6 g. of a ketone resin, e.g. "Kunstharz AW 2" of Badische Anilin and Soda-Fabrik, in 40 cc. of ethylene perchloride and 75 cc. of pure ethylene perchloride.

This mixture is applied to transparent paper in a thin layer and dried. If the coated transparent paper is placed in contact with a master in accordance with the instructions given in Example 1 and subjected to the action of radiant heat, a brown-black image of the master is formed.

(5) Mercury-N-benzyl-dithiocarbamate corresponding to Formula 2 is prepared by mixing 10.7 g. of benylamine with 50 cc. of methanol, and adding 6 cc. of carbon disulphide with cooling and following with a solution of 14 g. of mercury-II-chloride in 50 cc. of methanol with thorough stirring. The precipitated colorless mercury salt is purified with methanol and ether and dried in the air, as described in Example 4. The pale yellowish product melts with decomposition (black coloration) within one second if put on a metal plate (melting bed) heated to 166° C.

4.1 g. of mercury-N-benzyl-dithiocarbamate are finely ground in 50 cc. of carbon tetrachloride and mixed with the similarly finely ground suspension of 4.2 g. of N,N'-di-phenylguanidine in 50 cc. of carbon tetrachloride. To the mixture thus obtained 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride are added. A thin coat of this material is applied to transparent paper. The coating is then dried. Deep brown images are obtained by the copying process described in Example 1.

(6) Lead-3-methoxypropyl-dithiocarbamate corresponding to Formula 7 is prepared from 3-methoxypropylamine-1 in a manner analogous to that described in Example 1. It melts with decomposition (black coloration) if it is placed for one second on a plate (melting bed) heated at 130° C.

Suspension A.—27 g. of the product are ground in 200 cc. of carbon tetrachloride in a ball mill.

Suspension B.—12 g. of 1,6-diaminohexane are dissolved in a mixture consisting of 200 cc. of a 3% solution of ethyl cellulose in carbon tetrachloride and 600 cc. of pure carbon tetrachloride; dry carbon dioxide is then introduced until saturation is reached. The resultant product is an extremely finely divided suspension of 1,6-diaminohexane carbamate corresponding to Formula 14.

Suspensions A and B are intimately mixed and applied to transparent paper. This heat sensitive reproduction paper gives black images when subjected to the process described in Example 1.

(7) *Suspension A.*—2.8 g. of lead benzyl dithiocarbamate corresponding to Formula 1, the preparation of which is described in Example 1, are finely ground with 25 cc. of benzene in a ball mill.

Suspension B.—Lead-N-phenylethyl-dithiocarbamate corresponding to Formula 4 (melting point 170° C., with decomposition within 1 second) is prepared from phenylethylamine in a manner analogous to that described in Example 1. 3 g. of this compound are likewise finely suspended in 25 cc. of benzene by means of a ball mill.

Suspension C.—2 g. of the benzylamine salt of monochloroacetic acid are finely suspended in 20 cc. of benzene.

Suspensions A, B and C are mixed and 50 cc. of a 5% solution of polyvinylcarbazole in benzene and 100 cc. of pure benzene are added to the mixture. The product thus obtained is applied in a thin coating to a glass plate and dried. Black-brown images are obtained if this reproduction material is treated in the manner described in Example 1.

(8) Tin benzyl dithiocarbamate corresponding to Formula 3 is prepared as follows: 10.7 g. of benzylamine are mixed with 50 cc. of methanol; 6 cc. of carbon disulphide are added with stirring and as soon as the benzylamine salt of benzyldithiocarbamic acid begins to pre-

cipitate, 9.5 g. of tin-II-chloride dissolved in 50 cc. of water are added to the reaction mixture with cooling. The pale yellowish tin salt of benzyl-dithiocarbamic acid is separated by suction filtration and washed with methanol and ether. The product is then dried in the air. The pale yellowish product decomposes without melting if it is put for 1 second on a plate (melting bed) heated to 178° C.

5 g. of tin benzyl dithiocarbamate are finely ground in a ball mill with 50 cc. of carbon tetrachloride and then mixed with a finely divided suspension of 6 g. of N,N'-diphenylguanidine in 50 cc. of ethylene perchloride.

To this mixture 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride and also 100 cc. of pure ethylene perchloride are added and the mixture is thoroughly stirred. When this is coated on a suitable base material, dark brown images are obtained by the process described in Example 1.

(9) Lead-N-(carboxymethyl)-dithiocarbamate corresponding to Formula 9 is prepared by the solution of 22.3 g. of glycocoll hydrochloride in 20 cc. of water and the addition with external cooling of 35 g. potassium hydroxide dissolved in 30 cc. of water. The alkaline solution is then shaken with 15.2 g. of carbon disulphide until the greater part of the carbon disulphide is dissolved. Potassium chloride is precipitated and is filtered off. The filtrate is freed from any remaining carbon disulphide by ether extraction. From the solution of the dipotassium salt of dithiocarbamic acetic acid the di-lead salt is precipitated by careful addition of a solution of 76 g. of crystalline lead acetate in 200 cc. of water. The lead salt is washed with acetone and ether to form a colorless product. It is then dried in the air. The product decomposes with black coloration if it is placed for 1 second on a plate (melting bed) heated to 212° C.

8 g. of the lead salt are finely ground in a ball mill together with 50 cc. of ethylene perchloride and then mixed with a suspension of 4 g. of the acetone dicarboxylic acid salt of piperazine (see Formula 15) in 50 cc. of ethylene perchloride likewise prepared in a ball mill.

To the resultant mixture 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride are added and the product is coated upon transparent paper. The coating is dried. If this reproduction paper is used with the process described in Example 1, dark brown images are obtained.

(10) Lead-1,4-diamino-butane-bis-dithiocarbamate corresponding to Formula 8 is obtained if 8.4 g. of 1,4-diaminobutane are dissolved in 50 cc. of methanol and 12 cc. of carbon disulphide are added to the solution with stirring and external cooling and the mixture is then quickly poured into 50 cc. of a cooled normal lead acetate solution. Colorless lead salt corresponding to Formula 8 precipitates out and is separated by suction, washed consecutively with water, a little methanol and ether and dried in the air. The product decomposes without melting if it is put for one second on a plate (melting bed) heated to 131° C.

4.7 g. of the dry product are finely ground in a ball mill together with 50 cc. of carbon tetrachloride. The suspension obtained is mixed with a suspension of 3 g. of the cyanoacetic acid salt of 1,6-diaminohexane (see Formula 16) in 50 cc. of carbon tetrachloride. To this mixture 60 cc. of a 5% solution of ethylcellulose in carbon tetrachloride and 75 cc. of pure ethylene perchloride are added. The resultant product is coated upon transparent paper and the coating is then dried. This reproduction paper gives practically black images with the process described in Example 1.

(11) Lead-β-naphthmethyl-dithiocarbamate corresponding to Formula 11 is obtained if 15.7 g. of 2-naphthmethylamine are dissolved in 100 cc. of concentrated methanolic ammonia and 6 cc. of carbon disulphide

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are added with stirring and external cooling. The reaction mixture is then diluted with three times its quantity of ether (300 cc.) and the ammonium salt of 2-naphthmethyl dithiocarbamic acid thus formed is separated by suction, washed with ether and dried. The solid product is ground for 24 hours in a ball mill with 100 cc. of normal aqueous lead acetate solution. The conversion to the lead salt of 2-naphthmethyl-dithiocarbamic acid will by this time be complete. The product, which is practically colorless, decomposes without melting (black coloration) if put for one second on a plate (melting bed) heated to 234° C.

The lead salt is separated by suction, suspended in methanol, thoroughly mixed therein, again separated by suction, washed with ether and dried in the air.

4.4 g. of the product thus obtained are finely ground in a ball mill together with 50 cc. of ethylene perchloride and the resultant suspension is mixed with a suspension of 4.6 g. of 2-naphthmethyl carbamate corresponding to Formula 17 in 50 cc. of carbon tetrachloride. To this mixture 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride and 75 cc. of pure ethylene perchloride are added. This mixture is coated thinly upon transparent paper and the coating is dried. The reproduction paper thus obtained gives dark brown images when subjected to the process described in Example 1.

(12) Lead piperidino-dithioformate corresponding to Formula 12 is obtained as follows:

8.5 g. of piperidine are dissolved in 100 cc. of ethanol and 6 cc. of carbon disulphide are added with stirring, after which the reaction mixture is cooled to 20–25° C. 10 g. of lead acetate dissolved in 30 cc. of water are added with shaking. The lead salt of piperidino-dithioformic acid precipitates out. It is separated by suction, washed with methanol and ether, and dried in the air. The colorless product decomposes with black coloration if it is placed for one second on a plate (melting bed) heated to 254° C.

5.3 g. of the product are finely ground in a ball mill with 50 cc. of carbon tetrachloride. 2.5 g. of free 1,6-diaminohexane dissolved in 50 cc. of carbon tetrachloride are added to this suspension and the mixture is mixed with 60 cc. of a 5% solution of ethyl cellulose in carbon tetrachloride and with 75 cc. of ethylene perchloride. The resultant product is coated in a thin layer upon transparent paper and dried. With this reproduction paper black-brown images are obtained by the process described in Example 1.

(13) Lead-n-dibutyl-dithiocarbamate corresponding to Formula 13 is obtained when 4 g. of carbon disulphide are added with stirring to a mixture of 6.5 g. of n-dibutylamine and 50 cc. of ethanol and the reaction mixture is cooled to 25° C. and then poured with shaking into a solution of 10 g. of lead acetate in 30 cc. of water. The colorless lead salt of n-dibutyl-dithiocarbamic acid precipitates out; it is separated by suction, washed with methanol and ether and dried in the air. The product melts at 76° C. without decomposition, but decomposes within one second if it is out on a plate (melting bed) heated to 250° C.

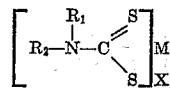
6.2 g. of the lead salt are finely ground in a ball mill with 50 cc. of carbon tetrachloride. The suspension thus obtained is mixed with a solution of 2.5 g. of free 1,6-diaminohexane in 50 cc. of carbon tetrachloride, 60 cc. of a 5% solution of ethyl cellulose in ethylene perchloride and 75 cc. of pure ethylene perchloride. The product thus obtained is applied in a thin coating to transparent paper and dried. The reproduction paper prepared in this manner gives black-brown images when processed in the manner described in Example 1.

Having thus described the invention what is claimed is:

1. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including at least one heavy

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metal salt of an N-substituted amino-dithioformic acid of the general formula



wherein:

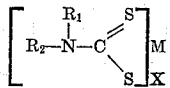
R₁ is selected from the group consisting of hydrogen and a lower alkyl residue,

R₂ stands for an organic residue selected from the group consisting of alkyl, aryl, aralkyl, substituted alkyl, substituted aryl, and substituted aralkyl radicals, and wherein R₁ and R₂ may join to form a ring which may be substituted by lower alkyl residues,

M is a heavy metal selected from the group consisting of metals of the b-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and

X is an integer equal to the valence of the heavy metal.

2. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including a binding agent and at least one heavy metal salt of an N-substituted amino-dithioformic acid of the general formula



wherein:

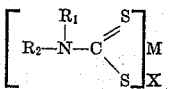
R₁ is selected from the group consisting of hydrogen and a lower alkyl residue,

R₂ stands for an organic residue selected from the group consisting of alkyl, aryl, aralkyl, substituted alkyl, substituted aryl, and substituted aralkyl radicals, and wherein R₁ and R₂ may join to form a ring which may be substituted by lower alkyl residues,

M is a heavy metal selected from the group consisting of metals of the b-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and

X is an integer equal to the valence of the heavy metal.

3. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including a binding agent selected from the group consisting of cellulose derivatives, polyvinyl compounds, polyamides and silicone resins and at least one heavy metal salt of an N-substituted amino-dithioformic acid of the general formula



wherein:

R₁ is selected from the group consisting of hydrogen and a lower alkyl residue,

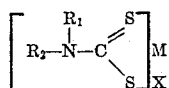
R₂ stands for an organic residue selected from the group consisting of alkyl, aryl, aralkyl, substituted alkyl, substituted aryl, and substituted aralkyl radicals, and wherein R₁ and R₂ may join to form a ring which may be substituted by lower alkyl residues,

M is a heavy metal selected from the group consisting of metals of the b-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and

X is an integer equal to the valence of the heavy metal.

4. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including at least one heat sensitive substance selected from the group consisting of amine salts and ammonium salts of readily heat-decom-

possible acids and heavy metal salts of N-substituted amino-dithioformic acids of the general formula



wherein:

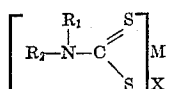
R_1 is selected from the group consisting of hydrogen and a lower alkyl residue,

R_2 stands for an organic residue selected from the group consisting of alkyl, aryl, aralkyl, substituted alkyl, substituted aryl, and substituted aralkyl radicals, and wherein R_1 and R_2 may join to form a ring which may be substituted by lower alkyl residues,

M is a heavy metal selected from the group consisting of metals of the *b*-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and

X is an integer equal to the valence of the heavy metal.

5. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including at least one binding agent and at least one heat sensitive substance selected from the group consisting of amine salts and ammonium salts of readily heat-decomposable acids, and a heavy metal salt of N-substituted amino-dithioformic acids of the general formula



wherein:

R_1 is selected from the group consisting of hydrogen and a lower alkyl residue,

R_2 stands for an organic residue selected from the group consisting of alkyl, aryl, aralkyl, substituted alkyl, substituted aryl, and substituted aralkyl radicals, and wherein R_1 and R_2 may join to form a ring which may be substituted by lower alkyl residues,

M is a heavy metal selected from the group consisting of metals of the *b*-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and

X is an integer equal to the valence of the heavy metal.

6. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including lead benzyldithiocarbamate.

7. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including lead-N-(*o*-phenyl-n-pentyl)-dithiocarbamate.

8. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated

with a heat sensitive layer including lead-N-(carboethoxymethyl)-dithiocarbamate.

9. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including lead benzyldithiocarbamate.

10. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including lead-diphenylmethyl-dithiocarbamate.

11. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including mercury-N-benzyl-dithiocarbamate.

12. A heat sensitive material for the reproduction of images comprising a base material in sheet formed coated with a heat sensitive layer including lead benzyldithiocarbamate and 1,6-diamino-hexane.

13. A heat sensitive material for the reproduction of images comprising a base material in sheet form coated with a heat sensitive layer including lead benzyldithiocarbamate and N,N'-diphenyl-guanidine.

14. A process for the manufacture of a heat sensitive reproduction material which comprises applying to a support a coating consisting of an N-substituted heavy metal dithiocarbamate, the heavy metal being selected from the group consisting of the heavy metals of the *b*-sub-groups and the transition group VIII of the periodic table having an atomic number of at least 26 and at most 83, and at least one heat sensitive substance selected from the group consisting of salts of amines and ammonium salts of readily heat-decomposable acids.

15. A process for the manufacture of reproductions which comprises subjecting the heat sensitive material claimed in claim 1 to heat differentially in correspondence with the desired image by placing the heat sensitive material and a master one upon the other and exposing the combined material from one side to radiant heat without subjecting to immediate heat radiation the surface carrying the heat sensitive layer.

16. A process for the manufacture of reproductions claimed in claim 15 which comprises contacting the heat sensitive material with a heated surface.

17. A process as claimed in claim 15 which comprises the step of fixing the image formed by subjecting the material to heat by exposing the material to the action of a volatile acid.

18. A process as claimed in claim 15 which comprises the step of fixing the image formed by subjecting the material to heat by exposing the material to the action of vapors of volatile acids selected from the group consisting of formic acid, acetic acid, and hydrochloric acid.

References Cited in the file of this patent

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