United States Patent Office 3,573,958 Patented Apr. 6, 1971

3,573,958

HEAT SENSITIVE RECORDING SHEET

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No Drawing. Filed May 31, 1968, Ser. No. 733,260
Int. Cl. B41m 5/18, 5/26
U.S. Cl. 117—36.8 7 Claims

ABSTRACT OF THE DISCLOSURE

A heat marking process using a novel heat sensitive recording sheet. The recording sheet comprises a substrate impregnated or coated with a heat sensitive composition of an indicator material, preferably ninhydrin or a derivative of ninhydrin, and an adduct of an amine ligand and an acceptor molecule of a halide or an organometallic halide of a member selected from the group consisting of germanium, tin, lead, and silicon; said adduct being stable at room temperature and dissociating at elevated temperatures, preferably temperatures in excess of 50° C., and most preferably, within the temperature range of 50° C. to 150° C. A record is formed by selective heating in a desired pattern to dissociate the adduct and liberate the amine for reaction with the indicator material. The recording sheet is more stable than prior art all organic recording sheets both prior to and subsequent to recording and forms deeper colored marks of high intensity.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to a recording sheet containing heat reactive components, and more particularly, to recording sheets capable of use in a thermographic copying process.

(2) Description of the prior art

Heat sensitive sheets useful for copying and recording and characterized by the ability to form a mark of contrasting colors when heated to an activation temperature above 50° C. are known in the art. They are commonly used in thermographic copying process wherein a recording sheet is placed next to a graphic original and exposed to infrared radiation to cause selective heating of the dark areas of the original sufficient to form a copy thereof on the heat sensitive sheet. A more detailed description of processes of this nature is set forth in United States Pat. No. 2,704,896 incorporated herein by reference.

In U.S. Pat. No. 3,076,707, there is disclosed heat sensitive sheets and compositions useful therefor containing an indicator material which changes color in the presence of a basic organic amine in combination with a latent developer. On heating, the latent developer dissociates yielding an amine effective to give a color reaction. The latent developers employed are the thermally dissociable crystalline molecular compounds consisting of an organic amine in combination with urea, thiourea, or a bisphenol. Under normal storage conditions, they are solids which exhibit no substantial amine characteristics, and may therefore be intimately associated with an indicator material without causing a color reaction.

The usefulness of the above noted compositions has been limited to the fact that the molecular compounds of urea, thiourea and bisphenols are relatively unstable in the presence of moisture, They cannot be applied to the sheet from aqueous systems, and the binder in which they

are dispersed must be one that is soluble in an organic liquid in which the latent developer is not soluble. In addition, the sheets employing these complexes have a reduced shelf life when stored at high humidity.

In U.S. Pat. No. 3,149,992, there is described an improved composition comprising an indicator material which changes color in the presence of a basic organic amine and an amine adduct of a hydroxyphenyl substituted chroman. Upon heating to a temperature between 50° C. and 150° C., the adduct decomposes liberating the amine for reaction with the indicator material to give a color change.

STATEMENT OF THE INVENTION

The present invention provides a heat marking process and a novel heat sensitive sheet useful for copying and recording purposes characterized by improved stability upon color change prior to recording and improved stability against discoloration and fading subsequent to recording. The heat sensitive sheet comprises a substrate impregnated or coated with an indicator material, preferably ninhydrin or a derivative thereof and an adduct of an amine ligand and an acceptor molecule that is a halide or an organometallic halide of a member selected from the group consisting of germanium, silicon, lead and tin. The adducts are stable at room temperature, and heat dissociable at elevated temperatures, preferably in excess of 50° C. and most preferably, within the temperature range of 50° C. to 150° C. In a thermal recording process, heat applied to the recording sheet in an image pattern causes dissociation of the adduct liberating amine for reaction with an indicator material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Heat sensitive sheets are produced by providing a sheet of suitable backing material, such as paper of an optically transparent plastic such as polycarbonate, polyamide, polystyrene, polyethylene or the like, with a coating containing both the indicator material and the adduct in intimate potentially reactive association such that upon decomposition of the adduct, the amine is present throughout the coating. The adduct will generally be retained on the sheet by means of a resin binder, and the components may be applied together in a single coat in which each is separately dispersed. Alternatively, the latent developer and indicator material may be applied in separate layers. In a second embodiment of the invention, the indicator material and adduct in solution may be impregnated into a porous substrate. In all cases, it is contemplated that additional material such as pigments, antistatic and antifriction ingredients may be incorporated in any of the heat sensitive compositions.

The adduct is one stable at room temperature and capable of dissociating at elevated temperatures, preferably at temperatures in excess of 50° C. and most preferably, capable of dissociating within the temperature range of 50° C. to 150° C. The adduct is formed from an amine ligand and an acceptor molecule that is a halide or an organometallic halide of a member selected from the group consisting of germanium, silicon, lead or tin in accordance with procedures known in the art. The following table sets forth examples of ligands and acceptor molecules for the formation of adducts suitable for purposes of the invention. Procedures for formation of the adduct are known in the art and publications describing the process and adduct are referenced in the table.

Example No.	Reactants: Ligands	Reactants: Acceptor molecules	Reference [1]
1	Ammonia	GeF_4 (1:2)	(2)
2	do	$GeCl_4$ (1:6)	(3)
3	do	H_3GeF_4(1:1)	(4)
4	do	$(C_2H_5)_3GeBr$ (1:1)	(5)
5	Hydrazine	GeF_4 (1:2)	(2)
6	Methylamine	CH_3GeBr_3 (1:1)	(6)
7	Ethylenediamine	GeF_4 (1:1)	(2)
8	Dimethylamine	CH_3GeBr_3 (1:1)	(6)
9	Diethanolamine	$GeCl_4$ (1:1)	(7)
10	Pyrolidine	GeF_4 (1:2)	(2)
11	Piperidine	GeF_4 (1:1)	(8)
12	Trimethylamine	GeF_4 (1:1)	(2)
13	do	$GeCl_4$ (1:1)	(9)
14	do	CH_3GeBr_3 (1:1)	(6)
15	do	$GeCl_4$ (1:1)	(7)
16	Dimethylanaline	GeF_4 (1:2)	(2)
17	Triethylanaline	$GeCl_4$ (1:4)	(10)
18	do	GeI_4 (1:5)	(11)
19	Cyclohexylamine	GeI_4 (1:4)	(3)
20	Acetonitrile	GeF_4 (1:2)	(2)
21	Pyridine	GeF_4 (1:2)	(2)
22	do	$GeCl_4$ (1:2)	(12)
23	do	$GeBr_4$ (1:2)	(12)
24	2,2'-bipyridyl	$GeCl_4$ (1:1)	(12)
25	do	$GeBr_4$ (1:1)	(12)
26	1,10-phenathroline	$GeCl_4$ (1:1)	(13)
27	do	$GeBr_4$ (1:1)	(12)
28	Hudroxyethyl-piperazine.	$GeCl_4$ (1:1)	(7)
29	Tetra-N-methyl-ethylenediamine.	Same.	(9)
30	Diethylenetriamine	do	(7)
31	Ethylenediamine-tetraacetic acid.	do	(7)
32	Diaminopropane	do	(7)

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NOTE.—The number in parenthesis above represents the moles of ligand to acceptor molecule necessary to form the adduct.

Equivalent compounds of silicon compounds, lead and tin can be formed by substitution of the appropriate halide or organometallic compound thereof for the germanium compound in accordance with procedures known in the art.

All of the above compounds are stable at room temperatures and decompose at elevated temperatures. The preferred compounds are those that dissociate above 50° C. and most preferably, within the temperature range of 50° C. to 150° C. Election of a suitable compound is governed by the temperature generated by the thermocopying apparatus used.

The indicator material is selected from that class of materials known to change colors in the presence of an amine and heretofore used for heat marking processes. Such indicator materials are disclosed in the above noted U.S. Pat. 3,149,992 incorporated herein by reference.

The following examples describe various formulations of indicator material suitable for use in this invention:

EXAMPLE 33

	Parts by weight
Water	450
Thiourea	33
Citric acid	15
2,3-dihydroxynaphthalene-6-sulfonic acid	24
p-Diazodiethylaniline	6.6
Ethylene glycol	12
Zinc chloride	15
Saponin	0.03

The materials may be added to the water in the order listed and mixed into solution for coating.

EXAMPLE 34

	Parts by weight
Ninhydrin	6
Polyvinyl formal resin (Formvar 7/70)	8
Trichloroethylene	84

The resin binder may be dissolved in the trichloroethylene and the ninhydrin added.

EXAMPLE 35

	Parts by weight
Hydrindantin	129
Pliolite VT	49
VM & P naphtha	369

The ingredients may be mixed together and ground for 24–48 hours in a ball mill.

EXAMPLE 36

	Parts by weight
2,3-dichloronaphthoquinone	10
Trichlorethylene	88.8
Polyvinyl butyral resin (Butvar B–76)	2.2

The materials may be combined and ground for 24–48 hours in a ball mill.

EXAMPLE 37

	Parts by weight
Tetrahydroquinone	10
Trichlorethylene	88.8
Polyvinyl butyral resin (Butvar B–76)	2.2

The materials may be combined and ground for 24–48 hours in a ball mill.

In the following examples, typical pH indicators are exemplified by dissolving the indicator in water or in a 50:50 methanol-water mixture at a concentration in the range of 0.5–2 percent.

Example:	Indicator
38	Azolitmin.
39	Bromcresol purple.
40	Clayton yellow.
41	Cresol red.
42	Alizarin blue.
43	Orange I.
44	Rosolic acid.
45	Chlorophenol red.

The heat marking sheets are prepared by coating a sheet of paper or other suitable webs such as an optically clear plastic film with a resin solution which contains both an adduct and indicator material capable of reacting with the amine to form a colored change. This may be accomplished by providing separate layers by first coating the substrate with a dispersion of the adduct in a binder solution followed by application of a coating of an indicator material as a separate layer, either before or after the application of the adduct layer. Alternatively, the adduct and indicator material may be combined in a single solution and coated onto the paper with a suitable binder or impregnated into the paper.

The following examples represent an overall process for the formation and use of heat recording sheets in accordance with the invention.

EXAMPLE 46

Form a first solution comprising one mole of ethylene-diamine dissolved in one liter of benzene. Prepare a second solution comprising one mole of germanium tetrachloride dissolved in one liter of benzene. Blend the two solutions allowing sufficient time for the adduct to form and precipitate from solution. Filter the solids from the solution and allow to dry.

Blend one gram of the adduct and one gram of the ninhydrin into a heptane solution of ethylhydroxyethylcellulose to form a dispersion. Coat paper with the

so formed dispersion and dry. Pass the so coated paper in contact with a graphic original through a Thermofax machine having a 350 watt infrared heater to produce a sharp deep purple image of the original.

EXAMPLES 47 to 50

Repeat the procedure of Example 46 substituting the following amines for the ethylenediamine.

Example No.	Amine	Remarks
47	Hydroxyethylpiperazine	Sharp, light reddish image.
48	Diethylenetriamine	Sharp, blue-black image.
49	Triethylamine	Sharp, dark blue image.
50	Diethanolamine	Sharp, dark purple image.

EXAMPLE 51

Following the procedure of Example 46, form an adduct of hydroxymethylpiperazine and germanium tetrachloride. Form a solution of one gram adduct, one gram ninhydrin and ethylhydroxyethyl cellulose dissolved in ethanol. Coat a polystyrene sheet to form a transparency suitable for projection.

EXAMPLE 52

Prepare a first solution comprising one mole of silicon tetrachloride dissolved in one liter of benzene. Prepare a second solution comprising one mole of 1,3-diaminopropane dissolved in one liter of benzene. Mix the two solutions and allow time for the adduct to precipitate from solution.

Blend three grams of the adduct and one gram hydrindantin in a heptane solution of ethylhydroxyethylcellulose. Coat onto a sheet of paper and allow to dry.

Pass the so-coated sheet of paper in contact with a graphic original through a standard Thermofax machine having a 350 watt infrared heater to produce a sharp image having an intense purple coloration. This formulation is characterized by very rapid color formation.

EXAMPLE 53

Repeat the procedure of Example 52 with a 1:1 weight ratio of adduct to hydrindantin. The purple image so formed is less intense in color with slower speed.

EXAMPLE 54

Repeat the procedure of Example 52 using a 2:1 weight ratio of adduct to hydrindantin. This produces the most desired color at moderate speed and is a preferred composition.

EXAMPLE 55

Repeat the procedure of Example 52 substituting ethylene-diamine for the 1,3-diaminopropane to yield a reproduction having a sharp, intense purple coloration.

It should be obvious that modifications can be made in the embodiments described above without departing from the scope of the invention as defined by the appended claims.

I claim:

1. In a marking sheet responsive to heating to an elevated temperature by changing visually to a contrasting color, comprising, in combination, a support carrying indicator material which changes color by chemical reaction with an amine, and a room temperature stable heat dissociable adduct in intimate association with said indicator material; the improvement wherein said adduct comprises an amine ligand in combination with an acceptor molecule selected from the group consisting of halides and organometallic halides of silicon, germanium tin and lead which adduct dissociates liberating amine at a temperature of at least 50° C.

2. The heat marking sheet of claim 1 where the adduct dissociates liberating amine at a temperature within the range of 50° C. to 150° C.

3. The heat marking sheet of claim 2 where the acceptor molecule is silicon tetrachloride.

4 The heat marking sheet of claim 2 where the acceptor molecule is germanium tetrachloride.

5. The heat marking sheet of claim 4 where the amine ligand is selected from the group consisting of diethylenetriamine, hydroxyethylpiperazine, triethylamine, ethylenediaminetetraacetic acid, 1,3 - diaminopropane and diethanolamine.

6. The heat marking sheet of claim 4 where the indicator material and adduct are coated onto the support dispersed in a resinous binder.

7. In a heat marking sheet responsive to heating to an elevated temperature by changing visually to a contrasting color, comprising, in combination, a paper or clear plastic support carrying indicator material selected from the group consisting of ninhydrin and hydrindantin which indicator material changes color by chemical reaction with an amine, and a room temperature stable heat dissociable adduct in intimate association with said indicator material; the improvement wherein said adduct comprises an amine ligand in combination with an acceptor molecule selected from the group consisting of halides and organo-metallic halides of silicon, germanium, tin and lead capable of dissociating to liberate an amine at a temperature of at least 50° C.

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U.S. Cl. X.R.

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