

[54] **MULTICOLOR ELECTROTHERMIC
RECORDING SHEET**

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[22] Filed: **Mar. 22, 1974**
[21] Appl. No.: **453,907**

[52] U.S. Cl. **346/135, 8/2, 117/36.7,**
204/2, 346/76 R
[51] Int. Cl. **G01d 15/34**
[58] Field of Search 346/135, 76 R; 204/2;
117/36.7; 8/2; 96/1.7; 250/316

[56] **References Cited**

UNITED STATES PATENTS

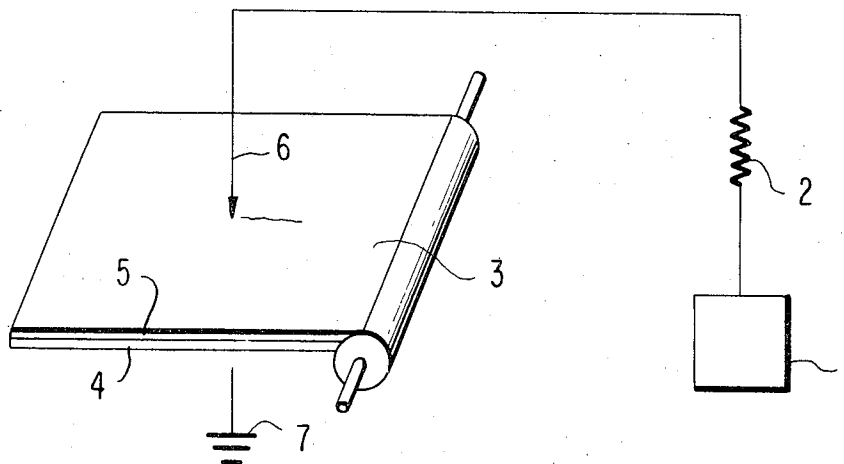
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[57] **ABSTRACT**

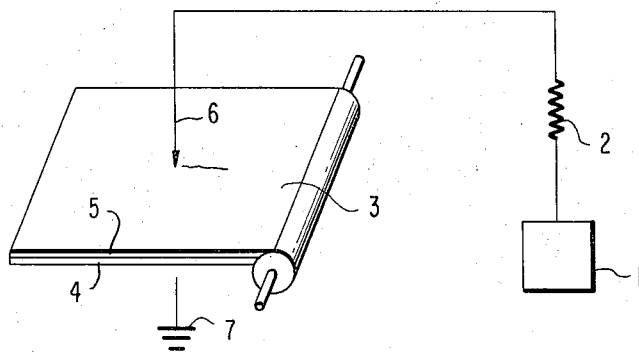
A multicolor electrothermic recording sheet which comprises a support having thereon a layer of a metal compound which can be electrically reduced to a metal or a lower valency metallic compound in a heat sensitive element layer comprising a combination of (1) a polyhydroxy compound or a weak acid compound and (2) a color forming leuco dye which undergoes a color forming reaction upon contact with the polyhydroxy compound or the weak acid compound and a high molecular weight binder, whereby the metal compound is electrically reduced by electrothermic energy to form a metallic color and the leuco dye is thermally developed.

7 Claims, 1 Drawing Figure



PATENTED FEB 4 1975

3,864,684



MULTICOLOR ELECTROTHERMIC RECORDING SHEET

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

This invention relates to a multicolor electrothermic recording sheet wherein multicolor recorded images can be formed by utilizing electrothermic energy and by controlling the signals provided by such energy.

2. DESCRIPTION OF THE PRIOR ART

Hitherto, a method for obtaining electric recording sheets wherein color images are formed by electrical energy is known wherein recorded images are formed on the free metal background having a different color from that of the recorded images by a dry type of electrolysis of a metal compound as disclosed in Japanese Patent Publication No. 22341/63. In the case of forming monochromatic recorded images, such a conventional method is suitable because odorless stable images having a comparatively high density are obtained without the necessity for a high electrical voltage as in an electric discharging recording paper or electrostatic recording paper.

However, in such electrolytic recording papers, it is difficult to obtain distinguishable multicolor recorded images having two or more colors, because the hues of the images are limited by the metal even if two or more metal compounds are used together so as to obtain metal images having a different hue from each other. Further, it is necessary to strictly control the electric voltage - electric current for the electrolysis. Accordingly, such a method is not practically used.

On the other hand, recently it has been necessary to obtain recording sheets which can be recorded at a high speed without carrying out any treatment and can form multicolor recorded images having a high contrast.

In order to meet such requirements and desires for obtaining distinct multicolor recorded images, attempts have been made to combine the element wherein metallic developed images are formed by electrically reducing a metal compound to a free metal or a lower valency metal compound, such as the above described electrolytic recording element, with a heat sensitive element wherein color images are formed thermally and preferably at a temperature of above 100°C. Thus, the production of multicolor images having a high density at a high speed by controlling the electric voltage and the electric current have been successful.

SUMMARY OF THE INVENTION

In the electric recording device used for the present invention, the recording sheet is brought into contact with a recording needle through which an electric current passes by means of the circuit device which can control the electric voltage and the electric current so as to provide a definite electrolysis value to the recording sheet, and thus thermographic development is carried out due to the Joule heat of the electric energy. If necessary, it is possible to change a very low electric energy into a heat energy in an intrinsic sensitive range using two recording devices.

It is also possible in another embodiment of the invention to develop the recording element by controlling the resistance using a resistor while the electric

current or the electric voltage is set at a definite value by a closed circuit.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWING

The drawing is an oblique view of an example of the recording process of the present invention, wherein 1 is a power source, 2 is a resistor, 3 is a recording sheet, 4 is a conductive layer, 5 is an electrothermic layer, 6 is a recording needle and 7 is a ground.

DETAILED DESCRIPTION OF THE INVENTION

In the present invention, it is necessary that the metal compound be stable at a temperature of above 200°C, and thus the heat sensitive element generally causes a color forming reaction at a temperature in the range of above 100 to 200°C. It is also possible that both of the metal compound and the heat sensitive element are subjected to reacting at the same condition.

Accordingly, thermographic color formation does not compete with the gray - black color formation of the metal compound. Further, it is possible to obtain each of the color images even if both of the elements are mixed together, because both image forming materials developed are not compatible with each other. In this case, if a high molecular weight binder is carbonized itself, further excellent metallic color formation can be carried out.

Namely, thermographic color formation is usually carried out at a lower temperature and metallic color formation is carried out at a higher temperature. Further, the resulting images are not only non-transparent but also have a conductivity such as carbon black because the high molecular weight binder is carbonized. Consequently, mixing of both colors hardly occur because a deep gray - black color is formed and bleeding of images which has been often resulted in the prior heat-sensitive elements containing two materials having a different melting point hardly occur in the present invention.

In the following, each component used in the present invention will be illustrated.

The requirements desired for the metal compound used in this invention are as follows: (1) it must be possible to electrically reduce the metal compound to a metallic compound having a different color, (2) the metal compound should be a white or a light color and should be insoluble in water and certain kinds of organic solvents (e.g. petroleum solvents), and (3) the metal compound must be comparatively conductive. Of course, the metal compound should be non-toxic and stable.

Examples of metal compounds are zinc oxide, lead oxide, barium sulfate, lithopone, basic lead carbonate and tin oxide. However, zirconium oxide, titanium oxide, bismuth oxide, silver oxide, nickel oxide, vanadium oxide, antimony oxide, aluminium oxide and calcium oxide, which do not satisfy all of the above described requisites completely, can also be used, if desired.

These metal compounds can be used alone or as a mixture of two or more thereof. Further, the metal compounds can be mixed with a high molecular weight binder or mixed with an aluminum powder, a zinc powder or stainless steel flakes.

Suitable examples of heat sensitive elements which can be used are those described in Japanese Patent

Publication Nos. 4160/1968 and 3680/1969 and U.S. Pat. Nos. 3,451,338 and 3,239,366.

Namely, as polyhydroxy compounds, those compounds having two hydroxy groups are preferably used. The melting point of these compounds basically controls the temperature of thermographic color formation.

Examples of suitable polyhydroxy compounds include 4,4'-isopropylidene diphenol, 4,4'-sec-butylidene-bis-(2-methylphenol), 4,4'-cyclohexylidene-bis-(2-methylphenol), 2,2'-dihydroxydiphenyl, 2,2'-methylene-bis-(4-fluorophenol), halogenated phenol resins, novolak phenol resins and α or β -naphthol, etc. Examples of weak acid compounds are benzoic acid, succinic acid, tartaric acid, citric acid, guanidine nitrate, urea nitrate, boric acid, carbonic acid and other inorganic solid acids (e.g., Kaolin, Bentonite, acidic clay), etc. However, the weak acids are not limited to these compounds. They are added, if desired, in order to control the temperature of color formation.

Typical examples of the leuco dye compounds (especially containing a lactone ring) include Crystal Violet lactone, benzo leuco Methylene Blue, Malachite Green lactone, Rhodamine B-lactam, benzindolino-spiropyran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-7-(N-methylanilino)-fluoran, spiro-(1-benzopyran-2,2'-naphthopyran), 3-diethylamino-6-methoxyfluoran, 3,3-bis-(p-diethylaminophenyl)-phthalide and 1,3,3-trimethyl-6'-chloro-8'-ethoxyindolino-benzospiropyran. These compounds may be used as a mixture of two or more thereof in order to form a different color. It is necessary to add a high molecular weight binder to these leuco dye compounds. Typical examples of suitable high molecular weight binders include gelatin, polyvinyl alcohol, hydroxyethylcellulose, gum arabic, casein, carboxymethylcellulose, methylcellulose and polyvinyl methyl ether-maleic acid anhydride copolymers for an aqueous medium and terpene, cyclized rubber, petroleum resins, acrylic rubber, styrene-butadiene resins, alkyl methacrylate resins, vinylidene chloride resins and nitrocellulose for an organic solvent medium. These resins sometimes change into black carbonized products at the carbonization temperature by controlling the electric current - electric voltage. The composition of these compounds depends upon the thickness of the coating film, conditions of the recording device and kind of dispersion medium. However, the following composition is usually used. Hereinafter, all percentages, ratio and the like are by weight unless otherwise indicated.

Basic Leuco Dye	100 (base)
Polyhydroxy Compound	50 to 1000
Metal Compound	50 to 500
High Molecular Weight Binder	10 to 500

A decrease in the amount of the high molecular weight binder sometimes causes a collapse of the coating layer and an increase thereof interferes with the color forming reaction. Therefore, the amount of the high molecular weight binder should be determined according to the conditions adopted.

As the dispersion medium, water or petroleum is particularly preferred. Alternatively, materials which dissolve only the high molecular weight binder, such as toluene, xylene and ligroin, can be used.

In the present invention, other components such as wax, paraffin, talc, microfine particles of polymers, metal powders, starch, glass powders, calcium carbonate, clay, carbon black, carbon fibers, Orange Yellow, guanidine, polyoxyalkylene derivatives, polyol compounds, surface active agents, ultraviolet ray absorbing agents, fluorescent brightening agents, defoaming agents, hardening agents, etc. can be added thereto. As the support of the sheet, a conductive paper treated so as to have a resistivity below $10^5 \Omega/\text{cm}^2$, thermoplastic films having a vacuum evaporated film of copper iodide, aluminium or zinc, and metal foils can be used.

In the present invention, the recording device shown in the appended drawing can be used. As the power source, either a direct current source or an alternative current source can be used. However, a direct current source is more preferred.

A device having a variable resistor in a closed circuit so as to control the electric current - electric voltage and a device which can control the intrinsic reduction value of the metal compound by increasing the electric current - electric voltage can be used. Such devices are described in U.S. Pat. No. 3,299,433 and Japanese Patent Publication No. 22341/1963.

The electrothermic recording sheets of the present invention can be used, for example, for computer outputs, printing typewriters electric calculators, tachometers, automatic recording devices, facsimiles, oscillography, reproduction of television images, automatic drawing instruments, astronomical observation recorders and electrocardiograms, etc.

In the following, the present invention will be illustrated in greater detail by reference to the examples. However, the scope of the present invention is not to be interpreted as being limited to these examples. Unless otherwise indicated, all parts, percents, ratios and the like are by weight.

EXAMPLE 1

A sheet of paper having a weight of 40 g/m² was laminated with an aluminium foil having a thickness of 1.5 microns. A coating solution having the following composition was applied to this sheet in a thickness of 5 μ .

A	ZnO	80 g
	Terpene Resin	20
	Petroleum (kerosine)	100
	(boiling point, about 200°C)	
B	Crystal Violet lactone	12
	Terpene Resin (Piccolite,	30
	produced by Esso Co.)	
	Petroleum (kerosine)	500
B'	4,4'-Isopropylidene-diphenol	45
	Terpene Resin	20
	Petroleum	250

(Ratio of A, B and B' is 5 : 1 : 1)

Using the resulting recording sheet, recording was carried out under the following conditions in the same manner as that shown in the appended drawing.

Electric Voltage:	100 V	} A blue color appeared.
Electric Current:	80mA	
Electric Voltage:	70 V	} A black color appeared.
Electric Current:	40mA	

The electric current - electric voltage condition depends upon the film thickness, the ratio of each component and the type of the recording device, etc.

EXAMPLE 2

A dispersion having the following composition was applied as a first layer in a thickness of 3.5 microns to a white film sheet comprising polycarbonate (50 μ) and cupric iodide (5 μ) prepared by vacuum evaporation which was treated so as to be conductive (10.3 Ω/cm^2).

A	Ligroin	100 g
	Styrene-Butadiene Resin (8:2) (Dow Latex No. 620, produced by Dow Chemical Company)	12.5
	4,4'-Isopropylidene-diphenol	12.5
B	Ligroin	100
	Styrene-Butadiene Resin (as defined above)	12.5
	N-Phenyl Rhodamine B Lactam	12.5

To the coated layer, the following coating solution was applied in a thickness of 30 microns.

Zinc Oxide	40 g
Barium Sulfate	40
Polymethyl Methacrylate Resin	20
Toluene	100

This recording sheet had a somewhat light grayish color. Images having the following colors were obtained using this recording sheet at an electric voltage of 100 V by changing the electric current as follows.

85mA Reddish violet color

50mA Grayish black color

It can be understood that the images obtained were those which had been reproduced as a distinguishable distinct signal image.

EXAMPLE 3

Zinc was deposited by evaporation (50 - 120A) on a polyester film having a thickness of 70 microns, and then a coating solution having the following composition was applied to the resulting zinc layer so as to form a recording layer having a thickness of 3.5 microns.

A	Phthalic Acid Anhydride	15 g
	Polyethyl Methacrylate	7
	Toluene	50
B	Ligroin	80
	Polyethyl Methacrylate	15
	3,3-bis-(p-Di-n-butylamino-phenyl)phthalide	5
C	Aluminum Flakes	5
	Zinc Oxide	65
	Zirconium Oxide	10
	Saran (trade name of Asahi Dow Chemical Company, vinylidene chloride : vinyl chloride = 8:2)	20
	Xylene	100
	A : B : C = 1 : 2 : 5	

In this recording sheet, a brownish black image was formed at 160V and 25mA, a deep blue image was formed at 120V and 70mA, and a nearly black image was formed at 160V and 50mA.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A multicolor electrothermic recording sheet which comprises a support having thereon a layer of a metal compound which can be electrically reduced to a metal or a lower valency metallic compound in a heat sensitive element layer comprising a combination of (1) a polyhydroxy compound or a weak acid compound and (2) a color forming leuco dye which undergoes a color forming reaction upon contact with said polyhydroxy compound or said weak acid compound and a high molecular weight binder, whereby said metal compound is electrically reduced by electrothermic energy to form a metallic color and said leuco dye is thermally developed.

2. The recording sheet of claim 1, wherein said polyhydroxy compound is a dihydroxyphenol.

3. The recording sheet of claim 1, wherein said weak acid compound is an organic acid.

4. The recording sheet of claim 1, wherein said leuco dye is a leuco dye containing a lactone ring.

5. The recording sheet of claim 1, wherein said metal compound is a compound of a metal in a low oxidation state.

6. The recording sheet of claim 5, wherein said metal compound is an oxide or hydroxide.

7. The recording sheet of claim 6, wherein said metal compound is zinc oxide, lead oxide, antimony oxide, zinc hydroxide, barium hydroxide, or barium sulfate.

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