Patented May 5, 1953

2,637,657

UNITED STATES PATENT OFFICE

2,637,657

THERMOSENSITIVE PAPERS AND COMPOSITIONS THEREFOR

Karlis V. Ozols, Brooklyn, N. Y., assignor to Product Development Laboratories, Inc., New York, N. Y.

No Drawing. Application June 10, 1946, Serial No. 675,817

6 Claims. (Cl. 106—178)

1

The present invention relates to thermosensitive recording papers and to compositions for surfacing or coating the same, and it particularly relates to thermosensitive papers upon which a permanent record may be made by the use of a heated tracing device or arrangement.

In making heat sensitive papers or, as they may also be termed, pyro-recording sheets or thermographic papers, it has been necessary to use materials sensitive to light and to expose them to light before subjection to heat which required quite a high temperature and did not give as satisfactory a trace in color and permanency as would be desired.

Many of these papers require complicated and delicate mechanism effectively to apply the heat to the composition or coated paper and to obtain the desired record and subsequently require special handling or after-developing and in all cases are very sensitive to temperature and humidity changes of the surrounding atmosphere.

It is among the objects of the present invention to provide improved thermosensitive recording papers and compositions therefor which are more sensitive to heat than other known compounds or compositions and which may be readily utilized without specific treatment beforehand or development afterward and which will be highly stable regardless of varying temperature and humidity, and upon heat inscription thereon will give a trace or record of desirable dark color and contrast which will have superior permanency.

Another object is to procure a coating composition which may be readily applied to a recording sheet of paper or other fabric, which will be non-cracking and which will flex with the paper and not flake or peel off, which after application will readily dry without efflorescence, hygroscopicity of deliquescence and may be readily handled, and which will produce non-smudging and non-fading recordings of high permanency regardless of exposure to atmosphere, prolonged storage under ordinary conditions.

A further object is to prepare an improved inexpensive thermosensitive recording paper upon which recordings may be readily produced without expensive or delicate mechanisms and without elaborate controls and which may be operated upon by a heated stylus, by focused infra-red rays, by high voltage spark discharge or by

2

passing current through a conducting or graphited sheet, by concentrated blasts of hot air or superheated steam or other heat sources.

A further object is to provide thermosensitive recording paper, devoid of wax, which will make satisfactory non-smudging dark recordings of desired contrast to a white background at a relatively low temperature without loss of all the fine detail of the recording, which paper will not be sensitive to varying atmospheric temperatures and humidities.

Still further objects and advantages will appear in the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes therein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

It has been found that certain metal salts, particularly heavy metal salts which are stable at ordinary temperatures, may be decomposed at high temperatures to form a marking or recording of the metal or metal oxide, but these high temperatures cannot normally be attained by the recording instruments employed for marking thermosensitive recording sheets. Lead formate has been found to be the most effective heavy metal salt, although other heavy metal salts, such as mercury salts, iron salts, lead salts, zinc salts, silver salts and titanium salts may also be employed.

It has been discovered, however, that when these metal salts are mixed with other salts or compounds which decompose at a lower temperature within the effective heat range of a recording instrument, the heat given off by the decomposition of said last mentioned salt or compound added to that applied by the recording instrument will result in effective decomposition of the first mentioned salt giving the recordation. The last mentioned salt or compound giving rise to the exothermic decomposition may or may not give a visible recording on decomposition, but in the preferred form the decomposition products of both salts or compounds give rise to the desired recordation or marking.

For example, although a heated recording instrument may actually have a temperature of

350° C. to 550° C. due to the speed of the instrument, conditions of contact and conductivity of the recording sheet, a much lower decomposition temperature will be produced in the body of the decomposable salt or compound on the recording sheet. Actually, often effective temperatures of between 100° C. and 250° C. will be produced upon and in the recording sheet. On the other hand, the most satisfactory record producing salts or compounds may not decompose at temperature below 250° C. and may require temperatures of between 260° C. to 300° C.

A feature of the present invention resides in the provision of a mixture of high temperature (e. g. 250° C. to 300° C.) decomposable trace producing salts, such as lead salts with low temperature (e. g. 150° C. to 250° C.) decomposable heat producing salts, such as mercury or iron salts. Generally it has been found most satisfactory to use a synergistic mixture of relatively heavy metal salts, and desirably of monobasic or dibasic-carboxylic acids, which apparently will sensitize each other and which individually will not be satisfactory in obtaining a recording of desired density and permanency.

Generally a mixture of mercury organic acid salts on one hand and lead organic acid salts on the other hand are most satisfactory and the most desirable combination includes both formates and oxalates.

For example, as lead salts it is possible to employ:

Lead formate (preferred)
Lead thioacetate
Lead thiosulphate
Lead oxalate
Lead thiocyanate
Lead acetate
Lead benzoate
Lead citrate

As mercury salts, it is possible to employ:

Mercuric oxalate (preferred)
Mercurous oxalate
Mercuric acetate
Mercurous acetate
Mercuric thiocyanate
Mercuric benzoate
Mercuric citrate
Mercuric formate
Mercuric tartrate

Mercuric oxide may also be used in lieu of the mercury salts stated.

For example, in connection with the above preferred salts, lead formate will decompose at about 250° C., while mercuric oxalate will decompose at 200° to 250° C. It will be noted that the preferred acids are organic acids, or inorganic acids which are not stable particularly when heated.

The best combination is lead formate and mercury oxalate and it has been found that this combination will not only result in a most permanent dense non-fading dark recording, but will satisfactorily adhere to sulphite paper or bond paper.

The preferred combinations should include a relatively small amount (e. g. 1% to 25%) of a lead or mercury salt which will decompose exothermically on heating and produce sufficient heat to catalyze the reduction or decomposition of a relatively large amount of another trace or record producing salt to similar condition, the final recording consisting of a combination of metals and/or suboxides of the metals in dark contrast to the unaffected white metal salts.

Various non-hygroscopic binders may be used, such as ethyl cellulose, casein, gelatin, albumin, starch, vinylite resins, phenol-formaldehyde resin lacquers and shellac.

As a general example, the following proportionment of the various components may be given:

60 to 80% of lead formate;
5 to 30% of mercuric oxalate;
2 to 15% of ethyl cellulose.

The mercury salt is the preferred sensitizer or activator and usually should be present in minor proportion—say, for example, from 1% to 25% of the lead salt and both salts should be present in a state of subdivision of less than 20 microns and desirably from 2 to 10 microns.

Zinc sulphide and titanium oxide in amounts from 2% to 10% may be added to improve the color and background of the material.

To give several examples:

Example 1

One gram of ethyl cellulose is dissolved in 100 cc. of carbon tetrachloride and 10 grams of finely ground lead formate are added. Then 1 gram of finely ground mercuric oxalate is added. The mixture is brushed or caused to flow upon a strip of sulphite or rag bond paper. Cellophane, plastic strips and metal foil may also be used as a sheet carrier. The paper or carrier may be graphite filled where passage of electric current supplies the heat. When the paper is to be used for marking with a heated stylus, the thickness of the coating may be 0.00020 to 0.00100 inch.

Example 2

Ten grams of lead formate are dispersed in 100 cc. of xylol containing 1 gram of ethyl cellulose. Then there is added 0.7 gram of mercuric nitrate and 0.3 gram of sodium oxalate and the mixture is then pebble milled for 24 hours. Finally it is applied to a carrier.

Example 3

A decomposable salt composition composed of the following may be used:

	Preferred	Range
Lead thiosulphate	30	10 to 40
Lead formate	60	50 to 70
Mercury oxalate	10	5 to 15

All parts by weight.

Example 4

As another decomposable salt composition:

	Preferred	Range
Lead formate	55	45 to 65
Lead oxalate	10	5 to 15
Mercurous oxalate	5	0 to 15
Mercuric formate	5	0 to 15
Lead thiosulphate	20	0 to 30
Zinc sulphide	5	0 to 10

All parts by weight.

Titanium oxide may be used instead of zinc sulphide. Mercuric salts generally are preferred to mercurous salts and give better results.

Example 5

As a most satisfactory composition:

	Preferred	Range
Lead formate	80	60 to 90
Mercuric oxalate	10	5 to 15
Ethyl cellulose binder medium viscosity grade	10	5 to 15

All parts by weight.

As other decomposable salt compositions which may be employed:

Example 6

	Parts by weight
Lead formate	45
Lead oxalate	45
Mercuric oxalate	10

Example 7

	Parts by weight
Lead formate	90
Mercuric oxalate	5
Mercuric acetate	5

Example 8

	Parts by weight
Lead formate	90
Mercurous acetate	10

Example 9

	Parts by weight
Lead oxalate	75
Mercuric thiocyanate	25

Example 10

	Parts by weight
Lead thiosulfate	80
Mercuric acetate	20

Example 11

	Parts by weight
Lead formate	90
Lead oxalate	10

In the above examples, the salts present in smaller quantity may be regarded as the low temperature decomposable heat producing salts, while the salts present in large quantity may be regarded as the high temperature decomposable trace producing salts.

Examples 3, 4 and 6 to 11 above omit the binder.

In these compositions a medium viscosity grade of ethyl cellulose, as a binder, may be used up to 10% by weight, and zinc sulphide or titanium oxide may be used up to 10% by weight. These salts may be placed in the paper pulp when the paper is being made.

Although silver oxalate may be added to the lead and mercury combination, this is not preferred since the lead and mercury decomposition products produce a superior trace in the absence of silver.

Although monobasic and dibasic carboxylates are preferred, tribasic carboxylic acid salts may be used.

The above compositions give much more desirable results than dark colored blue or black wax coated recording papers, in which case the

hot stylus will melt the wax into the paper. These wax coated papers are susceptible to varying atmospheric temperatures and humidities and will frequently smudge very badly and in any case will usually not show fine detail. By "exothermic" as used in the present specification and claims, the applicant includes salts which give off heat upon being decomposed.

As many changes could be made in the above composition and methods of making the same, and many widely varying embodiments of this invention could be made without departing from the scope of the claims, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A thermosensitive salt composition, useful in the form of a thin adherent surfacing provided with a binder to hold it on a flexible carrier sheet and capable of recording a permanent contrasting colored trace when locally heated to an elevated temperature, said composition including a binder and comprising

60 to 80 parts by weight of lead formate
5 to 30 parts by weight of mercuric oxalate
2 to 15 parts by weight of ethyl cellulose.

2. As a thermosensitive composition, a major proportion of lead formate and a minor proportion of mercuric oxalate to sensitize the lead formate.

3. A thermosensitive recording sheet coated with a mixture of a minor proportion of mercuric oxalate and a major proportion of lead formate.

4. A coating composition for a thermosensitive recording paper comprising 1 gram ethyl cellulose, 100 cc. carbon tetrachloride, 10 grams lead formate and 1 gram mercuric oxalate.

5. A coating composition for a thermosensitive recording paper comprising ethyl cellulose, carbon tetrachloride, lead formate and mercuric oxalate, the amount of the mercuric oxalate ranging between 1% to 25% of the lead formate.

6. A thermosensitive composition for surfacing a recording paper comprising one part by weight of ethyl-cellulose, ten parts by weight of finely divided lead formate and one part by weight of finely ground mercuric oxalate.

KARLIS V. OZOLS.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
150,722	Smith	May 12, 1874
423,530	Raymond	Mar. 18, 1890
1,434,432	Donohue	Nov. 7, 1922
1,515,495	Kolle et al.	Nov. 11, 1924
1,685,715	Molz	Sept. 25, 1928
1,689,842	Pauschenberg	Oct. 30, 1928
1,693,369	Cochran	Nov. 27, 1928
1,939,232	Sheppard et al.	Dec. 12, 1933
2,046,823	Johnson et al.	July 7, 1936
2,137,456	Palm	Nov. 22, 1938
2,210,565	Asher	Aug. 6, 1940
2,251,742	Kline	Aug. 5, 1941
2,294,150	Kline	Aug. 25, 1942