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THERMO-SENSITIVE COPY SHEET AND METHOD OF MAKING

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This invention relates to thermo-sensitive copy sheets for the reproduction of printed and written or other graphic matter under influence of heat. More particularly, this invention relates to paper and other similar sheet material coated or impregnated with a heat sensitive material which changes color upon exposure to heat, such as high intensity irradiation. The present invention is also concerned with thermo-sensitive sheet material which undergoes a visual color change in response to contact with a heated stylus or stamp.

Broadly stated, the present invention comprises providing sheet material with a heat sensitive layer including at least two reactants which at normal room temperature do not come into reactive relationship with each other but which, upon the application of heat, undergo a chemical change which results in a change in color. The heat sensitive material includes the combination of at least one substantially colorless zinc lower alkyl or aryl di-substituted di-thiocarbamate, and at least one heavy metal salt of a higher fatty acid which is non-reactive with the zinc salt at normal room and storage temperatures and reactive with the zinc salt to produce a color change at temperatures above the melting point of the zinc salt. These materials are dispersed as a solution or a suspension in an organic solvent. A suitable base material, such as paper, may be coated or impregnated with this liquid material directly. Where the heat sensitive material is desired to be present as a layer on one side of a sheet of base material only, the heat sensitive material is preferably incorporated into a film former or binder and then applied to the base material as a surface coating. The binder may be plasticized as desired or needed. A pigment or filler may be incorporated into the mixture to enhance the appearance of the coated sheet material.

Exemplary zinc di-substituted di-thiocarbamates include the methyl, ethyl, butyl, amyl and phenyl salts. For the preparation of copying paper for use in commercially available thermocopying machines, which operate within the range of about 60° to 120° C., the butyl, amyl and phenyl substituted di-thiocarbamates are preferred materials. Because of their higher melting points, heat sensitive copying paper made with corresponding methyl and ethyl salts require exposure at higher temperatures.

Exemplary heavy metal salts of fatty acids include ferric stearate, ferrous stearate, copper stearate, cobalt stearate, etc. Many different film formers or binders may be used. Exemplary binding agents include cellulose derivatives such as ethyl cellulose, methyl cellulose, cellulose acetate, cellulose acetate butyrate, etc.; vinyl compounds such as polyvinyl chloride and its copolymers, polyvinyl alcohol, polyvinyl butyral, polyvinyl acetal, polyvinyl carbazole, etc.; polyamides; silicone resins; natural rubber and synthetic rubberlike materials; etc. Similarly, wide variation is permitted in the selection of a solvent. It should preferably be a good solvent for the film former or binding agent, but a relatively poor solvent for the zinc salt. The zinc salt preferably exists in the liquid coating as a dispersion or suspension, rather than as a true solution. Exemplary solvent materials include, for example, methylene chloride and a mixture of one part ethanol to four parts toluol. The choice of solvent depends upon the particular film forming binder which is used. The plasticizer must, of course, be compatible with the film former. Suitable inert fillers or pigments include finely divided titanium dioxide, clays, antimony oxide, white lead, calcium carbonate, etc.

The zinc di-substituted di-thiocarbamate and heavy metal salt of a long chain fatty acid are present in the heat sensitive compositions in stoichiometrical amounts, or preferably with an excess of the heavy metal fatty acid salt. The excess of the fatty acid salt insures complete color change of all of the exposed zinc salt. Although not desiring to be bound by any particular theory, it is believed that the color change, which occurs upon the exposure to heat of the thermo-sensitive sheets according to the present invention, is due to displacement of the metal (zinc) of the salts by the metal of the heavy metal fatty acid salt. It is believed that softening or melting of the zinc salt in the heat sensitive layer is necessary to initiate the reaction with the metal fatty acid salt. The reactive ingredients are maintained physically separated in the heat sensitive layer until the layer is softened or melted. Then, there must be sufficient of the metal fatty acid salt to cause substantially complete displacement of the zinc in the zinc di-substituted di-thiocarbamate in order to produce as sharp and clear an impression as possible.

Thin paper sheet is the preferred supporting base material for the heat sensitive coating or layer. The sheet material need only have the ability to pass radiant energy of the wave lengths employed in the copying process. Sources of radiation such as are conventionally used in thermographic copying processes may be used. These include, by way of example, high intensity incandescent lamps, photoflash lamps, electric arc lamps, high energy infrared lamps, and the like. Other film or sheet material capable of being penetrated by radiant energy may be used such as cellophane, transparent plastic film, glass, and the like.

The thermo-sensitive copying sheet material produced according to the present invention may be utilized for contact printing, reflex printing or the inscribing of markings by means of a heated stylus or heated stamp, all as well understood in the thermographic copying art.

The thermo-sensitive copying sheets according to the present invention may be used for the reproduction of printing, writing or other graphic materials as either positives or negatives and from material appearing on one side or both sides of the master sheet being copied.

The invention is further illustrated by the following examples of specific heat sensitive compositions. It is to be understood, however, that these examples are illustrative only and not intended to limit the scope of the invention, which is defined by the claims.

Example 1

A typical heat sensitive composition according to the presnt invention was prepared by admixing ten parts by weight of zinc dibutyldithiocarbamate and ten parts by weight of ferric stearate with 4.9 parts by weight of titanium dioxide and blending in a mixture of 5.4 parts by weight of cellulose acetate butyrate film former and 1.6 parts by weight of a polyester plasticizer therefor in 66 parts by weight of methylene chloride. The solid ingredients were finely divided before incorporation into the composition. This material was applied as a coating to greaseproof paper. The coating was tan or light brown in color. The coating was dried and thereafter exposed to radiant energy in a commercial thermographic copying machine while in contact with printed material. A color change from tan to black occurred in the heat sensitive layer coated on the paper, corresponding to the indicia on the master sheet which was copied. A print of uniform intensity and good fidelity of detail was obtained. The heat sensitive coating had a useful pot

life after mixing of about 8 hours before application to the paper support. The coated paper had good heat stability as determined by exposure overnight in an oven maintained at 150 degrees F. Such paper could still be used to make readable copies.

According to a preferred method, when large quantities of this composition are being prepared, the ferric stearate, titanium dioxide, plasticizer, solvent and binder are initially admixed. This mixture can be stored indefinitely under normal conditions. Then, just prior to use, a portion of this initial mixture as needed is withdrawn and the zinc salt is admixed with it in the required proportion.

Example 2

A further heat sensitive composition was prepared, as described in Example 1, with the exception that the methylene chloride solvent was replaced by a mixture of ten parts of ethanol and 40 parts of toluol. Because this solvent mixture is apparently a better solvent for the reactants, the pot life of the mixture is reduced to about two hours. Apart from this, good results were obtained from copy paper coated with the heat sensitive material, dried and then exposed to a printed master in a commercial thermographic copying machine.

Example 3

A further heat sensitive composition was prepared according to Example 1 with the exception that copper stearate was substituted for ferric stearate. The resulting material, when applied to paper, produced a light green coating. Upon exposure to a master sheet in a thermographic copying machine, the copied indicia appeared in a dark green color in the printed areas.

Example 4

A still further heat sensitive material was prepared according to the formulation of Example 1 with the exception that zinc diethyldithiocarbamate was substituted as the zinc salt. This material was applied to a paper backing as a coating. In order to produce satisfactory copies, exposure to temperature somewhat higher than those attained in commercially available thermographic copying machines is necessary.

Example 5

A heat sensitive material according to Example 4 was prepared substituting zinc dimethyldithiocarbamate. Paper coated with this material likewise requires exposure at temperatures higher than the melting point of the zinc salt which are somewhat higher than those normally attained in present commercially available thermographic copying machines.

Example 6

In a further heat sensitive composition zinc diamyldithiocarbamate is substituted. This material, when applied to paper as a coating and exposed to radiant energy in a conventional thermographic copying machine while in contact with a printed master, produces good copies.

Example 7

In another heat sensitive composition zinc diphenyldithiocarbamate was substituted. Good copies may be produced on paper coated with this composition and exposed in a commercial thermographic copying machine in contact with a printed master sheet.

Example 8

A solution was prepared, according to the formulation of Example 1, of zinc dibutyldithiocarbamate and ferric stearate, but omitting the film former or binder material. Paper was saturated with this material and dried. Upon exposure to radiant energy in contact with a master sheet in a commercial thermographic copying machine good copies were produced. This example suggests the feasibility of incorporating the heat sensitive material into the paper base at some stage in the paper-making operation.

Example 9

Another heat sensitive composition was prepared according to Example 1 with the exception that ferrous stearate was substituted. This material performed similarly to the material containing ferric stearate, both in solution and on a coated sheet.

Example 10

A further heat sensitive coating composition was prepared according to the following formulation in parts by weight:

	Parts
Ethanol	57
Ethyl cellulose	5.4
Ferric stearate	10
Zinc dibutyldithiocarbamate	10
TiO_2 dispersion	6.5
Total	98.9

The ferric stearate and zinc salt are not soluble in the ethanol but are present in the form of a slurry. The ethyl cellulose binder forms a cloudy solution in the straight ethanol. This insolubility of the two active ingredients (stearate and zinc salt) is believed to be the cause of the lighter color coating which resulted and longer pot life of the composition of this example. This material when coated on paper and exposed to radiant energy produced good copies.

Example 11

A still further formulation in parts by weight is as follows:

	Parts
Methylene chloride	25
Cellulose acetate butyrate, ½ sec.	1.2
Cobalt stearate	3
Zinc dibutyldithiocarbamate	3
TiO_2 dispersion	2
Total	34.2

Upon application to paper and exposure to a master sheet in a thermographic copying machine, the copied material produced a green colored print.

It is apparent that many modifications and variations of this invention as hereinbefore set forth may be made without departing from the spirit and scope thereof. The specific embodiments described are given by way of example only and the invention is limited only by the terms of the appended claims.

We claim:

1. A thermo-sensitive copying sheet for the reproduction of graphic images which comprises a base material in sheet form carrying thereon a heat sensitive material comprising a uniformly dispersed mixture of at least one zinc salt selected from the class consisting of zinc lower alkyl di-substituted di-thiocarbamates, the substituted radicals of which have from one to five carbon atoms, and zinc aryl di-substituted di-thiocarbamates, and at least one heavy metal salt of a higher fatty acid which is non-reactive with said zinc salt at normal room and storage temperature and is reactive therewith at temperatures above the melting point of said zinc salt to produce a color change.

2. A thermo-sensitive copying sheet according to claim 1 further characterized in that said zinc salt and heavy metal salt are present on a paper base as a coating dispersed in a film forming binder.

3. A thermo-sensitive copying sheet according to claim 1 further characterized in that said heavy metal salt is present in stoichiometric excess.

4. A thermo-sensitive copying sheet according to claim

1 further characterized in that said fatty acid salt is a heavy metal stearate.

5. A thermo-sensitive copying sheet according to claim 1 further characterized in that said zinc salt is zinc dibutyldithiocarbamate and said fatty acid salt is ferric stearate.

6. A thermo-sensitive copying sheet for the reproduction of graphic images which comprises a paper sheet material coated with a heat sensitive material comprising a uniformly dispersed mixture of zinc dibutyldithiocarbamate and a stoichiometric excess of ferric stearate in a film forming binder.

7. A method of making a thermo-sensitive copying sheet for the reproduction of graphic images which comprises uniformly dispersing in a solvent a heat sensitive material comprising a mixture of at least one zinc salt selected from the class consisting of zinc lower alkyl di-substituted di-thiocarbamates, the substituted radicals of which have from one to five carbon atoms, and zinc aryl di-substituted di-thiocarbamates, and at least one heavy metal salt of a higher fatty acid which is non-reactive with said zinc salt at normal room and storage temperature and is reactive therewith at temperatures above the melting point of said zinc salt to produce a color change; applying said heat sensitive material to a base material in sheet form; and drying.

8. A method according to claim 7 further characterized in that a film forming binder is incorporated into said dispersion of heat sensitive material and said heat sensitive material is applied to a paper base as a coating.

9. A method according to claim 7 further characterized in that said heavy metal salt is present in said heat sensitive material in stoichiometric excess.

10. A method according to claim 7 further characterized in that said fatty acid salt is a heavy metal stearate.

11. A method according to claim 7 further characterized in that said zinc salt is zinc dibutyldithiocarbamate and said fatty acid salt is ferric stearate.

12. A method of making a thermo-sensitive copying sheet for the reproduction of graphic images which comprises uniformly dispersing in a solvent a heat sensitive material comprising zinc dibutyldithiocarbamate, a stoichiometric excess of ferric stearate and a film forming binder therefor; applying said material to a paper sheet material; and drying.

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