THERMOGRAPHIC RECORDING PROCESSES AND MATERIALS

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BY

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THERMOGRAPHIC RECORDING PROCESSES AND MATERIALS

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16 Claims

ABSTRACT OF THE DISCLOSURE

A heat-sensitive recording material comprising a support, a water-permeable hydrophilic colloid layer adjacent said support and an external water-impermeable hydrophilic layer in contact with said colloid layer are subjected to an image-wise action of heat, so that a decrease of hydrophilicity is effected in the heat-exposed areas of said external layer.

The present invention relates to thermographic recording and materials suited therefor.

From the U.S. patent application Ser. No. 421,861 filed Dec. 29, 1964, it is known to record a heat pattern as a differentiation of hydrophilicity and water-permeability in a recording material containing a layer comprising hydrophilic thermoplastic polymer particles, which are dispersed in a hydrophilic binder. The heat-exposed parts of said hydrophilic layer become less water-permeable and less hydrophilic than the unexposed parts so that by treating the exposed recording layer with an aqueous dyestuff solution, a dye-image is obtained.

The image obtained is a legible negative if the heat-sensitive material is exposed to heat in correspondence with the image-markings of a positive original.

The present invention provides recording materials with methods that permit the direct production of positive records from positive originals.

In accordance with the invention, a recording material comprising a water-impermeable hydrophilic surface layer containing (a) hydrophilic melttable substance(s), wherein said surface layer is in contact with a hydrophilic interlayer that in its turn is supported directly or indirectly (i.e. through one or more intervening layers) by a base e.g. a sheet of paper, is subjected to an image-wise or record-wise action of heat, so that a decrease of hydrophilicity is effected in the heat-exposed areas of the surface layer.

In other words, as a result of the modulated heating the recording layer comprising said melttable substance bears a record of the heating pattern in terms of a difference in hydrophilicity and water-permeability. Depending on the composition of the recording material a visible image can be formed by a subsequent development step, e.g., application of an aqueous dyestuff solution, which becomes selectively or differentially absorbed.

The methods and materials according to the invention are intended primarily for document copying and like purpose, but the invention is nevertheless capable of wider application, e.g., for recording data applied as a heat pattern to the recording material responsive to transmitted signals.

The application of the heat pattern may be achieved by heating the image markings of an original while these are in heat-conductive relation with the recording material. Such heating may, e.g., be performed by exposing the original to infrared radiation, the image markings being capable of absorbing such radiation, or by exposing the original to visible light of sufficient intensity, if the image-markings are light-absorbing, the absorbed light being transformed into heat.

One way in which reproductions of matter such as typewritten documents may be performed is by placing the copying sheet with its fusible surface layer against the back or unprinted surface of the document, and then exposing the printed face of the document to infrared radiation. Absorption of radiation by the printed characters results in generation of heat, which is then conducted through the backing e.g. to the heat-sensitive surface, thus producing the desired change in hydrophilicity therein. This "back-printing" method is capable of producing direct reproductions if the original is printed on a satisfactorily thin and heat-conductive paper or other material. This method is not suited, however, for copying from heavy book paper or thin papers heavily printed on both sides.

In "front-printing" the effective radiation first passes through the heat-sensitive copying sheet, which consequently should be sufficiently permeable to the radiation used.

The heat pattern resulting from absorption of radiation at the image markings of the document causes the necessary image-wise heating of the recording material according to whether the image markings make contact with the heat-sensitive surface layer during the exposure or stand in contact with the support, i.e. a very thin heat-conductive support, an image, which is legible through the support (transparent support) or an image, which is legible by reflected light, is obtained.

Selective heating of a recording material of use in the invention can also be realized by image-wise exposing a recording material which contains infra-red and/or visible light-absorbing substance(s) converting absorbed light into heat to infra-red and/or visible light. Said substances can be incorporated in the recording layer itself (the layer comprising the fusible substance), and/or in the adjacent hydrophilic interlayer and/or in the paper or other support. If such radiation-absorbing substance is not incorporated into the recording layer itself, it must nevertheless be in heat-conductive relationship with such layer.

Other heat-sensitive recording materials, which materials comprise light- and/or infra-red-absorbing substances that generate heat in the material to bring about some modification of the properties of a heat-sensitive layer when the material is exposed to suitable radiation, are useful in connection with the present invention. Some specific examples of substances that absorb visible light and infra-red radiation, and which may be incorporated into recording materials according to the invention, are i.e. finely divided carbon particles, e.g. carbon black, and heavy metals in finely divided state e.g. silver, bismuth, lead, iron, cobalt, and nickel. The particle size of these substances preferably does not exceed 0.1μ.

In recording an original according to the invention, the recording material incorporating light- and/or heat-absorbing substance(s), is preferably subjected to a short duration high intensity exposure. During such exposure the image markings may be in heat-conductive relationship with the hydrophilic surface layer. The exposure time preferably does not exceed 10⁻⁴ seconds. In such very short exposure there is insufficient time generated in the image markings to be sufficiently conducted to the said surface layer to bring about an effective change therein; on the other hand the light-absorbing substance(s) in the surface layer are heated and thus provide the necessary heat for melting or softening that layer.

The short duration exposure may be performed by using a flash lamp supplying a light energy of 100 to 1000 watt sec. in a time interval of 10⁻⁴ to 10⁻² seconds.
For obtaining a sufficient image differentiation an energy of at least 0.3 watt sec/cm.² is required.

Of course, gas discharge lamps with a much lower energy output can be used if the emitted energy is homogenously distributed over the image carrier or the recording material. Obviously the exposure may be carried out progressively or intermittently, e.g., it may be a scanning-wise exposure by means of a high-intensity light spot image-wise modulated and rapidly line-wise scanning the heat-sensitive surface layer, or it may be a progressive exposure extending over the entire area thereof, e.g., light of a tube-like radiation source is focussed.

On exposure, the hydrophilic interlayer normally acts as a receiving layer for the molten substance(s) of the hydrophilic layer. The hydrophilic layer and the hydrophobic layer can be composed in such a way that substances thereof become compatible by heating (melting).

The hydrophilic layer is preferably composed of or mainly contains (preferably more than 80% by weight) a hydrophilic substance or a mixture of such substances having preferably a melting point comprised between 40 and 200 °C and a low melt viscosity.

Substances that are preferred in this respect are water-like hydrophilic organic compounds preferably containing higher aliphatic groups with e.g. 10 to 20 carbon atoms more particularly fatty acids and the metal salts thereof, fatty alcohols and esters, fatty acid esters, sterols, fatty ketones, and paraffinic compounds.

Thus, waxes of the known six classes i.e. vegetable, mineral, insect, petroleum, animal, and synthetic waxes can be used.

Carnauba wax, cunicryl wax, candelilla wax, and sugar cane wax belong to the vegetable wax class. Ozokerite, montan wax, and Utah wax are mineral waxes. Bees-wax, shellac wax, and Chinese insect wax belong to the insect class. Paraffin wax is a member of the petroleum class. Woodwax and spermaceti wax from the sperm whale is in the animal class. Chemically modified natural waxes such as the "IG" waxes made from the natural montan wax can also be used. Another modified natural wax is a partly oxidized paraffin that can be a substitute for carnauba wax. Long chain polymers of ethylene e.g. "Epoleine N" marketed by Eastman Chemical Products, Inc., Kingsport, Tenn., U.S.A., halogenated hydrocarbons, e.g. chlorinated or fluorinated paraffin and silicone waxes belong to the synthetic class.

All these waxes can be mixed with each other and/or to some extent with oil. Among the above-mentioned waxes carnauba wax has the best flow characteristics and the best oil retention properties. Vegetable, insect, and animal waxes are usually composed of a mixture of various high-melting fatty acids, alcohols, and esters.

For more details about waxes and wax-like hydrophilic thermoplastic materials reference can be made to "The Chemistry and Technology of Waxes" by A. H. Warth, 2nd ed. 1956, Reinhold Publishing Corporation, New York, U.S.A.

Suitable hydrophobic organic compounds having a wax-like consistency and a melting point comprised between 40 and 200 °C are water-insoluble aromatic compounds e.g. phthalic acid anhydride, biphenyl, solid terpene compounds, and the derivatives thereof such as camphene, camphane, and camphor. Higher aliphatic aldehydes, ketones, ethers, nitrogen-containing hydrophobic organic compounds such as amides, anilides, sulfides, contain e.g. biphenyl sulfone and thiophenone quinone. Halogenated organic compounds such as bromocamphor, carbon tetrabromide, trichlorobenzene, hexachloroethane, and iodofrom.

The hydrophilic interlayers preferably contain or are composed of hydrophobic hardenened or unhardened organic hydrophilic colloids e.g.: (A) Water-soluble natural polymeric substances e.g. agar-agar, alginate, amylose, amylepectin, dextrin, gum arabic, casein, and gelatin;

(B) Modified natural polymeric substances derived from starch, cellulose, and algic acid.

Suitable water-soluble starch derivatives e.g.: (1) Anionic starches—starch acetate, e.g. corn acetate containing 1 to 4% of acetyl groups; starch hydroxyethyl ethers; hydroxyalkylstarch derivatives (e.g. hydroxymethyl- and hydroxypropylstarch derivatives).

(2) Ionic starches (the introduction of carboxyl, sulfonate, sulfate, or phosphate groups into starch permits the preparation of water-soluble alkali metal or ammonium salts of anionic starches. Usually the introduction of amino groups permits the preparation of cationic starches e.g. tertiary aminoalkyl corn starch).

Suitable water-soluble cellulose derivatives are e.g.: (1) Non-ionic cellulose derivatives (this category includes methylcellulose, hydroxyalkylcellulose derivatives and polyoxymethylcellulose derivatives).

(2) Ionic cellulose derivatives (the introduction of carboxy, sulfonate, sulfate, or phosphate groups into cellulose permits the preparation of water-soluble alkali metal or ammonium salts of anionic cellulose derivatives).

Suitable anionic cellulose gums are e.g.: carboxymethylcellulose, methylcellulose-m-sulphobenzoate, ethylcellulose sulphonate and acetylsulphonate cellulose sulphonate.

(C) Completely synthetic water-soluble resins.

Among these resins there can be mentioned: (1) Water-soluble homo- and co-vinyl polymers containing e.g. vinyl alcohol, N-vinyl-pyrrolidone, vinyl methyl ether, acrylic acid, methacrylic acid, maleic acid, acrylamide, or styrene sulphonate acid units.

(2) Water-soluble homo- and copolymers containing alkylene oxide units such as ethylene oxide units.

(3) Water-soluble polycondensates e.g. water-soluble alkyl resins and water-soluble polyester compounds.

(D) Hydrophilic water-insoluble but water-permeable polymers, e.g. ethylcellulose.

Among the above-mentioned polymers particularly those with polar and non-polar groups in the same molecule, e.g. wetting or emulsifying agents.

Examples of suitable ionic emulsifying and wetting agents are: the sodium salt of oleylauride, sodium stearate, beudatdecylbenzimidazolium sulphonate acid sodium salt, sodium sulphonates of higher aliphatic alcohols e.g. 2-methylhexanol sodium sulphonate, sodium di-isocetyl sulphosuccinate, sodium dodecyl sulphate and tetradecyl benzene sulphonate acid sodium salt. Examples of suitable non-ionic emulsifying agents are: saponine, condensation products of alkyl phenols and ethylene oxide, e.g. octylphenyl polyglycol ether, isononyl oxyethyl ether, and polyethylene glycol oleate.

A survey of emulsifying agents and wetting agents, representatives of which can be applied according to the present invention, is given by Gerhard Grawalek "Wasch- und Netzmittel," Akademieverlag, Berlin (1962).

The hydrophilic interlayer may contain all kinds of image-forming substances, e.g. the hydrophilic interlayer may contain light-sensitive silver halide, developing substances thereof, developing nuclei for complexed silver halide, catalysts for colour reactions, dyes, which are soluble in water and/or organic solvents, metal particles, which can be etched away and fillers with a substantially hydrophilic character e.g. barium sulphate, zinc oxide, titanium dioxide, and silica.

The support of the recording material may be porous or non-porous. For instance it may be composed of fibers such as paper, or it has a screen-printed record as a nylon gauze or it can be a non-porous material such as glass, glazed porcelain, a metal foil, a natural or synthetic resin film, a resin impregnated porous material, or a support coated with a metal film, foil, or hydrophobic resin layer.
When applied to a porous support the hydrophilic interlayer prevents the hydrophobic substances from penetrating into the support. A particularly suitable base material is glassine paper, which is a hydrophilic transparent paper base material and which is preferably coated with a fat-absorbing hydrophilic interlayer containing emulsifying or wetting agents.

Suitable fat-permeable paper supports are coated papers (papier couché e.g. art printing paper).

The hydrophilic interlayer, if any, preferably has a thickness not greater than 10μ. The hydrophobic meltably layer preferably has a thickness varying between 2 and 20μ.

The hydrophobic meltably recording layer is preferably applied in the form of a solution in an organic solvent that does not dissolve the hydrophilic interlayer, e.g. a solvent that is not miscible with water. After coating the hydrophobic layer must possess a tight structure, i.e. it should be water-impermeable. Depending on the type of hydrophobic substance the hydrophobic layer can also be applied advantageously by sublimation e.g. in vacuum or under atmospheric conditions at elevated temperature. Sublimable substances, which can be applied in that way, are e.g. phthalic anhydride, diphenyl, and camphor.

A result of the image-wise or record-wise heating, the hydrophobic substances in the hydrophobic layer melt in correspondence with the heat pattern. If the underlying hydrophilic layer contains polymeric hydrophilic substances that become compatible with the molten hydrophobic substances, said hydrophobic substances diffuse into the hydrophilic layer in other words they fuse homogeneously with the hydrophilic substances.

In order to determine, whether a hydrophobic substance is suited or not to become compatible, while in fused state, with a given hydrophilic polymer, a method can be applied, which consists in determining the melting point of the hydrophobic fusible material alone and of the mixture of said fusible material with the polymer chosen. Prior to the determination of the melting point the mixture must have been heated beyond the melting point of the hydrophobic substance and then cooled. In this test a substantial increase in the melting point of the said mixture beyond that of the fusible material alone indicates that the substances are compatible, whereas a substantially unchanged melting point indicates a lack of compatibility. In this type of test the hydrophilic polymer alone has a melting or softening point higher than that of the hydrophobic fusible substance.

The heat-exposed material can be developed e.g. by applying to the image-wise or record-wise heat-treated hydrophobic layer a hydrophilic solution e.g. an aqueous dyestuff solution that penetrates into the recording material in correspondence with the heated areas.

When penetrating into the heated areas that are rendered water-permeable, the hydrophilic solution, which can be considered to be a developing solution, can according to a special embodiment form therein a dyestuff image upon reaction with colour-forming components. The developing solution according to the latter embodiment may contain a diazo coupling agent whereas the recording material may comprise a suitable coupling partner therefor. The developed element can now be used as such, or as a master for making multiple copies by printing. If the dyestuff has a water-soluble character, the obtained copy can be used as a hydrotype printing master. If the dyestuff absorbed in the recording material is soluble in a lower aliphatic alcohol, the obtained master can be used for hectographic printing. In the latter case the hydrophobic layer is obviously insoluble in the alcohol used for the printing.

In this connection it is interesting to note that according to a particularly interesting embodiment a hectographic printing master can be obtained by simple image-wise heating of a recording material according to the present invention, which in the hydrophilic interlayer or a layer in water-permeable relationship therewith contains a dyestuff, which is suited for hydrotype or hectographic printing. Dyes suited for hectographic printing have a hydrophilic character, such as ethanol- or water-soluble dyes e.g. triphenylmethane dye salts.

According to another special embodiment a recording material is used containing in the porous and/or hydrophilic element substances that can be bleached or etched by the action of substances present in a hydrophobic developing liquid.

In this respect reference is made e.g. to colloidal silver, which can be bleached by a common photographic bleaching bath preferably containing potassium hexacyanoferrate (III). Use can also be made of oxonol dyes, which as generally known are used in dischargeable filter and antihalation dye layers in common silver halide photography and can be bleached by a solution having reducing properties e.g. a photographic silver halide developing bath.

The following examples illustrate the present invention.

**EXAMPLE 1**

Onto a porous paper web a hydrophilic interlayer was coated at a rate of 20 sq. m. per litre from the following composition:

- Carboxymethylcellulose, g. .......... 20
- 12.5% aqueous solution of saponine, cc. ---- 10
- Water, cc. .................................. 970

After having been dried this interlayer was coated twice at a rate of 20 sq. m. per litre with the following hydrophobic composition:

- Carbon tetrachloride, cc. ............... 975
- Behenic acid, g. ................................ 25

The material was then dried at room temperature.

**EXAMPLE 2**

On a translucent glassine paper of 60 g./sq. m. a hydrophilic interlayer of the following composition:

- Hydroxyethylstarch, g. .................. 20
- 12.5% aqueous solution of saponine, cc.---- 10
- Water, cc. .................................. 970

was coated at a rate of 20 sq. m. per litre.

To the dried interlayer a hydrophobic layer of the following composition:

- Carbon tetrachloride, cc. ............... 950
- Beeswax, g. ................................ 50

was applied at a rate of 20 sq. m. per litre. After having been coated the material was dried at room temperature.

**EXAMPLE 3**

A cellulose triacetate support provided with a gelatin nabbing layer was coated at a rate of 20 sq. m. per litre with a hydrophilic interlayer from the following composition:

- Gelatin, g. ................................ 50
- 12.5% aqueous solution of saponine, cc.---- 10
- Water, cc. .................................. 940

To the dried interlayer a hydrophobic layer was applied at a rate of 20 sq. m. per litre from the following composition:

- Microcrystalline petroleum wax having a melting point of 76-79° C. sold under the trade name Warco Wax 170A Yellow (a wax manufactured by Warwick Wax Co., Inc., U.S.A.), g. .............. 50
- Carbon tetrachloride, cc. ............... 950

The layer was dried at room temperature.

![Image](image-url)
### EXAMPLE 4

A hydrophobic coating consisting of biphenyl was applied by sublimation to a starch-coated paper weighing 90 g. per sq. m. The sublimation was carried out by heating the biphenyl to 70° C.

The resulting material was processed in the same way as the materials of Example 1 according to the following procedure:

- The image markings of an original presenting a carbon-ink printed text on a paper base were brought in contact with the support of the recording material. The recording material in contact with the original was reflectographically exposed to infrared radiation by means of an Ormig (trade mark) thermographic copying apparatus. The hydrophobic layer side of the exposed recording material was then brought in contact with an aqueous dye solution containing 2% by weight of a 50:50 mixture of malachite green and fuchsin. In this way a legible positive copy was obtained from the original.

- The materials described in the Examples 2 and 3 were exposed to infra-red light in the same way as described above, with the proviso however, that during the exposure the hydrophobic layer was placed in contact with the image cylinder of 44 having a diameter of 8 cm. of the above-described aqueous dye solution to the hydrophobic layer a very sharp positive image, which was legible through the transparent support, was obtained.

### EXAMPLE 5

The following hydrophobic composition:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Behenic acid</td>
<td>2.8</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>97.3</td>
</tr>
<tr>
<td>Colloidal carbon having an average particle size of 0.1 μ</td>
<td>2.5</td>
</tr>
</tbody>
</table>

This coated twice at a rate of 20 sq. m. per l on a porous paper base of 60 g. per sq. m. provided with a gelatin interlayer coated from a solution of 50 g. of gelatin in 940 cc. of water at a rate of 20 sq. m. per l.

As schematically represented in FIG. 1, the obtained hydrophilic paper 27 containing the hydrophobic meltable layer 20, which contained the infrared and visible light-absorbing carbon particles in such a concentration that the optical density of the layer was 0.50, was pressed against the original 21 (which was a transparency) and a black paper 28 against a glass cylinder 24 having a diameter of 8 cm. of the axis of this cylinder a xenon gas discharge lamp 25, which on discharge between the electrodes 26 produced a radiation energy of 600 watt. sec. in 1/200,000 sec. was placed at a distance of 4 cm. from the original 21 having visible light-absorbing image-markings 22 and background areas 23, which are transparent to visible light.

After exposure the paper 20 was brought in contact with an aqueous dyestuff solution by means of a roller, the dyestuff solution containing 2% by weight of a mixture of malachite green and fuchsin (50:50). The dye was absorbed in the areas of the copying material corresponding to the transparent areas 23 of the original.

### EXAMPLE 6

A subbed polyethylene terephthalate support was coated in a proportion of 50 g. per sq. m. with a layer from the following solution:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gelatin, g.</td>
<td>24</td>
</tr>
<tr>
<td>Sodium stearate, g.</td>
<td>10</td>
</tr>
<tr>
<td>Water to cc.</td>
<td>1000</td>
</tr>
</tbody>
</table>

After drying, a heat-sensitive layer was applied thereto from a suspension of the following composition, which has been ground for 8 hours in a ball mill:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearic acid, g.</td>
<td>200</td>
</tr>
<tr>
<td>Carbon black, g.</td>
<td>1.5</td>
</tr>
<tr>
<td>Carbon tetrachloride, cc.</td>
<td>1000</td>
</tr>
</tbody>
</table>

After evaporation of the solvent, the thickness of this layer amounted to 3 μ.

The material obtained was placed with its heat-sensitive side into contact with the printed side of an original to be copied, and irradiated reflectographically with a flash lamp, irradiating the recording material with an energy of 0.5 watt sec. per sq. cm.

The heat-sensitive material became hydrophilic on the areas corresponding with the white areas of the original. By moistening the irradiated material with a 20% aqueous solution of methylene blue, a transparent negative print of the original was obtained.

### EXAMPLE 7

A cellulose triacetate film base was coated consecutively with the compositions A and 8.

Composition A, after drying, forming a hydrophilic layer of 10 μ:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol, cc.</td>
<td>50</td>
</tr>
<tr>
<td>n-Butanol, cc.</td>
<td>50</td>
</tr>
<tr>
<td>Crystal violet, g.</td>
<td>5</td>
</tr>
<tr>
<td>A 10% solution of bleached shellac dissolved in ethanol, cc.</td>
<td>50</td>
</tr>
</tbody>
</table>

Composition B, after drying, forming a hydrophilic layer of 2 μ:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montan wax, g.</td>
<td>10</td>
</tr>
<tr>
<td>White spirit, cc.</td>
<td>100</td>
</tr>
</tbody>
</table>

The recording layer was reflectographically exposed with its hydrophobic layer in contact with the infrared light-absorbing image markings of a text typed on a common paper sheet. After exposure a hectographic printing master ready for printing with the aid of ethanol as printing liquid was obtained.

### EXAMPLE 8

A polyethylene terephthalate film base was coated consecutively with the following compositions C and D.

Composition C, after drying, forming a hydrophilic layer of 10 μ:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol, cc.</td>
<td>100</td>
</tr>
<tr>
<td>n-Butanol, cc.</td>
<td>50</td>
</tr>
<tr>
<td>Crystal violet, g.</td>
<td>5</td>
</tr>
</tbody>
</table>

Composition D, after drying, forming a hydrophilic layer of 2 μ:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline petroleum wax having a melting point of 76-79° C., sold under the trade name Warco Wax 170A Yellow (a wax manufactured by Waxcray Wax Co. Inc.—U.S.A.), g.</td>
<td>12.5</td>
</tr>
<tr>
<td>Carbon tetrachloride, cc.</td>
<td>100</td>
</tr>
</tbody>
</table>

The recording layer was reflectographically exposed to infra-red light with its hydrophilic layer in contact with the infra-red light-absorbing image markings of a text typed on a common paper sheet.

After exposure a hectographic printing master ready for use with ethanol as printing liquid was obtained.

### EXAMPLE 9

A transparent glassine paper was coated pro rata of 80 g. per sq. m. with the following composition:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polacrylamide, g.</td>
<td>50</td>
</tr>
<tr>
<td>Sodium thioaluminate, g.</td>
<td>1000</td>
</tr>
<tr>
<td>Water, cc.</td>
<td>5</td>
</tr>
</tbody>
</table>

On the dried hydrophilic layer of hydrophobic layer was applied from the following composition:

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcrystalline petroleum wax having a melting point of 76-79° C., sold under the trade name Warco Wax 170A Yellow (a wax manufactured by Waxcray Wax Co. Inc.—U.S.A.), g.</td>
<td>5</td>
</tr>
<tr>
<td>Carbon tetrachloride, cc.</td>
<td>100</td>
</tr>
</tbody>
</table>

The dried hydrophobic layer had a thickness of 5 μ.
9 The recording material was reflectographically exposed to infrad-red radiation with the hydrophobic surface layer in contact with the infrad-red absorbing image markings of a typed text.

After the exposure the surface layer was rubbed with a cotton swab soaked with a 5% aqueous solution of silver nitrate. A very dense black, sharp copy which was legible through the transparent paper support was obtained from the original.

What we claim is:

1. A heat-sensitive recording material comprising a support, a water-permeable hydrophilic colloid layer adjacent said support and an external water-impermeable hydrophobic layer in contact with said colloid layer, said hydrophobic layer consisting essentially of at least one hydrophobic substance which melts on heating and in such molten condition is compatible with said hydrophilic colloid layer.

2. A heat-sensitive recording material according to claim 1, wherein said substance is an organic substance melting between 40 and 200° C.

3. A heat-sensitive recording material according to claim 1 wherein said support is formed of non-porous material.

4. A heat-sensitive recording material according to claim 1, wherein the hydrophobic layer is composed of or mainly contains fatty acids, the metal salts thereof, fatty alcohols, fatty ethers, fatty esters, fatty ketones, paraffinic compounds, or a mixture of such substances.

5. A heat-sensitive recording material according to claim 1, wherein the hydrophobic layer is composed of or mainly contains a natural wax, a chemically modified natural wax, or a synthetic wax.

6. A heat-sensitive recording material according to claim 1, wherein the hydrophobic layer is composed of or consists mainly of an organic sublimable hydrophobic substance.

7. A heat-sensitive recording material according to claim 1, wherein the hydrophilic layer contains a hydrophilic dye.

8. A heat-sensitive recording material according to claim 1, wherein the support is transparent.

9. A heat-sensitive recording material according to claim 1, wherein at least one of the layers of the recording material contains a visible and infrared light-absorbing pigment that converts absorbed light into heat.

10. A recording method, wherein said heat-sensitive material of claim 9 is exposed to a pattern of said light.

11. A recording method according to claim 10, wherein said exposure is of high intensity and short duration.

12. A recording method, wherein said heat-sensitive recording material of claim 1 is subjected to the action of information-wise modulated heat to form a latent image according to said information.

13. A recording method according to claim 12, wherein said latent image is developed with a liquid selectively wetting the heated portions of the surface layer.

14. A recording method according to claim 13, wherein said liquid is an aqueous liquid.

15. A recording method according to claim 14, wherein the aqueous liquid contains a substance selected from the group consisting of a dye, a colour coupler, a catalyst for a colour reaction, and a bleaching agent.

16. A thermographic recording method according to claim 12, wherein the hydrophilic colloid layer contains a dyestuff suited for application in hydrotype or hectographic printing and the external hydrophobic layer, after having been image-wise subjected to the action of heat, is moistened with a hectographic printing liquid and pressed against a printing paper.

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