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PROTECTION OF INFORMATION IN RECORDING MATERIAL

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5 Claims

ABSTRACT OF THE DISCLOSURE

A relief image is formed by exposing to a heat pattern a heat-sensitive recording material comprising a generally uniform layer consisting essentially of a continuous phase of hydrophilic binding agent having distributed therethrough in substantially discrete, generally contiguous relationship a dispersed phase of particles consisting essentially of a hydrophobic thermoplastic polymer, in a weight ratio relative to the binder phase in excess of 1:1, the heat of such pattern being sufficient to at least partially coalesce the polymer particles in the heated area and thereby significantly reduce the fluid permeability of the layer in the heated regions thereof, and thereafter developing the exposed heat-sensitive recording material by washing off the unheated regions thereof of substantially unreduced permeability while leaving the remaining portions of the coalesced particles to form the relief image, is given a protective covering by applying to the relief image with pressure a hydrophilic colloid layer carried on a temporary hydrophobic sheet support, and stripping off the temporary sheet support so as to leave the colloid layer superimposed upon the relief image. Preferably, the colloid protective layer has a thickness of 3–10 μ and preferably the hydrophilic colloid layer is wet with an aqueous liquid which can contain a softening agent for the hydrophilic colloid when the colloid layer is applied to the relief layer.

The present invention relates to the protection of images that are present in or built up by portions of coatings of a rather soft structure.

The present invention more particularly relates to the use of a protective coating that is transferred according to a stripping off technique to a thermographic recording material containing an image to be protected against mechanical damage.

In practice each rather soft recording layer composed e.g. of hydrophilic colloids and not containing a protective surface coating has to be handled with great care in order to avoid complete or local degradation of an image contained therein.

In the silver halide photography specially hardened protective coatings known under the name "antistress-coating" are generally used for the surface protection of light-sensitive silver halide emulsions and silver or colour images formed therewith.

Thermosensitive materials comprising recording layers that are composed so that they undergo a change of water-permeability by the action of heat are also rather soft and

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they can be scratched easily. Therefore, it is desirable for improving the durability of the patterns or copies obtained therewith, to protect them by means of a surface protective coating.

A method has been found for protecting an image present in or built up by portions of a heat-sensitive recording layer that has been exposed information-wise to heat and has the property of undergoing a change in water-permeability by the action of heat, comprising the step of transferring to such exposed layer or portions thereof a hydrophilic protective colloid layer stripped off from a temporary support.

Heat-sensitive recording materials undergoing a change in water-permeability by the action of heat are described e.g. in U.S. Pat. 3,476,937 granted Nov. 4, 1969.

A heat-sensitive recording material that is preferably used in conjunction with a protective layer applied according to the present invention comprises a heat-sensitive recording layer undergoing a reduction in water-permeability by heating and incorporating particles composed wholly or mainly of a hydrophobic thermoplastic polymer dispersed in a hydrophilic binder. Preferably the ratio of said polymer particles to said binder is at least 1:1 (by weight) and more preferably at least 3:2. The heat-sensitive recording layer contains preferably at least 50% by volume of the dispersion of said polymer particles in said hydrophilic binder. More particulars about the polymer particles and suitable hydrophilic binding agents are described in the above-identified U.S. patent.

The information-wise heating of the above-described heat-sensitive materials may proceed according to any heating technique useful in the art. According to a particularly suited information-wise heating a recording layer comprising a hydrophilic binder incorporating said dispersed hydrophobic thermoplastic particles in heat-conductive relationship with infrared and/or visible light-absorbing substances is image-wise exposed to infrared radiation and/or visible light. The exposure is preferably a short duration exposure with a flash lamp as described in the published Dutch patent application 6606719. The heat produced in said substance(s) and conducted to the thermoplastic particles produces in the recording layer a decrease in water-permeability and water-solubility.

In the heat-sensitive recording layers described above a visible image can be developed in different ways. A survey of developing methods is given in the above-identified U.S. patent.

Preferred developing techniques are based on (1) the use of the difference in water-permeability created in the recording layer by information-wise heating and (2) the use of a different removability of selected portions after information-wise heating and wherein the removal of the more water-permeable portions is carried out e.g. by washing away preferably whilst softly rubbing the information-wise heated recording layer.

According to the first developing technique black-and-white or colour images can be produced by image-wise diffusion of substances into the information-wise heated recording layer. Said substances can image-wise colour the recording layer or image-wise etch or bleach out coloured substances contained therein.

According to the second developing technique the recording layer is image-wise removed and contains (a) non-differentially coloured substance(s) before its image-wise

heating. As a result of the removal of selected portions of the recording layer a relief colour image is left. When applying this technique it is important to use a recording layer, which is adhered strongly enough to its support in order to prevent complete removal by rubbing. Suitable subbing layers for the above recording layers containing hydrophobic thermoplastic polymer particles dispersed in a hydrophilic binder are described in the U.S. application Ser. No. 608,571 filed Jan. 11, 1967, now abandoned and replaced by application Ser. No. 91,864, filed Nov. 23, 1970.

Both types of images i.e. those produced by selective penetration of colouring or bleaching developing liquids and those produced by selective washing away of the portions of the recording layer having a higher permeability to water are protected according to the present invention by means of a covering layer applied thereto by stripping off from a temporary support.

The article of manufacture used in the present invention is a sheet material that contains a stripping layer composed of (a) hydrophilic colloids(s) and that is coated on a rather hydrophobic temporary support. The adhering power of the transferable stripping layer to its temporary support, preferably a flexible one, has to be adjusted in such a way that an easy stripping off of the temporary support is possible after pressing, preferably in wet state, of the image-containing or image-forming portions of the heat-sensitive recording layer against the stripping layer.

So, a relatively hydrophobic temporary support e.g. an unsubbed cellulose triacetate sheet, a polystyrene sheet or sheet of copoly(vinyl acetate/vinyl chloride) is used. According to a preferred embodiment the stripping coating is composed in such a way that its adherence in wet state to the temporary support is weaker than in dry state. This can be attained by the use of hygroscopic agents e.g. a water-soluble organic hygroscopic compound such as glycerol and the use of wetting agents and plasticizing agents, e.g. latices, among which the soft latices i.e. those having a softening point below room temperature (20° C.), are preferred.

The stripping layer is preferably a hydrophilic colloid layer e.g. composed of gelatin or modified gelatin forming a hydrophilic membrane.

The thickness of the stripping layer is usually less than 10 μ , and is preferably comprised between 3 and 10 μ .

The contacting of the image-containing recording layer or remaining relief portions thereof is performed advantageously between pressure rollers made of not too hard a material e.g. made of a not too highly vulcanized rubber or a synthetic rubber such as chloroprene. Leaving the nip between the rollers, the temporary support is peeled off from the stripping layer, which as a protective layer covers the image-containing recording layer or relief portions thereof.

The contacting of the stripping layer with the recording layer or portions thereof preferably proceeds in wet or slightly moist state. In order to improve the stripping, the wetting liquid may contain a softening agent for the colloid of the stripping layer, which colloid preferably acts as binder in the recording layer. A preferred softening agent for gelatin is urea. The aqueous wetting liquid used in the stripping operation may also have a temperature above room temperature e.g. 35° C., providing a same effect as the softening agent.

In order to improve the protection offered by the transferred protective colloid layer the latter is hardened to some extent after its transfer. Suitable hardening agents for hydrophilic colloids are generally known to those skilled in the art, e.g. a stripping layer containing gelatin, is hardened with formaldehyde.

The present invention is particularly useful for the protection of thermographically produced half-tone images, wherein the image parts are built up by lines or screen dots produced by selectively washing out of a heat-sensitive recording layer containing said thermo-

plastic polymer particles dispersed in a hydrophilic binder.

A detailed description will now be made of the composition and structure of a preferred stripping material, the use thereof, and the results obtained. The ratios given are by weight if not otherwise indicated.

EXAMPLE 1

A polyethylene terephthalate support (permanent support) of 0.1 mm. in thickness was coated with the following composition at a ratio of 15 g. per sq. m.

G.

40% aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000	15
20% aqueous dispersion of copoly(vinylidene-chloride/N-butylmaleimide/itaconic acid) (88/10/2) with an average particle size of 0.1 μ	15
30% aqueous dispersion of silica with an average particle size of 0.025 μ	15
Water	864
Ethanol	100

The subbing layer thus obtained was dried at 45° C. A green heat-sensitive layer for use in a washing-away development by rubbing with a cotton pad soaked with water at 20° C., was coated on this subbing layer at a ratio of 18 g. per sq. m. from the following composition:

G.

20% aqueous dispersion of poly-N-vinyl pyrrolidone	75
Water	433
40% aqueous dispersion of polyethylene as described above	156
Luconyl-grün CN Teig (a green pigment insoluble in water, sold by Badische Anilin- & Soda-Fabrik A.G., W. Germany)	110
3% aqueous dispersion of the sodium salt of tetradecyl sulphate	40
Ethanol	80

The heat-sensitive layer was dried at 40° C. and it was contacted with an opaque separation line-work positive (on white paper base) containing a silver image corresponding with those parts that are green on a geographic map (the original) and exposed to infrared radiation in a thermographic copying apparatus, whereby the recording layer was heated in correspondence with the infrared-absorbing image-markings of the positive. After the exposure the recording layer was removed at the non-heated areas by rubbing it with a plug of cotton soaked with water. A positive green transparent copy of the original was obtained.

Onto the green relief image formed on the said permanent support a red heat-sensitive recording layer was transferred by stripping off from a temporary cellulose triacetate support (thickness 0.08 mm.) coated with a stripping layer at a ratio of 50 g. per sq. m. with following composition:

G.

10% aqueous gelatin solution	400
Water	550
5% aqueous solution of saponine	15
5% aqueous solution of Hostapon T (a surfactant sold by Hoechst A.G., W. Germany)	15
Glycerol	5

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After setting and drying at 25° C. the red heat-sensitive recording layer was coated thereon at a ratio of 18 g. per sq. m. from the following composition:

	G.
10% aqueous gelatin solution -----	60
Water -----	628
40% aqueous dispersion of polyethylene as described above -----	160
3% aqueous dispersion of the sodium salt of tetradecyl sulphate as wetting and dispersing agent --	50
Permanent carmin FBB Colanyl Teig (C.I. Pigment Red 146, which is a pigment sold by Hoechst A.G., W. Germany) -----	80

After setting and drying the recording layer was slightly moistened with a 2% aqueous solution of urea and water at a temperature of 20° C. The recording layer, while still being attached through its stripping layer to its temporary support, was then conveyed between two pressure rollers of synthetic rubber and thereby was brought in pressure-contact with the side of the permanent support carrying the green relief image. After a contact time of 5 sec. the cellulose triacetate support (temporary support) was stripped off, thus leaving the recording layer with its stripping layer on the side of the permanent support carrying the green relief image.

After drying the red heat-sensitive recording layer was exposed in the same way as the green heat-sensitive recording layer but using an opaque line-work separation positive (on white paper base) containing a silver image corresponding with those parts that are red in the geographic map.

After the exposure the non-heated portions of the red recording layer were removed with a plug of wadding soaked with a 2% aqueous solution of urea at 20° C.

In an analogous way as described for the red recording layer a blue recording layer was applied that contained instead of Permanent carmin FBB Colanyl Teig 80 g. of Luconylblau B Teig (a pigment sold by Badische Anilin- & Soda-Fabrik, W. Germany).

The thus obtained multicolour image was protected by a surface coating which was a stripping layer applied to a cellulose triacetate support (thickness 0.08 mm.) at a ratio of 50 g. per sq. m. from the following composition:

	G.
10% aqueous gelatin solution (the Bloom Number of the gelatin is 230) -----	400
Water -----	480
5% aqueous solution of saponine -----	15
5% aqueous solution of Hostapon T (a surfactant sold by Farbwerke Hoechst A.G., W. Germany) and having the following structure: -----	15
$\text{H}_3\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CO}-\text{N}-\underset{\text{CH}_3}{\text{CH}_2}-\text{CH}_2-\text{S O}_3\text{Na}$	
Glycerol -----	5

After setting and drying at 25° C. the said stripping layer was slightly moistened with water at 35° C. and pressed in contact by means of pressure rollers against the relief image side of the multicolour copy. When leaving the pressure rollers the cellulose triacetate support was stripped off from the stripping layer, which remained on the multicolour recording layer relief pattern and strongly adhered thereto also after drying.

The finally obtained multicolour transparency was a copy of a geographic map which was suited for projection with an overhead-projector and was sufficiently protected against normal risks of image-damage during normal projection manipulations.

EXAMPLE 2

A poly(ethylene terephthalate) support of 0.1 mm. in thickness, provided with a subbing layer for gelatin,

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was coated with the following composition at a ratio of 30 g. per sq. m.:

	G.
10% aqueous gelatin solution -----	400
40% aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	320
Water -----	240
10% aqueous saponine -----	40
3% aqueous solution of the sodium salt of the condensation product of oleic acid and methyltaurine -----	40
4% aqueous formaldehyde -----	20

The interlayer thus obtained was dried at 30° C.

On this layer a heat-sensitive layer, for use in a washing-away development by rubbing with a cotton pad soaked with water of 20° C., was coated at a ratio of 30 g. per sq. m. from the following composition:

	G.
10% aqueous solution of polyvinyl alcohol -----	45
40% aqueous dispersion of polyethylene as described above -----	60
Water -----	320
Aqueous carbon dispersion containing per 100 g. 53 g. of carbon (average particle size 0.1 μ), 23 g. of water, 18 g. of glycol and 6 g. of nonylphenyl poly(ethylene oxide) -----	8
3% aqueous solution of the sodium salt of tetradecyl sulphate -----	25

After drying, the material was exposed in contact through a negative transparency (a reproduction of a printed text). The exposure was carried out by means of a xenon gas discharge lamp placed at a distance of 4 cm. from the recording layer and having a capacity of 1000 watts/sec., producing light within an exposure time of 1/2000 sec.

After exposure the recording layer was rubbed with a cotton pad wetted with water of 20° C., so that the non-exposed and still water-permeable parts of the recording layer were removed.

The thus obtained black-and-white transparency was protected by a surface coating, which was a stripping layer applied to a cellulose triacetate support (thickness 0.08 mm.) at a ratio of 50 g. per sq. m. from the following composition:

	G.
10% aqueous gelatin solution (the Bloom Number of the gelatin was 230) -----	400
Water -----	480
5% aqueous solution of saponine -----	15
5% aqueous solution of Hostapon T (a surfactant sold by Farbwerke Hoechst A.G., W. Germany) and having the following structure: -----	15
$\text{H}_3\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CO}-\text{N}-\underset{\text{CH}_3}{\text{CH}_2}-\text{CH}_2-\text{S O}_3\text{Na}$	
Water -----	5

After setting and drying at 25° C. the said stripping layer was slightly moistened at room temperature with water containing 2% by weight of urea and then pressed in contact by means of pressure rollers with the relief image side of the black-and-white transparency. When leaving the pressure rollers the cellulose triacetate support was stripped off from the stripping layer, which remained on the recording layer relief pattern and strongly adhered thereto also after drying.

EXAMPLE 3

To a paper support coated with polyethylene and weighing 120 g./sq. m. an interlayer was applied from the fol-

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lowing composition at a ratio of 30 g./sq. m. and then dried at 30° C.

	G.
10% aqueous gelatin -----	200
40% aqueous dispersion of polyethylene (see Example 1) -----	160
Water -----	120
10% aqueous saponine -----	20
50% aqueous solution of the sodium salt of the condensation product of oleic acid and methyltaurine -----	20
4% aqueous formaldehyde -----	10
Polyethylene glycol with an average molecular weight of 20,000 -----	10

On this layer a heat-sensitive layer was coated at a ratio of 30 g./sq. m. from the following composition:

	G.
20% aqueous solution of polyethylene glycol with an average molecular weight of 200,000 -----	200
40% aqueous dispersion of polyethylene (see Example 1) -----	80
Water -----	145
Aqueous carbon dispersion (see Example 1) -----	40
3% aqueous solution of sodium tetradecylsulphate --	25

Recording, development and application of protective coating occurred as described in Example 2.

EXAMPLE 4

A poly(ethylene terephthalate) support of 0.1 mm. in thickness provided with a subbing layer was coated with the following composition at a ratio of 30 g./sq. m.:

	Ccs.
10% aqueous solution of saponified poly(vinyl acetate) containing 98% of vinyl alcohol units, a 4% aqueous solution thereof having a viscosity of 6 cps. at 20° C. -----	200
Water -----	330
40% aqueous dispersion of polyethylene having a particle size of less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	320
50% aqueous dispersion of carbon black -----	100
5% aqueous solution of sodium tetradecyl sulphate --	520

After drying the material had an optical density of 3.5 as measured by transmittance. The material was exposed in contact with a xenon gas discharge lamp having a capacity of 1000 watts/sec. and producing light within $\frac{1}{2000}$ sec., through a continuous-tone negative transparency and a contact screen, each having a maximum optical density of 0.5. For a schematic view of the exposure arrangement, reference can be made to FIG. 1 of the Canadian patent specification 808,106.

After exposure, whereby the exposed areas were rendered relatively water-insoluble, the material was dipped into water and gently rubbed with a cotton pad. The heat-sensitive layer was removed at the non-exposed areas.

A positive true image of the continuous-tone transparency was obtained. It consisted of tiny dots with an equal optical density varying in diameter.

The same results were obtained when the polyethylene dispersion mentioned hereinbefore was replaced by a 40% aqueous dispersion of poly(vinyl chloride) particles having an average size of 0.16 μ and having a molecular weight of 200,000 or a 40% aqueous dispersion of polystyrene particles having an average size of 0.13 μ and having a molecular weight of 50,000.

The thus obtained screen images were protected with a surface coating, which was a stripping layer applied to

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a cellulose triacetate support (thickness 0.08 mm.) at a ratio of 50 g. per sq. m. from the following composition:

	G.
10% aqueous gelatin solution (the Bloom Number of the gelatin was 230) -----	400
Water -----	480
5% aqueous solution of saponine -----	15
5% aqueous solution of Hostapon T (a surfactant sold by Farbwerke Hoechst A.G., W. Germany) and having the following structure: -----	15
$\text{H}_3\text{C}-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CO}-\text{N}-\underset{\text{CH}_3}{\text{CH}_2}-\text{CH}_2-\text{S O}_3\text{Na}$	
Glycerol -----	5

After setting and drying at 25° C. the said stripping layer was slightly moistened with water at 35° C. and pressed in contact by means of pressure rollers against the relief image side of the multicolour copy. When leaving the pressure rollers the cellulose triacetate support was stripped off from the stripping layer which remained on the screen image portions and strongly adhered thereto also after drying.

The transferred stripping layer was hardened by a treatment in a 20% aqueous solution of formaldehyde.

EXAMPLE 5

A 7% aqueous solution of gelatin containing per liter 2 g. of infrared-absorbing colloidal silver was applied in a proportion of 7 g. of gelatin per sq. m. to a polyethylene glycol terephthalate support bearing a subbing layer.

The following composition was coated to the dried support in a proportion of 50 g./sq. m.:

	ML.
1% aqueous solution of gelatin -----	1000
40% aqueous colloidal dispersion of polyethylene having a particle size less than 0.1 μ and an average molecular weight comprised between 15,000 and 30,000 -----	75

The resulting layer was dried below 35° C.

The heat-sensitive recording material was reflectographically exposed to infrared radiation. The heat-sensitive layer became hydrophobic and impermeable to water at the areas corresponding with the areas of the original that reflected infrared radiation. By treating the thus irradiated recording element in a silver-bleaching bath, a negative copy of the original was obtained. The silver image was protected against wear by a protective layer as described in Example 1. Said layer was hardened with formaldehyde.

I claim:

1. In a method of recording information which comprises subjecting a heat-sensitive recording material comprising a generally uniform layer having a thickness of about 0.5–10 μ and consisting essentially of a continuous phase of hydrophilic binding agent having distributed therethrough in substantially discrete, generally contiguous relationship a dispersed phase of particles consisting essentially of a hydrophobic thermoplastic polymer, the weight ratio of said polymer particles to said binder being in excess of 1:1, to heat applied to said layer in a pattern according to said information, said heat being in quantity sufficient to at least partially coalesce said particles in the area of said layer corresponding to said pattern and thereby significantly reduce the fluid permeability of said layer in said at least partially coalesced area, and treating said layer to develop or reproduce said information by washing off the portions of said layer that have a substantially unreduced permeability, leaving the remaining portions of said at least partially coalesced particles forming a relief image, the improvement which comprises wetting with aqueous liquid a protective layer having a thickness of about 3–10 μ carried on a hydrophobic temporary sheet support, said protective layer consisting essentially of hydrophilic colloid containing a

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compound rendering said colloid less adherent to said hydrophobic temporary support when wet than when dry and selected from a hygroscopic compound, a wetting agent, or a plasticizing agent, applying the wetted colloid layer on said support to said relief image under generally uniform mechanical pressure to securely adhere the protective colloid layer to said relief image, and stripping off said hydrophobic support to leave said protective colloid in superimposed adhering relation upon said relief image.

2. A method according to claim 1, wherein said colloid layer is a gelatin-containing layer.

3. A method according to claim 1, wherein said compound is glycerine.

4. A method according to claim 1, wherein the temporary support is a cellulose triacetate sheet.

5. A method as in claim 1 wherein said aqueous liquid contains a softening agent for said hydrophilic colloid.

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