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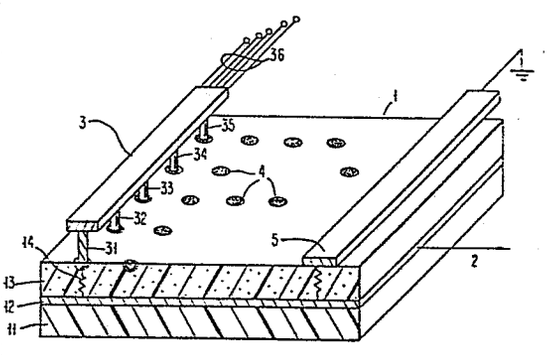
(54) **Printable media for use in non-impact printing and methods of producing such media.**

(57) The drawing illustrates a printable medium 1 comprising paper support 11, conductive film 12 and printing layer 13 associated with writing current probes 31 and 35 and common return electrode 5. A printed letter P is shown.

The layer 13 comprises a thermally sensitive image forming compound and a finely divided conductive material embedded in a suitable carrier. The carrier may comprise a polymer binder e.e. polycarbonate, polyester, polyurethane, Kapton* and the conductive material may comprise suspended particles of, for example, zinc iodide, zinc oxide, tin oxide, titanium dioxide or a mixture. The image forming compound may comprise for example silver behenate, leucoform triphenylmethane dye. Appropriate dye precursors and/or a roughening agent may also be present.

FIG. 1



EP 0 116 313 A2

PRINTABLE MEDIA FOR USE IN NON-IMPACT PRINTING AND METHODS OF PRODUCING SUCH MEDIA

The invention relates to printable media for use in non-impact printing and methods of producing such media. The invention is particularly concerned with an electrothermic printing material on which printing takes place without impact and without application of external heat, by application of electric currents at selected print element positions.

There are a number of prior art non-impact printing techniques, generally involving electroerosion to expose selected print elements, image forming techniques to alter the pigment coloration of areas exposed to radiation, and various offset techniques including electrostatic image development with toners according to copying machine techniques. These techniques may be broadly characterised as treated paper and plain paper techniques.

Each of the prior art techniques has its own advantages and disadvantages, and tradeoffs may be found. Three parameters are paramount in most situations, as follows:

1. Paper cost,
2. Investment in printer,
3. Print quality.

For certain high-quality applications of low volume, image forming techniques such as photography may be used. At higher volumes, however, the cost of image forming treated paper may be prohibitive. For high volume applications, paper cost becomes the major criterion for choice, and it becomes advantageous to make a significant investment in printer equipment in order to use plain paper.

There is a class of medium volume users in which a relatively inexpensive treated paper, even though somewhat more costly than plain paper, is economically advantageous because the related investment in

printer equipment provides sufficient savings to outweigh the extra cost of treated paper. Certain uses demanding high reliability might accept the extra cost of treated paper in order to permit the use of relatively expensive, but very reliable printer equipment, even though the total cost might be greater than that of a plain paper system.

The treated paper systems, in order of paper cost, are:

1. photographic,
2. thermal,
3. electroerosion.

For volume printing, thermal techniques provide a high quality but are relatively slow because of the need for the print element to cool between activations. Electroerosion does not require print element cooling but can be unreliable because the removed material often tends to be redeposited on the print head and significantly affect print quality.

In both thermal printing and electroerosion printing the print element may be subjected to wear because of the need for good thermal contact or because of arc-sputtering electrode loss.

Various techniques for treated paper printing may be typified by the following prior patents:

U. S. Patent 3,074,809, Owen, HEAT-SENSITIVE COPYING-PAPER, January 22, 1963. Heat sensitive back printing copying using a carrier, a heat sensitive layer and a protective layer. The heat sensitive layer, which may be an organic- acid salt of a noble metal (e.g., silver behenate) is reduced by the heat of black portions of the item to be copied.

U. S. Patent 3,320,089, Bourgeois, METHOD OF MAKING BLUSH COATED RECORDING SHEET, COATED SHEET AND COATING COMPOSITION, May 16, 1967. Multi- layer treated stylus-printing heat sensitive paper using a

blushed layer which is rendered clear by local heat so as to expose the underlying dark layer.

U. S. Patent 3,425,858, Echeagaray, HEAT SENSITIVE RECORDING MATERIAL, February 4, 1969. Stylus printing treated heat sensitive paper with a phenolphtalein/acid/alkali oxide composite opaque layer. The composite is of adequate pH for a white indication. Local heat causes the alkali to activate the phenolphtalein as a result of the formation of hydroxides which decrease the pH and result in a localized red indication by the phenolphtalein.

U. S. Patent 4,042,936, Yoshikawa, ELECTRO- SENSITIVE RECORDING METHOD, August 16, 1977. Multilayer thermographic erosion printing by conduction of current from a conductive layer (on a paper substrate) through a dark conductive intermediate layer and a non-conductive white surface layer. The white surface layer is destroyed, leaving the visible image of the dark intermediate layer showing as printing.

U. S. Patent, 4,273,602, Kosaka et al, HEAT- SENSITIVE RECORDING MATERIAL, June 16, 1981. Heat sensitive transfer printing.

U. S. Patent, 4,305,082, Kusakawa et al, ELECTRIC RECORDING SYSTEM AND ELECTRIC HEAT RECORDING SHEET, December 8, 1981, shows a heat sensitive printing material in which heat is generated adjacent to a stylus by an arc or a current from the stylus through a resistance layer to a conductive metal layer, and printing occurs in an underlying thermographic layer heated by heat from the arc or the resistance transmitted by conduction through the conductive metal.

SUMMARY OF THE INVENTION

The invention is a composite electrothermic printing material i.e. a printable medium operating by selective application of electric current to selected print elements. The material includes a substrate treated with a conductive composite electrothermic layer of polymer containing a

thermally sensitive image forming material together with conductive material. Selective application of electric current provides for localized heating of areas of conductive material within the composite electrothermic layer. This localized heating causes thermally sensitive image forming material to change colour. The result of the localized selective current caused heating of appropriate print elements is matrix character or facsimile printing.

Accordingly the invention provides printable medium for use in non-impact printing, said medium comprising a substrate supporting a composite electrothermic layer comprising a thermally sensitive image forming compound and a finely divided conductive material embedded in a carrier.

The printing material includes a substrate coated with a conductive composite electrothermic printing layer of polymer (polycarbonate, polyester, polyurethane, Kapton*) made conductive by suspended conductive particles (zinc iodide, zinc oxide, tin oxide, titanium dioxide, zinc, silver, etc. or a mixture of these). Also incorporated in the polymer layer along with the conductive material is a finely divided, thermally sensitive image forming material (e.g., silver behenate).

The printing stylus does not need to be hot in order to print but must merely carry current. The localized current passing from a printing stylus into the treated paper, provides a localized hot spot which changes colour. The amount then dissipates into a broad area of the conductive polymer to a broad area return electrode for return to ground. An optional aluminium thin layer between the paper base and the thermally sensitive resistive polymer layer provides a convenient and effective dissipating current flow path for return to the broad area return electrode and also results in increased current localization and hence higher resolution and quality printing. The current is dissipated over such a broad area at the broad area return electrode that it does not raise the temperature above the threshold for printing.

*TM

The invention will now be further described with reference to the accompanying drawings in which:

FIG. 1 is an isometric view, semi-diagrammatic in form, showing the treated paper operatively juxtaposed to a multi-stylus print element and to a broad area return electrode.

FIG. 2 is a semi-diagrammatic elevation view showing the relationship of treated paper to print element and broad area return electrode.

FIG. 1 illustrates the preferred embodiment. The printing head 3 or the treated paper composite 1 is driven by means not shown, so that the motion of the paper composite relative to the printhead is as shown by the direction of arrow 2 so as to pass multi- element stylus printing head 3 in a fashion to present spot printing elements in any one of several well known dot printing attitudes toward the moving paper. Broad area return electrode 5 makes broad area contact to paper 1 at the surface of the paper.

Paper 1 is actually a composite of:

layer 11, a paper base of ordinary paper, or inexpensive polymer such as polypropylene;

layer 12, a very thin film of conductive metal such as aluminium overlaid on the entire surface of paper base layer 11;

layer 13, electrothermic composite.

In operation, the printhead has its several styli 31-35 selectively energized via conductors 36 so as to provide selective spot producing currents at respective styli 31, 32, 33, 34 and 35 as required by the configuration of the desired character (P shown in FIG. 1).

A representative spot producing circuit includes a potential on the appropriate conductor of conductor bundle 36 to provide a potential at a selected stylus, e.g., stylus 31. A conductive path for electrical current from stylus 31 is via resistance 14 to a surrounding area on aluminium film 12; and thence via aluminium film 12 to the area under broad area return electrode 5 and thence back through the conductive material in polyester composite 13 and broad area return electrode 5 to ground.

FIG. 2 is a simplified elevation diagram showing operation of another preferred embodiment. Composite thermographic printing paper 1 is drawn in the direction of arrow 2 under printhead 3 so as to provide selective printed dots 4 by application of respectively related currents. The currents are dissipated via the conductive capability 12' of the printing composite carried by paper substrate 11 and returned via broad area electrode 5 to ground. The resolution of printed spots in this latter embodiment is usually not as good as is obtained by using the thin metallic aluminium return conductor beneath the electrothermic polymer due to greater current spreading in the conductive electro-thermic polymer.

One preferred mechanism for providing broad area conductivity to the treated composite thermographic paper is thin film aluminium layer 12 as shown in FIG. 1. This preferred embodiment results in higher point resolution and quality. A second preferred embodiment eliminates the specific return layer 12 by providing sufficient conductivity 12' (FIG. 2) within composite polyester layer 13 to carry the desired currents. This conductivity may be provided by a homogenous dispersion of current carrying particles within polyester layer 13 or by a graded dispersion with the heavier occurrence of conductive particles on the inside next to substrate paper layer 11. The greater current spreading in the conductive polymer, however, usually results in adequate, but lower resolution printing compared to the prior embodiment.

The electrothermal recording sheet according to this example consists of a paper or polymer substrate 11 such as polyester (e.g., MYLAR*) or polypropylene, on which is deposited an electrically conductive film 12 of aluminium by vacuum evaporation or sputtering. The aluminium film 12 is overcoated with a chromogenic resistive layer 13 composed of one or a mixture of conductive particulate materials (zinc iodide, zinc oxide, tin oxide, titanium dioxide) dispersed in a binder containing thermally sensitive additives. A roughening agent selected from silica, alumina, aluminium hydroxide, $CaCo_3$, TiO_2, etc., can also be incorporated in the resistive formulations in order to eliminate polymer debris accumulation on the print head during writing.

Application of an electric signal to the printing device is accompanied by the generation of resistance heat which results in facsimile printing or direct image formation characterised by localized bleaching, colour formation or colour change. The intensity, contrast and hue of the imaged region depends on the chemical system selected for image definition. The electric signal may be on the order of 5-25 volts, 10-30 milliamperes as short as .02 milliseconds.

Various binders suitable for dispersion of semiconductive particles and other additives to form resistive coatings can be selected from the following classes:

- Cellulose derivatives such as cellulose acetate butyrate, ethyl cellulose, cellulose acetate, hydyroxyethyl cellulose, nitrocellulose, carboxymethyl cellulose, etc.

- Acrylate polymers including polymethylmethacrylate, polyacrylonitrite, polyacrylamides, polyvinylacetate, polyvinyl-acetal resis such as polyvinylbutyral.

- Polystyrenes and poly x-methylstyrene and related systems.

- Polycarbonates, novolaks, epoxy resins.

*TM

- Crosslinked polymers such as polyurethanes formed from the reaction of free hydroxyl carrying binders with polyisocyanates or melamines.

- Hydroxyethylene polymers such as hydroxypropylene, poly(ethylene glycols), polyvinylalcohol, etc.

Various conductive materials that can be utilized for this application are:

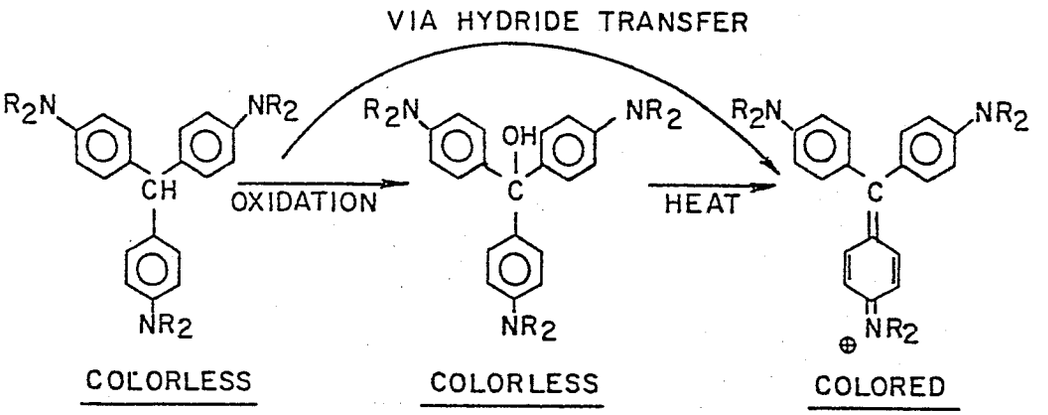
ZnO, ZnI_2, CuI_2, Sb_2O_3, MoO, Cds, TiO_2, molydisulfide, conducting polymers that can be employed as alternate binders for inorganic conductive particles such as oligostyrene sulfonate, polyethylene imine salts, doped polyacetylenes, polyphenylenes, etc.

Image definition, according to the electrothermal technique described in this invention, can be obtained by incorporation of various thermally sensitive additives in the resistive formulations so that their heat-induced chemical reactions are accompanied by bleaching, colour formation or colour change. Some of the preferred chromogenic materials and their thermal transformations are:

Leucoform dyes that undergo dye formation when subjected to electrical resistance heat generated during printing, e.g.

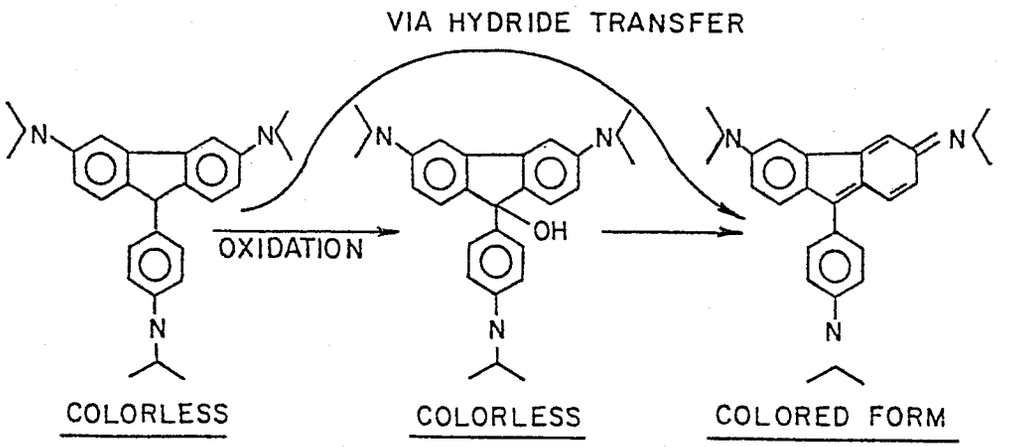
a) Leuco bases of triphenylmethane series or fluorene analogs of crystal violet which undergo oxidation-elimination reactions to colored forms, as shown in FORMULAS 1A and 1B. (In FORMULA 1A, (R=H, CH_3, C_2H_5, etc.)

FORMULA 1A



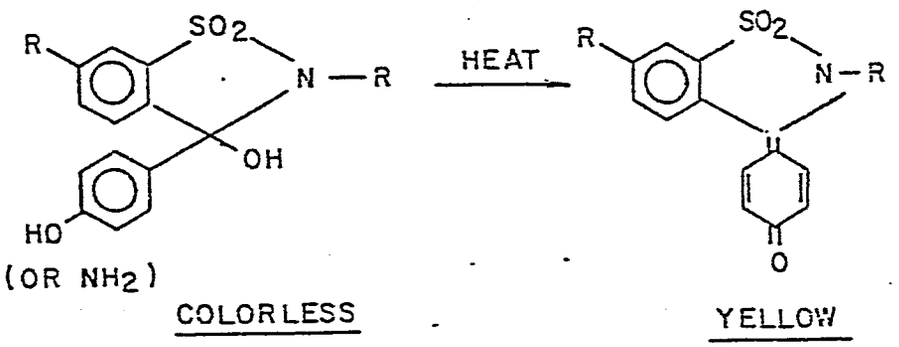
R = H, CH_3, C_2H_5 ETC

FORMULA 1B



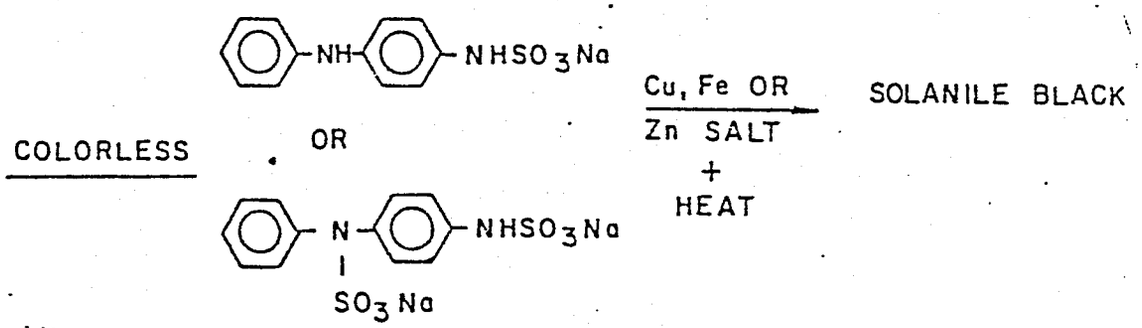
b) Saccharine derived leuco carbinol systems which under irreversible colour change upon heating, as shown in FORMULA 2. (In FORMULA 2, R=CH_3, Ethyl, OH, OCH_3, $-NH_2$, $N(CH_3)_2$, Halogen, etc. R' = alkyl groups as CH_3, etc. or hydroxyethyl, akloxyethyl, etc.)

FORMULA 2



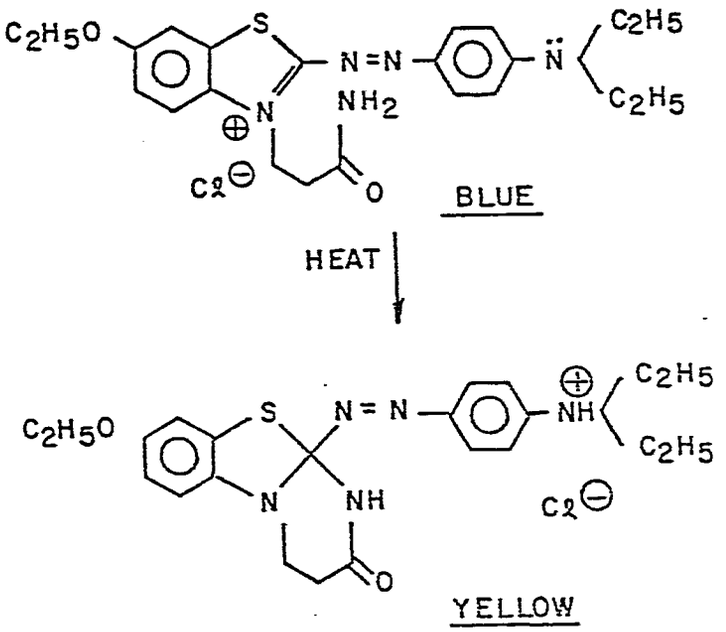
c) Diazahemicyanine dyes in benzothiazole series which can be permanently bound to polymers with free reactive sites (e.g. diazahemicyanine dyes with 2-carbamoylethyl side chain) as shown in FORMULA 3.

FORMULA 3



Dye precursors such as sulfamino derivatives of 4-amino diphenylamine can be incorporated in the resistive coatings to obtain deep black images due to the formation of polyzines similar to "Aniline Black," Solanile Black" (and related systems) in the presence of metal salts at 180°-200°C, as shown in FORMULA 4.

FORMULA 4

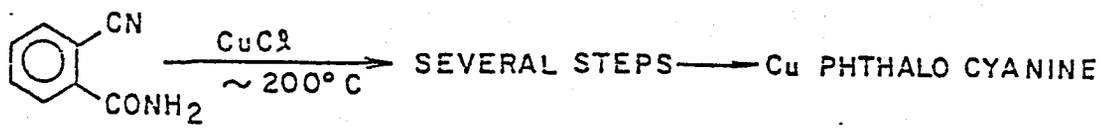


Solanile Black gives a fast black image on cellulosic polymers.

Electrothermal printing can also be accomplished by resistive heat induced in situ generation of metallic phthalocyamine.

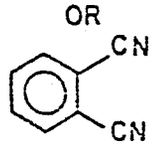
Preferred materials for these pigments are 0-cyanobenzamide or phthalonitrile and a small amount of copper salts such as cuprous or cupric chloride which can be incorporated in the resistive formulations prior to coatings, as shown in FORMULA 5.

FORMULA 5



O-CYANO BENZAMIDE

OR



PHTHALONITRILE

Similar phthalocyanine derivatives can be formed from other metals as nickel, cobalt, zinc, aluminium are generally brilliant blue and green.

Various coating formulations for the image forming resistive layers in the fabrication of electrothermal printing material according to this invention are illustrated by the following representative examples:

Example 1

Mixture A	Parts by Weight
Silver Behenate	10
Butyral Resin	5
Methyl Ethyl Ketone	45
2Propanol	15
Pluthalazinone	0.2 (optional)

Mixture B	
Semi Conductive Titanium Oxide	10
Butyral Resin	8
Novolak Resin	2
MEK	60
2-Propanol	40
Dispersing agent (such as R22175)	0.5

Mixture A and B are ball milled separately to form uniform dispersions which are then combined and briefly ball milled (1-2 hours) to insure thorough mixing. The resulting composition is coated on aluminized plastic (e.g., Mylar*, polypropylene, etc.) or paper support and dried/cured at 50-60°C to obtain 2-10 μm thick dry resistive film. Resistive heat generated during the electrothermal printing according to the present invention is accompanied by reduction of ionic silver to silver metal to provide a permanent black image. The novolak resin or related easily oxidizable systems when incorporated in these formulations, a more efficient reduction of ionic silver can be brought about.

*TM Alternate binders such as ethyl cellulose, cellulose acetate, cellulose acetate butyrate (CAB), polymethylmethacrylate, 2-methyl - styrene - methylmethacrylate, etc. can be substituted for polyvinylbutyral resin.

Example 2

	Parts by Weight
Semiconductive -	
Titanium Oxide or	
Zinc Oxide	10 to 40
Polymethylmethacrylate	50
Methyl Ethyl Ketone	400

The mixture is ball milled to form a uniform dispersion and combined with 10 parts of a leuco form of triphenylmethane dyes or fluorene analogs of crystal violet. The final composition is thoroughly mixed and applied on aluminized plastic or paper support as described in Example 1 to obtain a resistive layer with thickness of the dry coating between 2mm - 10mm.

Example 3

Electric resistant coatings formed with urethane-crosslinked cellulose derivatives as binders for semiconductive particulate material:

Semiconductive TiO_x or ZnO	1 - 3 parts
Cellulose Acetate Butyrate (CAB)	5
MEK	20
Toluene	5
Multron R 221-75 (dispersing agent)	0.3

This mixture is ball milled to form the Mill Base Coating Formulation:

Mlll Base	10
CB-75 (Polyisocyanate)	2
MEK	8
Toluene	2
Stannous octoate (catalyst)	0.01
FC-430 (Surfactant)	0.03
Diazahemicyanine - dye	0.5 to 1.0

The ingredients are thoroughly mixed together and approved on a plastic or paper support as described in Examples 1 and 2, and cured at 80-90°C for 10 minutes.

Example 4

	Parts by Weight
Ethyl Cellulose (N-22)	50
Semiconductive TiO_X or ZnO	5 to 20
MEK	300
Toluene	100
Dispersing agent (R221-75)	2
Surfactant (FC-430)	0.2
Sodium disulfonate of 4-amino diphenylamine	5 to 20

A solution of ethylcellulose is first prepared in a part of the solvent mixture, combined with the rest of the ingredients and the final composition is ball milled for 6 to 16 hours to form a uniform dispersion. After adjustment of viscosity to a desired consistency the formulation is coated on plastic or paper support as described in Example 1. The resulting structure when subjected to electrothermal printing according to this invention, an intense black image is formed due to resistive heat medicated oxidative transformation of the color forming ingredients (sulfonic derivatives of 4-amino diphenylamine) to polyazine dyes such as "Solanil Black."

Alternate binder systems that can be substituted for ethyl cellulose are: CAB, cellulose acetate, nitrocellulose, polyvinylbutyral, etc.

Example 5

	Parts by Weight
Cellulose Acetate Butyrate (CAB)	70
Semiconductive TiO_x or ZnO	10 to 30
MEK	400
Toluene	100
Dispersing Agent (R22175)	3
Ortho Cyano benzamide	5 to 10
or	
Phthalonitrile	
Copper Iodide or cuprous chloride	0.5

CAB is first dissolved in a portion of the solvent mixture, combined with the rest of the ingredients, and ball milled for 6-16 hours to form a homogeneous slurry which is applied onto the aluminized support to obtain a dry coating thickness of 2mm to 10mm after dry/cure cycle at 80-90°C. Electrothermal printing on such a recording material is accompanied by colour image formation due to copper phthalocyanine generated in the electric resistance layer containing colour forming precursors such as orthocyanobenzanide and the copper salts such as Cucl, $Cucl_2$, CuI_2, CuO, Cu_2O etc.

A variation of the above formulation includes the use of copper powder or copper paste as substitute for ZnO or TiO_x in cellulosic binders such as CAB or ethylcellulose with the rest of the ingredients being the same as in Example 5, to form electric resistant coatings of this invention.

CLAIMS

1. Printable medium for use in non-impact printing, said medium comprising a substrate supporting a composite electrothermic layer comprising a thermally sensitive image forming compound and a finely divided conductive material embedded in a carrier.

2. A printable medium as claimed in claim 1, further comprising a thin conductive layer between the substrate and the composite layer.

3. A printable medium as claimed in claim 1 or 2, in which said composite electrothermic layer comprises (by weight) approximately:

15 parts polymer carrier;

10 parts thermally sensitive dye; and

10 parts finely divided conductive materials.

4. A printable medium as claimed in claim 1, 2 or 3, in which said finely divided conductive material is one of or a mixture of zinc iodide, copper iodide, antimony trioxide, molybdenum oxide, cadmium sulfide, molybdenum disulfide, zinc oxide, tin oxide, titanium dioxide, oligostyrene sulfonate, polyethylene imine salts, doped polyacetylenes and polyphenylenes, metallic conductive particles such as zinc, tin or silver.

5. A printable medium as claimed in any one of claims 1 to 4, in which said composite electrothermic layer further comprises a roughening agent.

6. A printable medium as claimed in claim 5, in which said roughening agent is one or a mixture of silica, alumina, aluminium hydroxide, calcium carbonate, and titanium dioxide.

7. A printable medium as claimed in any one of claims 1 to 6, in which said image forming compound is a leucoform dye of a leuco base of the

triphenylmethane series that undergoes dye formation when subjected to electrical resistance heat.

8. A printable medium as claimed in any one of claims 1 to 6, in which said image forming compound is a fluorene analog of crystal violet that undergoes an oxidation elimination reaction to a colored form when subjected to electrical resistance heat.

9. A printable medium as claimed in any one of claims 1 to 6, in which said image forming compound is a saccharine derived leuco carbinol system which undergoes irreversible colour change when subjected to electrical resistance heat.

10. A printable medium as claimed in any one of claims 1 to 6, in which said image forming compound is a said thermally sensitive dye and is a diazohemicyanine dye in the benzothiazole series which can be permanently bound to a polymer with free reactive sites when subjected to heat.

11. A printable medium as claimed in claim 10, in which said diazohemicyanine dye includes a 2- carbamoyl ethyl side chain.

12. A printable medium as claimed in claim 1 or 2, in which said composite electrothermic layer comprises a carrier, a thermally sensitive dye, a finely divided conductive material and a dye precursor.

13. A printable medium as claimed in claim 12, in which said dye precursor is a sulfamino derivative of 4-amino-diphenylamine.

14. A printable medium as claimed in claim 12, in which said thermally sensitive dye is a mixture of a first component selected from the group (0-cyanobenzamide and phtalonitrile) and a second component is a salt of a metal selected from the group (copper, cobalt, zinc, aluminium, tin).

15. A method of producing a printable medium as claimed in claim 1, 2 or 3, said medium being produced by separately mixing a first mixture and a second mixture, combining the mixtures briefly, and coating the combined mixture on a substrate,

said first mixture comprising approximately (by weight)

silver behenate	10
oxidizable resin binder	5
volatile solvents	60, and

said second mixture comprising approximately (by weight)

semiconductive metal oxide	10
oxidizable resin binder	10
volatile solvents	100
dispersing agent	0.5

16. A method of producing a printable medium as claimed in claim 7, said medium being produced by mixing a first mixture and a second mixture, combining the mixtures briefly, and coating the combined mixture on a substrate,

said first mixture comprising approximately (by weight)

semiconductive metal oxide	10-40
polymethylmethacrylate	50
volatile solvents	400, and

said second mixture comprising approximately (by weight)

leucoform triphenylmethane dye	10.

17. A method of producing a printable medium as claimed in claim 7, said medium being produced by mixing a first mixture and a second mixture, combining the mixtures briefly, and coating the combined mixture on a substrate, in which said first mixture comprises approximately (by weight)

fluorene analog of crystal violet 10.

18. A method of producing a printable medium as claimed in claim 1, 2 or 3, said medium being prepared by separately mixing a first mixture and a second mixture, combining the mixtures briefly, and coating the combined mixture on a substrate,

said first mixture comprises approximately (by weight)

	semiconductive metal oxide	1-3
Mill Base	cellulose acetate butyrate	5
	volatile solvents	25
	dispersing agent	0.3, and

said second mixture comprising approximately (by weight)

mill base	10
polysocyanate	2
volatile solvents	10
catalyst	0.01
surfactant	0.03
diazahemicyanine dye	0.5 - 1.0.

19. A method of producing a printable medium as claimed in claim 1, 2 or 3, said medium being prepared by separately mixing a first mixture and a second mixture, combining the mixtures briefly, and coating the combined mixture on a substrate,

said first mixture comprises approximately (by weight)

binder solution	(ethyl cellulose)	50
	volatile solvents	200, and

said second mixture comprises approximately (by weight)

binder solution	250
semiconductive metal oxide	5-20
volatile solvents	200
dispersing agent	2
surfactant	0.2
sodium disulfonate of 4-amino diphenylamine	5-20.

FIG. 1

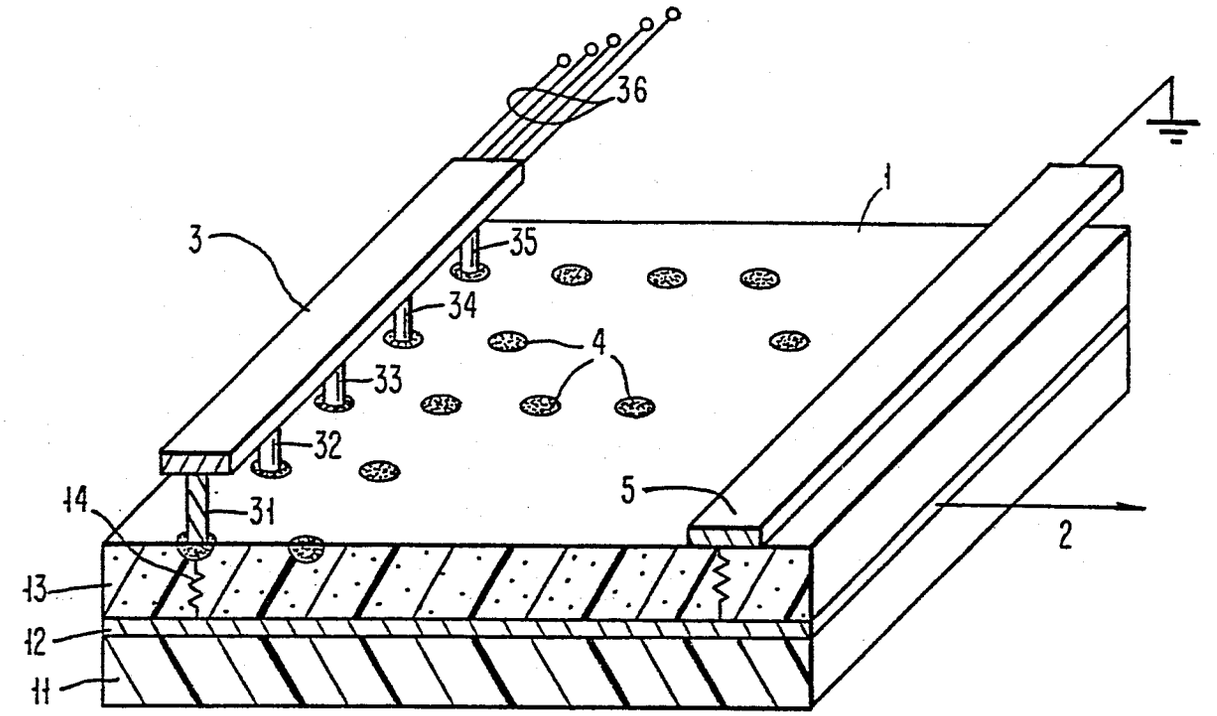


FIG. 2