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

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⑦③ Proprietor: **International Business Machines Corporation**
Old Orchard Road
Armonk, N.Y. 10504 (US)

⑦② Inventor: **Pennington, Keith Samuel**
Londonberry Lane
Somers New York 10589 (US)
Inventor: **Sachdev, Krishna Gandhi**
14 Candlewood Drive
Wappinger Falls New York 12590 (US)

⑦④ Representative: **Burt, Roger James, Dr.**
IBM United Kingdom Limited Intellectual
Property Department Hursley Park
Winchester Hampshire SO21 2JN (GB)

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Description

The invention relates to current sensitive printable media for use in the non-impact non-electroerosion 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 high 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 system, 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 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 phenolphthalein/acid/alkali oxide composite opaque layer. The composite is of adequate pH for a white indication. Local heat causes the alkali to activate the phenolphthalein as a result of the formation of hydroxides which decrease the pH and result in a localized red indication by the phenolphthalein.

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 colour

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 of facsimile printing.

5 Accordingly the invention provides current sensitive printable medium for use in non-impact non-electroerosion printing, said medium comprising a substrate supporting a composite electrothermic layer comprising a carrier encompassing a thermally sensitive colour forming system and a conductive material.

The printing material includes a substrate coated with a conductive composite electrothermic printing layer of polymer (polycarbonate, polyester, polyurethane, Kapton*) made conductive by suspended
10 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 benhenate).

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
15 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
20 area return electrode that it does not raise the temperature above the threshold for printing.

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
25 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
30 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;

35 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
40 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.
45 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
50 polymer due to greater current spreading in the conductive electrothermic 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
55 currents. This conductivity may be provided by a homogeneous 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 of polymer substrate
60 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 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, hydroxyethyl cellulose, nitrocellulose, carboxymethyl cellulose, etc.

Acrylate polymers including polymethylmethacrylate, polyacrylonitrile, polyacrylamides, polyvinylacetate, polyvinylacetal resins such as polyvinylbutyral.

Polystyrenes and poly x-methylstyrene and related systems.

Polycarbonates, novolaks, epoxy resins.

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, ZnI₂, CuI₂, Sb₂O₃, MoO₃, CdS, TiO₂, 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.

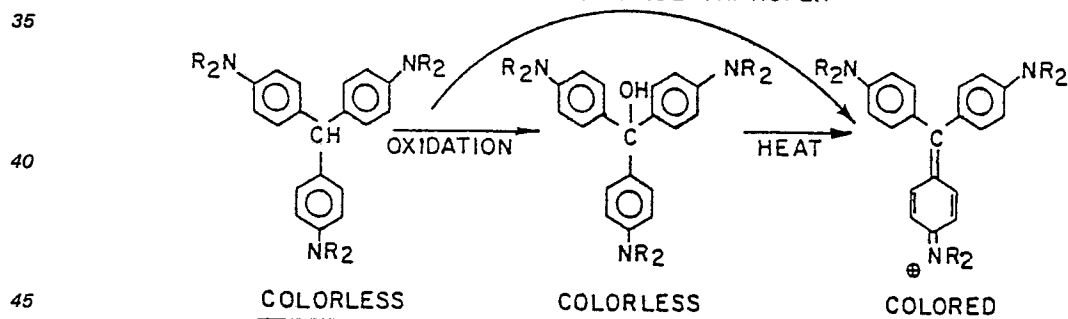
Image definition, according to the electrothermal technique described in this invention, can be obtained by incorporation of various thermally sensitive additives in the resistive formulations so that their heat-induced chemical reactions are accompanied by bleaching, colour formation or colour change. 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 of 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, CH₃, C₂H₅, etc.)

FORMULA 1A

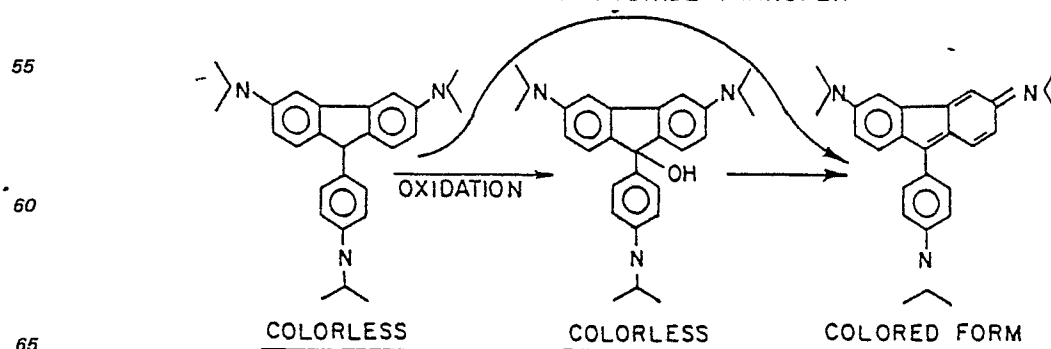
VIA HYDRIDE TRANSFER



R = H, CH₃, C₂H₅ ETC

FORMULA 1B

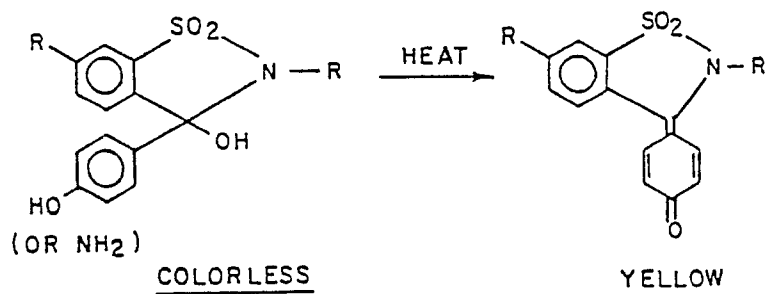
VIA HYDRIDE TRANSFER



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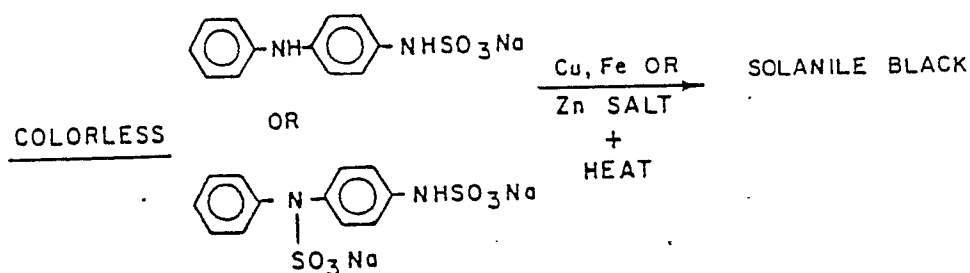
b) Saccharine derived leuco carbinol systems which under irreversible colour change upon heating, as shown in formula 2. (In formula 1, R=CH₃, Ethyl, OH, OCH₃, —NH₂, N(CH₃)₂, Halogen, etc. R' = alkyl groups as CH₃, etc. or hydroxyethyl, alkoxyethyl, etc.)

FORMULA 2



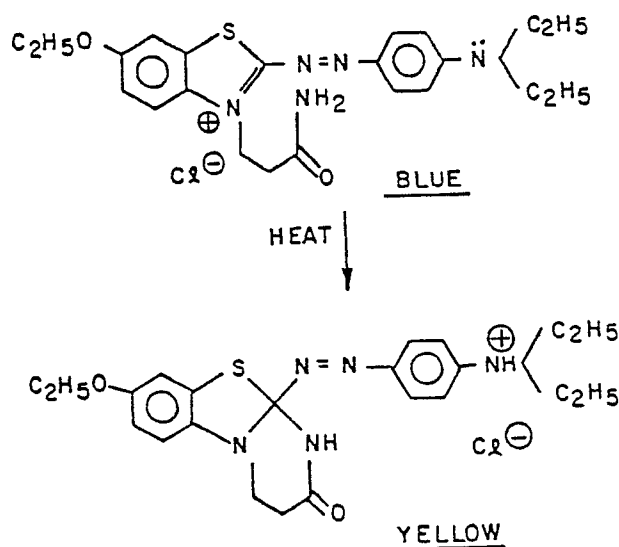
c) Diazahemicyanine dyes in benzothiazole series which can be permanently bound to polymers with free reactive sites (e.g. diazahemicyanine dyes with 2-carbomoyl ethyl side chain) as shown in formula 3.

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.

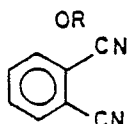
Electrothermal printing can also be accomplished by resistive heat induced in *in situ* generation of metallic phthalocyanine.

Preferred materials for these pigments are O-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



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
30	Silver Behenate	10
	Butyral Resin	5
	Methyl Ethyl Ketone	45
35	2Propanol	15
	Phthalazinone	0.2 (optional)
40	Mixture B	
	Semi Conductive Titanium Oxide	10
45	Butryal Resin	8
	Novolak Resin	2
	MEK	60
50	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-methylstyrene — methylmethacrylate, etc. can be substituted for polyvinylbutyral resin.

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Example 2

		Parts by Weight
5	Semi-conductive — Titanium Oxide or Zinc Oxide	10 to 40
	Polymethylmethacrylate	50
10	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
15 applied on aluminized plastic or paper support as described in Example 1 to obtain a resistive layer with thickness of the dry coating between 2 μm —10 μm .

Example 3

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

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

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

35	Mill Base	10
	CB—75 (Polyisocyanate)	2
40	MEK	8
	Toluene	2
45	Stannouse octoate (catalyst)	0.01
	FC—430 (Surfactant)	0.03
	Diazahemicyanine — dye	0.5 to 1.0

50 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.

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Example 4

	Parts by Weight
5 Ethyl Cellulose (N—22)	50
Semiconductive TiO_x or ZnO	5 to 20
MEK	300
10 Toluene	100
Dispersing agent (R221—75)	2
Surfactant (FC—430)	0.2
15 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 mediated oxidative transformation of the colour 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
30 Cellulose Acetate Butyrate (CAB)	70
35 Semiconductive TiO_x or ZnO	10 to 30
MEK	400
Toluene	100
40 Dispersing agent (R22175)	3
Ortho Cyano benzamide or Phthalonitrile	5 to 10
45 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 homogenous 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 orthocyanobenzamide 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 coating of this invention.

Claims

1. Current sensitive printable medium for use in non-impact non-electroerosion printing, said medium comprising a substrate supporting a composite electrothermic layer comprising a carrier encompassing a thermally sensitive colour forming system and a conductive material.
2. A printable medium as claimed in claim 1 in which said composite electrothermic layer comprises a carrier encompassing a thermally sensitive colour forming system and a finely divided conductive material.

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

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

- 5 15 parts polymer carrier;
 10 parts thermally sensitive dye; and
 10 parts finely divided conductive materials.

5. A printable medium as claimed in claim 2, 3 or 4, in which said finely divided conductive material is one of or a mixture of zinc iodide, copper iodide, antimony trioxide, molybdenum oxide, cadmium sulfide, 10 molybdenum disulfide, zinc oxide, tin oxide, titanium dioxide, metallic conductive particles such as zinc, tin or silver.

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

7. A printable medium as claimed in claim 6, in which said roughening agent is one or a mixture of 15 silica, alumina, aluminium hydroxide, calcium carbonate, and titanium dioxide.

8. A printable medium as claimed in any one of claims 1 to 7, in which said colour forming system is a leucoform dye of a leuco base of the triphenylmethane series that undergoes dye formation when subjected to electrical resistance heat.

9. A printable medium as claimed in any one of claims 1 to 7, in which said image forming system is 20 fluorene analog or crystal violet that undergoes an oxidation elimination reaction to a colored form when subjected to electrical resistance heat.

10. A printable medium as claimed in any one of claims 1 to 7, in which said image forming system is a saccharine derived leuco carbinol system which undergoes irreversible colour change when subjected to electrical resistance heat.

25 11. A printable medium as claimed in any one of claims 1 to 7, in which said image forming system 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.

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

30 13. A printable medium as claimed in claim 1, 2 or 3 in which said composite electrothermic layer comprises a carrier, a finely divided conductive material and a dye precursor.

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

35 15. A printable medium as claimed in claim 13, in which said dye precursor is a mixture of a first component selected from the group (o-cyanobenzamide and phthalonitrile) and a second component is a salt of a metal selected from the group (copper, cobalt, zinc, aluminium, tin).

16. A method of producing a printable medium as claimed in claim 1, 2, 3 or 4, 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)

40	silver behenate	10
	oxidizable resin binder	5
45	volatile solvents	60

and said second mixture comprising approximately (by weight)

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

17. A method of producing a printable medium as claimed in claim 8, said medium being produced by mixing a first mixture and further component, combining the mixture briefly, and coating the combined mixture on a substrate, said first mixture comprising approximately (by weight)

60	semiconductive metal oxide	10—40
	polymethylmethacrylate	50
65	volatile solvents	400

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and said further component comprising approximately (by weight)

leucoform triphenylmethane dye	10
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5 18. A method of producing a printable medium as claimed in claim 8, said medium being produced by mixing a first mixture and a further component, combining the mixture 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

15 and said further component comprising approximately (by weight)

fluorene analog of crystal violet	10.
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19. A method of producing a printable medium as claimed in claim 1, 2, 3 or 4, said medium being prepared by mixing a first mixture to form a mill base and adding components to said first mixture to form a second mixture, combining the mixture briefly, and coating the combined mixture on a substrate, said first mixture comprises approximately (by weight)

25	Mill Base	{	semiconductive metal oxide	1—3
			cellulose acetate butyrate	5
			volatile solvents	25
			dispersing agent	0.3

30 said second mixture comprising approximately (by weight)

mill base	10
polyisocyanate	2
volatile solvents	10
catalyst	0.01
surfactant	0.03
diazahemicyanine dye	0.5—1.0

45 20. A method of producing a printable medium as claimed in claim 1, 2, 3 or 4 said medium being prepared by mixing a first mixture to form a binder solution with further components to form a second mixture, combining the mixture briefly, and coating the combined mixture on a substrate, said first mixture comprises approximately (by weight)

50	binder solution	{	ethyl cellulose	50
			volatile solvents	200

and 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

Patentansprüche

1. Stromempfindliches bedruckbares Medium zur Verwendung beim anschlagfreien, elektroerosionfreien Drucken, wobei das Medium ein Substrat umfaßt, welches eine zusammengesetzte elektrothermische Schicht trägt, welche einen ein wärmeempfindliches farbbildendes System und ein leitfähiges Material enthaltenden Träger umfaßt.
2. Bedruckbares Medium nach Anspruch 1, bei welchem die zusammengesetzte elektrothermische Schicht einen ein wärmeempfindliches farbbildendes System und ein feinverteiltes leitfähiges Material enthaltenden Träger umfaßt.
3. Bedruckbares Medium nach Anspruch 1 oder 2, welches ferner eine dünne, leitfähige Schicht zwischen dem Substrat und der zusammengesetzten Schicht umfaßt.
4. Bedruckbares Medium nach Anspruch 1 oder 2, welchem die zusammengesetzte elektrothermische Schicht ungefähr umfaßt (in Gewichtsteilen):
- | | |
|--|--|
| 15 Teile Polymerträger, | |
| 10 Teile wärmeempfindlichen Farbstoff, und | |
| 10 Teile feinverteilte leitfähige Materialien. | |
5. Bedruckbares Medium nach Anspruch 2, 3 oder 4, bei welchem das feinverteilte leitfähige Material Zinkiodid, Kupferiodid, Antimontrioxid, Molybdänoxid, Cadmiumsulfid, Molybdändisulfid, Zinkoxid, Zinnoxid, Titandioxid, metallisch leitende Teilchen wie Zink, Zinn oder Silber, oder ein Gemisch davon ist.
6. Bedruckbares Medium nach irgendeinem der Ansprüche 1 bis 5, bei welchem die zusammengesetzte elektrothermische Schicht ferner ein Rauungsmittel umfaßt.
7. Bedruckbares Medium nach Anspruch 6, bei welchem das Rauungsmittel Silika, Tonerde, Aluminiumhydroxid, Calciumcarbonat, Titandioxid oder ein Gemisch davon ist.
8. Bedruckbares Medium nach irgendeinem der Ansprüche 1 bis 7, bei welchem das farbbildende System ein Leukoformfarbstoff einer Leukobase der Triphenylmethanreihe ist, welcher ein Farbstoffbildung durchmacht, wenn er elektrischer Widerstandswärme unterworfen wird.
9. Bedruckbares Medium nach irgendeinem der Ansprüche 1 bis 7, bei welchem das bildbildende System ein Fluorenanaloges von Kristallviolett ist, das eine Oxidationseliminationsreaktion in eine gefärbte Form durchmacht, wenn es elektrischer Widerstandswärme unterworfen wird.
10. Bedruckbares Medium nach irgendeinem der Ansprüche 1 bis 7, bei welchem das bildbildende System ein saccharinabgeleitetes Leukocarbinolesystem ist, welches eine irreversible Farbänderung durchmacht, wenn es elektrischer Widerstandswärme unterworfen wird.
11. Bedruckbares Medium nach irgendeinem der Ansprüche 1 bis 7, bei welchem das bildbildende System ein wärmeempfindlicher Farbstoff ist und ein Diazohemicyanin-Farbstoff in der Benzothiazolreihe ist, welcher bleibend an ein Polymer mit freien reaktiven Stellen gebunden werden kann, wenn er Wärme unterworfen wird.
12. Bedruckbares Medium nach Anspruch 11, bei welchem der Diazohemicyanin-Farbstoff eine 2-Carbamoyl-ethyl-Seitenkette enthält.
13. Bedruckbares Medium nach Anspruch 1, 2 oder 3, bei welchem die zusammengesetzte elektrothermische Schicht einen Träger, ein feinverteiltes leitfähiges Material und ein Farbstoffvorstufe enthält.
14. Bedruckbares Medium nach Anspruch 13, bei welchem die Farbstoffvorstufe ein Sulfamino-Derivat von 4-Aminodiphenylamin ist.
15. Bedruckbares Medium nach Anspruch 13, bei welchem die Farbstoffvorstufe ein Gemisch aus einer ersten Komponente ausgewählt aus der Gruppe (o-Cyanobenzamid und Phthalonitril) und einer zweiten Komponente, die ein Salz eines Metalls ausgewählt aus der Gruppe (Kupfer, Kobalt, Zink, Aluminium, Zinn) ist, ist.
16. Verfahren zur Herstellung eines bedruckbaren Mediums nach Anspruch 1, 2, 3 oder 4, wobei das Medium durch getrenntes Mischen eines ersten Gemischs und eines zweiten Gemischs, kurzes Kombinieren der Gemische und Beschichten eines Substrats mit dem kombinierten Gemisch hergestellt ist, wobei das erste Gemisch ungefähr umfaßt (in Gewichtsteilen)
- | | |
|-------------------------|----|
| Silberbehenat | 10 |
| oxidierbaren Harzbinder | 5 |
| flüchtige Lösungsmittel | 60 |
- und das zweite Gemisch ungefähr umfaßt (in Gewichtsteilen)
- | | |
|--------------------------|-----|
| halbleitendes Metalloxid | 10 |
| oxidierbaren Harzbinder | 10 |
| flüchtige Lösungsmittel | 100 |
| Dispersierungsmittel | 0,5 |

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17. Verfahren zur Herstellung eines bedruckbaren Mediums nach Anspruch 8, wobei das Medium durch Mischen eines ersten Gemischs und einer weiteren Komponente, kurzes Kombinieren des Gemischs und Beschichten eines Substrats mit dem kombinierten Gemisch hergestellt ist, wobei das erste Gemisch ungefähr umfaßt (in Gewichtsteilen)

5	halbleitendes Metalloxid	10—40
	Polymethylmethacrylat	50
10	flüchtige Lösungsmittel	400

und die weitere Komponente ungefähr umfaßt (in Gewichtsteilen)

15	Leukoform-Triphenylmethan-Farbstoff	10.
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18. Verfahren zur Herstellung eines bedruckbaren Mediums nach Anspruch 8, wobei das Medium durch Mischen eines ersten Gemischs und einer weiteren Komponente, kurzes Kombinieren des Gemischs und Beschichten eines Substrats mit dem kombinierten Gemisch hergestellt ist, wobei das erste Gemisch ungefähr umfaßt (in Gewichtsteilen)

20	halbleitendes Metalloxid	10—40
	Polymethylmethacrylat	50
25	flüchtige Lösungsmittel	400

und die weitere Verbindung ungefähr umfaßt (in Gewichtsteilen)

30	Fluorenanaloges von Kristallviolett	10.
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19. Verfahren zur Herstellung eines bedruckbaren Mediums nach Anspruch 1, 2, 3 oder 4, wobei das Medium durch Mischen eines ersten Gemischs zur Bildung einer Mühlenbasis und Zugabe von Komponenten zum ersten Gemisch zur Bildung eines zweiten Gemischs, kurzes Kombinieren des Gemischs und Beschichten eines Substrats mit dem kombinierten Gemisch hergestellt ist, wobei das erste

35 Gemisch ungefähr umfaßt (in Gewichtsteilen)

	Mühlen- basis	halbleitendes Metalloxid	1—3
40		Zelluloseazetatbutyrat	5
		flüchtige Lösungsmittel	25
		Dispergierungsmittel	0,3 und

45 das zweite Gemisch ungefähr umfaßt (in Gewichtsteilen)

	Mühlenbasis	10
	Polyisocyanat	2
50	flüchtige Lösungsmittel	10
	Katalysator	0,01
55	oberflächenaktives Mittel	0,03
	Diazahemicyanin-Farbstoff	0,5—1,0.

20. Verfahren zur Herstellung eines bedruckbaren Mediums nach Anspruch 1, 2, 3 oder 4, wobei das

60 Medium durch Mischen eines ersten Gemischs zur Bildung einer Binderlösung und Kombinieren der Binderlösung mit weiteren Komponenten zur Bildung eines zweiten Gemischs, kurzes Kombinieren des Gemischs und Beschichten eines Substrats mit dem kombinierten Gemisch hergestellt ist, wobei das erste Gemisch ungefähr umfaßt (in Gewichtsteilen)

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Binder- lösung	Ethylzellulose	50
	flüchtige Lösungsmittel	200

5 und das zweite Gemisch ungefähr umfaßt (in Gewichtsteilen)

	Binderlösung	250
	halbleitendes Metalloxid	5—20
10	flüchtige Lösungsmittel	200
	Dispergierungsmittel	2
15	oberflächenaktives Mittel	0,2
	Natriumdisulfonat von 4-Aminodiphenylamin	5—20.

20 Revendications

1. Matière imprimable sensible aux courants, utilisable en impression ne faisant pas appel aux impacts ni à l'électroérosion, ladite matière comprenant un substrat portant une couche électro-thermique composite comprenant un véhicule contenant un système générateur de couleur thermosensible et une substance conductrice.

2. Matière imprimable selon la revendication 1, dans laquelle ladite couche électro-thermique composite comprend un véhicule contenant un système générateur de couleur thermosensible et une substance conductrice finement divisée.

3. Matière imprimable selon la revendications 1 ou 2, comprenant en outre une couche mince conductrice entre le substrat et la couche composite.

4. Matière imprimable selon la revendication 1, 2 ou 3, dans laquelle ladite couche électro-thermique composite comprend (en poids) approximativement:

- 15 parties de véhicule polymère;
- 10 parties de colorant thermosensible; et
- 10 parties de substances conductrices finement divisées.

5. Matière imprimable selon la revendication 2, 3 ou 4, dans laquelle ladite substance conductrice finement divisée est un composé, ou un mélange de composés, choisi parmi l'iodure de zinc, l'iodure de cuivre, le trioxyde d'antimoine, l'oxyde de molybdène, le sulfure de cadmium, le bisulfure de molybdène, l'oxyde de zinc, l'oxyde d'étain, le bioxyde de titane, des particules métalliques conductrices comme le zinc, l'étain ou l'argent.

6. Matière imprimable selon l'une quelconque des revendications 1 à 5, dans laquelle ladite couche électro-thermique composite comprend en outre un agent granuleux.

7. Matière imprimable selon la revendication 6, dans laquelle ledit agent granuleux est un composé, ou un mélange de composés, choisi parmi la silice, l'alumine, l'hydroxyde, d'aluminium, le carbonate de calcium et le bioxyde de titane.

8. Matière imprimable selon l'une quelconque des revendications 1 à 7, dans laquelle ledit système générateur de couleur est un leucodérivé de colorant ou une leucobase de la série du triphénylméthane qui subit la formation d'un colorant quand il est soumis à de la chaleur produite par effet Joule.

9. Matière imprimable selon l'une quelconque des revendications 1 à 7, dans laquelle ledit système générateur d'images est un dérivé fluorène du violet cristallisé qui subit une réaction d'oxydation-élimination pour donner une forme colorée, lorsqu'il est soumis à de la chaleur produite par effet Joule.

10. Matière imprimable selon l'une quelconque des revendications 1 à 7, dans laquelle ledit système générateur d'images est un système leucocarbinol dérivé de la saccharine qui subit un changement de couleur irréversible lorsqu'il est soumis à de la chaleur produite par effet Joule.

11. Matière imprimable selon l'une quelconque des revendications 1 à 7, dans laquelle ledit système générateur d'images est un colorant thermo-sensible et est un colorant diazohémicyanine de la série du benzothiazole, qui peut être lié de façon permanente à un polymère à l'aide de sites réactifs libres, lorsqu'il est soumis à de la chaleur.

12. Matière imprimable selon la revendication 11, dans laquelle ledit colorant diazohémicyanine contient une chaîne latérale 2-carbomoyléthyle.

13. Matière imprimable selon la revendication 1, 2 ou 3, dans laquelle ladite couche électrothermique composite comprend un véhicule, une substance conductrice finement divisée et un précurseur de colorant.

14. Matière imprimable selon la revendication 13, dans laquelle ledit précurseur de colorant est un dérivé sulfamino de 4-aminodiphenylamine.

15. Matière imprimable selon la revendication 13, dans laquelle ledit précurseur de colorant est un

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mélange d'un premier constituant choisi dans le groupe (o-cyanobenzamide et phthalonitrile) et d'un second constituant qui est un sel d'un métal choisi dans le groupe (cuivre, cobalt, zinc, aluminium, étain).

16. Procédé de production d'une matière imprimable selon la revendication 1, 2, 3 ou 4, ladite matière étant produite par une opération de mélange séparée d'un premier mélange et d'un second mélange, la réunion rapide des mélanges, et l'application du mélange combiné sur un substrat, ledit premier mélange comprenant approximativement (en poids)

	béhénate d'argent	10
10	liant à base de résine oxydable	5
	solvants volatiles	60

et ledit second mélange comprenant approximativement (en poids)

15	oxyde métallique semi-conducteur	10
	liant à base de résine oxydable	10
20	solvants volatils	100
	agent dispersant	0,5

17. Procédé de production d'une matière imprimable selon la revendication 8, ladite matière étant produite par une opération de mélange d'un premier mélange et d'un autre constituant, la réunion rapide du mélange et l'application du mélange combiné sur un substrat, le premier mélange comprenant approximativement (en poids)

30	oxyde métallique semi-conducteur	10—40
	poly(méthacrylate de méthyle)	50
	solvants volatils	400

35 et ledit autre constituant comprenant approximativement (en poids)

	le codérivé de colorant triphénylmétane	10
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18. Procédé de production d'une matière imprimable selon la revendication 8, ladite matière étant produite par l'opération de mélange d'un premier mélange et d'un autre constituant, la réunion rapide du mélange et l'application du mélange combiné sur un substrat, le premier mélange comprenant approximativement (en poids)

45	oxyde métallique semi-conducteur	10—40
	poly(méthacrylate de méthyle)	50
	solvants volatils	400

50 et ledit autre composé comprenant approximativement (en poids)

	dérivé fluorène du violet cristallisé	10.
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19. Procédé de production d'une matière imprimable selon la revendication 1, 2, 3 ou 4, ladite matière étant préparée en mélangeant un premier mélange pour former une base de broyage et en ajoutant des constituants audit premier mélange pour former un second mélange, en réunissant rapidement le mélange et en appliquant le mélange combiné sur un substrat, ledit premier mélange comprenant approximativement (en poids)

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5	base de broyage	oxyde métallique semi-conducteur	1—3
		acétate-butyrat de cellulose	5
		solvants volatils	25
		agent dispersant	0,3

et ledit second mélange comprenant approximativement (en poids)

10	base de broyage	10
	polyisocyanate	2
15	solvants volatils	10
	catalyseur	0,01
	tensio-actif	0,03
20	colorant diazahémicyanine	0,5—1,0

20. Procédé de production d'une matière imprimable selon la revendication 1, 2, 3 ou 4, ladite matière étant préparée en mélangeant un premier mélange pour former une solution de liant et en réunissant ladite solution de liant avec d'autres constituants pour former un second mélange, en réunissant rapidement le mélange et en appliquant le mélange combiné sur un substrat, ledit premier mélange approximativement (en poids)

30	solution de liant	éthylcellulose	50
		solvants volatils	200

ledit second mélange comprenant approximativement (en poids)

35	solution de liant	250
	oxyde métallique semi-conducteur	5—20
40	solvants volatils	200
	agent dispersant	2
	tensio-actif	0,2
45	disulfonate sodique de 4-aminodiphénylamine	5—20

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60

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FIG. 1

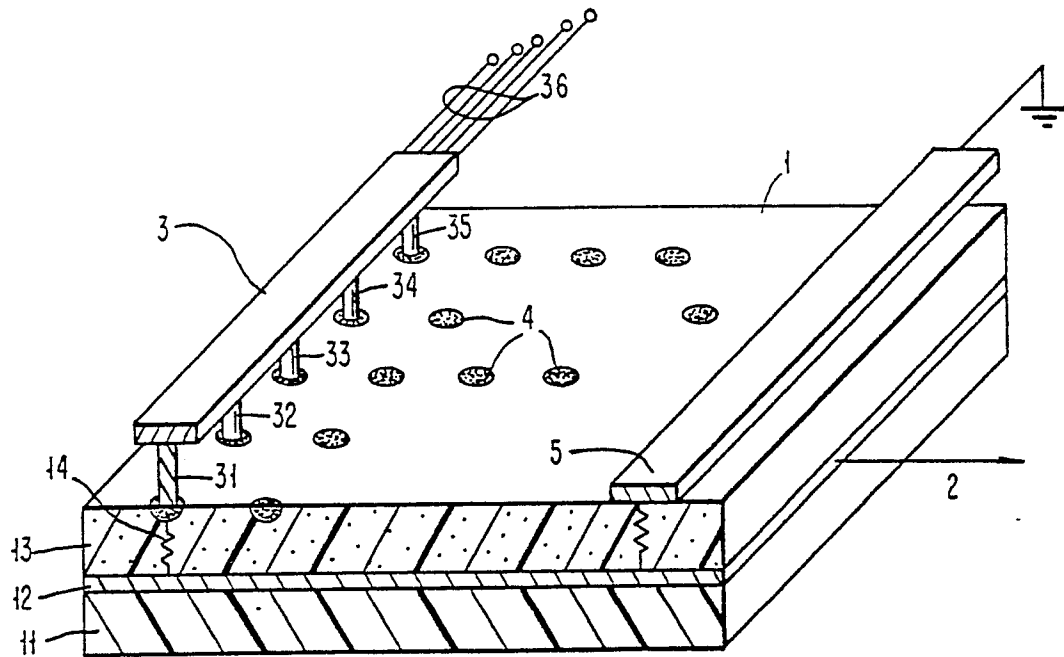


FIG. 2

