(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 982 718 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.03.2000 Bulletin 2000/09

(21) Application number: **98202898.7**

(22) Date of filing: **28.08.1998**

(51) Int. Cl.^{7}: **G11B 7/24**, B41M 5/24

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: **AGFA-GEVAERT N.V.**
2640 Mortsel (BE)

(72) Inventor:
Quintens, Dirk
c/o Agfa-Gevaert N.V.
2640 Mortsel (BE)

(74) Representative:
Ramon, Charles Lucien
Agfa-Gevaert N.V.
Dienst Intellectuele Eigendom 3800
Septestraat 27
2640 Mortsel (BE)

(54) Heat mode recording element with two antistatic layers

(57) A heat mode recording element is disclosed based on a thin metallic layer comprising an antistatic layer on both outermost sides.

Printed by Xerox (UK) Business Services
2.16.7/3.6

Description

FIELD OF THE INVENTION

[0001] The present invention relates to an improved heat mode recording material based on a thin metallic layer.

BACKGROUND OF THE INVENTION

[0002] In a particular type of heat mode recording materials information is recorded by creating differences in reflection and/or in transmission on the recording layer. The recording layer has high optical density and absorbs radiation beams which impinge thereon. The conversion of radiation into heat brings about a local temperature rise, causing a thermal change such as evaporation or ablation to take place in the recording layer. As a result, the irradiated parts of the recording layer are totally or partially removed, and a difference in optical density is formed between the irradiated parts and the unirradiated parts (cf. US Pat. Nos. 4,216,501, 4,233,626, 4,188,214 and 4,291,119 and British Pat. No. 2,026,346)

[0003] The recording layer of such heat mode recording materials is usually made of metals, dyes, or polymers. Recording materials like this are described in 'Electron, Ion and Laser Beam Technology", by M. L. Levene et al.; The Proceedings of the Eleventh Symposium (1969); "Electronics" (Mar. 18, 1968), P. 50; "The Bell System Technical Journal", by D. Maydan, Vol. 50 (1971), P. 1761; and "Science", by C. O. Carlson, Vol. 154 (1966), P. 1550.

[0004] Recording on such thermal recording materials is usually accomplished by converting the information to be recorded into electrical time series signals and scanning the recording material with a laser beam which is modulated in accordance with the signals. This method is advantageous in that recording images can be obtained on real time (i.e. instantaneously). Recording materials of this type are called "direct read after write" (DRAW) materials. DRAW recording materials can be used as a medium for recording an imagewise modulated laser beam to produce a human readable or machine readable record. Human readable records are e.g. micro-images that can be read on enlargement and projection. An example of a machine readable DRAW recording material is the optical disc. To date for the production of optical discs tellurium and its alloys have been used most widely to form highly reflective thin metal films wherein heating with laser beam locally reduces reflectivity by pit formation (ref. e.g. the periodical 'Physik in unserer Zeit', 15. Jahrg. 1984/Nr. 5, 129-130 the article "Optische Datenspeicher" by Jochen Fricke). Tellurium is toxic and has poor archival properties because of its sensitivity to oxygen and humidity. Other metals suited for use in DRAW heat-mode recording are given in US-P-4499178 and US-P-4388400. To avoid the toxicity problem other relatively low melting metals such as bismuth have been introduced in the production of a heat-mode recording layer. By exposing such a recording element very shortly by pulses of a high-power laser the writing spot ablates or melts a small amount of the bismuth layer. On melting the layer contracts on the heated spot by surface tension thus forming small cavitations or holes. As a result light can pass through these cavitations and the density is lowered to a certain Dmin value depending on the laser energy irradiated.

[0005] According to EP 0 384 041 a process is provided for the production of a heat mode recording material having "direct read after write" (DRAW) possibilities wherein a web support is provided with a heat mode recording thin metal layer, preferably a bismuth layer, characterized in that in the same vacuum environment a protective organic resin layer in web form is laminated to said supported recording layer by means of an adhesive layer.

[0006] A commercially available material manufactured according to the principles of cited EP 0 384 041 is MASTERTOOL MT8, registered trade name, marketed by Agfa-Gevaert N.V.. It is mostly used after recording as master in the manufacturing of microelectronic circuits and printed circuit boards. We refer to the description in Circuit World, Vol. 22, No. 3, April 1996. The material comprises a double-sided subbed polyethylene terephthalate (PET) support, carrying on one side a bismuth layer of about 0.25 mm thickness deposited in vacuo, a 8 mm thick weak adhesive layer, and a thin PET protective foil of 12 mm thickness. On the other side of the subbed PET support a backing layer is provided containing an antistatic and a matting agent (or roughening agent, or spacing agent, terms that will be used as synonyms furtheron). The matting agent prevents sticking to each other of packaged MASTERTOOL sheets, a phenomenon that is likely to lead to transport problems in exposure devices.

[0007] It is known that hydrophobic resin sheet and web materials of low conductivity readily become electrostatically charged by frictional contact with other elements during their manufacture, e.g. during coating or cutting, and during use, e.g. during the recording of information in exposure devices. Since the protective PET top foil of the commercial MASTERTOOL described above is such a hydrophobic resin it is no wonder that transport problems tend to occur in the laser exposure devices due to electostatic sticking.

OBJECTS OF THE INVENTION

[0008] It is an object of the present invention to provide a heat mode recording element based on a thin metallic layer with impoved antistatic properties, and, as a consequence, improved transport properties.

[0009] Further advantages and embodiments of the present invention will become apparent from the following description.

SUMMARY OF THE INVENTION

[0010] The objects of the present invention are realized by providing a heat mode recording element comprising, in order,

(a) a first antistatic layer,
(b) a transparent polymeric support,
(c) a thin metallic recording layer,
(d) a protective layer or layer pack,
(d) a second antistatic layer.

[0011] In a preferred embodiment these antistatic layers show a lateral resistance smaller than 10^{11} Ohm/□ thanks to the presence of a conductive compound, preferably a polythiophene derivative, most preferably polyethylene dioxythiophene (PEDT). This compound is preferably incorporated in the antistatic layer as an aqueous dispersion also containing a polymeric anion, most preferably polystyrene sulphonate.

[0012] In an alternative embodiment the outermost layers are rendered antistatic by controlling their triboelectric chargebility.

DETAILED DESCRIPTION OF THE INVENTION

[0013] As explained above, in a preferred embodiment one or both of the antistatic layers contain(s) a conductive compound the nature of which will be now explained in detail.

[0014] Such a compound can show ionic or electronic conductivity. Ionic conducting compounds are e.g. high molecular weight polymeric compounds having ionic groups, e.g. carboxylic sodium salt groups, built in at frequent intervals in the polymer chain [ref. Photographic Emulsion Chemistry, by G.F. Duffin, - The Focal Press - London and New York (1966) - Focal Press Ltd., p. 168]. To further enhance the permanence of the conductivity of ionic conductive polymers it has been proposed to cross-link these polymers with hydrophobic polymers (ref. e.g. US-P 4,585,730, US-P 4,701,403, US-P 4,589, 570, US-P 5,045,441, EP-A-391 402 and EP-A-420 226).

[0015] The conductivity however of an antistatic layer containing said ionic conductive polymers, even after cross-linking, is moisture dependent.

[0016] Therefore electronically-conducting conjugated polymers have been developed that have electronic conductivity. Representatives of such polymers are described in the periodical Materials & Design Vol. 11, No. 3 - June 1990, p. 142-152, and in the book "Science and Applications of Conducting Polymers" - Papers from the 6th European Physical Society Industrial Workshop held in Lothus, Norway, 28-31 May 1990, Edited by W R Salaneck Linkoping University, D T Clark ICI Wilton Materials Research Centre, and E J Samuelson University of Trondheim, published under the Adam Hilger imprint by IOP Publishing Ltd Techno House, Redcliffe Way, Bristol BS1 6NX, England.

[0017] Substances having electronic conductivity instead of ionic conductivity have a conductivity independent from moisture. They are particularly suited for use in the production of antistatic layers with permanent and reproducible conductivity.

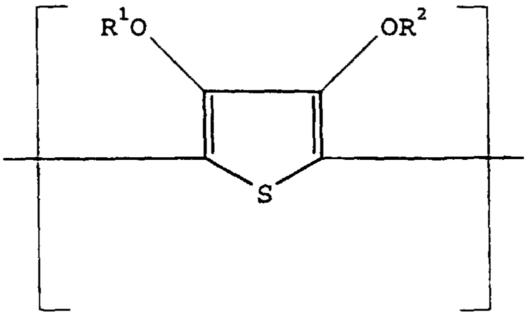
[0018] Many of the known electronically conductive polymers are highly coloured which makes them less suited for use in photographic materials, but some of them of the group of the polyarenemethylidenes, e.g. polythiophenes and polyisothianaphthene are not prohibitively coloured and transparent, at least when coated in thin layers. As a result polythiophene derivatives are a preferred type of conductive compounds for use in the present invention.

[0019] The production of conductive polythiophenes is described in preparation literature mentioned in the above mentioned book : "Science and Applications of Conducting Polymers", p. 92.

[0020] For ecological reasons the coating of antistatic layers should proceed where possible from aqueous solutions by using as few as possible organic solvents. The production of antistatic coatings from aqueous coating compositions being dispersions of polythiophenes in the presence of polyanions is described in published European patent application 0 440 957. Thanks to the presence of the polyanion the polythiophene compound is kept in dispersion.

[0021] Preferably said polythiophene has thiophene nuclei substituted with at least one alkoxy group, or -$O(CH_2CH_2O)_nCH_3$ group, n being 1 to 4, or, most preferably, thiophene nuclei that are ring closed over two oxygen atoms with an alkylene group including such group in substituted form.

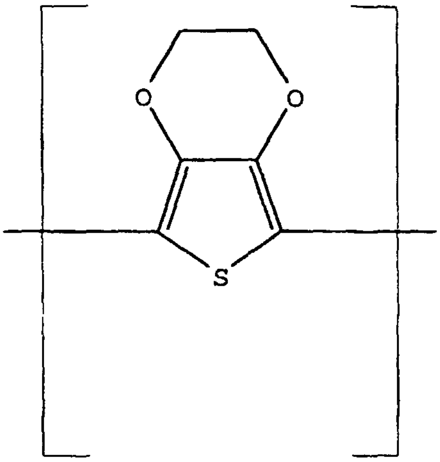
[0022] Preferred polythiophenes for use according to the present invention are made up of structural units corresponding to the following general formula (I):



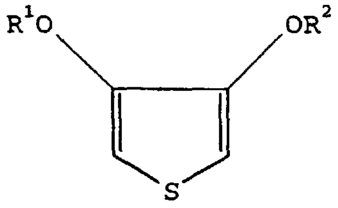
in which :

each of R^1 and R^2 independently represents hydrogen or a C_{1-4} alkyl group or together represent an optionally substituted C_{1-4} alkylene group or a cycloalkylene group, preferably an ethylene group, an optionally alkyl-substituted methylene group, an optionally C_{1-12} alkyl- or phenyl-substituted 1,2-ethylene group, a 1,3-propylene group or a 1,2-cyclohexylene group.

[0023] The most preferred compound is poly(3,4-ethylenedioxy-thiophene), (PEDT) with following formula Ibis :



[0024] The preparation of said polythiophene and of aqueous polythiophene-polymeric polyanion dispersions containing said polythiophene is described in published European patent application 0 440 957, cited above. The synthesis proceeds in the presence of said polymeric polyanion compounds by oxidative polymerization of 3,4-dialkoxythiophenes or 3,4-alkylenedioxythiophenes according to the following general formula (II):



wherein :

R^1 and R^2 are as defined in general formula (I), with oxidizing agents typically used for the oxidative polymerization of pyrrole and/or with oxygen or air in the presence of said polyacids, preferably in aqueous medium containing optionally a certain amount of organic solvents, at temperatures of 0 to 100°C.

[0025] The polythiophenes get positive charges by the oxidative polymerization, the location and number of said charges is not determinable with certainty and therefore they are not mentioned in the general formula of the repeating units of the polythiophene polymer.

[0026] The size of the polymer particles in the coating dispersion is in the range of from 5 nm to 1mm, preferably in the range of 40 to 400 nm.

[0027] Suitable polymeric polyanion compounds required for keeping said polythiophenes in dispersion are provided by acidic polymers in free acid or neutralized form. The acidic polymers are preferably polymeric carboxylic or sulphonic acids. Examples of such polymeric acids are polymers containing repeating units selected from the group consisting of acrylic acid, methacrylic acid, maleic acid, vinyl sulfonic acid and styrene sulfonic acid or mixtures thereof.

[0028] The anionic acidic polymers used in conjunction with the dispersed polythiophene polymer have preferably a content of anionic groups of more than 2% by weight with respect to said polymer compounds to ensure sufficient stability of the dispersion. Suitable acidic polymers or corresponding salts are described e.g. in DE-A -25 41 230, DE-A-25 41 274, DE-A-28 35 856, EP-A-14 921, EP-A-69 671, EP-A-130 115, US-P 4,147,550, US-P 4,388,403 and US-P 5,006,451.

[0029] The polymeric polyanion compounds may consist of straight-chain, branched chain or crosslinked polymers. Cross-linked polymeric polyanion compounds with a high amount of acidic groups are swellable in water and are named microgels. Such microgels are disclosed e.g. in US-P 4,301,240, US-P 4,677,050 and US-P 4,147,550.

[0030] The molecular weight of the polymeric polyanion compounds being polyacids is preferably in the range from 1,000 to 2,000,000 and more preferably in the range from 2,000 to 500,000. Polyacids within the above criteria are commercially available, for example polystyrene sulfonic acids and polyacrylic acids, or may be produced by known methods (ref. e.g. Houben-Weyl, Methoden der Organischen Chemie, Vol. E20, Makromolekulare Stoffe, Teil 2, (1987), pp. 141 et seq.).

[0031] Instead of the free polymeric polyacids applied in conjunction with the polythiophenes it is possible to use mixtures of alkali salts of said polyacids and non-neutralized polyacids, optionally in the presence of monoacids. Free acid groups of the polyanionic polymer may be allowed to react with an inorganic base, e.g. with sodium hydroxide, to obtain a neutral polymer dispersion before coating.

[0032] The weight ratio of polythiophene polymer to polymeric polyanion compound(s) can vary widely, for example from about 50/50 to 15/85.

[0033] The most preferred polymeric polyanion for use in combination with the polythiophene derivative, e.g. PEDT, is polystyrene sulphonate (PSS).

[0034] Having described the invention extensively on the hand of its preferred embodiment wherein the conductive compound is a polythiophene derivative it will be clear that any other compound showing ionic or electronic conductivity can be used in one or both of the antistatic layers without departing from the scope of the invention. Also mixtures of different types of compounds can be used in order to achieve the antistatic effect. As examples of other conductive compounds we cite :

- metal oxides, such as vanadium pentoxide, as disclosed e.g. in WO 91/02289, US 5,221,598; ZnO, SnO_2, MgO, as disclosed in e.g. US 5,238,801, colloidal manganese dioxide as disclosed in EP 504826 ; oxides from Zn, Ti, In, Si, Mg, Ba, Mo, W, V, as disclosed in EP 569821; in combination with a fluorine containing (co)polymer according to EP 552617, ; a reaction product of a metal oxide sol and a chitosan salt cf. EP 531006; heteropolycondensates of tin and boron oxide as described in WO 90/013851; doped metal oxides;
- silica and modified silica compounds, see e.g. US 4,895,792, EP 334400, US 5,385,986, US 5,236,818, EP 438621, EP 296656, EP 444326
- conductive polymers with acidic groups optionally further crosslinked e.g. by aziridines or other compounds, such as disclosed in US 4,960,687, EP 318909, US 4,891,308, US 5,077,185, EP 439181, US 5,128,233, EP 486982, DE 4103437, EP 505626;
- mixtures of a water-soluble conductive polymer, containing e.g. sulphonic acid groups, sulphuric acid groups or carboxylic acid groups + a hydrophobic polymer + a crosslinking or curing agent as disclosed e.g. in US 5,013,637, US 5,079,136, US 5,098,822, US 5,135,843, EP 432654, EP 409665, EP 391402
- (poly)phosphazene derivatives, see e.g. US 4,948,720, WO 90/08978, US 4,898,808 ; graft polymers of polyphosphazenes with polyalkylene glycols as disclosed in EP 304296;,
- (co)polymers of a diallyldialkylammonium salt as disclosed in EP 320692,
- polyalkyleneimine grafted vinyl polymers such as disclosed in US 5,153,115,
- copolymer of styrene sulphonic acid and a hydroxyl group containing monomer crosslinked by methoxyalkylmela-

mine as described in WO 91/18061,; the same copolymer but crosslinked by a hydrolyzed metal lower alkoxide as disclosed in WO 91/18062 ;

- polymer complexes containing polyalkylene oxide units as disclosed in JN 62/286038;
- a combination of polymerized oxyalkylene oxide units and a fluorine containing inorganic salt as disclosed in EP 170529 ; a polyoxyalkylene in combination with a thiocyanate, iodide, perchlorate, or periodate cf. US 4,272,616;
- a highly crosslinked vinylbenzyl quaternary ammonium polymer in combination with a hydrophobic binder as described in *Research Disclosure*, June 1977, Item 15840 and US 3,958,995 ;
- sulphonated anionic microgel latices as described in *Research Disclosure*, October 1977, Item 16258;
- polymers and copolymers of pyrrole, furan, aniline, vinylcarbazole, pyridine, and other heterocycles and their deivatives as disclosed in several patents, usually outside imaging science, e.g. in EP 537504, DE 3940187, EP 326864, DE 3743519, DE 3734749, DE 3716284, EP 264786, EP 259813, EP 195381, WO 96/01480, EP 469667;
- so-called TCNQ-complexes, e.g. N-butyl-isochinolinium-tetracyanoquinone-dimethane; references to TCNQ-complexes can be found in *Handbook of organic conductive molecules and polymers*, Vol. 1, Chapter 4 p. 229, and *J. Am. Chem. Soc.*, Vol. 84, (162) p. 3370.

[0035] It will be clear that mixtures of these different types of conductive compounds may be used, e.g. combinations of metal oxides and conductive polymers.

[0036] Apart from being rendered antistatic by the presence of a conductive compound the outermost layer(s) can be made antistatic by adding a compound or mixtures of compounds which reduce the so-called triboelectric chargebility of the layer. Usually one of these compounds is a perfluorated surfactant.

[0037] The triboelectric chargebility of a layer versus a reference material is expressed as its Q_{Far} value which is determined as follows.

[0038] The experimental mounting consists of two concentric cylinders isolated from each other. The external cylinder is connected to the earth potential and the internal cylinder, functioning as cage of Faraday, is connected to an electrometer. The internal cylinder contains a flat metal plate to which a 275 x 35 mm strip of the sample to be measured (e.g. the top layer of MASTERTOOL) is applied. A 60 x 35 strip of the reference material (e.g. the backing layer of MASTERTOOL) is applied to a PTFE-block (polytetrafluorethylene, a strong insulator) of dimensions 55 x 30 x 15 mm. Materials and test equipment are conditioned for at least 24 h in a clima room with fixed temperature and relative humidity. After discharging of the whole the block is put in the Faraday cage. The triboelectric charge is generated by rubbing the PTFE-block containing the reference sample under its own weight (0.53 N) over the metal plate containing the sample to be measured. The block is moved five times there and back at an average speed of 10 cm/s. Then the reference material is removed from the inner cylinder and the countercharge is measured. An average (median) of twenty repeated measurements is calculated. It was found experimentally that in order to avoid problems with static charging a Q_{Far} value not surpassing 3.6×10^{-6} C/m^2 could be allowed for an outermost layer.

[0039] Materials and methods wherein a material is made antistatic by reducing its triboelectric chargebility are disclosed in e.g. :

- US 3,775,126 and US 3,850,640; disclose a combination of a cationic perfluorinated alkyl surfactant and a non-ionic alkyl phenoxy polypropylene oxide surfactant;
- US 3,850,642 ; the surface layer contains a so-called "charge control agent';
- GB 1330356 ; a fluoro substituted quaternary ammonium compound is combined with another wetting agent;
- US 4,956,270; describes the combination of an organic fluoro compound and a non-ionic surfactant;,
- EP 288059 ; discloses particular compounds containing polyalkylene groups;
- EP 319951 and US 5,258,276 ; combination of an anionic, a non-ionic and a fluorinated non-ionic surfactant;
- EP 534006 ; combination of a polyalkylene compound and a fluorinated surfactant containing oxyethylene groups.

[0040] Apart from the conductive compound or the compounds reducing the triboelectric position the antistatic layers can contain several other types of ingredients.

[0041] For instance, a matting agent also called roughening agent or spacing agent may be present.

[0042] This roughening agent can be chosen from a wide variety of chemical classes and commercial products provided the particles chosen show an excellent mechanical and thermal stability. Preferred roughening agents include following :

- the spherical polymeric beads disclosed in US 4,861,818 ;
- the alkali-soluble beads of US 4,906,560 and EP 0 584 407 ;
- the insoluble polymeric beads disclosed in EP 0 466 982 ;
- polymethylmethacrylate beads ;
- copolymers of methacrylic acid with methyl- or ethylmethacrylate ;

- TOSPEARL siloxane particles (e.g. types T105, T108, T103, T120), marketed by Toshiba Co ;
- SEAHOSTAR polysiloxane - silica particles (e.g. type KE-P50), marketed by Nippon Shokubai Co ;
- ROPAQUE particles, being polymeric hollow spherical core/sheat beads, marketed by Rohm and Haas Co, and described e.g. is US-P's 4,427,836, 4,468,498 and 4,469,825 ;
- ABD PULVER, marketed by BASF AG ;
- CHEMIPEARL, spherical poymeric particles, marketed by Misui Petrochemical Industries, Ltd.m

[0043] The spacing particles must be chosen so that they are not optically disturbing.

[0044] In a most preferred embodiment the roughening agent is based on polymethylmethacrylate beads which are preferably cross-linked. They preferably have an average particle size of 0.5 to 5 mm, and most preferably 1 to 4 mm. Other preferred roughening agents are disclosed in EP 0 080 225, EP 0 466 982, and EP 0 698 625.

[0045] Furtheron, the antistatic layer(s) may contain an adhesion promoting agent, preferably a (co)polymer with hydrophilic groups (see example section furtheron), and a so-called anti-scratch agent, e.g. a polysiloxane-polyether copolymer.

[0046] The different other layers and sheets constituting the heat mode recording material of the present invention, apart from the antistatic layers, will be explained now in more detail.

[0047] Useful transparent polymeric supports (b) include e.g. cellulose nitrate film, cellulose acetate film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film, polycarbonate film, polyvinylchloride film or poly-α-olefin films such as polyethylene or polypropylene film. The thickness of such organic resin film is preferably comprised between 0.03 and 0.35 mm. In a most preferred embodiment of the present invention the support is a polyethylene terephthalate layer provided with a subbing layer. This subbing layer can be applied before or after stretching of the polyester film support. The polyester film support is preferably biaxially stretched at an elevated temperature of e.g. 70-120°C, reducing its thickness by about 1/2 to 1/9 or more and increasing its area 2 to 9 times. The stretching may be accomplished in two stages, transversal and longitudinal in either order or simultaneously. The subbing layer is preferably applied by aqueous coating between the longitudinal and transversal stretch, in a thickness of 0.1 to 5 mm. In case of a bismuth recording layer the subbing layer preferably contains, as described in European Patent Application EP 0 464 906, a homopolymer or copolymer of a monomer comprising covalently bound chlorine. Examples of said homopolymers or copolymers suitable for use in the subbing layer are e.g. polyvinyl chloride, polyvinylidene chloride, a copolymer of vinylidene chloride, an acrylic ester and itaconic acid, a copolymer of vinyl chloride and vinylidene chloride, a copolymer of vinyl chloride and vinyl acetate, a copolymer of butylacrylate, vinyl acetate and vinyl chloride or vinylidene chloride, a copolymer of vinyl chloride, vinylidene chloride and itaconic acid, a copolymer of vinyl chloride, vinyl acetate and vinyl alcohol etc.. Polymers that are water dispersable are preferred since they allow aqueous coating of the subbing layer which is ecologically advantageous.

[0048] Possible metals for the recording layer (c) in this invention include Mg, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Re, Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt, Cu, Ag, Au, Zn, Cd, Al, Ga, In, Si, Ge, Sn, As, Sb, Bi, Se, Te. Due to their low melting point Mg, Zn, In, Sn, Bi and Te are preferred. The most preferred metal for the practice of this invention is Bi. Also metal oxides and metal chalcogenides can be used.

[0049] The metallic recording layer may be applied by vapor deposition, sputtering, ion plating, chemical vapor deposition, electrolytic plating, or electroless plating.

[0050] In the preferred case of Bi the recording layer is preferably provided by vapor deposition in vacuo or, according to a more recent process, by coating from an aqueous medium.

[0051] A method and an apparatus for a deposition are disclosed, in EP 0 384 041, cited above. According to this disclosure an adhesive layer and a top thin polymeric resin, preferably PET, are applied to the vacuum deposited bismuth layer on line in the vacuum chamber.

[0052] In a more recent method, described in pending European patent application appl. No. 97201117, the metal layer, preferably bismuth, is coated from an aqueous medium by conventional coating techniques after chemical reduction of a metal salt.

[0053] In a first step an aqueous solution of bismuth ions is prepared. As most suitable bismuth salt bismuth nitrate is chosen. Almost all bismuth salts are poorly soluble in water. In order to maintain a sufficient amount of bismuth ions in solution, it is necessary to add a complexing agent. A preferred complexant is simply the well-known ethylenediaminetetraacetic acid (EDTA) or a homologous compound or a salt thereof. Another preferred one is citrate, e.g. triammonium citrate. Other suitable complexants include diethylenetriamine-pentaacetic acid (DTPA), trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CDTA), ethyleneglycol-O,O'-bis(2-aminoethyl)-N,N,N',N'-tetraacetic acid (EGTA), N-(2-hydroxyethyl)ethylenediamine-N,N,N'-triacetic acid (HEDTA), etc.. In order to keep the metal bismuth that will be formed by reduction in the next step in dispersion a protective binder is preferably added to the aqueous medium. A particularly preferred protective binder is carboxymethylcellulose (CMC), preferably of the high viscosity type. Other possible binders include gelatin, arabic gum, poly(acrylic acid), cellulose derivatives and other polysaccharides. However, it will be clear from the examples furtheron that the use of CMC favours a low Dmin. The solution can further contain a so-called dispersing aid (also called co-dispersing agent). Suitable dispersing aids in the case of bismuth are pyrophosphates, more particularly a hexametaphosphate such as sodium hexametaphosphate. Probably, the hexametaphosphate adsorbs to the surface of the bismuth particles so that they become negatively charged. By electrostatic repulsion they are kept in dispersion.

[0054] In a following step the bismuth ions in the solution are reduced to metal bismuth particles by means of the addition of a reducing agent. The metal particles are kept in dispersion by the presence of the binder and dispersing aid as described above. A preferred reducing agent is sodium hydrosulphite. Another suitable reducing agent is KBH_4. Others include glucose, formaldehyde, tin(II)chloride. The reducing agent can be added to the original bismuth salt solution as a solid powder. On the other hand the reducing agent can be dissolved separately and added to the bismuth salt solution according to a single jet or a double let procedure. When the reduction is substantially completed the aqeous medium can directly be coated, but more preferably the superfluous salts are first removed from the aqueous medium in a step 2bis, by well-known methods such as ultracentrifugation followed by redispersing, flocculation and washing followed by redipersing, or ultrafiltration. In the case of ultracentrifugation, and using CMC as binder a bismuth-CMC deposit is separated. The ultracentrifugation step may be repeated after washing with fresh water. The final deposit is redispersed in an aqueous medium, preferably containing the same or different binder and/or dispersion aid as the original solution. In the case of a bismuth-CMC deposit the redispersing aqueous medium preferably contains the same dispersing aid as the original solution, e.g. sodium hexametaphosphate. In the final aqueous medium preferable an antioxidant, added at any stage of the preparation, such as ascorbic acid or a derivative thereof is present in order to avoid oxidation to bismuth oxide which would lead to an unacceptable density loss during drying after coating or during conservation of the unprotected bismuth layer. Finally, after the addition of one or more coating agents the obtained aqueous medium is coated on the transparent substrate by means of a conventional coating technique.

[0055] Suitable coating agents include non-ionic agents such as saponins, alkylene oxides e.g. polyethylene glycol, polyethylene glycol/polypropylen glycol condensation products, polyethylene glycol alkyl esters or polyethylene glycol alkylaryl esters, polyethylene glycol esters, polyethylene glycol sorbitan esters, polyalkylene glycol alkylamines or alkylamides, silicone-polyethylene oxide adducts, glycidol derivaties, fatty acid esters of polyhydric alcohols and alkyl esters of saccharides; anionic agenst comprising an acid group such as a carboxy, sulpho, phospho, sulphuric or phosphoric ester group; ampholytic agents such as aminoacids, aminoalkyl sulphonic acids, aminoalkyl sulphates or phosphates, alkyl betaines, and amine-N-oxides; and cationic agents such as aklylamine salts, aliphatic, aromatic, or heterocyclic quaternary ammonium salts, aliphatic or heterocyclic ring-containing phosphonium or sulphonium salts. Other suitable surfactants include perfluorinated compounds.

[0056] The particle size of the reduced metalic bismuth is preferably comprised between 5 and 300 nm, most preferably 10 and 200 nm. The thickness of this Bi layer is preferably comprised between 0.05 and 1.5 mm, and most preferably between 0.05 and 0.6 mm. When this thickness is too low the recorded images do not have sufficient density. When on the other hand the thickness is too high the sensitivity tends to decrease and the minimal density, i.e. the density after laser recording on the exposed areas tends to be higher.

[0057] Since the metallic layer is very sensitive to mechanical damage a protective element (e) must be provided on top of the metallic layer.

[0058] Three types of protectives element are preferred.

[0059] In a first preferred particular embodiment this protective element comprises a transparent organic resin, acting as outermost cover sheet, and an adhesive layer. A method for applying such a protective element by lamination in the same vacuum environment as wherein the deposition of the metal layer took place is also disclosed in EP 0 384 041, cited above. The cover sheet can be chosen from the group of polymeric resins usable for the support of the heat mode element. In a preferred embodiment the cover sheet is also polyethylene terephthalate but preferably substantially thinner than the polyethylene terephthalate of the support. The cover sheet may be provided with a subbing layer to improve the adhesion to the adhesive layer.

[0060] The adhesive layer may contain a pressure-adhesive or a thermoadhesive.

[0061] Pressure-sensitive adhesives are usually composed of (a) thermoplastic polymer(s) having some elasticity and tackiness at room temperature (about 20°C), which is controlled optionally with a plasticizer and/or tackifying resin. A thermoplastic polymer is completely plastic if there is no recovery on removal of stress and completely elastic if recovery is instantaneous and complete.

[0062] Particularly suitable pressure-sensitive adhesives are selected from the group of polyterpene resins, low density polyethylene, a copoly(ethylene/vinyl acetate), a poly(C_1-C_{16})alkyl acrylate, a mixture of poly(C_1-C_{16})alkyl acrylate with polyvinyl acetate, and copoly(vinylacetate-acrylate) being tacky at 20°C.

[0063] Examples of pressure-adhesive resins are described in US-P 4,033,770 for use in the production of adhesive transfers (decalcomanias) by the silver complex diffusion transfer process, in the Canadian Patent 728,607 and in the United States Patent 3,131,106.

[0064] In the production of a pressure-adhesive layer an intrinsically non-tacky polymer may be tackified by the adding of a tackifying substance, e.g. plasticizer or other tackifying resin. Examples of suitable tackifying resins are the terpene tackifying resins described in the periodical "Adhesives Age", Vol. 31, No. 12, November 1988, p. 28-29.

[0065] According to another embodiment the protective element is laminated or adhered to the heat mode recording layer by means of a heat-sensitive also called heat-activatable adhesive layer or thermoadhesive layer, examples of which are described also in US-P 4,033,770. In such embodiment the laminating material consisting of adhesive layer and abrasion resistant protective layer and/or the recording web material to be protected by lamination are heated in their contacting area to a temperature beyond the softening point of the adhesive. Heat may be supplied by electrical energy to at least one of the rollers between which the laminate is formed or it may be supplied by means of infra-red radiation. The laminating may proceed likewise by heat generated by high-frequency micro-waves as described e.g. in published EP-A 0 278 818 directed to a method for applying a plastic covering layer to documents.

[0066] A survey of pressure and/or heat-sensitive adhesives is given by J. Shields in "Adhesives Handbook", 3rd. ed. (1984), Butterworths - London, Boston, and by Ernest W. Flick in "Handbook of Adhesive Raw Materials" (1982), Noyens Publications, Park Ridge, New Jersey - USA.

[0067] More recent reviews on adhesives include Creton, "Material science of pressure-sensitive adhesives", *Fr. Mater. Sci. Technol.* (1997), 18, p. 707 ; Baghdachi, "Fundamentals of adhesion", *J. Coat. Technol.* (1997), 69 (870), p. 85 ; Clemens, "The developing chemistry of pressure sensitive adhesives", *Proc. Ann. Meet. Adhes. Soc.* (1997), 20th, p. 351.

[0068] In a second preferred type of protective layer pack two layers are coated on top of the metal layer, a soft polymeric layer and an outermost hard polymeric layer. Combinations of useful compositions for the soft and the hard polymeric layers are described in European patent application appl. No. 98201117 cited above. In a particular preferred embodiment the soft polymeric layer is based on neocryl or ucecryl, and the hard polymeric layer is based on copoly(ethylacrylate-methacrylic acid).

[0069] A third type of protective element consists of just one coated layer which due to the presence of a reactive monomer is radiation-curable, preferably UV-curable. Protective elements of this type are disclosed in pending European patent application appl. No. 97203857.

[0070] For the formation of a heat mode image using the element of the present invention any laser can be used which provides enough energy needed for the production of sufficient heat for this particular process of image formation. In a preferred embodiment a powerful infra-red laser is used, most preferably a Nd-YLF laser or diode laser.

[0071] The present invention will now be illustrated by the following examples without however being limited thereto.

Examples

-1. preparation of MASTERTOOL samples

[0072] The application of a bismuth layer by vacuum deposition onto a PET support and of a protective laminate consisting of an adhesive layer and of a PET protective layer were performed according to the process described in EP 0 384 041, cited above. A cylindrical vacuum chamber contained an electrically heated refractory tray in which bismuth is present as metal vapour source. Under high vacuum (a pressure in the range of 10^{-2} Pa to $8x10^{-1}$ Pa) the obtained metal vapour was directed towards a web made of polyethylene terephthalate having a thickness of 175 mm and was deposited thereon at a thickness of about 300 nm. The web was supplied by an unwinding roll and was conveyed over a guiding roller against a cooled support roller. After passing the zone of the metal vapour deposition the web traveled upwardly to meet a laminating web. The laminating web consisted of a three layer pack composed of (i) a 23 mm thick releasable temporary support (siliconised PET), (ii) a 8 mm thick pressure adhesive layer (acrylate based), and (iii) a 12 mm PET protective layer. By a mechanism explained in the cited patent the releasable layer (i) was first peeled off, and the layers (ii) and (iii) were laminated by means of pressure rollers to the deposited bismuth layer.

[0073] The backing layer, corresponding to the first antistatic layer (a), had following ingredients :

- antistatic complex polyethylenedioxythiophene/polystyrene sulphonic acid;
- binder polymethylmethacrylate latex (0.15-0.4 mm);
- thickener polysaccharide KELZAN S (trademark of Kelco Co.);
- polyethylene latex (0.2 mm) PERAPRET PE40 (tradename of BASF);
- colloidal silica KIESELSOL 100F (trade name of Bayer AG);
- wetting agent ULTRAVON W (trade name of Ciba-Geigy AG).

[0074] The backing layer was coated from a mixture of N-methylpyrrolidone and isopropanol.

[0075] The antistatic top layer, being the second antistatic layer (e) was composed as follows :

[0076] A coating composition was prepared containing the following ingredients the preparation of which will be explained hereinafter:

- 37.5 g of dispersion PT being the dispersion of the PEDT-polystyrene sulphonate complex;
- 30 ml of latex A being a film-forming polymer improving a.o. he adhesion of the antistatic layer to the protective thin PET foil;
- 10 ml of latex B being a film-forming polymer having the same function;
- 0.15 ml of a 5.7 % aqueous dispersion of a matting agent in the form of polymethylmethacrylate beads having an average particle size of 3 µm;
- an admixture of the solvents N-methylpyrrolidone/water up to 1 liter.

[0077] These different ingredients were prepared as follows :

- **Preparation of 3,4-ethylenedioxy-thiophene**

[0078] The 3,4-disubstituted thiophenes of the above general formula (II) can be obtained by processes known in principle by reacting the alkali metal salts of 3,4-dihydroxy-thiophene-2,5-dicarboxylic esters with the appropriate alkylene vic-dihalides and subsequently decarboxylating the free 3,4-(alkylene-vicdioxy)thiophene-2,5-dicarboxylic acids (see, for example, Tetrahedron (1967) Vol. 23, 2437-2441 and J. Am. Chem. Soc. 67 (1945) 2217-2218).

- Preparation of poly(3,4-ethylenedioxy-thiophene)/polyanion dispersion (also called dispersion PT)

[0079] Into 1000 ml of an aqueous solution of 20 g of polystyrene sulfonic acid (109 mmol of SO_3H groups) with number-average molecular weight (Mn) 40,000, were introduced 12.9 g of potassium peroxidisulfate ($K_2S_2O_8$), 0.1 g of $Fe_2(SO_4)_3$ and 2.8 g of 3,4-ethylenedioxy-thiophene. The thus obtained reaction mixture was stirred for 24 h at 20 °C and subjected to desalting.

[0080] 500 ml of the above prepared reaction mixture were diluted with 500 ml of water and stirred for 6 hours at room temperature in the presence of a granulated weak basic ion exchange resin LEWATIT H 600 (tradename of Bayer AG) and strongly acidic ion exchanger LEWATIT S 100 (tradename of Bayer AG. After said treatment the ion exchange resins were filtered off and the potassium ion and sulfate ion content were measured which were respectively 0.4 g K^+ and 0.1 g $(SO_4)^{2-}$ per liter.

- preparation of latex A

[0081] A mixture of 306 ml of 10 % aqueous solution of HOSTAPAL B [tradename of Hoechst AG, Frankfurt, Germany, for nonyl-phenyl-(oxyethylene)$_5$-O-SO_3Na] and 5940 ml of water was heated to 85 °C while nitrogen gas was bubbled through. 383 ml of methylmethacrylate and 225 ml of a 1 % aqueous solution of $K_2S_2O_8$ were added and the reaction mixture was stirred for 30 minutes. Thereupon an additional amount of 1532 ml of methylmethacrylate and 450 ml of a 1% aqueous solution of $K_2S_2O_8$ were added dropwise and stirring was continued for a further 2 h at 85 °C. The solids content of the latex was 20.9 % and the avarage particle size of the latex particles being dispersed polymethylmethacrylate was 69 nm. The glass transition temperature (T_g) of the obtained polymethylmethacrylate was 119 °C.

- preparation of latex B

[0082] An addition copolymer of vinylidene chloride, methylmethacrylate and itaconic acid, containing 88 % by weight of vinylidene chloride units, 10 % by weight of methylmethacrylate units, and 2 % by weight of itaconic acid units was prepared as a latex by classical emulsion polymerisation conducted in aqueous medium in the presence of persulphate as initiator.

[0083] A comparative sample was prepared being the same MASTERTOOL material as described above but without the second antistatic layer (e).

- 2. evaluation of the samples

[0084] The lateral electrical resistance and the Q^{Far} as defined above were determined.

[0085] The results are summarized in table 1.

TABLE 1

	invention ex.	compar. ex.	dimension
lateral resist.	$4x10^6$	$> 10^{12}$	Ω/□

TABLE 1 (continued)

	invention ex.	compar. ex.	dimension
Q_{Far}	1.7×10^{-7}	3.6×10^{-6}	C/m^2

[0086] The results prove the superior antistatic properties of the invention example versus the comparative example.

Claims

1. Heat mode recording element comprising, in order :

    (a) a first antistatic layer,
    (b) a transparent polymeric support,
    (c) a thin metallic recording layer,
    (d) a protective layer or layer pack,
    (e) a second antistatic layer.

2. Heat mode recording element according to claim 1 wherein one or both of said antistatic layers (a) and (e) contain(s) an effective amount of a conductive compound lowering the lateral electrical resistance to a value smaller than 10^{11} Ohm/□.

3. Heat mode recording element according to claim 2 wherein said conductive compound is a polythiophene compound.

4. Heat mode recording element according to claim 3 wherein said polythiophene compound is incorporated in said antistatic layer(s) as an aqueous dispersion of a polythiophene compound / polymeric anion complex.

5. Heat mode recording element according to claim 4 wherein said polymeric anion is polystyrene sulphonate.

6. Heat mode recording element according to claim 3, 4 or 5 wherein said polythiophene compound is polyethylene dioxythiophene (PEDT).

7. Heat mode recording element according to claim 2 wherein said conductive compound is a member chosen from the group consisting of tin oxide, indium tin oxide, and vanadium oxide.

8. Heat mode recording element according to claim 2 wherein said conductive compound is a member chosen from the group consisting of polyaniline, a tetracyanoquinone (TCNQ) complex, a quaternary ammonium compound, and a sulphonated compound.

9. Heat mode recording element according to claim 1 wherein one or both of said antistatic layer(s) contain(s) a compound or a mixture of compounds reducing the triboelectrical chargebility of said layer(s) in such a way that it (they) show(s) a Q_{Far} value, defined and determined as explained in the specification, lower than 3.6×10^{-6} C/m^2.

10. Heat mode recording element according to claim 9 wherein said compound or said mixture of compounds is or comprises a perfluorinated surfactant.

11. Heat mode recording element according to any of claims 1 to 10 wherein said thin metallic layer (c) is a bismuth layer having a thickness between 0.05 and 0.6 μm.

12. Heat mode recording element according to any of claims 1 to 11 wherein said thin metallic layer has been applied by evaporation in vacuo.

13. Heat mode recording element according to any of claims 1 to 11 wherein said thin metallic layer has been applied by coating from an aqueous solution.

14. Heat mode recording element according to any of claims 1 to 13 wherein said protective layer pack (d) comprises an adhesive layer and a rigid polymeric resin.

15. Heat mode recording element according to any of claims 1 to 13 wherein said protective layer pack (d) comprises a coated soft polymeric layer and a coated hard polymeric layer.

16. Heat mode recording element according to any of claims 1 to 15 wherein one or both of said antistatic layers (a) and (e) further contain(s) a matting agent.

17. Heat mode recording element according to claim 16 wherein said matting agent is PMMA.

18. Heat mode recording element according to any of the previous claims wherein one or both of said antistatic layers further contain(s) an anti-scratch agent.

19. Heat mode recording element according to claim 18 wherein said anti-scratch agent is a polysiloxane-polyether copolymer.

20. Method for the formation of a heat mode image comprising exposing information-wise by intense laser radiation a heat mode recording element according to any of the previous claims.

21. Method according to claim 19 wherein said intense laser radiation is produced by an infra-red laser.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 2898

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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