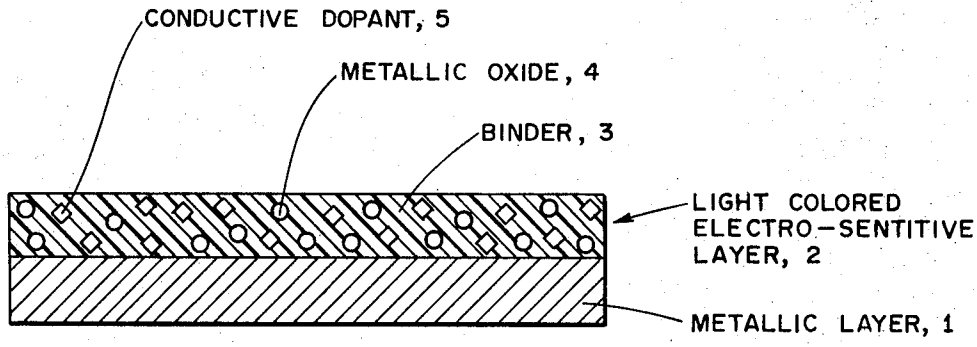
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ELECTROSENSITIVE RECORDING MATERIAL

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ELECTROSENSITIVE RECORDING MATERIAL

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ABSTRACT OF THE DISCLOSURE

A dry electrosensitive recording sheet consists of a substrate of a metal which forms a dark oxide and a topcoat containing a light colored metallic oxide which is electrically reducible to a color contrasting dark lower oxide. An electrochemically inert additive is preferably included in the topcoat to increase its conductivity.

SPECIFICATION

This invention relates to a dry electrosensitive recording material useful for marking or image formation by means of an electrically energized stylus or the like. The recording material of this invention consists essentially of a base or substrate of a metal which forms a dark oxide and a coating containing a light colored oxide which is reducible to a lower preferably dark colored oxide. A stylus of negative potential relative to the substrate causes both the light oxide to become reduced to a dark oxide and the base to oxidize to a dark oxide.

The transmission of continuous tone images, as in facsimile reproduction processes, requires a recording sheet which produces sharp color contrasts and fine gradations in tonal value. In particular, facsimile reproduction of the superior quality obtainable with this invention has many applications in business and scientific copying. For example, high quality facsimile reproduction is increasingly important for recording photographs and other information transmitted from aircraft and satellites.

The prior art contains many recording papers and other multiple layer media which produce local color changes upon the application of an electric current.

An early technique was to impregnate papers with conductive solutions which were decomposed by an electrical signal, thereby leaving a dark mark as a record. These recordings do not produce fine gradations in the darkness of the mark and are therefore suitable only for coarse work such as the reception of telegraphic messages. The same objection applies to the known use of an electric current to burn holes in a paper recording blank. Another widely used electrosensitive paper has a powdery light grey coating on one surface which smudges, is readily pressure marked, and is physically displaced by the passage of a current through the paper.

Recording sheets employing an electrolytic reaction, such as the indium oxide sheet disclosed by Hamm in U.S. Pat. No. 3,087,869, must be moistened prior to use, as by fixing a sponge ahead of the stylus delivering the electrical signal.

In U.S. Pat. No. 3,138,547, Clark discloses a dry electrosensitive recording sheet that largely avoids the above mentioned problems. The recording process utilized in this sheet is the reduction of a metallic oxide to a free metal which can then be either visually or electronically scanned. The present invention is aimed to producing a visible record or image of superior quality and to that end a metallic oxide is reduced to a lower oxide (not a free metal), and, a supporting metal base is oxidized to a dark colored oxide which additionally contributes to the production of a color contrasting image.

The preferred embodiment of the invention consists of two electrically conductive layers including a continuous substrate of metal and a uniform adherent electrosensitive topcoat. The electrosensitive layer is adhered to the metallic layer by a binder in which a particulate, electrically reducible, metallic oxide and an electrochemically inert but electrically conductive dopant have been uniformly distributed. In operation, the passage of a current between a electronegative stylus in contact with the topcoat and the metal substrate causes the metallic oxide to become reduced to a dark lower oxide in sharp color contrast to the surrounding unreduced portions of the electrosensitive layer. The same current results in oxidation of the metal of the metallic layer to a dark oxide which contributes to the image formation, making the image clearer and the tonal gradations finer than if the metal did not participate in the reaction.

The invention is described in detail with reference to the accompanying drawing in which:

FIG. 1 is a fragmentary cross section of the preferred embodiment.

The metallic layer 1 may be a sheet of metal, a metal foil, a metal coated on a film, or a metal impregnated paper. All of these forms of metallic substrate except the paper have the advantages of flexibility and high tear strength. The metal coated films are particularly useful in conjunction with computer read out use. Any metal which produces a dark colored oxide may be used. Suitable metals include copper (which was used in actual tests), silver, lead, tin, nickel, cadmium, iron, chromium, and molybdenum.

The electrosensitive layer 2 consists of particles of a metallic oxide 4, such as stannic oxide and molybdic oxide, a binder 3, and preferably also particles of an "inert" dopant 5, such as zinc oxide. These particles are uniformly dispersed in the binder 3 which has a relatively low electrical conductivity. The resistance offered by the topcoat to a passage of current between the stylus and the metallic layer 1 can be controlled by varying the thickness of this topcoat, or by varying the dimensions to which the particles 4 and 5 are milled. Both the thickness of the topcoat 2 and the dispersion of the metallic oxide 4 and dopant 5 in the binder 3 must be uniform or else variances in the resistance will cause tonal gradation which are not due to the varying strength of the applied electrical signal. For ease in storage and handling, the electrosensitive layer 2 should not under normal conditions be sensitive to light, heat or pressure. Also, the passage of the reducing current should not physically disrupt the topcoat 2.

The metallic oxide 4 must electrically reduce to a lower oxide. For example, a stannic oxide (SnO_2) reduces to stannous oxide (SnO) and molybdic oxide (MoO_3) reduces to molybdous oxide (MoO_2). The combined choice of the metallic oxide 4 and the metallic layer 1 is such that the formation of a lower oxide of the metallic ion forming the metallic oxide 4 rather than the formation of metal is both (and simultaneously) thermodynamically and kinetically favored. The lower oxide must be dark in sharp contrast to the light color of the unreduced surrounding portions of the topcoat 2. In the above mentioned examples, the unreduced oxide is white and the lower oxide is black. This color contrast is sharper than that obtained by reducing an oxide to a free metal, resulting in an image of superior quality. In order to have tonal gradations, the metallic oxide 4 must be such that the amount of lower oxide deposited varies directly with the strength of the recording current. The reduction reaction does not require the presence of moisture or the deposit of a free metal. Moreover, no color additives or color-contrasting layers are necessary.

The topcoat **2** is made more conductive by adding a white conductive dopant **5**. This additive appears to increase the conductivity of the electrosensitive layer **2** without itself being chemically changed. A suitable additive has thermodynamic properties, such that the free energy change for the reduction of the dopant material **5** by the metal substrate **1** or the oxidation of this material by the reducible metallic oxide **4** is algebraically less than the free energy change of the primary oxidation-reduction reaction.

The binder **3** is an organic nonconductive film forming on adhesive compound which functions both to hold the particles **4** and **5** in a fixed position within the topcoat **2** and to firmly adhere these particles to the metal substrate. Before reduction the particles **4** and **5** must be held by the binder **3** in a uniform dispersion to prevent tonal gradations not due to variations in the recording current. During the actual recording reaction, the binder **3** must be strong enough ot prevent "blasting" or other physical disruption of the continuity of the topcoat **2**. Once the facsimile image has been formed on the recording sheet, image permanence depends on the ability of the binder **3** to hold the particles of reduced oxide in a fixed location. Suitable binders which have the above properties include ethyl cellulose (Ethocel) and Pliolite S–6.

The fixative properties of the binder **3**, and in particular its ability to resist blasting and arcing, depend not only on the type of binder used, but also on the ratio of the binder **3** to the particles **4** and **5**. A preferred mixture which was used in actual tests and yielded good fixative and recording results consisted of 16 gms. of stannic oxide, 16 gms. of zinc oxide and 4 gms. of Ethocel (100 cps.) dissolved in 150 grams of solvent. This mix was ball milled for 24 hours to produce a moist, cohesive paste which was coated on metal substrates of both aluminum impregnated paper and copper foil. The coatings were applied at a thickness of 5.0 mils. When the coatings had dried, dark marks of facsimile reproduction quality were produced by using a recording current of 2.7 milliamperes applied at 200 volts. In the preferred embodiment, the above mixture is coated on a copper base. An alternative mixture equivalent to the preferred mixture is obtained by substituting molybdic oxide for stannic oxide. The molybdic oxide mixture has the same ratio of metallic oxide to binder as the preferred mixture.

Alternative chemical compounds, mix ratios, milling times, and coating thicknesses which achieve the same results are of course within the scope of this disclosure. Such factors as costs, the availability of materials, the desired electrical resistance of the top-coat, and the requirements of the particular recording instrument will determine these choices.

It is contemplated that these and other modifications will occur to those skilled in the art without departing from the scope of this invention.

Having disclosed my invention in detail, what I claim is:

1. An electrosensitive nonelectrolytic recording material comprising a continuous metallic layer, the metal of said layer forming a dark oxide, and a uniform, nondisplaceable, electrosensitive layer coated on the metallic layer, said electrosensitive layer comprising: (1) an electrically reducible particular metallic oxide to a lower oxide which is dark in contrast to the light unreduced electrosensitive layer, and (2) an insulating binder in which said electrically reducible metallic oxide and the dopant are uniformly dispersed.

2. The electrosensitive recording material of claim **1** in which the metallic oxide is stannic oxide.

3. The electrosensitive recording material of claim **1** in which the metallic oxide is molybdic oxide.

4. The electrosensitive recording material of claim **1** including additionally zinc oxide.

5. The electrosensitive recording material of claim **1** in which the binder is ethyl cellulose.

6. The electrosensitive recording material of claim **1** in which the electrosensitive oxide-binder ratio is about 4:1.

7. The process for forming images on the recording material of claim **1** which comprises passing an electric current through the two layers to reduce the oxide in the electrosensitive layer to a lower oxide dark in contrast to the unreduced oxide and to oxidize the metal in the metal layer to an oxide dark in contrast to the metal.

8. The process of claim **7** wherein the unreduced metallic oxide is stannic oxide.

9. The process of claim **7** wherein the unreduced metallic oxide is molybdic oxide.

10. The process of claim **7** wherein the dopant is zinc oxide.

11. The process of claim **7** wherein the binder is ethyl cellulose.

12. The process of claim **7** wherein the electrosensitive oxide-binder ratio is about 4:1.

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