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IMPREGNATED PAPER FOR REPRODUCTION PROCESSES

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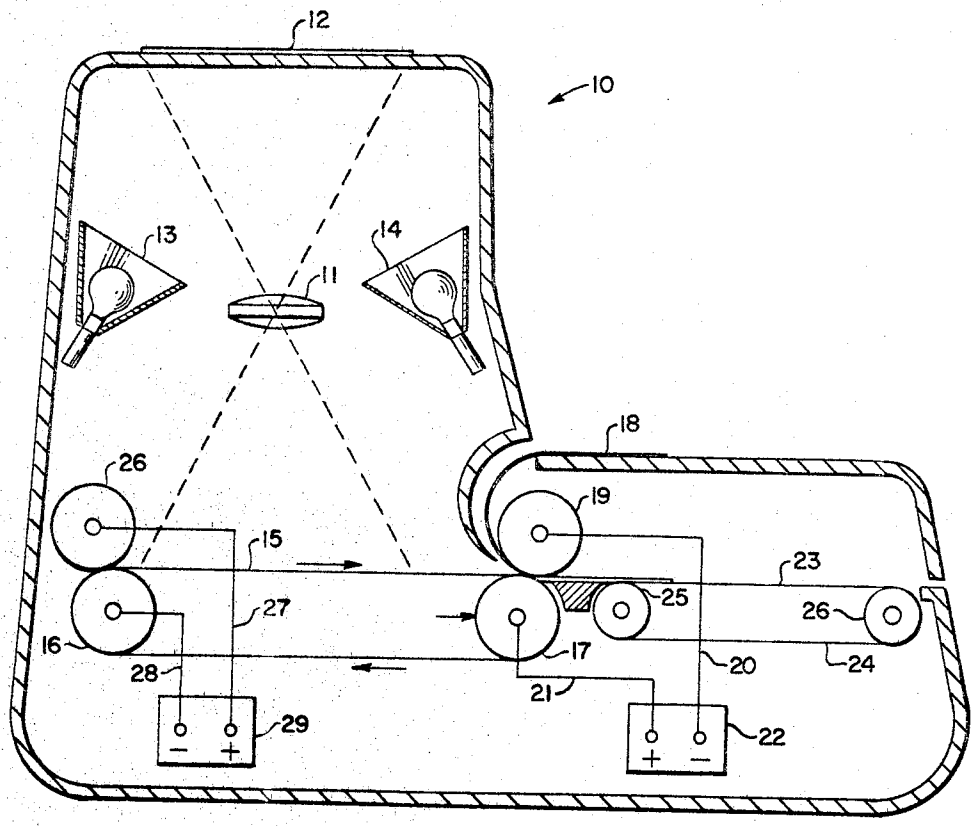

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IMPREGNATED PAPER FOR REPRODUCTION PROCESSES

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ABSTRACT OF THE DISCLOSURE

A copy sheet impregnated with a semiconductor oxide and having no electrically conductive backing is described. The copy sheet is prepared by forming a precipitate on the recording surface and subsequently converting the precipitate to the oxide by immersion of the sheet in boiling water.

The present invention relates to a novel electro-sensitive paper. More particularly, the invention relates to an electro-sensitive recording sheet which does not contain or require a distinct electrically conductive backing layer.

Electro-sensitive recording sheets heretofore known generally comprised an electrically conductive backing and a contiguous layer of a suitable electro-sensitive material. The electrically conductive backings that have been employed in the art include metal foil, paper or fabric impregnated with conductive particles such as aluminum flakes, vapor deposited metal films, conductive plastics, etc. The contiguous electro-sensitive layer usually comprises a dispersion of electro-sensitive material in a binder having a low electrical conductivity.

In my copending U.S. patent application Ser. No. 205,600 filed June 27, 1962 and now Patent No. 3,355,290, there is disclosed a reproduction process for the introduction of a small amount of catalyst ions into a semiconductor layer under the application of an electric field. The introduction of the catalyst ions into the semiconductor layer provides a stable, high contrast record of an original image projected onto the recording structure. There is disclosed, as an embodiment of the invention set forth therein, an electro-photographic sandwich structure consisting of, in the order named, an electrode which may be formed of conductive glass, a photoconductive layer which may be formed of cadmium selenide, zinc oxide or antimony trisulfide, a catalyst layer which acts as a source of catalytic ions, a recording layer comprising a semiconductor material, and a conductive backing for the material. A suggested conductive backing, which functions as an electrode, is aluminum foil.

Also in my co-pending application Ser. No. 463,841 filed June 14, 1965, there is disclosed a positive-to-positive reproduction system. According to the invention disclosed therein, a substantially permanent positive image is formed by having an image projected onto a catalytic layer supported on a conductive backing and then placing the catalytic layer in contact with a copy sheet comprising a semiconductor oxide supported on an electrically conductive backing and applying an electric field between the conductive base of the catalytic layer and the conductive base of the copy sheet.

It is an object of the present invention to provide a recording medium such as a copy sheet which does not require the use of a conductive backing such as aluminum foil, or the like.

It is another object of the invention to provide an electrosensitive copy sheet capable of reproducing highly stable images with good definition and high contrast.

Another object of this invention is to provide a copy sheet which can be employed in the reproduction processes

disclosed in my aforementioned co-pending applications as well as in other prior art reproduction processes employing sensitive materials heretofore deposited on an electrically conductive backing.

A still further object of the present invention is to provide methods for producing the electro-sensitive recording sheet of the present invention.

Other objects and advantages of the present invention will become apparent from the consideration of the following description in conjunction with the appended drawing.

The figure, is a schematic diagram of a photocopy apparatus that employs the electro-sensitive copy sheet of the present invention.

According to the present invention an electro-sensitive recording sheet is obtained which does not require the presence of an electrically conductive backing layer. It has been found that electro-sensitive materials can be uniformly precipitated inside of the fibers of a suitable recording sheet. The electro-sensitive materials comprise those materials known in the art such as semiconductor oxides. These oxides are known as materials suitable for use in electro-sensitive paper because they undergo a change in color upon reduction to a lower oxidation state.

The process of the present invention results in the precipitation of a suitable oxide pigment inside the fibers of the recording sheet. The oxide pigment introduced according to the process of the present invention is evenly distributed throughout the recording sheet. After the pigment has been introduced in the manner to be described below, the electro-sensitive material is "doped" to bring out the semiconductive properties of the material. The doping material and procedure will vary somewhat with the semiconductor material considered, as will be understood by those skilled in the art.

An electro-sensitive material which has been found particularly suitable is antimony trioxide. This oxide results in a recording sheet which can be employed without any electrically conductive backing layer. One manner of preparing a recording sheet containing antimony trioxide inside the fibers is by passing an untreated recording sheet into a bath comprising an acid solution of an antimony trihalide (such as antimony trichloride) in hydrochloric acid. After the recording sheet has been thoroughly soaked in the solution of antimony trichloride, the sheet is transferred to another bath containing cool running water (a temperature of 15° C. is suitable). Upon transfer of the sheet from the acid solution of antimony trichloride to the bath containing cool water, a white precipitate of antimony oxychloride is formed which covers the surface of the recording sheet. The formation of this precipitate is due to the hydrolysis of the antimony trichloride according to the following equations:

$$SbCl_3 \rightarrow Sb^{3+} + 3Cl^-$$

$$Sb^{3+} + H_2O \leftrightharpoons SbO + 2H^+$$

$$SbO + Cl \leftrightharpoons SbOCl$$

If desired, an aqueous ammonium hydroxide bath can alternatively be employed to bring about precipitation on the recording sheet. The antimony oxychloride which covers the surface of the recording sheet is converted into the corresponding oxide by imersing the recording sheet in water, preferably boiling water. The oxychloride precipitate is converted into oxide according to the following equation:

$$2SbOCl + H_2O \rightarrow Sb_2O_3 + 2HCl$$

As a result of this precipitation technique, the antimony trioxide pigment is formed inside of the fibers of the recording sheet. After the oxide has been formed

in the sheet the semiconductive properties are brought out by "doping" the oxide. The doping material and procedure is determined from the semiconductor's energy band structure and solid state properties. In the case of antimony trioxide, a solution of copper sulfate may be employed to dope the crystal. The doping of the oxide can be simply accomplished by immersing the recording sheet in a solution of a suitable doping agent. After the oxide has been doped, the recording sheet is dried by suitable means known in the art, such as, for example, under tension between two layers of blotting paper. This avoids wrinkling of the recording sheet.

Alternatively, a recording sheet containing antimony trioxide uniformly distributed inside the fibers of the sheet may be prepared by passing the untreated sheet into a bath comprising an alcohol (e.g. methanol) solution of antimony trichloride. After the recording sheet has been thoroughly soaked in the alcoholic solution of antimony trichloride, the sheet is transferred to a bath containing cool water. This transfer to a water bath results in the precipitation of antimony oxychloride which covers the surface of the recording sheet. The precipitation can also be effected by employing an aqueous ammonium hydroxide bath in place of the water bath. The precipitate on the recording sheet is then converted to the corresponding oxide in the manner described above.

Another semiconductor oxide that can be precipitated inside the fibers of a recording sheet and eliminates the necessity of having an electrically conductive base layer is bismuth trioxide. The processes described above for the introduction of antimony trioxide inside the fibers of a recording sheet are the same for bismuth trioxide.

For example, the bismuth trioxide is introduced inside the fibers of the recording sheet by first immersing the untreated sheet in an acid solution of bismuth trichloride in hydrochloric acid. After the recording sheet has been immersed in the acid solution, it is immersed in a bath of cool water. This immersion results in the formation of a preciptate of bismuth oxychloride on the surface of the recording sheet. The formation of this precipitate upon the immersion of the sheet in the water bath is shown by the following equations:

$$BiCl_3 \rightarrow Bi^{3+} + 3Cl^-$$
$$Bi^{3+} + H_2O \leftrightharpoons BiO^+ + 2H^+$$
$$BiO^+ + Cl^- \leftrightharpoons BiOCl$$

The conversion of the oxychloride into the corresponding oxide takes place in the same way as for antimony in a subsequent immersion in boiling water.

The doping of the sheet containing bismuth trioxide inside the fibers is performed by immersion of the sheet in a doping solution containing a suitable doping agent. The doping solution comprises an ionic salt such as ammonium nitrate in water, a minor amount of humectant such as glycerol, sorbitol or other glycol and the desired doping material, in this case, nickel chloride.

Specific illustrative but non-limiting examples of the preparation of the recording medium of the present invention are as follows:

EXAMPLE 1

A paper to be used as an electro-sensitive recording sheet was soaked for about one minute in an acid solution comprising 100 grams bismuth trichloride in 100 cc. 37% hydrochloric acid and 100 cc. water. After immersion in the acid solution of bismuth trichloride, the sheet is transferred to another solution comprising 70 cc. of ammonium hydroxide in 200 cc. water and immersed in that solution for about ten minutes while agitating the solution.

After about ten minutes immersion in the aqueous ammonium hydroxide solution the sheet was removed and washed with boiling water which resulted in precipitation of bismuth trioxide inside the fibers of the sheet.

The semiconductive properties of the bismuth trioxide are brought out by immersing the sheet, wth agitation for ten minutes, in a solution comprising 0.6 gram nickel chloride, 160 grams ammonium nitrate, 25 cc. glycerol and 380 cc. of water. After immersion in the doping solution the sheet is dried between blotters.

A recording of a 60 cycle per second electrical signal on the bismuth trioxide sheet was obtained.

EXAMPLE 2

A recording sheet was prepared according to Example 1, except that the untreated sheet was immersed in an alcoholic solution comprising 100 grams bismuth trichloride and 300 cc. methanol for about five minutes in place of the acid solution of Example 1.

EXAMPLE 3

A recording sheet was prepared according to Example 1, except that precipitation was brought about by immersion of the sheet in a distilled cool water bath in place of the aqueous ammonium hydroxide solution of that example.

EXAMPLE 4

A recording sheet was prepared according to Example 1, except that antimony trichloride was used in place of bismuth trichloride and the doping material was 0.5 gram of copper sulfate instead of the nickel chloride of that example.

While the examples are given in specific quantities, it will be appreciated that in practice the total quantities may be adjusted to be appropriate for the processing apparatus. Unless otherwise indicated the process steps are conducted at room temperature approximately.

The semiconductor oxide recording sheet of the present invention which does not contain an electrically conductive backing layer, is particularly useful in photocopy applications, and may be utilized in an apparatus such as that illustrated in the drawing, for example.

Photocopy apparatus **10** comprises a lens **11** for focussing an image of a document **12**, or other subject to be reproduced. The image of a document is focussed by lens **11** under illumination from light sources **13** and **14** on to a catalytic belt **15**. The composition used for the catalytic belt **15** can be a mixture of a metal thiocyanate with an oxide capable of being reduced to a lower state of oxidation. A preferred catalytic composition includes a mixture of cuprous thiocyanate with titanium dioxide. A more detailed disclosure of the preparation of suitable catalytic compositions for use in the apparatus of the figure, is found in my copending application Ser. No. 463,841, filed on June 14, 1965.

The catalytic belt **15** is driven by rollers **16** and **17**. The copy sheet **18**, which is the electro-sensitive recording sheet of the present invention impregnated with a semiconductor oxide in a higher state of oxidation, and which does not contain an electrically conductive backing, is contacted with the catalytic belt **15** under the pressure of rollers **17** and **19**. These rollers **17** and **19** are electrically connected by leads **20** and **21** to a source of electrical potential **22** providing the necessary electrical field for the transfer of the latent image formed on the catalytic belt **15** onto the copy sheet **18**.

The positive reproduction **23** of the original image is transferred outside the machine by belt **24** driven by pulleys **25** and **26**.

The latent image on the catalytic belt **15** can be erased by providing an electrical potential between rollers **16** and **26** which are connected by leads **27** and **28** to a source of electrical potential **29**. The image is erased due to the reactivation of the deactivated catalyst in the catalytic belt **15**. The electric field applied between roller **26** and the base of the catalytic belt causes electrons to be accepted by the neutralized metal ions in the belt and, therefore, reinstates the original ionic nature of the catalytic surface so that it can be used continuously.

The electro-sensitive recording sheet of the present invention can also effectively be employed in the photocopy processes of my copending application Ser. Nos. 487,480 now abandoned and 491,786 now U.S. Patent 3,309,198, filed Sept. 15, 1965 and Sept. 30, 1965, respectively. The disclosure of U.S. Patent 3,309,198 is incorporated herein by reference, particularly as to the semiconductor oxides disclosed therein. Furthermore, the copysheet of the present invention may be utilized in numerous reproduction processes of the prior art which employ semiconductor oxides.

Other variations and modifications of the present invention are possible and will be apparent to those of skill in the art. For example, the processes described above for the impregnation of the copysheet may be used to impregnate zinc oxide or equivalent materials to make a xerographic paper for a process of the Electrofax type.

It is accordingly desired that the scope of the invention not be limited to those embodiments specifically illustrated or suggested, but that the scope of the invention be defined by reference to the appended claims.

What is claimed is:

1. A recording sheet consisting essentially of a semiconductor oxide selected from the class consisting of antimony trioxide and bismuth trioxide, said semiconductor oxide being impregnated into the fibers of said medium, said medium being free of any electrically conductive backing layer and said semiconductor oxide being in a higher state of oxidation and undergoing a change in color upon reduction to a lower oxidation state.

2. A recording medium according to claim **1** wherein said medium is a copy sheet.

3. A copy sheet according to claim **1** wherein the semiconductor oxide impregnated in the fibers of said copy sheet is doped with a doping composition.

4. A copy sheet according to claim **3** wherein the semiconductor oxide is antimony trioxide.

5. A copy sheet according to claim **4** wherein said doping composition comprises a doping agent of copper sulfate in a solution of an ionic salt and a humectant.

6. A copy sheet according to claim **3** wherein the semiconductor oxide is bismuth trioxide.

7. A copy sheet according to claim **6** wherein said doping composition comprises a doping agent of nickel chloride in a solution of an ionic salt and a humectant.

8. The method of preparing a semiconductor oxide recording sheet which does not contain any electrically conductive backing layer which comprises immersing an untreated sheet in an acid solution or an alcoholic solution containing a corresponding halide of the semiconductor oxide to be impregnated inside of the fibers of said recording sheet subsequently, immersing said sheet in a medium selected from the class consisting of water and an aqueous ammonium hydroxide solution, thereby forming a precipitate on said recording sheet, immersing said recording sheet in boiling water to convert said precipitate to the semiconductor oxide and drying said recording sheet.

9. The method according to claim **8** wherein said untreated sheet is immersed in an acid solution or an alcoholic solution containing a member selected from the class consisting of antimony trichloride and bismuth trichloride.

10. The method according to claim **9**, including the additional step of immersing said sheet in a doping composition comprising a doping agent in a solution of an ionic salt and a humectant, subsequent to the immersion of said sheet in boiling water.

11. The method according to claim **10** wherein the untreated sheet is immersed in an hydrochloric acid solution containing antimony trichloride, and wherein after immersion of said sheet in said acid solution said sheet is immersed in an aqueous ammonium hydroxide solution.

12. The method according to claim **11** wherein the doping agent is copper sulfate.

13. The method according to claim **10** wherein the untreated sheet is immersed in methanol solution containing bismuth trichloride and wherein after immersion of said recording sheet in said alcoholic solution, said sheet is immersed in a water bath.

14. The method according to claim **13** wherein the doping agent is nickel chloride.

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