Jan. 21, 1964 C. M. WISWELL ETAL 3,118,789

ELECTRICALLY CONDUCTIVE COATED PAPER

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Fig. 1.

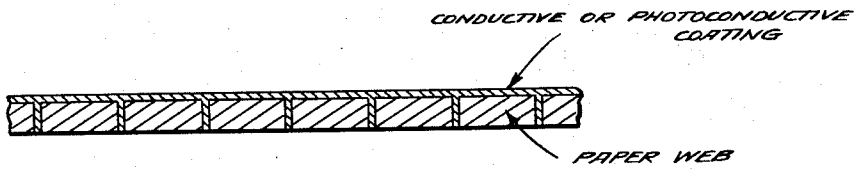


Fig. 2.

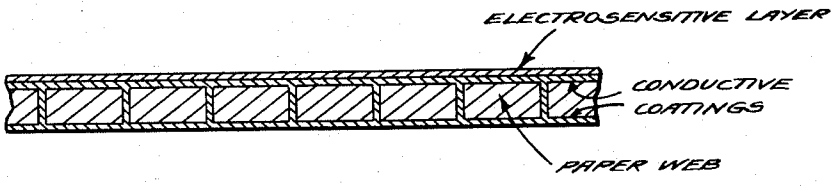
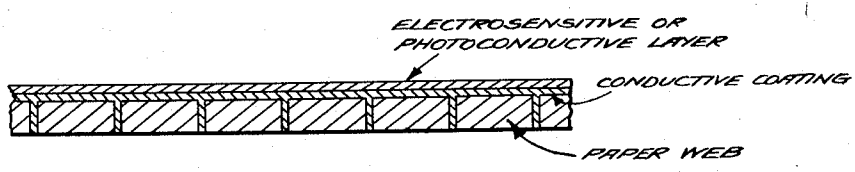


Fig. 3.



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ELECTRICALLY CONDUCTIVE COATED PAPER

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This invention relates to coated paper which is electrically conductive.

Ordinary paper, which normally consists of cellulosic fibers, filler such as clay, and some water-repellent sizing material such as rosin-size, has a relatively high electrical resistivity. Though the actual resistivity of such paper will vary considerably depending upon the relative humidity to which it is exposed, it will always be so high that the paper can be considered as an insulator rather than as a conductor of electricity.

In some applications it is desired that paper should have a considerable degree of electrical conductivity. For instance, in one form of facsimile transmission of messages or photographs in which the message is recorded on electrosensitive blanks by an electric stylus it is desirable that the current shall pass through the paper base of the blank and into the grounded conductive supporting platen or revolving drum to which the blank is attached.

Another instance where good electrical conductivity is desirable is in the base paper for electrographic recording in which an insulating layer capable of being electrostatically charged is supported by a conductive carrier sheet. Good conductance right up to the insulating layer on the one hand makes easier the attainment of a high electrostatic charge on that layer and on the other hand at the desired time permits the rapid dissipation of the balancing charge present under the insulating layer.

A similar instance is in the case of electrophotographic coatings on paper. As pointed out by Carlson in U.S. Patent No. 2,297,691, the support for such a coating should be conductive, both to facilitate charging of the coating and to permit ready discharge of the areas subsequently exposed to light.

Of the many proposed methods for increasing the electrical conductivity of paper webs, most have involved inclusion in the paper web of material which improves conductivity under conditions of medium to high relative humidity, but has little effect at low relative humidity. Substantially the only generally successful method of ensuring good conductivity in a paper web at low humidity has been to fill the web during manufacture with conductive carbon-black.

To produce carbon-black filled paper the carbon-black must be included in the fibrous furnish from which the paper web is formed. This ordinarily requires having the paper custom-made to order some time before it is to be converted to the special use for which its conductivity is desired. Moreover when such paper is once formed on the paper machine its conductivity is fixed and cannot thereafter be altered in any substantial degree to fit the needs or requirements of the moment.

The present invention enables a paper-coater to start with substantially any available paper supply and to produce therefrom a coated paper web which is readily conductive through the sheet from front to back. Moreover the paper-coater can to a considerable degree regulate the conductivity of the paper to fit specific requirements.

According to the invention a web of paper of substantially any type is coated with a layer of coating which is electrically conductive. To ensure electric conductance through the paper base, the web prior to being coated is pricked or punctured, as by small diameter pins, so that

during the coating process the coating composition penetrates the resulting holes and forms tiny paths of conductive matter from the coated surface to the under surface of the sheet. Considerable variation in the degree of conductance can be obtained by varying the composition of the coating and/or by varying the size of the pin-holes and the number thereof per unit area. The holes however should preferably always be so small that they do not show through the coating layer on the coated side of the web to cause visible pits or blemishes thereon. It is therefore better merely to pierce the web rather than to use a perforating die which actually cuts away portions of the web. Piercing pins having diameters from about 0.01 inch to about 0.05 inch have been used satisfactorily. Piercing may provide an additional advantage by raising a ring of fibers beyond the surface of the reverse side of the web so that the plug of coating which subsequently fills the puncture can also extend slightly beyond the general level of the paper surface. The piercings or punctures should preferably be fairly close together. Spacings between about ¼ inch and 1½ inches are of the order of those considered most feasible.

Probably the most effective conductive coating is composed of conductive carbon-black and organic adhesive or binding material. Substantially any convenient adhesive may be used, such as casein, starch, latex, resin, etc. In cases where the effect of humidity might be undesirable resinous adhesives are preferable.

To make sure that the electrical paths formed by the plugs of conductive coating which penetrate such punctures can make connection with a grounded support on which the coated paper may be placed in use, it is usually advisable to take some special step to ensure that result. One step which will usually ensure good electrical contact of the conductive plugs with a smooth metal support is to pass the coated paper through a calender to make it smooth. Even greater assurance of good electrical contact with the metal support may be achieved by also coating the reverse side of the web with a conductive coating so that the plugs or paths through the punctures or pin-holes actually join together the conductive coating layers borne on the opposite sides of the web.

Embodiments of the invention are described in the following examples.

Example 1

A sized web of paper containing both long and short chemical wood fibers and a small quantity of clay filler and weighing about 50 pounds per 25" x 38"—500 sheet ream, or about 75 grams per square meter, was pierced by pins of 0.02 inch diameter at one inch intervals. The web was then coated on one side with about 10 pounds per ream, dry weight (or 15 grams per square meter), of an aqueous coating mixture containing the following ingredients:

50 parts by weight of electrically conductive carbon-black (added in the form of a paste).
100 parts by weight of internally plasticized vinyl acetate copolymer (added in the form of a latex, "Flexbond 800" sold by Colton Chemical Co. of Cleveland, Ohio.)
Water to make solids content 32%.

The black coating composition penetrated the pin-holes, as could be seen by observing the reverse side of the web. The coated web was then dried and smoothed by being passed through a supercalender.

Thereafter over the black conductive coating was applied an electrosensitive coating of about 10 pounds per ream, dry weight (or 15 grams per square meter), of the following composition:

100 parts by weight of cuprous thiocyanate powder.

40 parts by weight of "Penford Gum" a partial hydroxyethyl starch ether.
1 part by weight of "Tergitol 4."
½ part by weight of tributyl phosphate, an anti-foam agent.
Water to make solids content 30%.

"Tergitol 4" is the trade name of a wetting agent said to be the sodium sulfate derivative of 7-ethyl-2-methyl-undecanol-4.

As is well known the normally white cuprous thiocyanate when subjected to electric current as when a coated paper is electrically inscribed by a spark from a stylus is converted into black copper sulfide.

The coated paper was then dried.

A sheet of the paper was attached to the grounded revolving drum in a conventional facsimile receiver and was readily imaged by means of signal currents applied to an electric stylus. At any time during the recording of the facsimile image by the electrified stylus, the paper and the grounded machine could be simultaneously touched by the operator without experiencing the slightest electrical shock, thus showing the presence of an effective electrical path through the paper web to the grounded supporting drum.

Example 2

The procedure of Example 1 was repeated in every detail except that the paper web was not pierced before being coated. When this sheet was placed on the grounded drum in the facsimile receiver, conductivity through the web was insufficient to assure operator safety. Freedom from shock was not obtained until a grounding electrode having prongs to penetrate the paper into the conductive layer was applied to the top or coated surface of the web.

The pierced paper web bearing the calendered black conductive coating as described in Example 1 also makes a good conductive base for electrographic or electrophotographic coatings. For instance, coating such a base with about 10 grams per square meter of a clear layer of polystyrene desposited from a volatile solvent results in a product which is excellent for taking an electrostatic charge in the electrographic recording process. In this case, since the paper is black, the ink used to develop the charged image should be white or some other light color.

An excellent electrophotographic recording paper can be produced by applying to the same calendered black conductive coated base of Example 1 a layer of about 30 grams, dry weight, per square meter of photoconductive zinc oxide bound with about 15 percent of silicone resin dispersed in volatile solvent. This product is readily charged by corona discharge in the absence of actinic radiation. The product is gray because the underlying black layer shows through the white top coat. The charged image thereon can be developed by black or other colored electroscopic powder.

It is not necessary, however, for a satisfactory base of an electrophotographic recording paper to have as high a degree of conductivity as that provided by the conductive carbon-black coating previously described. For satisfactory results according to the invention it is adequate to have the photoconductive coating itself penetrate through pin-holes in the paper base to make contact with a supporting ground. Following Example 3 shows such an electrophotographic recording paper.

Example 3

A sized paper web weighing 80 grams per square meter was pierced at 3/8 inch (about 1 cm.) intervals with pins of 0.02 inch diameter. This pierced web was thereafter coated on one side by applying thereto 30 grams per square meter, dry weight, of an aqueous coating mixture containing, in parts by weight: 130 parts of water, 120 parts of photoconductive zinc oxide, and 20 parts of water-soluble resin made by reacting 1 part of diisopropylamine with 10 parts of a resinous copolymer of 95 parts vinyl acetate and 5 parts crotonic acid. The coated web was force-dried to insolubilize the resin, and then was smoothed by passage through a supercalender. The sheet was given an electrostatic charge by exposure to a corona discharge in the dark. The sheet while resting on a grounded metal support was then exposed to actinic radiation through a transparency. The latent image remaining on the unexposed area was then developed by application of electroscopic powder to the sheet. No powder was picked up by the exposed background area, showing that the charge thereon had been entirely dissipated.

The embodiments of the invention described above are illustrated in the accompanying drawings in which

FIG. 1 is an enlarged cross section of a web of paper having pin-holes therethrough and a conductive coating covering one surface of the web and extending through the pin-holes,

FIG. 2 is an enlarged cross section of a web of paper having a conductive coating on both sides and an additional electrosensitive layer and,

FIG. 3 is an enlarged cross section of a web of paper having a conductive coating on one side only and an additional electrosensitive or photoconductive layer.

In the drawings the paper web and the coatings are adequately identified by legends.

It will be understood that in the embodiment illustrated in FIG. 1 the conductive coating shown may be merely a conductive coating as described at the beginning of Example 1 or a photoconductive coating as described at the end of Example 2. Referring to FIG. 2 it will be appreciated that the electrosensitive coating may be omitted leaving only the paper web having a conductive coating on both sides. Also referring to FIGS. 2 and 3 it will be appreciated that an electrosensitive, photoconductive, electrographic, or electrophotographic coating may be superposed upon a paper web which has a conductive coating on only one side or both sides.

In the foregoing we have referred to electrically conductive paper, paper having a good electrical conductivity and paper having a considerable degree of electrical conductivity as compared with paper having a relatively high electrical resistivity or which is an insulator. These terms are well understood in the art but for completeness we may say that ordinary paper which is regarded as being non-conductive has an estimated resistance of at least about 10^{10} ohm-centimeters whereas paper having a higher degree of conductivity may have a resistance of the order of 10^6 ohm-centimeters or less, e.g., 10^2 ohm-centimeters. It is to be understood that our invention is not limited to paper having any particular conductivity but embraces all paper products which have been rendered more conductive by the application of an electrically conductive coating in the manner described.

Also for completeness we may say that a conductive coating is one which is conductive under normal conditions of illumination and atmosphere, a photosensitive coating is one which is non-conductive in the dark but is conductive when exposed to light, an electrophotographic coating is a photoconductive coating which can be electrostatically charged in the dark but loses its charge when exposed to light, and an electrographic coating is one which can be electrostatically charged in light as well as in the dark.

We claim:

1. A coated paper product comprising a paper web of negligible electrical conductivity, pin-holes extending through said paper web, and an electrically conductive coating forming a layer on at least one side of said web and also extending through said pin-holes to form electrically conductive paths from said coating layer to the reverse side of said web.

2. A product as set forth in claim 1 having upon said

electrically conductive layer another layer of coating of lower electrical conductivity than said conductive layer.

3. A product as set forth in claim 1 having a layer of electrically conductive coating on the reverse side of the web.

4. An electrosensitive recording blank comprising a paper base, pin-holes through said base, over said base and penetrating said pin-holes an electrically conductive layer comprising conductive carbon-black and vinyl acetate copolymer binder, and a top electrosensitive layer containing a pigment which is discolorable upon treatment by an electric stylus, said blank by reason of penetration of conductive matter through said pin-holes, having electrical paths from said conductive layer to the reverse side of said paper base.

5. Process of making a paper web electrically conductive from its front surface to its under surface which comprises piercing the web at intervals to form pin-holes therein, subsequently applying to at least one surface of the web and into the pin-holes therein a coating composition which after being dried will be electrically conductive, and drying the coated web.

6. Process of claim 5 in which the coated web is subsequently calendered to make the reverse side flat and smooth.

7. Process of claim 5 in which the reverse side of the web also is coated with an electrically conductive coating.

8. Process of claim 5 in which there is applied over the electrically conductive coating layer another layer of coating having less conductivity than said electrically conductive coating layer.

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