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R. B. GIBNEY
ELECTROGRAPHIC RECORDING

2,530,956

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FIG. 1

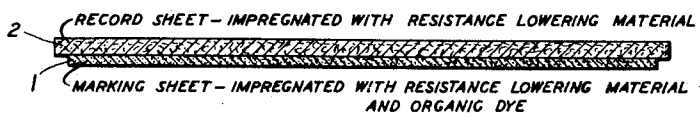


FIG. 2

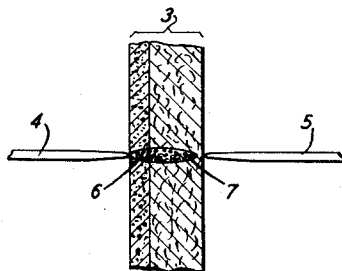


FIG. 3

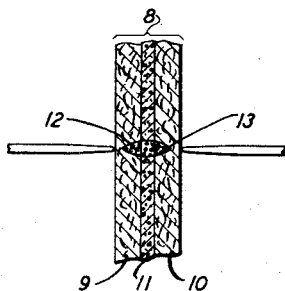
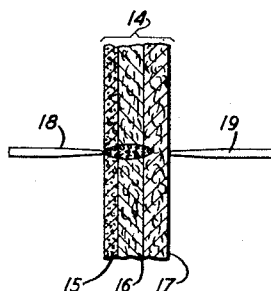


FIG. 4



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ELECTROGRAPHIC RECORDING

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7 Claims. (Cl. 204—2)

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This invention relates to electrochemical recording media and more particularly to the production of visible marks upon a paper by the passage of an electric current.

An object of the invention is to provide an improved form of electrographic recording medium which will provide clear stable marks of high definition when acted upon by high potential low density currents.

Another object is to provide an electrographic recording medium which is dry and requires no special preparation either before or after the recording process.

A further object is to provide an electrographic recording medium which is insensitive to light, stable in the atmosphere, and which may be handled with safety.

Methods of electrochemical recording are well known and, generally speaking, those methods depend upon either the electrolytic production of inorganic salts or metals or the electrolytic production of organic reaction products. Electrographic papers using either type of reaction have had substantial disadvantages, the former being characterized by requirements of high current density while the latter types have been unsatisfactory due to auto-oxidation of the organic agents or the instability of the colored reaction products.

Efforts to improve the known techniques have been directed primarily toward finding more satisfactory agents for the second type of reaction. United States Patent 1,970,539, issued August 21, 1934 to V. Bausch describes an electrographic paper which depends upon the volatility of certain of the amines or the light sensitivity of the diazo compounds to neutralize the active agent after marking to prevent the subsequent auto-oxidation and formation of colored products. United States Patent 2,367,113 issued January 9, 1945 to R. B. Gibney utilizes the electrolytic oxidation of the leuco bases in the presence of a weak acid in order to obtain a more stable colored product.

While the papers described in the referenced patents go far toward overcoming the disadvantages and shortcomings of the previously known techniques, they have certain limitations. Particularly, they are dependent upon the presence of moisture in order that the electrolytic action may take place, the primary agents tend to be light sensitive, and they require high current densities in order to obtain satisfactory marking speeds.

The recording process of the present invention

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overcomes the limitations referred to by utilizing the principle that charged ions in a conducting solution will move between electrodes in that solution upon the application of a potential to the electrodes. According, there is provided a composite recording sheet consisting of a dye impregnated marking sheet in close contact with a record sheet, the combination being impregnated with a solid compound which is electrically conducting in the molten state. The selection of dye and impregnant is such that the application of a high potential to point electrodes in contact with opposite sides of the composite sheet will melt the solid and cause colored ions to migrate to the record sheet, thus producing a characteristic mark.

Other features and aspects of the invention will be apparent from a consideration of the following detailed specification and appended claims taken in connection with the accompanying drawing, in which:

Fig. 1 shows a cross-section of the recording paper;

Fig. 2 shows an enlarged cross-section of the paper and a pair of electrodes to which a high potential has been applied;

Fig. 3 shows a composite sheet in which the marking sheet carries two dyes to produce mirror images upon the two record sheets; and

Fig. 4 shows a method of making duplicate record sheets.

Referring to Fig. 1, there is shown a cross-sectional view of the composite electrographic paper. The dye or marking sheet 1 consists of a tissue paper which has been impregnated with an organic dye and a resistance lowering material which will melt to form a conducting liquid. In close contact is a record sheet 2 of a strong white paper which has been impregnated only with the resistance lowering material.

Fig. 2 shows in enlarged cross-sectional view the manner in which the marking action takes place when the composite sheet 3 is placed between point electrodes as in a facsimile printer. Upon the application of a sufficiently high potential to point electrodes 4 and 5 in contact with opposite sides of the sheet 3 enough current will flow through the volumes 6 and 7 to cause a rapid increase in temperature. When the melting point of the impregnant is reached, it becomes highly conducting, thus providing an electrolytic medium. The high potential gradient will cause the ionized dye molecules in the volume 6 in the marking sheet to move toward the electrode 5 which must be of the opposite polarity

with respect to that of the colored dye ions. Upon removal of the potential, current ceases to flow and the impregnant hardens, leaving a dye impregnated volume 7 in the record sheet.

Fig. 3 shows an enlarged cross-sectional view of an electrographic sheet which may be used to produce marks which are mirror images. Composite sheet 3 is made up of two record sheets 9 and 10 on opposite sides of the marking sheet 11, all of which are impregnated with the resistance lowering material. Marking sheet 11 is impregnated also with two organic dyes, one forming color bearing ions, having a positive charge, the other forming color bearing ions having a negative charge. During the marking process, the groups of ions will separate to move towards the oppositely charged electrodes and form images in volumes 12 and 13. The record sheet bearing the inverted image may be useful in certain types of duplicating processes where a large number of copies are to be made.

Fig. 4 shows an electrographic sheet suitable for making duplicate copies of the recording. Composite sheet 14 is made up of marking sheet 15 and record sheets 16 and 17, impregnated as in the example of Fig. 1. By the use of relatively slow writing speeds and high potentials at electrodes 18 and 19, the color bearing ions from marking sheet 15 will pass through record sheet 16 into record sheet 17 thus producing identical copies.

In order to put the paper to its intended use, a series of point electrodes, such as those illustrated in Fig. 2 may be provided with means for switching the activating potential from electrode to electrode. A typical example of such a device is shown in United States Patent 2,273,433, issued February 17, 1942 to E. Bruce, where an electron beam is caused to sweep a mosaic of conductors over which the electrographic paper moves. As the beam strikes a given conductor, a potential is applied across the paper producing a mark by the described process. In actual use with such a device, the paper has been shown to be sensitive and fast, capable of marking at the rate of several inches per second and with currents as low as 150 microamperes. It is to be understood that this example is by way of illustration only as the paper will function satisfactorily when used with the drum and point electrode of the usual facsimile receiver.

In order to prepare the electrographic paper it is first necessary to select an impregnant which will function properly in conjunction with the volt-ampere characteristic of the printing device to be used. In operation, the impregnant must act both as a resistance lowering agent to facilitate the flow of current through the sheet and, after melting, as an electrolytic medium for the formation and movement of the color-bearing ions. The resistance of the impregnated paper must be such that it will not materially limit the maximum current available, as in the case of the cathode ray device referred to above, where the paper resistance may be of any value up to one megohm. Under such conditions the temperature of the region between the electrodes will reach a value which is limited only by the amount of current available from the printer and an impregnant must be chosen which will melt within that range.

It has been found that certain of the acid amides are well adapted to meet the requirements for the impregnant. Acetamide, a normally

solid crystalline compound melts at about 70° C. to form an electrically conducting liquid. In order to meet special requirements, propionamide may be used to obtain a higher melting point, while formamide, a normally liquid member of the series, may be added to the impregnant to lower the melting point and hence increase the speed of fusion. These three substances, propionamide, acetamide and formamide, constitute the entire group of saturated fatty acid amides containing not more than three carbon atoms. A typical and satisfactory solution may be made up of the following proportions: one hundred grams of acetamide; ten grams of formamide; and sufficient water to make up to a total of two hundred fifty cubic centimeters. The impregnant deposited from such a solution is, upon drying a solid solution of the amide components.

A base is selected for the record sheet which is sufficiently porous to be thoroughly penetrated by the impregnant. A strong bond paper which will not tear when wetted to saturation may be used. Paper is by nature a porous, flexible, electrically insulating sheet, when dry. Paper is not necessary however as any material may be used which is sufficiently strong mechanically and which is capable of carrying the impregnant when deposited from solution.

Impregnation may be accomplished in any desired manner, for example, by passing the paper, if paper is used, continuously through the solution in strip form and rolling it so as to insure thorough impregnation and removal of air bubbles and excess impregnant. If it is found that the impregnated paper dries too slowly for continuous processing, it is possible to utilize some other and more volatile solvent. Methyl alcohol may be used, but it then becomes necessary to use a relatively coarse and very absorbent material as the base, otherwise evaporation will take place with excessive rapidity and consequent crystallization in large needles on the surface of the sheet.

The preparation of the dye or marking sheet is very similar to the preparation of the record sheet described above. The base may be much lighter, such as a tissue paper, but of such composition that it will absorb the impregnant and yet provide sufficient strength for processing. The electrolytic impregnant used for the dye sheet should be the same as used for the record sheet, with the addition however for the proportions indicated of two to four grams of an organic dye.

The dye selected must have the following characteristics to fulfill its required function:

It must have a salt-forming group.

It must, when ionized, form a colored ion the net charge of which is not zero. Such ions are produced from any of the dye molecules which are in the form of salts and in which all of the salt radicals in any one molecule are salts of acid groups or salts of basic groups or in which the number of groups of acid salts and groups of basic salts are not equal.

It must be soluble in acetamide.

Of the groups of dyes which have the above-mentioned requisites further selection may be made as to color, or as to the formation of positive or negative color bearing ions, either of which will be dictated by the intended use of the electrographic paper. For example, Victoria blue may be selected for an application which requires a positively charged ion, while the dye known as

methyl orange may be selected where a negatively charged ion is necessary.

In order to complete the preparation of the paper it is necessary only that the marking sheet and record sheet be rolled together. This may best be accomplished just before the impregnant has fully dried in order that a maximum adhesion between the two sheets is secured with a minimum premature transfer of color. The best conditions are dependent upon the matrix and impregnant used and should be determined by experiment. No special precautions are necessary for storage for reasonable periods of time, however for longer periods the prepared papers must be stored in sealed containers to prevent loss of the impregnant by sublimation. A few crystals of acetamide may be placed in the container if storage for extended intervals is contemplated.

While the invention has been described and illustrated with reference to certain preferred embodiments, it is to be understood that a great latitude for substitution and alteration exists without departures from the scope of the invention as defined in the appended claims.

What is claimed is:

1. An electrographic recording medium comprising two essentially dry paper sheets in face to face contact, each impregnated with a mixture of acetamide and formamide in the proportions of about 100 parts of the former to 10 parts of the latter, one of said sheets being also impregnated with the dye, Victoria blue, in the proportion of about 2 parts of dye per 100 parts of acetamide.

2. An electrographic recording medium comprising two essentially dry paper sheets in face to face contact, each impregnated with a normally solid, saturated, fatty acid amide containing not more than three carbon atoms, one of said sheets being also impregnated with a salt-forming organic dye, soluble and ionizable in said amide in the molten state to form colored ions having a net electric charge.

3. An article as described in claim 2 wherein the amide is acetamide.

4. An electrographic recording medium comprising two essentially dry paper sheets in face to face contact, each impregnated with a solid solution of saturated fatty acid amides containing not more than three carbon atoms, one of said sheets being also impregnated with a salt-forming organic dye, soluble and ionizable in said mixture of amides in the molten state to form colored ions having a net electric charge.

5. An electrographic recording medium com-

prising two essentially dry porous sheets in face to face contact, each impregnated with a normally solid organic compound capable of melting locally at a point on the sheets to an electrically conducting liquid under the passage of a small electric current through the sheet at said point, said porous sheets being formed of a substance which imparts to the sheets in the unimpregnated state a resistivity higher than that of said organic compound in the solid state, one only of said sheets being also impregnated with an organic dye soluble in said organic compound in the molten state and ionizable in said molten organic compound to form color-bearing ions having a net electric charge.

6. An electrographic marking sheet comprising an essentially dry paper sheet containing an impregnant comprising acetamide, formamide and Victoria blue in the proportions of about 100 parts acetamide, 10 parts formamide and 2 to 4 parts Victoria blue, said sheet being adapted for electrographic recording by reason of its ability to form color-bearing ions and provide an electrolytic path for the movement of said ions to the medium to be marked.

7. An essentially dry paper sheet, for electrographic recording, impregnated with acetamide and formamide in the proportions of about 10 parts of acetamide to 1 part of formamide.

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