

## UNITED STATES PATENT OFFICE

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## ELECTROGRAPHIC RECORDING MEDIUM

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This invention relates to recording media, and particularly to a paper which becomes discolored or otherwise marked by the passage of an electric current therethrough.

An object of the invention is to provide an improved form of an electrographic recording medium. A study of the problem of improving such media led to the attempt to find one which shall be highly sensitive to electric current, producing easily recognizable marks when activated by a comparatively weak current; which shall be capable of producing clear marks of high definition with a minimum of fringes; which shall produce marks which are stable and persist over reasonable times; which shall give marks of a pleasing color on a back-ground of equally pleasing color; which may be manufactured with ease and safety; which is composed of materials readily obtainable through the ordinary channels of commerce; which may be handled without excessive precautions in that it is not unduly sensitive to ordinary daylight; which may be handled with safety in that it is not corrosive to the human skin; which does not require particular preparation, as distinguished from manufacture, prior to use; and which does not require any development or fixation process subsequent to use.

In accordance with the invention in its preferred specific form there is provided a medium having all of the desirable characteristics above mentioned. In a somewhat narrower aspect media are provided in which one or more of these characteristics are absent or are present in a lesser degree than in the specific preferred form but which are nevertheless improvements over the media heretofore used, as will hereinafter appear.

Other objects and features will be apparent from the following description of the invention.

To overcome the various disadvantages and objections which characterize the well-known electrographic papers of the inorganic salt type it has already been proposed to employ a paper impregnated with leuco bases, e. g., tetramethyl-p-diamino triphenyl methane and to produce a discoloration reaction therein on the passage of electric current by anodic oxidation to the corresponding dyestuff, e. g. malachite green. So far as is known, and as pointed out in U. S. Patent 1,970,539, August 21, 1934, papers so prepared have been unsatisfactory inasmuch as they either show a tendency to autooxidation or else the colored reaction products are themselves unstable, causing the electrographic record to disappear.

In contrast with the foregoing, however, it has been discovered that a particular member of the

group of dye-forming compounds known as leuco bases lends itself readily to this use, and also that many such compounds, and the one preferred in particular, may be admixed with certain other carefully chosen ingredients which add to their stability and generally to their reliability in operation and use.

Accordingly, and in pursuance of the objects of the invention in its preferred form there is prepared an alcohol solution of an organic leuco base, preferably a hydrocarbon substituted diamino-diphenylmethane, such as tetramethyldiaminodiphenylmethane, a weak, normally solid acid which is slightly soluble in water, such as boric acid, a substance such as potassium hydroxide, capable of forming a buffer by equilibrium reaction with the acid, and a hygroscopic agent such as sorbitol. In a preferred solution the constituents and their proportions are as follows:

|    |                             |                |
|----|-----------------------------|----------------|
| 20 | Tetramethyldiaminodiphenyl- |                |
|    | methane -----               | grams-- 5-10   |
|    | Boric acid-----             | do----- 50-100 |
|    | Potassium hydroxide-----    | do----- 5-10   |
|    | Sorbitol -----              | do----- 50-100 |
| 25 | Methyl alcohol-----         | liter-- 1      |

The preferred base is a strong white bond paper which shall not tear when wetted to saturation, but this preference is based only on the strength of the paper, and any paper, or indeed any web-like material capable of absorbing or otherwise carrying and holding the novel mixture, may be employed without departing from the spirit of the invention. The paper, if paper is used, may be impregnated with the mixture in any desired manner, for example by passing it in the form of a long strip through a vat or tub containing the mixture while pressing and rolling it to remove any air bubbles which may be attached to it and to ensure a thorough soaking. This method has the advantage that the manufacturing process for the paper itself is not modified or altered in any way. However, if desired the impregnation may be carried out as a part of the paper-making process and at any point therein at which subsequent operations will not disturb or be disturbed by the presence of any of the ingredients of the mixture. Indeed, if proper precautions be observed, the novel solution may be mixed with the batch itself prior to the felting operation.

It is, of course, advisable to see that the novel mixture be a thorough and intimate one, else the resulting treated paper might be non-homogeneous in its constituents and therefore non-uniform in its properties.

After the paper has been thoroughly saturated with the novel solution in order to secure an intimate and uniform dispersion of all the ingredients, the alcohol should be allowed to evaporate or otherwise removed, leaving dispersed in the paper an intimate and homogeneous mixture of substances all of which are solids, with the exception of a small quantity of moisture taken up from the atmosphere by the sorbitol. The paper is thus dry enough to be handled with safety without having to resort to especial precautions to avoid injury to it as might be the case were it soaking wet.

The removal of the alcohol should be complete, else the colored deposit formed by the passage of the current might spread and so degrade the definition of the marks, since the dye, as well as the leuco base, is soluble in alcohol. However, the presence of the moisture absorbed by the sorbitol in the proportions given above does not produce this effect since the organic compound is not appreciably soluble in water.

Since the novel mixture is practically colorless the natural color of the paper is preserved, and this provides the background for the markings. For most purposes plain white paper is to be preferred, but if desired a colored paper may be employed provided the color is one against which the color of the dye formed in use will provide good visual contrast. For example, the blue dye of tetramethyldiaminodiphenylmethane is clearly visible against the background of a scarlet paper.

The paper as thus prepared is slightly sensitive to bright light, but not so much so as to necessitate especial precautions in its handling. For example, it may safely be kept in a roll or in the drawer of a cabinet or desk, and may be unrolled and exposed to ordinary indoor light in order to place it in the recording apparatus for use without fear of discoloration. Furthermore, it need not be wetted with liquid water to prepare it for use. Under comparatively humid weather conditions the sorbitol in the quantity stated above absorbs from the atmosphere and holds an amount of moisture which enables the oxidation reaction to take place correctly. In drier weather it may be advisable to keep the paper in a controlled humidity chamber.

Furthermore, since the ingredients of the impregnating solution, with the exception of the alcohol, are all non-volatile, the composition of the impregnating mixture in the paper remains unchanged and therefore the properties of the impregnated paper remain unchanged also.

When the paper as thus prepared is to be put to its intended use it may be placed between the electrodes which are to carry the activating current. For example, it may be passed between the exposed tips of a plurality of conductors which extend through the end wall of a cathode ray tube and a knife edge anode in registry therewith, as disclosed in a copending application of E. Bruce, Serial No. 328,816, filed April 10, 1940 (Bruce 28), now Patent No. 2,273,433, Feb. 17, 1942, and advanced by rollers in a direction perpendicular to the row of conductors while the cathode beam plays from end to end of the row. As the beam strikes a particular conductor a current flows from it through the paper, which is rendered conductive by the presence in it of the electrolyte, to the external knife edge anode. In the presence of the weak acid oxidation of the leuco base takes place at the anode resulting in the formation of an organic dye of deep color and lasting charac-

ter. In an actual test with a cathode ray tube whose conductor tips were about 1.5 mils square, spaced about 10 mils apart, and an anode whose "knife edge" was about 10 mils wide, and through which a current of 500 microamperes was passed for 1/2000 second, the novel paper, prepared with tetramethyldiaminodiphenylmethane, gave good, strong, well defined marks of a deep blue color. In this case the discharge of electricity was of the order of 1/4 microcoulomb and the momentary current density at the anode during discharge was of the order of 5 amperes per square inch. To avoid electrolytic reaction with the materials of the comb conductors on the knife edge anodes, the latter are preferably of non-corrosive metal.

After the passage of the current, the process is complete, the paper requiring no finishing process in the nature of development or fixation. Furthermore, the dark marks are sufficiently durable for all practical purposes. It is only necessary to preserve the marked paper in such a manner that it will not be contacted by a dye solvent, such as alcohol, which might cause the marks to run, and to preserve it from excessive exposure to light which might darken the light background.

Although a paper bearing the organic substance alone will, when sufficiently wetted to render it conductive, become discolored on the passage of current, each of the auxiliary ingredients of the novel mixture offers specific advantages. The oxidation reaction takes place best in the presence of a weak acid, especially when stabilized by a buffer. In the presence of a strong acid the paper is unduly light sensitive and the strong acids cannot readily be stabilized. Boric acid meets these requirements, being a weak, readily stabilized acid. It offers the further advantage that it is normally solid and not deliquescent so that the paper containing it is not rendered wet by the acid or by atmospheric moisture absorbed by the acid. The only moisture in the paper is that absorbed by the sorbitol, and its quantity, which need only be small, is therefore controllable and independent of the amount of acid present.

The potassium hydroxide reacts with the boric acid to produce potassium borate which exists in equilibrium with the boric acid and the potassium hydroxide. The borate acts, along with the acid, as an electrolyte to conduct the current through the paper, and it also serves as a buffer to maintain the proper ion concentration to allow the oxidation reaction to take place.

A further advantage offered by the potassium borate and therefore by the potassium hydroxide from which it is formed by reaction with the boric acid, is that its anions in electrolysis are not discharged at an anode in preference to oxygen. Therefore the concentrations of the ingredients are not substantially altered in the course of the reaction, nor is the anode corroded or the paper discolored by the presence of secondary reaction products.

It is also true of the novel mixture as a whole that the oxidation reaction takes place without either cathode or anode taking part chemically therein. As a result both electrodes may be incorporated as permanent elements of the recording apparatus.

The sorbitol acts to absorb and hold sufficient moisture to dissolve a small quantity of the boric acid and the potassium hydroxide and so permit the electrolytic action to take place. The alcohol is employed because it is believed to be the best

known solvent for both the organic leuco base and the boric acid. The choices of potassium borate for the electrolytic salt and sorbitol for the hygroscopic agent are further dictated by the facts that these substances too are soluble in alcohol.

The considerations underlying the choice of the preferred proportions of the novel solution are as follows: About 5 grams of the organic dye-forming substance per liter of alcohol will impregnate paper of ordinary thickness sufficiently to give strong, clear marks when fully oxidized. Much less than 5 grams per liter would create a danger that, if the distribution of the organic substance in the paper were not completely uniform, certain regions of the paper might not be fully supplied. To ensure against this, it is preferred to provide somewhat more, so that the most poorly impregnated regions have enough while the most fully impregnated regions have a harmless excess. At the same time it is preferred not to attempt to use much more than 10 grams per liter of alcohol on account of the difficulty of dissolving a greater quantity.

The oxidation reaction takes place best in a weak acid medium, and it is desirable that the boric acid be substantially in excess of the potassium hydroxide so that the latter may be wholly neutralized with the formation of potassium borate in sufficient quantities to provide the buffer action. For this purpose 5 to 10 grams of potassium hydroxide have been found sufficient, and the use of a quantity of acid ten times as great assures that this reaction shall be substantially complete. Such a quantity, namely, 50 to 100 grams of the acid can be readily dissolved in a liter of the alcohol, whereas much more could not be.

50 to 100 grams of sorbitol per liter of alcohol provides a sorbitol concentration which is adequate to absorb from the atmosphere an amount of moisture which dissolves enough of the acid to render the paper conductive and allow the electrolytic action to take place, but not so much as to wet it enough to render handling difficult.

Diphenylmethane compounds are preferred to mono-, tri- or tetraphenylmethane compounds for the following reasons. The last named are so stable that they do not give an appreciable discoloration reaction on the passage of current. The triphenyl compounds are extremely sensitive to light and precautions must be taken to protect them from exposure, both before the recording operation and afterward. Therefore, they are believed to be less suitable than the preferred compound. However, they may be found useful in special cases, for example when only a small current is available and precautions against exposure to light are not objectionable.

The amino derivative of the monophenyl compound, otherwise known as toluidine, besides being comparatively insensitive to the electrolytic reaction, is self-oxidizing and becomes discolored in time. Furthermore, this substance is corrosive to the hands.

Each phenyl group may have attached to it one amino group, more than one, or none at all. Of these combinations it is found that all the compounds having more than one amino group per phenyl group require additional protection in order that the oxidation reaction may progress in a satisfactory manner, and consequently they are not recommended. Likewise, the presence of at least one amino group in the compound appears to be essential to the formation of the

dye. Hence consideration is limited to one amino group for monophenyl (toluidine), one or two amino groups for diphenyl, and one, two or three amino groups for triphenyl.

Toluidine and monoaminodiphenylmethane give faint colors of inferior character and, though their use is possible when sufficiently strong and prolonged currents are available, they are less sensitive than the preferred compounds.

Each amino group has connected to it two groups, one or both of which may be either hydrogen or a hydrocarbon radical. Of the compounds so constituted all are believed to be operative within the limits discussed above. In general, a stronger, deeper color is obtainable with a compound in which the replaceable hydrogen of the amino groups are all substituted with hydrocarbon radicals than with compounds not so substituted. Thus, for example, the tetramethyl compound is preferred to the tri-, di-, and monomethyl compounds and also to the unsubstituted compound, diaminodiphenylmethane. This particular compound offers the further advantage that it is readily obtainable in commerce.

Whatever the leuco base employed it is of advantage to employ with it a weak solid acid and a hygroscopic agent. Further, to insure that the light sensitivity shall not be excessive, it is desirable to employ in addition either a buffer or some compound which will form a buffer by reaction with the acid. The exact identity and proportions of the ingredients named above serve these purposes well, and are therefore recommended, though substances having like or equivalent properties may be employed without departing from the spirit of the invention.

While in the foregoing the invention has been described, for the sake of particularity, with reference to a sheet support capable of being impregnated, it is to be understood that it is equally applicable to a web-like or film-like material bearing the novel mixture on its surface but not impregnated therewith.

What is claimed is:

1. An electrographic porous recording medium in sheet form carrying in its pores a mixture of a compound selected from the group consisting of diaminodiphenylmethane, monomethyldiaminodiphenylmethane, dimethyldiaminodiphenylmethane, trimethyldiaminodiphenylmethane, and tetramethyldiaminodiphenylmethane, an excess of a weak, solid, slightly water-soluble acid which is not changed in electrolysis, and an electrolytically inactive hygroscopic agent, said acid and hygroscopic agent being present in such amounts that if humid air is permitted to penetrate the mixture in said pores a small amount of moisture is absorbed by the hygroscopic agent and a correspondingly small amount of the acid is dissolved in said absorbed moisture, said solution existing in equilibrium with the undissolved excess of acid.

2. The combination with a porous supporting medium adapted to hold solid material within its pores when deposited there from solution which material is suitable for electrographic recording by reason of its being responsive to oxygen released from the anode when a voltage is applied to electrodes in contact with the medium, of a readily volatilizable liquid within the pores of said medium in which has been dissolved boric acid, potassium hydroxide and tetramethyldiaminodiphenylmethane, the ratios of the weight of the boric acid to that of the tetramethyldiamino-

diphenylmethane and to that of the potassium hydroxide being within the range from five to twenty and the ratio of the weight of the tetramethyldiaminodiphenylmethane to that of the potassium hydroxide being within the range from one-half to two, and a quantity of hygroscopic substance sufficient only to make the material in said pores a good conductor of electricity when said volatilizable liquid has been evaporated and the medium is subsequently exposed to humid air.

3. The combination of claim 2 in which said hygroscopic substance is sorbitol.

4. The combination with a porous supporting medium adapted to hold solid material within its pores when deposited there from solution which material is suitable for electrographic recording by reason of its being responsive to oxygen liberated at the anode when a voltage is applied to electrodes in contact with said medium, of material within the pores of said medium comprising alcohol in which has been dissolved the following substances in the amounts specified per liter of alcohol: 5 to 10 grams of tetramethyldiaminodiphenylmethane, 50 to 100 grams of boric acid, 5 to 10 grams of potassium hydroxide and 50 to 100 grams of sorbitol.

5. The combination with a porous supporting medium of solid material within the pores of said medium adapted when in a substantially dry state for electrographic recording by reason of its being responsive to oxygen liberated at the anode when a voltage is applied to electrodes in contact with said medium which material comprises essentially tetramethyldiaminodiphenylmethane, boric acid, potassium hydroxide, potassium borate and a quantity of hygroscopic substance sufficient to make the material in its pores a good conductor of electricity when the medium is subsequently exposed to humid air.

6. The combination with a porous supporting medium adapted to hold solid material within its pores when deposited there from solution which material is suitable for electrographic recording

by reason of its being responsive to oxygen released from the anode when a voltage is applied to electrodes in contact with the medium, of a readily volatilizable liquid within the pores of said medium in which has been dissolved boric acid, potassium hydroxide and an organic dye-forming substance selected from the group consisting of diaminodiphenylmethane, monomethyldiaminodiphenylmethane, dimethyldiaminodiphenylmethane, trimethyldiaminodiphenylmethane, and tetramethyldiaminodiphenylmethane, the ratio of the weight of the boric acid to that of the dye-forming substance and to that of the potassium hydroxide being within the range from five to twenty and the ratio of the weight of the dye-forming substance to that of the potassium hydroxide being in the range from one-half to two, and a quantity of hygroscopic substance sufficient only to make the material in said pores a good conductor of electricity when said volatilizable liquid has been evaporated and the medium is subsequently exposed to humid air.

7. The combination with a porous supporting medium adapted to hold solid material within its pores when deposited there from solution which material is suitable for electrographic recording by reason of its being responsive to oxygen released from the anode when a voltage is applied to electrodes in contact with the medium, of a readily volatilizable liquid within the pores of said medium in which has been dissolved an organic dye-forming substance selected from a group consisting of diaminodiphenylmethane, monomethyldiaminodiphenylmethane, dimethyldiaminodiphenylmethane, trimethyldiaminodiphenylmethane, and tetramethyldiaminodiphenylmethane together with boric acid, potassium hydroxide, potassium borate, and a quantity of a hygroscopic substance sufficient only to make the material a good conductor of electricity when said volatilizable liquid has been evaporated and the medium is subsequently exposed to humid air.

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