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ELECTROLYTIC RECORDING

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The present invention concerns electrolytic recording and, in particular, sensitizing materials for facsimile electrolytic recording surfaces.

One object of the present invention is to provide sensitizing material for a facsimile recording sheet capable of improved image reproduction.

Another object is to provide a sensitized sheet for facsimile or other recording capable of yielding a sharper and more permanent print than has hitherto been obtainable.

Still another object is to provide materials capable of yielding a sharp electrolytic print which does not spread or lose its detail subsequent to recording.

A still further object is to provide recording materials which do not discolor subsequent to recording.

These and other objects will be apparent from the detailed description of the invention.

Electrolytic recording is the art of recording by means of the electrolytic action of an electric current upon a properly sensitized medium. The recording current is localized to produce marks under control of a machine or operator. In facsimile recording it is common practice to scan a record sheet with a stylus carrying current modulated according to the instantaneous density of the subject to be reproduced. A properly sensitized sheet, for instance, may be passed under a reciprocating stylus carrying the recording current or the equivalent scanning operation may be carried out in a number of ways well known to those skilled in the art.

In order to produce a mark or image on the recording sheet the sheet must carry on its surface or impregnated in its structure materials which change color or optical density or both in response to the passage on an electric current.

One method of preparing such a current sensitive surface is to impregnate a sheet of paper with pyrocatechin, sodium or potassium nitrate, and water, and to record by means of an iron stylus carrying the recording current. The sodium nitrate in water solution is electrolytically conductive and is decomposed upon the passage of the recording current. An alkali, sodium hydroxide, is produced at the cathode of the recording circuit. This alkali passes thru the paper to the anode where the iron of the recording electrode is dissolved and meeting the pyrocatechin in the presence of the alkali forms a color lake. The iron lake is dense and nearly black in color, providing a record of high contrast and density. A small amount of an acid strong enough to dissolve the lake may be added to sharpen detail and prevent spreading of the recorded image. The acid which prevents lake formation is neutralized by the above mentioned alkali at the recording point, allowing the lake to form, producing a desired image, but prevents spreading of the lake to non-recording points by destroying the lake beyond the point of marking.

It has been found that a second form of spreading and loss of detail in the recording is due to the fact that the color lake forming the image is a hydrated colloid, or hydrophyllic sol, and is composed of positively charged particles. If enough excess moisture remains after recording, or is picked up from a humid atmosphere, these charged particles repel each other and tend to migrate, especially when the H^+ ions from the unmarked part of the paper diffuse into the marked zones.

Dehydration sufficient to remove this excess moisture, subsequent to recording, is possible and is effective, but is cumbersome and slow. It would require a drying attachment to the recorder, which would increase both the weight of the instrument and its power consumption.

Migration may also be prevented by removal of the positive charge. This discharge or precipitation may be accomplished by the use of a salt or acid whose negative ion is of higher valence than the positive. It has been found that an ion with a valence of at least three is highly desirable, since the trivalent ion is much more effective than the divalent and the tetravalent than the trivalent. Since it must, in general, also be soluble and colorless, the number of available substances with polyvalent-ions is limited. Phosphates, citrates and naphthol disulfonates have been found to be particularly desirable.

It has been found that phosphoric acid is effective as a precipitating electrolyte when used in an amount as low as two per cent by weight of the amount of pyrocatechin used as sensitizer.

This phosphate ion is equally effective whether introduced as a phosphoric acid or as an acid phosphate.

It has been found that citric acid or naphthol disulfonic acid in amounts of the order of 0.5 per cent may also be used as precipitants.

It has been found that since many trivalent ions, such as PO_4, form insoluble ferric salts, the lake formed in their presence is in much lower concentration than if the insoluble ferric salts were not present. It has also been found that, in such cases, a satisfactory amount of lake can be obtained if a polyhydroxy compound, such as glycerine, dextrine, mannitol, citric acid, tar-

taric acid, or a glycol, is also present. The amount of such hydroxy body, which can be effectively used, varies with its nature. For instance, as much as 10 per cent of glycerine may be used, whereas as little as 0.5 per cent of citric acid may interfere with oxidation of the electrode.

It has been found that while the above materials and methods produce an initially sharp and contrasty print, the light colored background may be subject to discoloration due to oxidation, especially if the recording is exposed to sunlight or oxidizing oils, such as linseed and tung oils.

According to the present invention this discoloration by oxidation may be substantially prevented by the addition of a small amount of a powerful reducing agent to the sensitizing material. Among those substances, which have been found to be effective antioxidants when used in quantities small enough not to unduly increase the power requirements of recording, usually less than five per cent of the aromatic lake-forming compound, are salts of hydrazine and phenyl hydrazine, such as the sulfate or hydrochloride, allyl thiourea, thiourea, and salts of semi-carbazide, such as sulfate or hydro-chloride. Thiourea, because of its effectiveness and commercial availability, has been found to be particularly useful. Also, a mixture of more than one of these agents has been found to be more effective than one alone, as, for instance, thiourea and semi-carbazide hydrochloride; or a mixture of hydrazine sulfate and allyl thiourea.

By combining the precipitant and antioxidant in the same formula, the resulting sensitization is capable of giving very sharp detail in a print that is permanent, and at the same time, paper so prepared resists discoloration on exposure to sunlight, catalysts, and high humidity, over a much longer period of time than papers hitherto available.

A small amount of penetrant may be added to lower the surface tension during impregnation. Various compounds may be used for the purpose. Commonly used penetrants are sodium alkyl sulfonate, alkylated aryl sulfonate, and dioctylester of sodium sulfo succinic acid.

Specifically, recording papers may be prepared by impregnation with any of the following formulae:

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
$NaH_2PO_4 \cdot H_2O$	do	0.3
H_3PO_4 (85% strength)	cubic centimeter	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
H_3PO_4	cubic centimeters	0.1
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
Citric acid	do	0.5
Thiourea	do	0.1
Penetrant	cubic centimeters	0.1

4

Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
$NaH_2PO_4 \cdot H_2O$	do	0.3
H_3PO_4	cubic centimeters	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1
Glycerin	do	5

5

Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
$NaH_2PO_4 \cdot H_2O$	do	0.3
H_3PO_4	cubic centimeters	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1
Glycerin	do	5
Pyrocatechin sulfonic acid	grams	0.5

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
Salicyclic sulfonic acid	do	0.3
H_3PO_4 (85%)	cubic centimeters	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1
Glycerin	do	5
Pyrocatechin sulfonic acid	grams	0.5

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
$NaH_2PO_4 \cdot H_2O$	do	0.3
H_3PO_4	cubic centimeters	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1
Glycerin	do	5
Citric acid	grams	0.1

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Water	cubic centimeters	100
Potassium nitrate	grams	20
Pyrocatechin	do	5
$NaH_2PO_4 \cdot H_2O$	do	0.3
H_3PO_4	cubic centimeters	0.05
Thiourea	grams	0.1
Penetrant	cubic centimeters	0.1
Glycerin	do	5
Pyrocatechin sulfonic acid	grams	0.5
Citric acid	do	0.1

Electrolytic recording may be performed on the papers prepared according to the above specifications by scanning them with an iron-bearing electrode carrying modulated signal currents. It has been found that iron-bearing electrodes containing a hardening element are to be preferred. A stainless steel containing about 5 per cent molybdenum has been found to be highly satisfactory as the recording electrode.

The present invention has been described and a few specific examples have been given. Many combinations will be apparent to those skilled in the art within the spirit and scope of the invention, as set forth in the appended claims.

What is claimed is:

1. A medium for electrolytic recording with a lake-forming metal electrode, including a support treated with pyrocatechin, an aqueous solution of a strong electrolyte, a reducing agent chosen from the class consisting of thiourea, thio-

sinamine, hydrazine, phenyl hydrazine, semicarbazide, and their salts, and a charge neutralizer comprising a source of trivalent negative ions chosen from the class consisting of phosphates, citrates, and naphthol disulfonates.

2. The process of electrolytic recording which comprises passing a modulated current from an electrode consisting essentially of a lake-forming metal through a recording medium containing an aqueous solution of a colorless, lake-forming compound, an acidified solution of an electrolyte, a charge neutralizer that consists of a water soluble compound furnishing negative ions having a valence of at least three, the current passed being sufficient to oxidize the metal of the electrode and to cause it to react with the lake-forming compound to form charged colloidal particles, neutralizing the charge, and precipitating and fixing the color lake in place by means of said compound containing the polyvalent negative ion.

3. A medium for electrolytic recording with an electrode consisting essentially of lake-forming metal which comprises a support impregnated with an aqueous solution consisting of a colorless lake-forming compound which, upon passage of the current becomes a dye and forms an electrically charged, colloidal lake with the metallic ions from the electrode, a small quantity of a strong reducing agent sufficient to keep the background clear, a strong electrolyte to readily conduct an electric current during recording, and a small quantity of a charge neutralizer consisting of a water soluble compound furnishing negative ions of a valence of at least three, the medium being free from mordant forming salts.

4. A medium for electrolytic recording with a lake-forming metal electrode, including a support treated with an aqueous solution containing a lake-forming polyhydroxyphenol, a strong electrolyte, an anti-oxidant chosen from the group consisting of thiourea, thiosinamine, hydrazine, phenylhydrazine, semicarbazide and their salts; and a charge neutralizer comprising a source of trivalent negative ions, chosen from the group consisting of phosphates, naphtholdisulfonates, and citrates.

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