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ELECTROLYTIC RECORDING MEDIUM CONTAINING A POLYNUCLEAR PHENOL

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13 Claims. (Cl. 204—2)

This invention relates to the art of electrolytic recording and in particular to an improved electrolytic recording medium or paper containing a polynuclear phenol.

Recording paper of the electrolytic type is generally marked by passing the paper between a positive eroding metal anode electrode and a negative non-eroding cathode electrode. The paper is impregnated with an electrolytically conducting solution containing certain ingredients. When a voltage is applied between the electrodes and current is passed through the recording paper, metal ions are introduced into the paper from the anode and reacted with one or more of the ingredients of the paper impregnant to form a colored mark on the recording paper.

In order to be acceptable for facsimile recording purposes, the recording paper preferably should be white initially and should have the ability to produce marks having a density which is at least close in linear relationship to the current passed through the paper. The density of the marked area should be variable uniformly in a range from white for zero current flow through medium shades for currents of intermediate magnitude to darker shades for currents of maximum value. The mark should be optically dense so as to provide a good contrast with the white background.

There should also be a minimum of bleeding or fringing of the mark so as to provide good resolution. The unmarked paper while stored in moist condition in sealed containers for extended periods of time prior to use should remain stable without chemical decomposition of its ingredients which would cause discoloration of the paper or affect the reproducibility of results without recorder adjustment. Further, the marked recording paper should not become discolored, give off unpleasant or other odors, or be subject to the transfer of the mark to adjacent materials. The marked recording paper should be insensitive to light even after being repeatedly run through any of the conventional duplicating machines involving exposure to ultraviolet or other strong light sources.

Heretofore successful recording papers have been provided employing catechol as the marking compound, such as disclosed in U.S. Patent 2,339,267 to J. V. L. Hogan et al. and U.S. Patent 2,358,839 to E. R. Wagner. The Hogan patent discloses the use of catechol compounds in an acid solution thereby adding to the stability against discoloration during storage and further to enhance sharpness and detail of the recording.

Although such prior recording papers have been generally satisfactory, difficulty has been had in some cases because of the tendency of catechol to diffuse or transfer to and discolor adjacent sheets of paper in contact with or in close proximity thereto.

The present invention aims to overcome the difficulties and disadvantages of prior recording papers by providing an improved paper which includes a marking agent of lower vapor pressure thus providing a recording paper of low transfer characteristics.

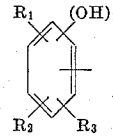
In accordance with the invention this is accomplished by providing a recording paper in which the marking agent is a polynuclear phenol.

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

In accordance with the present invention we have discovered agents which serve as excellent marking compounds in electrolytic media. The new marking agents are polynuclear phenols which are composed of two aromatic rings which are linked by an aliphatic group such that at least one of the aromatic rings contains two hydroxy groups ortho to each other. Such compounds constitute the class represented by the following general formula:

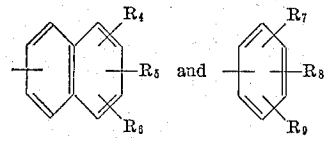
$$A_r—X—A_r'$$

where A_r is



where R_1, R_2, and R_3 are selected from the group consisting of H, OH, OR^e, SO_3H, COOH, Cl, Br, or lower aliphatic groups having one to six carbon atoms, where R^e is a lower aliphatic group having one to six carbon atoms; $(OH)_2$ designates two hydroxy groups ortho to each other;

where A_r' is selected from the group consisting of A_r,



where R_4 and R_9 may be SO_3H, OH, or COOH, R_5 and R_6 may be H, SO_3H, OH, or COOH, R_7 may be H, SO_3H or COOH and R_8 may be H, SO_3H or COOH;

and where X is selected from the group consisting of C_nH_{2n}, $C_nH_{2n-r}Y_r$; where n is 1 to 6, Y is Cl, Br, and r may have any value from 1 to $2n$.

Examples of the new marking agents are:

methylene-di-catechol
ethylidene-di-catechol
ethylidene-di-(3,4-dihydroxytoluene)
ethylidene-di-3-methoxy-catechol
ethylidene-di-pyrogallol
methylene-di-4-chlorocatechol
ethylidene-di-hydroxyhydroquinone
1,1,1-trichloro-(2-catechol 2-naphthalene sulfonic acid)-ethane
1,1,1-trichloro-(2,2-di-catechol)ethane
1,5-bis-(3,4-dihydroxy phenyl)pentane
(3,4 dihydroxy phenyl,naphthalenesulfonic acid) methane

The bridging of the aryl groups as depicted in the general formula provides a series of compounds which have a low vapor pressure and good electrolytic marking capability. Appropriate selection of substituent groups on one or both of the aromatic rings can be made to impart aqueous solubility to these compounds where desired.

The compounds above may be synthesized by modifications of known methods. For example, ethylidine-di-catechol may be synthesized by heating a mixture of 110 parts of catechol, 500 parts of water, 44 parts of paraldehyde, and 10 parts of 25% sulfuric acid for 55 hours at 50 to 60 degrees C. Upon washing the reaction mixture to a neutral pH and the elimination of unreacted catechol by distillation at reduced pressure, 75 parts of a water soluble brown oil remained which solidified to an amorphous mass on standing.

Similarly ethylidene-di(3,4-dihydroxytoluene) was synthesized by heating a mixture of 49.6 parts of 3,4-dihydroxytoluene, 200 parts of water, 17.6 parts of paral-

dehyde, and 4 parts of 25% sulfuric acid for 25 hours at 50 to 55 degrees C. A white solid formed during this period which was recrystallized from 70 parts of hot isopropanol, and washed with 25 parts of ligroin (low boiling). After air drying 23.5 parts of white crystals remained which melted at 117 to 118 degrees C. with decomposition. No description of this material has been found in the literature.

The new marking agents produce a sensitive recording medium wherein the mark density can be appreciably improved by the inclusion of oxidizing agents in the formulation, such as chlorates, bromates, and so forth, as known in the art. The marking agents give a high density mark at varying spot speeds.

An eroding anode electrode is used and may be made of any suitable material such as is well known in the art, including iron, stainless steel, chromium, copper and nickel, together with alloys of various metals as known in the art.

The cathode electrode may be made of any suitable conductive metal able to stand the abrasive effects of the moving recording paper. Metals found acceptable are platinum, platinum alloys, steel, and others as are well known in the art.

Recording media may be prepared by impregnating porous white paper or other porous support of a high wet strength with an impregnant in accordance with the examples herein. The porous support may be passed through a solution of the impregnant, excess impregnant being removed by passing the paper between pressure rollers so that when ready for use in a recorder the media will contain a uniformly distributed and controlled concentration of impregnant. In order to retard evaporation the impregnated paper preferably is stored in suitable sealed containers until needed for use.

Suitable formulations for impregnating into ten square feet of recording paper stock or other porous support are as follows:

Example 1

Ethylidene-di-catechol	2.5
Sodium chloride	10.0
Thiourea	0.25
Water	100.0

Example 2

Ethylidene-di-catechol	4.0
Sodium chloride	7.5
Sodium chlorate	4.0
Thiourea	0.25
Water	100.0

Example 3

Methylene-di-catechol	4.0
Sodium chlorate	4.0
Potassium nitrate	8.0
Thiourea	0.5
Water	100.0

Example 4

Ethylidene-di-(3,4-dihydroxytoluene)	4.0
Sodium chlorate	4.0
Sodium chloride	8.0
Thiourea	0.25
Water	100.0

Example 5

(3,4-dihydroxy phenyl, napthalene-sulfonic acid) methane	5.0
Sodium sulfate	10.0
Sodium chlorate	4.0
Thiourea	0.25
Water	100.0

Example 6

1,1,1-trichloro(2-catechol,2-napthalene sulfonic acid)-ethane	5.0
Sodium sulfate	10.0
Sodium chlorate	4.0
Thiourea	0.25
Water	100.0

Example 7

Ethylidene-dicatechol	4.0
Sodium chloride	7.5
Sodium chlorate	4.0
Oxalic acid	0.9
Sodium dihydrogenphosphate	0.1
Thiourea	0.25
Water	100.0

Example 8

Ethylidene-di-(3,4-dihydroxytoluene)	4.0
Sodium chloride	7.5
Sodium chlorate	4.0
Citric acid	0.08
Thiourea	0.25
Water	100.25

With all of the formulations of the examples satisfactory marks were obtained.

In the examples various concentrations of the marking agent have been used. It is to be understood that the amount of marking agent may be varied from a minimal amount up to the solubility limit thereof. Further, various combinations of the marking agent compounds may be used rather than a single compound. The concentration may be selected so as to be commensurate with conventional recording speeds and marking apparatus sensitivity.

In the examples sodium chloride, potassium nitrate, potassium chloride, and sodium sulfate have been set out as electrolytes. Suitable electrolytes which might be used may be chosen from the group consisting of the chlorides, bromides, nitrates, and sulfates of sodium, potassium, lithium, magnesium, rubidium, cesium, and ammonium. The concentration of the salt may be varied as desired for purposes of varying the electrical conductivity as is known in the art. Such variations may be from minimal amounts to the solubility limits of the respective salts. A suitable range is between 2 and 20 by relative weights. Combinations of the various salts may be used if desired.

It is desirable to provide a pH in the acid range because effective stabilization of the marking agent is thus best achieved. The pH may range between 1 and 5, the preferred range being between 2 and 3.

Thiourea serves as a stabilizer for the recorded marks and may be replaced by another suitable stabilizer such as an alkyl derivative of thiourea, or dithiobiuret. The stabilizer may be varied as desired from minimal amounts up to the solubility limit thereof, larger aounts affording increased stability of the recording medium but sacrificing mark density. A suitable range is between .01 and 1 by relative weight.

In the Examples 2 to 8 sodium chlorate is included as an oxidizing agent. The inclusion of an oxidizing agent in the impregnant formulation provides a marking medium with increased marking sensitivity and greater maximum marking density. Among the oxidants which may be used are the chlorates, bromates, perchlorates, iodates and periodates of the alkali metal salts. A suitable range is between 1 and 10 by relative weight.

The impregnant in any of the above formulations may also include an acidifier and one or more antifringing agents as included in Examples 7 and 8. Such agents are selected from the group including sulfuric acid, nitric acid, hydrochloric acid, cirtric acid and salts thereof, oxalic acid and salts thereof, phosphoric acid and salts

thereof, tartaric acid and salts thereof, and formic acid and salts thereof.

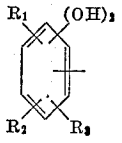
While the invention has been described and illustrated with reference to specific embodiments thereof, it is to be understood that other embodiments may be resorted to without departing from the invention. Therefore, the form of the invention set out above should be considered as illustrative and not as limiting the scope of the following claims.

We claim:

1. An electrolytic recording medium comprising an impregnated sheet containing in an electrolytically conducting solution at least one polynuclear phenol composed of two aromatic rings linked by an aliphatic group, at least one of the aromatic rings containing two hydroxy groups ortho to each other, such polynuclear phenol being selected from the class represented by the following general formula:

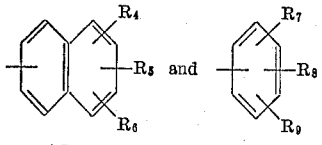
$$A_r—X—A_r'$$

where A_r is



where R_1, R_2, and R_3 are selected from the group consisting of H, OH, OR^e, SO_3H, COOH, Cl, Br, and lower aliphatic groups having one to six carbon atoms, where R^e is a lower aliphatic group having one to six carbon atoms; $(OH)_2$ designates two hydroxy groups ortho to each other;

where A_r' is selected from the group consisting of A_r,



where R_4 and R_9 are selected from the group consisting of SO_3H, OH, and COOH, R_5 and R_6 are selected from the group consisting of H, SO_3H, OH, and COOH, R_7 is selected from the group consisting of H, SO_3H and COOH, and R_8 is selected from the group consisting of H, SO_3H and COOH;

and where X is selected from the group consisting of C_nH_{2n}, C_nH_{2n-r} Y_r; where n is 1 to 6, Y is Cl, Br, and r has a value from 1 to $2n$.

2. An electrolytic recording medium comprising an impregnated sheet containing in an electrolytically conducting solution at least one polynuclear phenol selected from the class consisting of methylene-di-catechol, ethylidene-di-catechol, ethylidene-di-(3,4-dihydroxytoluene), ethylidene - di - 3 - methoxy - catechol, ethylidene - dipyrogallol, methylene-di-4-chlorocatechol, ethylidene-dihydroxyhydroquinone, 1,1,1-trichloro (2-catechol,2-naphthalene sulfonic acid)-ethane, 1,1,1-trichloro-(2,2-dicatechol) ethane, 1,5-bis (3,4-dihydroxy phenyl) pentane, and (3,4-dihydroxy phenyl, napthalene-sulfonic acid) methane.

3. An electrolytic recording medium according to claim 1 in which the solution has been rendered electrolytically conductive by at least one electrolyte selected from the group consisting of the chlorides, bromides, nitrates, and sulfates of sodium, potassium, lithium, magnesium, rubidium, cesium and ammonium.

4. An electrolytic recording medium according to claim 1 in which at least one acid is included therewith selected from the group consisting of sulfuric, nitric, hydrochloric, citric, oxalic, phosphoric, tartaric and formic acids and salts thereof in quantities sufficient to produce a pH of the impregnant solution in the range 1.0 to 5.0.

5. An electrolytic recording medium according to claim 1 in which the pH of the impregnant ranges between 2 and 3.

6. An electrolytic recording medium according to claim 1 in which a stabilizer is incorporated.

7. An electrolytic recording medium according to claim 1 in which a stabilizer is incorporated selected from the group consisting of thiourea, alkyl derivatives of thiourea, and dithiobiuret.

8. An electrolytic recording medium according to claim 1 in which a stabilizer and an acid are incorporated.

9. An electrolytic recording medium according to claim 1 in which an oxidizing agent is incorporated selected from the group consisting of chlorates, bromates, iodates, perchlorates, and periodates of the alkali metal salts.

10. An electrolytic recording medium according to claim 1 in which a stabilizer, an acid, and an oxidizing agent are incorporated.

11. An electrolytic recording medium according to claim 1 in which is included an electrolyte and a stabilizer, the impregnant consisting in essential parts by relative weights of polynuclear phenol between 2.5 and 5, electrolyte between 2 and 20, stabilizer between 0.01 and 1., oxidizing agent between 1 and 10, and water 100.

12. An electrolytic recording medium according to claim 1 in which the impregnant is an aqueous solution which includes a stabilizer and an oxidizing agent, the solution consisting in approximate parts by relative weights of ethylidene-di-catechol 4.0, sodium chloride 7.5, sodium chlorate 4.0, thiourea 0.25, and water 100.

13. An electrolytic recording medium according to claim 1 in which the impregnant is an aqueous solution which includes a stabilizer and an oxidizing agent, the solution consisting in approximate parts by relative weights of ethylidene-di-(3,4-dihydroxytoluene) 4., sodium chloride 8., sodium chlorate 4.0, thiourea 0.25, and water 100.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,342,704 September 19, 1967

Marcel A. Gradsten et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 62, for "diffculties" read -- difficulties --; column 4, line 24, for "100.25" read -- 100.00 --; line 57, for "aounts" read -- amounts --.

Signed and sealed this 12th day of November 1968.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents