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ELECTROLYTIC RECORDING MEDIUM CONTAINING A HALOGENATED POLYHYDRIC PHENOL

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This invention relates to the art of electrolytic recording, and in particular to an improved electrolytic recording medium or paper.

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. Wagner taught the use of catechol compounds together with a charge neutralizer such as phosphates, citrates and naphthol disulfonates in order to reduce spreading and loss of detail in the recording.

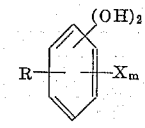
Although such prior recording papers have been generally satisfactory, difficulty has been had in some cases because of the tendency of catechol to diffuse or transfer to and discolor adjacent sheets of paper in contact with or in close proximity thereto.

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 halogenated polyhydric phenol in which at least two of the phenolic hydroxyl groups are ortho to each other.

Other objects and advantages of the invention will be apparent from the following description of an embodiment 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 halogenated polyhydric phenols in which at least two of the phenolic hydroxyl groups are ortho to each other. Such compounds constitute the class represented by the following general formula:



where R is H, OH or CH_3; X is halogen, *m* is 1 or 2; and $(OH)_2$ denotes two ortho phenolic hydroxyl groups.

Examples of the new marking agents are 4-chlorocatechol, 4,5-dichlorocatechol, 4-bromocatechol, 4-chloropyrogallol, 4-chloro-5-bromo catechol, and 4-chloro-3-methyl catechol.

The presence of the halogen group lowers the vapor pressure of the ortho-dihydric phenol without appreciably affecting its aqueous solubility. These halogenated polyhydric phenols produce a sensitive stabilizable 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. At 135 inches per second with a spot size of 0.0001 square inch electrode contact a good dense mark was obtained with 250 milliamperes and 64 volts.

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

	Grams
4-chlorocatechol	4.5
Sodium chloride	10.0
Thiourea	0.25
Water	100

Example 2

	Grams
4-chlorocatechol	4.5
Sodium chloride	7.5
Sodium chlorate	4.0
Thiourea	0.25
Water	100

Example 3

	Grams
4,5-dichlorocatechol	5.0
Sodium chlorate	4.0
Potassium nitrate	8.0
Thiourea	0.2
Water	100

Example 4

	Grams
4-bromocatechol	5.0
Sodium chlorate	4.0
Potassium chloride	8.0
Thiourea	0.25
Water	100

Example 5

	Grams
4-chloro 3-methyl catechol	5.0
Sodium sulfate	10.0
Sodium chlorate	4.0
Thiourea	0.25
Water	100

Example 6

	Grams
4-chlorocatechol	4.5
Sodium chloride	7.5
Sodium chlorate	4.0
Oxalic acid	0.9
Sodium dihydrogenphosphate	0.1
Thiourea	0.25
Water	100

Example 7

	Grams
4-chlorocatechol	4.5
Sodium chloride	7.5
Sodium chlorate	4.0
Citric acid	0.08
Thiourea	0.25
Water	100

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

In the examples a concentration of the marking agent has been set at approximately four percent by weight. However 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. 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 halogenated polyhydric phenols is thus best achieved. The pH may range between 1 and 5, the preferred value being about 2.

Thiourea serves as a stabilizer for the recorded marks and may be replaced by another suitable stabilizer such as one of the alkyl derivatives of thiourea, or dithiobiuret. The stabilizer may be varied as desired from minimal amounts up to the solubility limit thereof, larger amounts affording increased stability of the recording medium but sacrificing mark density.

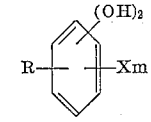
In the examples 2 to 7 sodium chlorate is included as an oxidizing agent. The inclusion of an oxidizing agent in the impregnant formulation provides a marking medium with increased marking sensitivity and greater maximum marking density. Among the oxidants which may be used are the chlorates, bromates, perchlorates, iodates and periodates of the alkali metal salts.

The impregnant in any of the above formulations may also include an acidifier and one or more anti-fringing agents as included in Examples 6 and 7. Such agents are selected from the group including sulfuric acid, nitric acid, hydrochloric acid, citric 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 a halogenated polyhydric phenol in which at least two of the phenolic hydroxyl groups are ortho to each other and selected from the class consisting of:



where R is selected from the group consisting of H, OH and CH_3; X is halogen, *m* is 1 or 2; and $(OH)_2$ denotes two ortho phenolic hydroxyl groups.

2. An electrolytic recording medium comprising an impregnated sheet containing in an electrolytically conducting solution a halogenated polyhydric phenol selected from the class consisting of 4-chlorocatechol, 4,5-dichlorocatechol, 4-bromocatechol, 4-chloropyrogallol, 4-chloro-5-bromocatechol, and 4-chloro-3-methyl catechol.

3. An electrolytic recording medium according to claim **1** in which the impregnant contains an 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 of acids consisting of sulfuric, nitric, hydrochloric, citric, oxalic, phosphoric, tartaric and formic 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 1 and 5.

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 oxidizing agent, and an acid are incorporated.

11. An electrolytic recording medium according to claim 1 in which is included an oxidizing agent and a stabilizer, the impregnant consisting in essential parts by relative weights of halogenated polyhydric phenol 4.5, electrolyte 7.5, stabilizer 0.25, oxidizing agent 4, and water 100.

12. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weights of 4-chlorocatechol 4.5, sodium

chloride 7.5, sodium chlorate 4.0, thiourea 0.25, and water 100.

References Cited

UNITED STATES PATENTS

2,459,521	1/1949	Greig	204—2
2,513,238	1/1950	Greig	204—2
2,949,409	8/1960	Richards	204—2
3,024,173	3/1962	Mandel	204—2
3,123,542	3/1964	Mandel et al.	204—2

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