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ELECTROLYTIC RECORDING MEDIUM CONTAINING A HYDROXYNAPTHOIC ACID

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13 Claims. (Cl. 204—2)

This invention relates to the art of electrosensitive recording, and in particular to an improved electrolytic recording medium or paper containing a hydroxynapthoic acid.

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 enchance sharpness and detail of the recording.

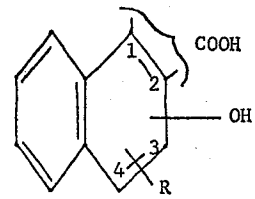
Although such prior recording papers have been generally satisfactory, there has been some difficulty because of the tendency of catechol to diffuse or transfer to and discolor adjacent sheets of paper in contact with or in close proximity thereto.

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 an ortho hydroxynapthoic acid.

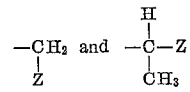
Other objects and advantages of the invention will be

apparent from the following description of an embodiment of the invention.

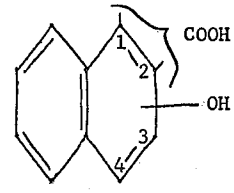
In accordance with the present invention we have discovered agents which serve as excellent marking compounds in electrolytic media. The new marking agents are ortho-hydroxy-napthoic acids. Such compounds are represented by the following general formula:



where the carboxyl group is in the 1 or 2 position, the hydroxyl is ortho to the carboxyl, and the group R is meta to the carboxyl. R is selected from the group including H, lower alkyls,



where Z is



with the same conditions on the carboxyl and hydroxyl as set forth above.

Typical ortho hydroxy napthoic acids include

1-hydroxy-2-napthoic acid,
2-hydroxy-1-napthoic acid,
3-hydroxy-2-napthoic acid,
4-methyl-3-hydroxy-2-napthoic acid,
4,4′-methylene-bis-(3-hydroxy-2-napthoic acid),
4,4′-methylene-bis-(1-hydroxy-2-napthoic acid),
3,3′-methylene-bis-(2-hydroxy-1-napthoic acid),
4,4′-ethylidene-bis-(3-hydroxy-2-napthoic acid),
4,4′-methylene-bis-(1,3′-dihydroxy-2,2′-dinapthoic acid).

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. One of the best alloys has been found to be a stainless steel containing about five percent molybdenum.

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 impregnated media will have about 25–50 percent moisture by weight. 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 of about .003 inch in thickness are as follows:

Example 1

	Grams
1-hydroxy-2-napthoic acid	2
Sodium chloride	10
Water	100

Example 2

1-hydroxy-2-napthoic acid	4
Sodium chloride	10
Water	100
Propylene glycol	25

Example 3

1-hydroxy-2-napthoic acid	4
Sodium sulfate	10
Water	100
Propylene glycol	25

Example 4

3-hydroxy-2-napthoic acid	4
Sodium chloride	10
Water	100
Propylene glycol	25

Example 5

4,4'-methylene-bis-(3-hydroxy-2-napthoic acid)	2
Sodium chloride	10
Water	100

Example 6

4,4'-methylene-bis-(3-hydroxy-2-napthoic acid)	10
Sodium chloride	10
Water	100
Propylene glycol	25

Example 7

4,4'-methylene-bis-(3-hydroxy-2-napthoic acid)	5
Sodium sulfate	10
Water	100
Propylene glycol	25

Example 8

2-hydroxy-1-napthoic acid	2
Sodium chloride	10
Water	100

Example 9

3-hydroxy-2-napthoic acid	4
Sodium nitrate	10
Water	100
Propylene glycol	25

Example 10

2-hydroxy-1-napthoic acid	4
Sodium chloride	10
Water	100
Propylene glycol	25

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

In the examples a concentration of the marking agent has been chosen to provide good solubility in each particular formulation. 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 may be used rather than a single agent. The concentration may be selected so as to be commensurate with conventional recording speeds and marking apparatus sensitivity. As would be expected, the sensitivity of the impregnated medium increases with an increase in concentration of the marking agent.

In the examples sodium chloride, sodium nitrate, and sodium sulfate have been set out as electrolytes. Other suitable salts which might be used as electrolytes are any of the alkali metal nitrates, chlorides and sulfates. 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 and may vary between 2 and 30 parts by relative weight. Combinations of the various salts may be used if desired.

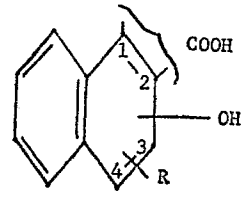
In some of the examples propylene glycol has been added as a solubilizer for the marking compounds. It is understood that other suitable solublizers might be substituted for the propylene glycol such as glycerine, ethylene glycol, trimethylolpropane, mannitol, etc.

The pH of the impregnant may be between 2 and 11, preferably between 3 and 7. It should be noted that the use of propylene glycol as a solubilizer permits a greater concentration of marking compound in the preferred pH range.

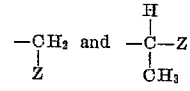
While the invention has been described and illustrated with reference to specific embodiments thereof, it is to be understood that other embodiments may be resorted to without departing from the invention. Therefore, the form of the invention set out above should be considered as illustrative and not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

We claim:

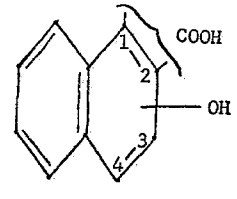
1. An electrolytic recording medium comprising an impregnated sheet containing in an electrolytically conducting solution as a marking agent at least one ortho hydroxy napthoic acid represented by the following general formula:



where the carboxyl group is in the 1 or 2 position, the hydroxyl is ortho to the carboxyl, and the group R is meta to the carboxyl; R is selected from the group consisting essentially of H, lower alkyls,



where Z is



where the carboxyl group is in the 1 or 2 position, and the hydroxyl is ortho to the carboxyl.

2. An electrolytic recording medium comprising an impregnated sheet containing in an electrolytically conducting solution at least one ortho-hydroxy-napthoic acid selected from the class consisting of 1-hydroxy-2-napthoic acid, 2-hydroxy-1-napthoic acid, 3-hydroxy-2-napthoic acid, 4-methyl-3-hydroxy-2-napthoic acid, 4,4'-methylene-bis-(3-hydroxy-2-napthoic acid), 4,4'-methylene-bis-(1-hydroxy-2-napthoic acid), 3,3'-methylene-bis-(2-hydroxy-1-napthoic acid), 4,4'-ethylidene-bis-(3-hydroxy-2-napthoic acid), and 4,4'-methylene - bis - (1,3'-dihydroxy-2,2'-dinapthoic acid).

3. An electrolytic recording medium according to claim

1 in which the impregnant contains at least one salt selected from the group consisting of the chlorides, sulfates and nitrates of the alkali metals.

4. An electrolytic recording medium according to claim 1 in which the pH of the impregnant ranges between 2 and 11.

5. An electrolytic recording medium according to claim 1 in which the pH of the impregnant ranges between 3 and 7.

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

7. An electrolytic recording medium according to claim 1 in which at least one solubilizer is incorporated selected from the group consisting of glycerine, ethylene glycol, propylene glycol, trimethylolpropane, and mannitol.

8. An electrolytic recording medium according to claim 1 in which is included an electrolyte, the impregnant consisting in essential parts by relative weights of hydroxynapthoic acid between 2 and 10 and electrolyte between 2 and 30.

9. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weights of 1-hydroxy-2-napthoic acid 2, sodium chloride 10, and water 100.

10. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weights of 4,4'-methylene-bis-(3-hydroxy-2-napthoic acid) 2, sodium chloride 10, and water 100.

11. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weights of 3-hydroxy-2-napthoic acid 4, sodium chloride 10, propylene glycol 25, and water 100.

12. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weights of 4,4'-methylene-bis-(3-hydroxy-2-napthoic acid) 10, sodium chloride 10, propylene glycol 25, and water 100.

13. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate weights of 4,4'-methylene-bis-(3-hydroxy-2-napthoic acid) 5, sodium sulfate 10, propylene glycol 25, and water 100

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