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3,344,044

# ELECTROLYTIC RECORDING MEDIUM CONTAINING A QUATERNARY AMMONIUM COMPOUND

Marcel A. Gradsten, Demarest, N.J., and Irving Lieblich, Elmhurst, N.Y., assignors to Hogan Faximile Corporation, New York, N.Y.

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8 Claims. (Cl. 204—2)

This invention relates to the art of electrolytic recording, and in particular to an electrolytic recording medium or paper containing a quaternary ammonium compound.

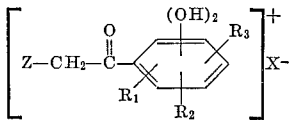
Electrolytic recording is the art of recording by means of the electrolytic action of an electric current upon a properly sensitized medium. The recording current is localized to produce marks under control of a machine or operator. In facsimile recording it is common practice to scan line-by-line a record sheet with a stylus which carries 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 marking compounds which change color or optical density, or both, in response to the passage of an electric current.

One of the most successful types of electrolytic recording paper using an eroding anode is that disclosed in U.S. Patent 2,358,839 to Wagner, in which a polyhydroxyphenolic compound is employed in a recording medium. Such a substance, which is normally colorless, has the characteristic of forming a colored complex compound in combination with iron or other heavy metal. The paper is marked between cathode and anode electrodes. The anode which contains the necessary metal required to form the complex compound dissolves into the paper and is gradually consumed during the recording process. This consumption or erosion of the anode has proven disadvantageous since frequent replacement of the anode is required. Heretofore, many attempts have been made to find ways of reducing erosion of the anode without success.

In U.S. Patent No. 3,122,488 issued to G. Mandel there is a teaching that it is possible to produce excellent marks in a recording medium marked between cathode and anode electrodes, without the erosion of either of the electrodes by incorporating a metal-bearing compound and a selected organic compound in an impregnant medium. An electrolytic recording medium formulated according to Mandel gives satisfactory results.

The present invention aims to provide another electrolytic recording medium which does not require erosion of either of the electrodes.

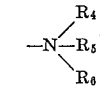
In accordance with the invention it has been found that an electrolytic recording medium is provided by impregnating paper with a manganous or nickelous salt and a quaternary polyhydric phenacyl ammonium compound in which at least two of the phenolic hydroxyl groups are ortho to each other. Such compounds constitute the class represented by the following general formula:



where $R_1$, $R_2$, and $R_3$ may be H, OH, lower alkyls, or



lower alkoxy groups; where Z may be an amine group represented by the formula



wherein $R_4$, $R_5$, and $R_6$ may be H, lower saturated or unsaturated alkyls, or aryl groups; or Z may be a heterocyclic ring structure wherein the phenacyl group is linked to a nitrogen in the ring, and X is halogen or another inorganic anion.

Typical polyhydric phenacyl quaternary ammonium compounds (salts) are

3,4-dihydroxyphenacyl-trimethylammonium chloride,
3,4-dihydroxyphenacyl-triethylammonium bromide,
3,4-dihydroxyphenacyl-triallylammonium nitrate,
3,4,5-trihydroxyphenacyl-trimethylammonium chloride,
3,4-dihydroxyphenacyl-pyridinum chloride,
3,4,5-trihydroxyphenacyl-N-dimethylanilinium chloride,
2-methyl-4,5-dihydroxyphenacyl-diethylmethylammonium iodide,
3,4-dihydroxyphenacyl-isoquinolinium bromide,
3,4-dihydroxyphenacyl-hexamethylene-tetraammonium chloride.

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

EXAMPLE 1

| | Grams |
|---|---|
| 3,4-dihydroxyphenacyl trimethylammonium chloride | 4.0 |
| Sodium chloride | 10.0 |
| Manganous chloride | 2.0 |
| Water | 100.0 |

EXAMPLE 2

| | Grams |
|---|---|
| 3,4-dihydroxyphenacyl trimethylammonium chloride | 2.0 |
| Sodium chloride | 10.0 |
| Sodium bisulfite | 0.2 |
| Manganous chloride | 1.0 |
| Water | 100.0 |

EXAMPLE 3

| | Grams |
|---|---|
| 3,4-dihydroxyphenacyl-pyridinum chloride | 4.0 |
| Sodium sulfate | 10.0 |
| Manganous chloride | 2.0 |
| Sodium bisulfite | 0.2 |
| Thiourea | 0.25 |
| Water | 100.0 |

EXAMPLE 4

| | Grams |
|---|---|
| 3,4-dihydroxyphenacyl-isoquinolinium bromide | 2.0 |
| Potassium chloride | 10.0 |
| Sodium bisulfite | 0.2 |
| Nickelous chloride | 2.0 |
| Water | 100.0 |

EXAMPLE 5

| | Grams |
|---|---|
| 3,4,5 - trihydroxyphenacyl - trimethylammonium chloride | 3.0 |
| Sodium nitrate | 10.0 |
| Hydrazine sulfate | 0.2 |
| Thiourea | 0.25 |
| Nickelous chloride | 2.0 |
| Water | 100.0 |

Recording paper impregnated with each of the formulations was electrolytically markable upon the passage

of current therethrough between electrodes which need not be consumed in the recording process. The mark, in all cases where the electrode was noneroding was a surface mark which appeared at the cathode side of the paper.

In the examples various concentrations of the quaternary ammonium salts have been used. It is to be understood that the amount of quarternary ammonium salt may be varied from a minimal amount up to the solubility limit thereof. Further, various combinations of quaternary ammonium salts may be used rather than a single one. 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, potassium chloride and sodium sulfate have been set out as electrolytes. Other suitable electrolytes which might be used are any of the alkali metal chlorides, nitrates and sulfates, and ammonium nitrate or sulfate. 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.

The pH may range between 1.5 and 6.5. Generally, better stability of the impregnated medium is obtained at the lower end of this range.

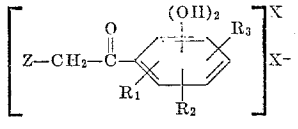
In this system suitable stabilizers are selected from the group including thiourea, alkyl derivatives of thiourea, alkali metal bisulfites, hydrazine and salts thereof, hydroxyl-amines and salts thereof.

The quantities of manganous and nickelous salts or combinations thereof may vary depending upon the intensity of the mark desired, the quantity and type of quaternary ammonium salt used, and the required stability of the system.

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 metal salt chosen from the manganous and nickelous salts and at least one quaternary polyhydric phenacyl ammonium compound in which at least two of the phenolic hydroxyl groups are ortho to each other as represented by the following general formula:




where $R_1$, $R_2$, and $R_3$ is selected from the groups consisting of H, OH, lower alkyls, and lower alkoxy groups; where Z is selected from the group consisting of a heterocyclic ring structure wherein the phenacyl group is linked to a nitrogen in the ring and an amine group represented by the formula




wherein $R_4$, $R_5$, and $R_6$ is selected from the group consisting of H, lower saturated or unsaturated alkyls, and aryl groups; and X is an inorganic anion.

2. An electrolytic recording medium according to claim 1 in which the quaternary ammonium compound is selected from the class consisting of 3,4-dihydroxyphenacyl-trimethylammonium chloride, 3,4-dihydroxyphenacyl-triethylammonium bromide, 3,4-dihydroxyphenacyltriallylammonium nitrate, 3,4,5-trihydroxyphenacyl-triethylammonium chloride, 3,4,5-trihydroxyphenacyl-N-dimethylanilinium chloride, 2-methyl-4,5-dihydroxyphenacyl-diethylmethylammonium iodide, 3,4-dihydroxyphenacyl-pyridinium chloride, 3,4-dihydroxyphenacyl-isoquinolinium bromide, 3,4-dihydroxyphenacyl-hexamethylenetetraammonium chloride.

3. An electrolytic recording medium according to claim 1 in which the pH of the medium ranges between 1.5 and 6.5.

4. An electrolytic recording medium according to claim 1 in which a stabilizer is included.

5. An electrolytic recording medium according to claim 1 in which a stabilizer is included which is selected from the group consisting of thiourea, alkyl derivatives of thiourea, alkali metal bisulfites, hydrazine and salts thereof, hydroxyl-amines and salts thereof.

6. An electrolytic recording medium according to claim 1 in which the metal salt is manganous chloride, the quaternary ammonium compound is 3,4-dihydroxyphenacyl-trimethylammonium chloride, and a stabilizer is included, the composition having a pH of at least 1.5.

7. An electrolytic recording medium according to claim 1 in which the metal salt is manganous chloride, the quaternary ammonium compound is 3,4-dihydroxyphenacyl-pyridinium chloride, and a stabilizer is included, the composition having a pH of at least 1.5.

8. An electrolytic recording medium according to claim 1 in which the impregnant consists in approximate parts by relative weight of manganous chloride 1, 3,4-dihydroxyphenacyl-trimethylammonium chloride 2, and sodium chloride 5.

**References Cited**

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JOHN H. MACK, *Primary Examiner.*

W. VAN SISE, *Assistant Examiner.*

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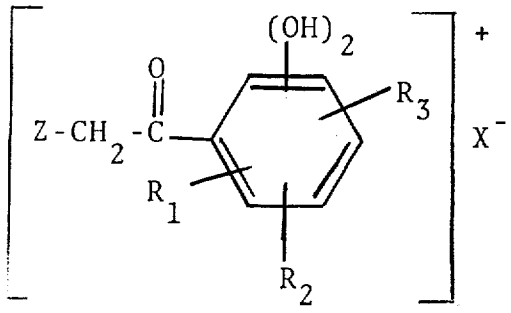
# CERTIFICATE OF CORRECTION

Patent No. 3,344,044 September 26, 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 3, lines 55 to 60, the formula should appear as shown below instead of as in the patent:




Signed and sealed this 19th day of November 1968.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents