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ELECTROLYTIC RECORDING MEDIUM

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4 Claims. (Cl. 204—2)

This invention relates to recording media for facsimile recorders employing an electrolytic recording process in which the medium is used in a moist condition.

Facsimile recorders of the type referred to may be used to receive and record graphical or pictorial matter transmitted by a facsimile transmitter over a wire or radio link, or for industrial purposes to record measurements or other data.

A well known type of electrolytic recording medium consists of a thin paper impregnated with an aqueous solution containing a small percentage, for example, 5 percent by weight, of a polyhydroxyphenolic compound such as catechol, in conjunction with an electrolyte, such as sodium nitrate, and possibly other chemical elements to provide specific characteristics in the record. The paper is used with an electrode containing iron or another metal which will go into solution in the impregnant under the influence of the current and react with the catechol to form a dark-coloured lake.

In the recorder the paper passes between two electrodes one of which is usually movable so as to provide a scanning line across the paper, and the recording current passes from one electrode to the other through the electroconductive paper, the optical density of the mark made on the record depending upon the instantaneous current density.

Recorders of the type referred to are frequently used for the reproduction of graphic material in which it is desired to have a long scale of graduation with a deep black and a pure white at two ends of the scale. In known recording media of the kind referred to the dark tones are not pure black but contain a tinge of purple and are not as deep as is desired. It has been found that papers of this kind may be intensified, that is to say, the blacks may be deepened and the contrast increased by heating the record to a temperature between 250° F. and 450° F. shortly after recording. There is a tendency, however, for the white areas of the record to become yellow at these high temperatures and unless the temperature is regulated very closely the paper base itself is affected by the heat and begins to turn brown.

In U.S. patent specification No. 517,659, now abandoned, there is described a recording medium containing a small proportion of an oxidizing compound which has the effect of substantially lowering the temperature at which intensification by heat takes place. By adding a suitable amount of chlorate and appropriately adjusting the proportions of other constituents it is possible to provide a recording medium which will, of its own accord, darken considerably after recording.

It is a disadvantage of this type of recording medium that the intense black mark is produced over a very narrow voltage range. For example, a paper which gives an intense black mark at an applied voltage of 35 to 36 volts under normal recording conditions, gives a weaker mauve mark below 35 volts and a pale brown mark above 36 volts. Below 35 volts the iron enters the solution as ferrous ions and reacts with catechol to give the mauve mark. Between 35 and 36 volts the iron entering the solution as ferrous ions is oxidized by decomposing chlorate to give ferric ions which react with catechol to give the intense black mark. Above 36 volts the catechol is also

oxidized to give o-benzoquinone which does not react with ferric ions.

We have investigated the effect of oxidation catalysts on these reactions. Many substances will cause the oxidation of ferrous ions at a lower applied voltage but most of them are incompatible with catechol or give coloured solutions which are undesirable. Cerium salts were found to be effective as catalysts even in very low concentrations. If they are introduced to the solution as the cerous salts they have no effect on catechol or the other normal constituents of the medium until the current is passed through it. The cerium is probably oxidized to a perceric compound which then oxidizes the ferrous ions. This causes an intense black mark at a potential lower than that required when no cerium salt is present. For example, when 0.04 percent by weight of cerous sulphate is added to the medium described above, an intense black is obtained over the range 32 to 36 volts.

The advantage of this is that the medium is less sensitive to minor variations in the electrical characteristics of different recording machines. A further advantage is that the medium is less sensitive to variations in its composition. When a paper is impregnated with a solution the final concentration of the solution depends on the amount of moisture in the paper prior to impregnation. This is difficult to control and varies between 0 and 6 percent. The effect is noticeable on papers which contain no cerium but disappears when 0.04 percent of cerium sulphate is added.

Any salt of trivalent cerium may be used provided it is sufficiently soluble. Cerous acetate, chloride, iodide, nitrate, oxalate and sulphate have been used with the described effect. Double salts such as ammonium cerium nitrate $2.NH_4NO_3.Ce(NO_3)_3.4H_2O$ and ammonium cerium sulphate $(NH_4)_2SO_4.Ce_2(SO_4)_5.8H_2O$ are also effective.

An example of a solution with which paper may be impregnated to give a satisfactory recording medium is:

	Percent by weight
Sodium chlorate	5
Sodium nitrate	5
Sodium sulphate	5
Catechol	3
Oxalic acid	0.5
Thiourea	0.5
Cerous sulphate	0.1
Water to	100

Sodium sulphate is added to promote drying as described in co-pending U.S. patent application No. 672,123, now Patent No. 2,949,409. Oxalic acid is added in known manner to maintain slight acidicity. Thiourea is added in known manner to prevent premature oxidation of the catechol. The sodium chlorate may be replaced by sodium perchlorate, potassium chlorate or potassium perchlorate in suitable proportions.

If the electrolyte includes a potassium compound the oxidizing compound conveniently comprises up to 6 percent by weight of solution.

If the electrolyte consists of a sodium compound the oxidizing compound conveniently consists of up to 30% by weight of solution.

We claim:

1. An electrolytic recording medium for facsimile or photoelegraphic receivers comprising a base impregnated with an aqueous solution of an amount in the range 2% to 8% of solution weight of a polyhydroxyphenolic compound, an amount in the range 5% to 20% of solution weight of a salt of a strong acid and an alkali metal acting as an electrolyte, an amount in the range 5% to 20% of solution weight of a chlorate of an alkali metal acting as

an oxidizing agent, and an amount in the range of 0.001% to 0.1% of solution weight of a water-soluble salt of trivalent cerium.

2. An electrolytic recording medium as claimed in claim 1, in which the polyhydroxyphenolic compound is catechol.

3. A method of electrolytic recording comprising the steps of passing an electrolytic recording medium as claimed in claim 1 between two electrodes in contact with the recording medium, passing a current between the electrodes through the recording medium to produce a dark coloured mark by electrolysis.

4. A method of electrolytic recording comprising the

steps of passing an electrolytic recording medium as claimed in claim 2 between two electrodes in contact with the recording medium, passing a current between the electrodes through the recording medium to produce a dark coloured mark by electrolysis.

References Cited in the file of this patent

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OTHER REFERENCES

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