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ELECTROLYTIC RECORDING

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5 Claims. (Cl. 204—2)

The present invention concerns electrical recording and in particular facsimile reproductions formed of metals or colored oxides on a supporting medium.

The object of the invention is to reproduce pictures and writings electrically by means faster and more sensitive than hitherto used and producing a more permanent, denser and more pleasing record than has been hitherto obtainable.

This application is a continuation-in-part of an application entitled "Electrolytic recording paper and process" filed on December 27, 1935, and bearing Serial No. 56,318.

Facsimile or telegraphic records are commonly made by recording upon a sensitized medium, usually a coated or impregnated sheet of paper. The recording, particularly of facsimile pictures, is usually accomplished by scanning elemental areas of the subject to be reproduced and reproducing the densities or the inverse on a record sheet a point at a time. The information obtained from the scanning process is transmitted by means of electrical impulses over wire or radio circuits in the form of current impulses or modulations of alternating current signals. Reproduction on the sensitized medium may be thermal by means of an electric spark or heated electrode or it may be electrochemical due to passage of a modulated current thru the medium.

The electro-chemical method has the advantages of greater speed and better control than the thermal method. A number of sensitizing substances suitable for electro-chemical recording have been used in the past. One of the oldest and best known is starch and iodine, although the record produced is not permanent or of great density. Colored records have been produced by combining the metal of the recording electrode with the chemicals in the medium, but this requires frequent replacement of the electrode. Silver salts have been used, but the record must be treated to fix it after recording, if a permanent record is desired.

It has been found that molybdenum trioxide and related white or light-colored compounds of molybdenum may be utilized as sensitizing substances and that these substances may be reduced to highly colored lower oxides of molybdenum or molybdenum itself at the cathode of an electric circuit. These substances have been found to be stable before and after marking without additional treatment; to be sensitive and rapid in reaction; and to produce a mark of high optical density and pleasing color.

The supporting medium may be a sheet having suitable conductivity which may be of the order of magnitude of one mho per square inch or greater. This conductivity may be obtained by impregnating a supporting medium with some suitable electrolyte, such as an aqueous solution of sodium or potassium chloride or sodium or potassium nitrate or any electrolyte which is otherwise compatible with the purposes of the invention. There may be in conjunction with said electrolyte a quantity of water sufficient to provide the conductivity desired. The sheet may be metallic or metal-filled or graphite or carbon-filled or may be of any conductive material which shall be compatible with the purposes of the invention. These various conductive sheets are well known in the art and the construction or the manufacture thereof or the conductive sheet of itself is not of my invention and therefore I do not wish to be limited to any one conductive sheet, above described.

To a conductive sheet, the molybdenum compound with suitable binder and to which an admixture of ancillary compounds may be added, is applied as a coating or, when all the sensitizing compounds are soluble, the sheet may be impregnated, or under some circumstances may be mixed with the pulp or otherwise incorporated in the conductive sheet during its manufacture. The method of coating, however, lends itself more readily to the purpose at hand and is more adaptable to machines in common use for the manufacture thereof.

In general, the compounds of molybdenum which are useful in this invention consist of molybdenum trioxide of the formula MoO_3 or derivatives thereof. They may be defined by the general expression $XR_nO_m \cdot YMoO_3$, where R indicates an element or radical such as sodium or ammonium, X indicates the number of molecules of R_nO_m and Y indicates the number of molecules of MoO_3. n indicates the number of the number of atoms of oxygen. Examples are atoms or groups designed by R and m indicates given below:

Sodium molybdate	$Na_2MoO_4 = Na_2O \cdot MoO_3$
Potassium molybdate	$K_2MoO_4 = K_2O \cdot MoO_3$
Antimony molybdate	$Sb_2(MoO_4)_3 = Sb_2O_3 \cdot 3MoO_3$
Lead molybdate	$PbMoO_4 = PbO \cdot MoO_3$
Sodium dimolybdate	$Na_2Mo_2O_7 = Na_2O \cdot 2MoO_3$
Sodium parsmolybdate	$Na_6Mo_7O_{24} = 3Na_2O \cdot 7MoO_3$
Sodium trimolybdate	$Na_2Mo_3O_{10} = Na_2O \cdot 3MoO_3$
Molybdic acid	$H_2MoO_4 = H_2O \cdot MoO_3$

In addition there are double salts such as $Na_2O \cdot CoO \cdot 7MoO_3$ which is sodium cobaltou:

paramolybdate, and complex molybdates of variable composition such as ammonium phosphomolybdate $3(NH_4)_2O \cdot P_2O_5 \cdot 24MoO_3 \cdot nH_2O$ which can be seen to be extensions of the above general formula. Many of these compounds are relatively colorless or light colored and may or may not be soluble. Molybdenum trioxide has a slight greenish tinge. When any of the above compounds are reduced a blue or blue-black color is produced known as "molybdenum blue" and which is of indefinite composition corresponding roughly to the formula Mo_3O_8. This compound may be fitted into the above general expression as $MoO_2 \cdot 2MoO_3$, which is an additive compound containing hexavalent and tetravalent molybdenum, the dark color being characteristic of the tetravalent molybdenum.

Ammonium molybdate also falls within the above general formula although no compound $(NH_4)_2O$ is known as such. In the literature ammonium paramolybdate is frequently written as $3(NH_4)_2O.7MoO_3.H_2O$. This expression may be found in "Comprehensive Treatise on Inorganic and Theoretical Chemistry" by J. W. Mellor, volume XI, pages 582 and 583, and includes the use of the general expression given herein.

The ancillary compounds which may be used consist of compounds of antimony such as antimony oxychloride; of lead such as lead acetate; of bismuth such as bismuth chloride which in marking produce colors which when combined with the blue of molybdenum produces a more pleasing black, also increasing the density of the record.

An intermediate reducing agent which is formed in the coat at the time of marking by the reduction of a compound such as stannic, ferric or cupric chloride or nitrate or in general any material which may be reduced by the action of an electric current and which then has sufficient reducing action to act upon the molybdenum compound may be used. Stannous or ferrous or cuprous salts are produced by the reduction of the corresponding stannic, ferric or cupric compounds. When molybdenum trioxide is used, the above reducible compound may also be used to produce additional density. The record produced upon marking consists of colored oxides of molybdenum, metallic molybdenum or antimony or various combinations of these substances against a background of white or light-colored unreduced substances and the supporting medium. These reduced substances in the case of molybdenum contain molybdenum atoms of a valence of less than 6 and may include blue molybdenum oxide (Mo_3O_8), molybdenum sesquioxide (Mo_2O_3), molybdenum di-oxide (MoO_2) and metallic molybdenum (Mo).

It has been found that tungsten compounds may be used in place of the molybdenum compounds with substantially equivalent results. It has also been found that bismuth and arsenic compounds may be used in place of the antimony compounds with substantially equivalent results although the toxic properties of arsenic render it usually undesirable.

It has been found that if current of the order of 50 milliamperes is passed thru an area of the order of .0001 square inch of recording surface, records may be produced at a speed of 30 linear inches a second or greater.

One method of preparing electrolytic recording paper utilizing molybdenum or tungsten compounds was disclosed in the above referred to application. In this method approximately 100 grams of molybdenum trioxide and 3 grams of starch are mixed with 100 grams of water to form a thick paste. A suitable support such as a paper sheet is coated with this paste. The coated paper is rendered highly conductive by impregnating it with a solution of a substantially neutral salt, such as potassium chloride. A solution of 10 grams of potassium chloride in 100 grams of water is satisfactory.

Another suitable recording medium may be prepared by coating a conductive sheet in the following manner: to 100 grams of molybdenum trioxide add 200 grams of antimony oxychloride ($Sb_4O_5Cl_2$), for example 200 cc. of water and grind to a fine slurry. Then to this mixture add 50 grams of ground gelatin dissolved in 200 cc. of water and continue the grinding or mixing process. Stannic chloride may be added to the extent of, for example, 50 grams. Other reagents such as chrome alum and formaldehyde may be added to render the gelatin water-resistant and the mixture may then be applied directly as a coat to the conductive sheet, containing, for example, potassium chloride, dried and then remoistened to obtain conductivity. Where antimony oxychloride is not used it may be advisable to substitute another binder for gelatin, as a binder such as starch or water soluble gum, as molybdenum trioxide will, when by itself and reduced slightly, precipitate gelatin from solution. It is also advisable to bring the pH of the above mixture within the range of 3 to 4 by the addition of an alkali such as sodium hydroxide.

The sensitizing substances herein described are intended for electrolytic reduction to produce a mark at the cathode of an electric circuit. Little or no mark is produced at the anode; the electrodes are not consumed; the substances are insensitive to thermal changes up to 200 or 300 degrees centigrade where most papers start to char; an electric spark has little effect on them, short of puncturing the paper, and they are photo-stable. The record produced needs no fixing, although it is desirable to dry the paper.

In the specification and claims light-colored is used in the sense of white, white lightly tinted and light grey. Also colored or dark-colored is used in the sense of dark colors, dark grey or black.

While only two examples of molybdenum or tungsten papers have been given, many modifications will be apparent to those skilled in the art within the spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. An electrolytic recording medium comprising a porous insulating support carrying an electrolytically sensitive composition consisting essentially of a light-colored oxygen-bearing compound of an element chosen from the group consisting of hexavalent molybdenum and hexavalent tungsten, and an electrolyte in sufficient quantity to make the medium conducting in the presence of water.

2. An electrolytic recording medium comprising a porous insulating support carrying an electrolytically sensitive composition consisting essentially of a light-colored oxide of an element chosen from the group consisting of tungsten and molybdenum, and an electrolyte in sufficient quantity to make the medium conducting in the presence of water.

3. An electrolytic recording medium comprising a porous insulating support carrying an elec-

trolytically sensitive composition consisting essentially of a compound chosen from the group consisting of molybdenum trioxide and tungsten trioxide, and an electrolyte in sufficient quantity to make the medium conducting in the presence of water.

4. An electrolytic recording medium comprising a porous insulating support carrying an electrolytically sensitive composition consisting essentially of a compound chosen from the group consisting of molybdenum trioxide and tungsten trioxide, and at least one electrolyte chosen from the group consisting of potassium chloride, sodium chloride, and calcium chloride.

5. An electrolytic recording medium comprising a porous insulating support carrying an electrolytically sensitive composition consisting essentially of a compound chosen from the group consisting of molybdenum trioxide and tungsten trioxide, stannic chloride, an alkali in sufficient quantity to at least partially reduce the acid reaction of said compound, and an electrolyte in sufficient quantity to make the medium conducting in the presence of water.

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