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ELECTROLYTIC RECORDING PAPER

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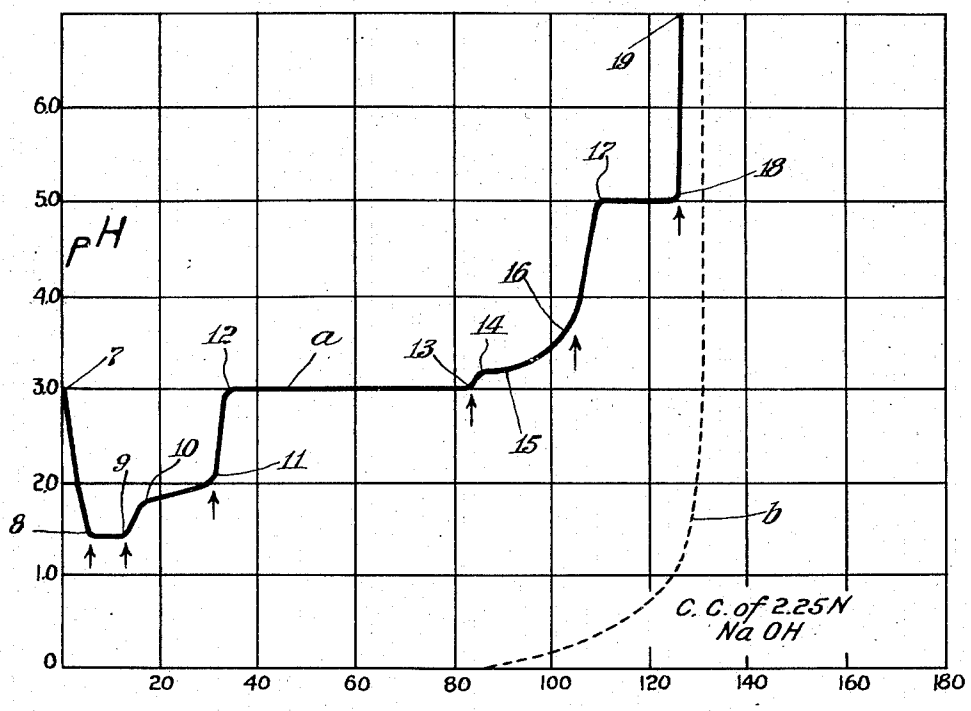

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ELECTROLYTIC RECORDING PAPER

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2 Claims. (Cl. 204—2)

The present invention relates to an electro-chemical recording medium suitable for use in facsimile recorders and the like.

One object of the present invention is to provide an electro-chemical recording medium capable of producing a record of high optical contrast and maximum density and with a high order of detail.

Another object is to provide an electro-chemical recording medium in which drag or tailing effects are eliminated.

A particular object is to provide an electro-chemical recording medium substantially permanently stable toward light and thermal effects yet capable of efficiently utilizing relatively high electrical currents for the marking thereof.

Other objects are set forth in the copending application entitled "Electrolytic recording paper," Serial No. 31,564, filed July 16, 1935 (now Patent Number 2,173,141 issued September 19, 1939) and to which this is to be considered a continuation in part. Certain features to be set forth below are also shown in the copending application entitled "Electrolytic recording paper and process," Serial No. 56,318 filed on December 27, 1935 in which certain molybdenum and tungsten compounds are disclosed.

Facsimile recording may be practiced in a number of ways as follows:

1. Records may be printed from an inked member or carbon paper as an electro-mechanical impression.

2. Records may be made by rendering transparent a light-colored opaque layer covering a darker layer on a prepared paper, usually by burning off the upper layer by means of an electric spark.

3. Records may be printed on a light-sensitive medium from a lamp fed with facsimile signals.

4. Records may be printed by oxidizing a light colored compound to produce a dark colored compound by means of an electric current, spark or by the application of heat. In the case of an applied current, the marking takes place at the anode.

5. Records may be printed by reducing light colored compounds to dark colored compounds or elements by means of an electric current. In this case the marking takes place at the cathode.

It has been found that when all the important characteristics of a recording medium, such as permanence, contrast, detail, simplicity and cost are taken into consideration that the last two methods offer the best solution to the recording problem. The last or reducing method has a unique advantage over the oxidizing method in that its product is less sensitive to atmospheric effects providing photo-sensitive materials are not used.

Sensitizing substances for electro-chemical reducing recording have been found to mark most easily when in an acid condition. If the acidity is too great, however, a paper supporting medium will be destroyed or the record will fade. If the substance exhibits strong buffer characteristics, that is, a strong resistance to change in pH (function of hydrogen ion concentration), it is possible to reduce a large percentage of the sensitizing substance starting with an acidity low enough not to injure a paper support without producing a reduction in acidity to a point where further reduction is blocked. If the sensitizing substance is insoluble and the reduced product is insoluble, fading and other deleterious effects, such as loss of detail due to "drag" are eliminated. The lighter the color of the initial substance and the darker the final reduced product, the greater will be the contrast of the resulting record. The oxyhalides and other compounds of antimony and bismuth have been found to fulfill the above requirements, as more fully set forth below.

The figure of the drawing shows a titration curve of antimony trichloride against sodium hydroxide and of a completely dissociated acid against sodium hydroxide.

In pure water or a solution of a salt of a highly ionized acid and highly ionized base, the concentration of hydrogen ions (H^+) and of hydroxyl ions (OH^-) is equal and equal to 10^{-7} mols per liter each. (There is a slight variation with temperature.) The term pH is defined as log

$$\frac{1}{(H^+)}$$

and hence the pH of pure water or a solution of certain salts as set forth above is 7. Substances or solutions having values of pH of less than 7 are said to be acid, due to an excess of hydrogen ions, while substances or solutions having values of pH of more than 7 are said to be basic, due to an excess of hydroxyl ions. Further, if a weak acid, such as acetic acid, is allowed to react with a strong base, such as potassium hydroxide, a salt having a basic reaction is produced. The reaction is as follows:

$$HAC+KOH \rightarrow KAC+H_2O$$

forming the normal salt KAC having basic char-

acteristics, as indicated by a pH greater than 7. This is due to the fact that if the potassium acetate is hydrolyzed, the potassium ion will not combine with the hydroxyl ion formed by the ionization of the water, since potassium hydroxide ionizes almost completely, whereas the acetate ion will combine with the hydrogen ion removing it from solution and leaving an excess of hydroxyl ion. Thus, we may have a normal salt with a basic characteristic. Similarly, we may have a normal salt with an acid characteristic formed by a reaction between a weak base and a strong acid. In addition, there are basic salts which are salts whose solution has a higher pH than the normal salt, although this pH may still be less than 7. Thus, antimony oxychloride (SbOCl), a basic salt, is more basic than antimony trichloride ($SbCl_3$), the normal salt, yet SbOCl has a pH of 3.0 in saturated solution which is well on the acid side.

The term buffer is used to describe an important characteristic of the final coatings to be utilized, according to the present invention. A titration curve (see the figure of the drawing) is a graphical representation of pH plotted against some added reagent. If this curve shows no points of inflection slope (see curve *b*), it shows that only normal compounds are being formed, or that the reaction has been completed. On the other hand, if the slope of the curve becomes less steep at some point, it indicates the start of an intermediate chemical reaction and a resumption of the initial slope indicates the completion of this reaction. These decreases in slope of the pH curve show resistance to a change in pH and are called buffer points. A buffer may be defined as a compound which resists a change in pH as shown by an intermediate region of decreased slope in the pH curve. A buffer may also be defined as a substance which, if added to another substance, causes the resulting substance to resist changes in pH. In general, the stronger the buffer action, the longer and flatter will be the portion of the pH curve associated with the buffer action.

In electro-chemical recording utilizing reducing effects of an electric current, one effect of the current is to increase the pH of the recording medium at the cathode. It has been found, however, that if the pH becomes greater than about 5, then the mark produced by the recorder will become increasingly faint. On the other hand, if the recording medium has too low a pH, the paper supporting the medium will be darkened or destroyed. Thus, it will be appreciated that a medium having strong buffer characteristics permits higher initial pH preserving the paper and also permits the use of a higher recording current producing a denser mark before the pH is raised to a point where recording becomes difficult or impossible.

The figure of the drawing shows a titration curve *a* of antimony trichloride which at certain points of the curve exhibits strong buffer characteristics. The $SbCl_3$ is titrated against cubic centimeters of 2.25 normal NaOH starting with 10 cubic centimeters of a solution of $SbCl_3$ containing 22.4 grams of the latter. The pH curve starts out at a little over 3 at point **7**, drops rapidly to about 1.4 at point **8**, is flat to point **9**, rises to point **10**, rises less rapidly to point **11**, rises rapidly to point **12**, is very flat to point **13**, rises to point **14**, is flat to point **15**, rises gradually to point **16**, rises rapidly to point **17**, is flat to point **18**, and then rises very rapidly to point **19**. The vertical arrows indicate points where calculations show new products are completely formed and fall as would be expected at the ends of flat or nearly flat portions of the curve. Flat portions of the curve between points **7** and **11** indicate the formation of oxychlorides whose definite identity has not been established by other independent means. The flat portion of the curve from points **12** to **13** indicates the formation of SbOCl, the gradual rise from points **14** to **16** indicates the formation of $Sb_4O_5Cl_2$, and the flat from points **17** to **18** indicates the formation of Sb_2O_3. As pointed out above, marking by electro-chemical reduction tends to increase the pH and if the pH rises above about 5, marking becomes very difficult. Hence, if the sheet to be marked contains $Sb_4O_5Cl_2$, as formed in the region of point **16** on the titration curve, the buffer action as shown between points **17** and **18** will resist an increase in pH permitting higher recording currents and hence denser markings in the recording process than would be possible without the buffer action. Point **16** thus indicates a region where a large percentage of reducible material is present ($Sb_4O_5Cl_2$) followed by a buffer region.

Curve "*b*" shows for comparison the theoretical titration of a completely dissociated acid (0.293 gram equivalents in 10 cubic centimeters of aqueous solution) titrated against cubic centimeters of 2.25 normal NaOH solution. The first part of this curve up to a pH of about 1.0 has a lower slope indicating chemical reaction (simple neutralization in this case) while above 1.0 the curve becomes very steep indicating that the reaction has been completed and no further reaction is taking place. This curve then represents a normal curve without buffer characteristics.

It is to be noted that less than 1 c. c. of solution of NaOH raises the pH from 3.6 to above 7.0 on curve *b*, whereas over 30 c. c. of NaOH solution is required to raise the pH of $Sb_4O_5Cl_2$ from 3.6 to above 5.0 on curve *a*.

While there are certain advantages in using a recording medium which in itself has strong buffer characteristics, the advantages of the buffer action may be obtained to a somewhat lesser degree by the addition of an ancillary buffer. Also, a medium exhibiting weak buffer characteristics may have its buffer action increased by the addition of ancillary buffers. The following compounds may be used as ancillary buffers: molybdenum trioxide, stannic chloride, stannous chloride, gallic acid, salycilic acid, benzoic acid and other acids, such as citric, boric and phosphoric, of slightly dissociated character which have buffer characteristics and may be brought by partial neutralization to a pH of over 3. Note, however, that the interaction of stannous chloride and molybdenum trioxide produces a dark blue discoloration and the two should not be used simultaneously. Likewise, gallic acid reacts with molybdenum trioxide to form a straw-colored discoloration.

Antimony oxychloride of the form $Sb_4O_5Cl_2$ is white, thermal and photo stable, insoluble, a strong buffer and has a suitable pH for use on a paper record sheet. Many other compounds of antimony and bismuth are white, thermal and photo stable, insoluble, have or may readily be brought to a suitable pH, and have sufficient buffer action or may readily be made to have satisfactory buffer characteristics by the addition of an ancillary buffer as set forth above. Some

of these antimony and bismuth compounds are as follows:

Antimony oxychloride (SbOCl)
Bismuth oxychloride (BiOCl)
Antimony oxybromide (SbOBr)
Bismuth oxybromide (BiOBr)
Antimony oxysulphate $(SbO)_2SO_4$
Antimony oxychloride (penta) ($SbOCl_3$)
Bismuth oxynitrate $(BiO)NO_3$
Bismuth oxycarbonate $(BiO)_2CO_3$
Bismuth oxyiodogallate
Bismuth subgallate
Bismuth salicylate (basic)

All of the above compounds are reducible at the cathode of an electric circuit to a dark colored lower oxide or the metallic element itself. These are all basic salts of antimony or bismuth and while other basic salts are known to exist and may be used in electrolytic recording, they have been omitted from the list either because they were colored or not readily obtainable. Since these compounds may be readily tested for their desirable qualities in electrolytic recording, once they are obtained, this is felt to be a complete disclosure of the basic salts of antimony and bismuth, organic and inorganic suitable for electrolytic recording.

Other compounds of antimony and bismuth are also reducible to dark colored substances. In general, they mark more slowly than the basic salts, due to lack of buffer action or even alkalinity. The tri-valent compounds are usually more easily reduced than the penta-valent compounds. Below is shown a list of these compounds with brief remarks as to their characteristics. With the use of an ancillary buffer, their characteristics, as far as ease and speed of electrolytic marking goes, are greatly improved.

Compound	Remarks
Antimony tribromide ($SbBr_3$)	Antimony oxybromide precipitates from solution.
Antimony triiodide (SbI_3)	Antimony oxyiodide precipitates from solution.
Antimony oxide (Sb_2O_3)	Very insensitive.
Potassium antimoniate (diaphoratic).	Sensitive.
Tartar emetic	Dissolved in HCl.
Potassium antimoniate (pyro)	Reduction products redissolve rapidly.
Antimony pentasulfide	Orange coat.
Bismuth subcarbonate	Insensitive.
Bismuth lactate	Solidmark.
Bismuth chromate	Orange coat.
Bismuth subiodide	Insensitive.
Bismuth triiodide (BiI_3)	Yellowish coat.
Bismuth oxide (Bi_2O_4) (tetra)	Do.
Bismuth tartrate	Poor mark.
Bismuth ammonium citrate	Good mark.
Bismuth citrate	Do.
Bismuth phosphate	Do.
Bismuth oxalate	Good mark (insensitive).
Bismuth tannate	Do.

The electrolytic recording medium will usually be in the form of a sheet and for economical reasons paper is most commonly used for the sheet. The above sensitizing materials may be incorporated in the paper by mixing with the paper pulp in the process of manufacture, coating on the paper or forming by chemical reactions within the pores of the paper. Various substances may be added to the primary compounds set forth above to improve the quality of the record produced on the recording medium. Gelatin may be added to the coating to act as a binder or for other purposes. Starch or other binders compatible with the acid condition required in the coating may be used. Isopropanol or almost any alcohol may be added with the gelatin or other binder to eliminate foam and produces a smoother coat. Glycerine or any glycerine substitute, such as "sorbitol" may be added to act primarily as a plasticizer. Chrome alum or any chrome salt of the same valency or which may be brought to the same valency may be added to the coating in order to increase the water-resistance of a gelatin binder. Formaldehyde or other aldehydes or any compound which liberates an aldehyde, such as hexamethyleneamine may be added to the coat and increases the water resistance of the binder and with the chrome salts gives a result which is in excess of what would be expected if the chrome salt and the formaldehyde acted as an aggregate. Lubrication, to facilitate marking with a moving electrode, may be added to the medium by adding "Proofit" or other emulsions containing wax or fatty substances. The above added substances may have beneficial actions other than those noted. For instance, gelatine may be used as an ancillary buffer, if previously treated with a weak solution of an acid such as hydrochloric.

In order to render the recording medium electrically conductive, so that electrolytic recording may be readily practiced, an electrolyte with sufficient water to render it conductive may be added. Suitable electrolytes are potassium chloride, sodium nitrate, potassium nitrate, sulphates or any strong, substantially neutral electrolyte. The moisture in the medium may be controlled by using a mixture of hygroscopic and non-hygroscopic electrolytes. Potassium chloride which is comparatively non-hygroscopic may be mixed with varying amounts of sodium nitrate which is hygroscopic to produce a desired moisture retaining characteristic. Many other combinations will be evident to produce this result.

Paper or other supports coated or impregnated according to the above process and variations of the process or with the above substitutes are intended for electro-chemical marking. The marking is a process of reduction of the antimony, bismuth and/or molybdenum and/or stannic compounds from substantially white or colorless compounds to colored lower oxides or the elements themselves at the cathode of an electrical circuit. For use in facsimile, the supporting sheet is fed so that facsimile signals may be passed between two electrodes thru the medium causing marking. While the coatings set forth herein are not limited by the use to which they are put, still it is pointed out that they are not substantially affected by heat or light. Hence, we may characterize the above coatings by saying that they may be reduced to colored substances by the direct application of an electric current, but are substantially unaffectable before and after marking by either heat or light. The active reducible substances (antimony, bismuth and molybdenum compounds) are also substantially insoluble, as are the colored reduced substances. The medium in condition for marking is further characterized by a pH in the neighborhood of 3.6 to 4.0 and substantial buffer characteristic.

The odd series of Group V of the periodic table, includes arsenic, antimony and bismuth. The characteristics of antimony and bismuth compounds in an electrical recording system have been described. Arsenic compounds, while representing differences in some of their characteristics, have been found to be reducible by an electric current to a dark-colored compound.

Arsenic trisulphide, As_2S_3, arsenic trioxide, As_2O_3, and arsenic oxide, As_2O_5 were separately tried by coating on a supporting sheet, rendering electroconductive and passing an electric current thru the coating. A dark mark appeared at the cathode of the electric circuit.

Whereas antimony trioxide, Sb_2O_3, has a very slight solubility and for practical purposes is considered insoluble, as is also bismuth trioxide, Bi_2O_3, the arsenic trioxide, As_2O_3 has a solubility of 2.04 grams per 100 c. c. of water at 25° C. Also, the oxychlorides of arsenic are considerably more acid than the equivalent oxychlorides of antimony and even more so than the oxychlorides of bismuth. The oxychlorides of arsenic readily decompose in water to the trioxide as is to be expected from their more acid nature. The disadvantage of arsenic is its intensely poisonous character, especially arsenic trioxide, As_2O_3. In general, arsenic compounds are the equivalent of antimony and bismuth compounds except that they are more poisonous, more soluble and more acid.

A large number of arsenic, antimony and bismuth compounds suitable for electro-chemical marking by reduction at the cathode of an electric circuit have been set forth. While some of these compounds are colored and others reduce with difficulty, they are as a class suited to such marking as above described. Many other compounds of arsenic, antimony and bismuth are known to exist. This disclosure of many readily available compounds is considered to be a disclosure of other compounds of these elements not noted which have similar desirable characteristics. Therefore the invention is limited only by the spirit and scope of the appended claims.

While not in any way intended to limit the invention, the following specifications have been found to be desirable.

With electrode areas of 0.0003 square inches; paper 0.0025 inch thick, the best operation has been obtained when operating at a surface speed of 30 inches per second when the medium had a resistance between 100 and 1000 ohms. Papers with resistances as high as 100,000 ohms may be useful, but, in general, at resistances of the order of 1,000,000 ohms or greater between the above specified electrodes the paper breaks down before sufficient current to produce a mark can be passed.

What is claimed is:

1. An electrolytic recording material which comprises a supporting surface carrying an electrolytically sensitive composition consisting essentially of a compound of the class consisting of, antimony trioxide, antimony oxysulphate, potassium antimoniate, tartar emetic, antimony pentasulfide, bismuth oxynitrate, bismuth oxyiodogallate, bismuth subgallate, bismuth salicylate (basic), bismuth lactate, bismuth chromate, bismuth trioxide, bismuth tetraoxide, bismuth ammonium citrate, bismuth citrate, bismuth phosphate, bismuth oxalate, and bismuth tannate, and an electrolyte in sufficient quantity to make the material conducting in the presence of water.

2. An electrolytic recording material which comprises a supporting surface carrying an electrolytically sensitive composition consisting essentially of a compound of the class consisting of, antimony trioxide, antimony oxysulphate, potassium antimoniate, tartar emetic, antimony pentasulfide, bismuth oxynitrate, bismuth oxyiodogallate, bismuth subgallate, bismuth salicylate (basic), bismuth lactate, bismuth chromate, bismuth trioxide, bismuth tetraoxide, bismuth ammonium citrate, bismuth citrate, bismuth phosphate, bismuth oxalate, and bismuth tannate, a buffer chosen from the class consisting of, gallic acid, salycilic acid, benzoic acid, citric acid, boric acid and phosphoric acid, and an electrolyte in sufficient quantity to make the material conducting in the presence of water.

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