Aug. 19, 1947. B. L. KLINE 2,425,742

ELECTROSENSITIVE RECORDING BLANK

Filed July 29, 1942

FIG. 1

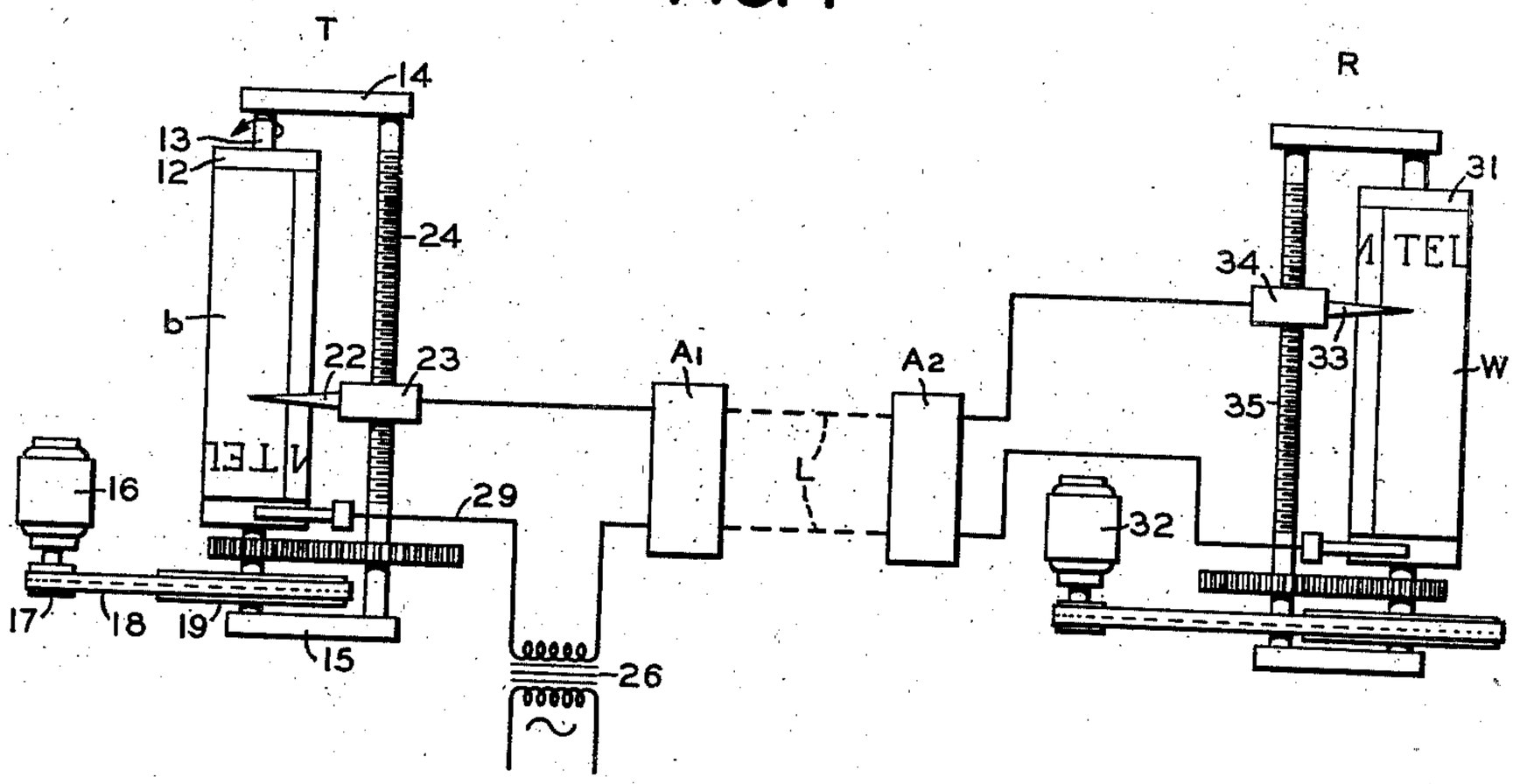
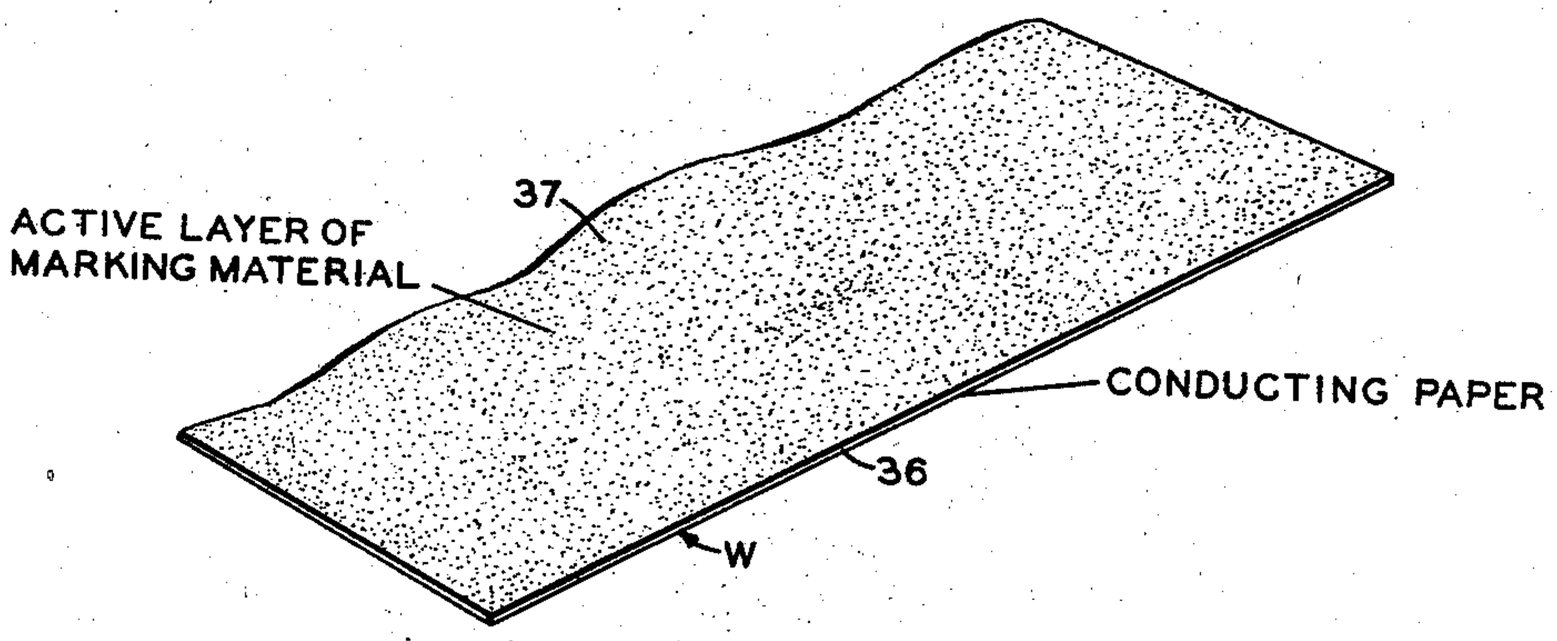


FIG. 2



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ELECTROSENSITIVE RECORDING BLANK

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This invention relates generally to an electrosensitive recording blank, and more particularly to a recording blank on which various kinds of subject matter may be recorded by means of telegraph facsimile or other types of electrical signals which are applied to selected elemental areas of the recording blank by means of an electrode that scans the surface of the blank for applying the signals to selected areas thereof.

Various methods of recording in facsimile by means of electrical signals and other marking agents, and various types of recording mediums, have heretofore been proposed, but in general the prior art methods and recording blanks employed required special handling or treatment prior to their use, as in the case where wet or other electrolytical recording papers were employed or required heaters or other mechanisms controlled by signals which in turn operated to mark the message sheet, or required special handling or development treatment after recording. None of the recording mediums of the prior art have enabled satisfactory recording to proceed at a sufficiently fast rate with relatively small amounts of marking energy whereby they are adapted for use with the currents and voltages ordinarily employed in telegraph recording systems, and none of the prior art methods and recording mediums have produced the sharp definition desired in facsimile recording consistent with producing records which may be scanned at a higher rate of speed and with small values of currents and voltages.

For example, it is old to have paper impregnated with electrically conducting solutions, or electrolytes, said solutions being adapted to be decomposed by signal impulses so that a record of the signals is made, and it is old to cause an electric arc to burn holes in a paper recording blank, the holes thus burned representing telegraphic signals or comprising the outline of the subject matter desired to be recorded. Such recordings, however, are only suitable for relatively coarse work where no fine gradations of tonal values are necessary, such as in the reception of telegraphic signals in general and recording of various types of curves in connection with the performance of instruments. However, in the transmission of matter, particularly of pictures and the like, where half-tones are encountered, the range of tonal values extends from what might be termed pure white to pure black.

Prior art methods of recording have suffered from the serious draw back of diffusion of the record area. Thus, for example, with the electrolytic paper method previously discussed, the capillary action of the paper often results in a spreading of the record element so that satisfactory definition for precise work becomes an impossibility under normal high speed operation. Also,

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where recording is effected by means of holes burned through a paper blank by the action of an arc discharge, it will be appreciated that the result would not produce fine definition and can produce no fine gradations or tonal values of the recorded subject matter; moreover, the disadvantages of having a record sheet with holes burned through the sheet will be obvious, and there is also an appreciable fire hazard involved in such a method of recording.

This invention provides a recording blank, and enables a method of recording to be used, which is remarkably free from the above objections. For example, high speed of facsimile recording is a prime requisite due to the customary diversion from other commercial services of the telegraph transmitting means in connection therewith. The need of high speed operation is further enhanced by requirements for sharp definition. Thus, in picture transmission, increasing the number of lines to the inch increases the length of time required for the marking of a record and, therefore, places a slow speed system at a further disadvantage. A further and desirable property of the record in accordance with the present invention is the fact that the recording blanks may be stored under normal conditions for long periods of time without any substantial deterioration and are ready for use at all times. No supplementary development or other treatment of the recording blank is necessary apart from the reception of the signal impulses and the transformation of such signal impulses to record elements during the normal process of recording. The blank is a dry blank which operates in the absence of moisture; it is capable of recording at an extremely fast rate and with very sharp definition; it does not require special handling; is not adversely affected by exposure to light or air; and is adapted for use with recording apparatus of a comparatively simple character.

The invention in general makes use of the phenomenon of the reduction or conversion of a chemical compound, when an electrical signaling potential or current is applied thereto, to form another compound which distinctively differs in appearance from the former compound, and to a varying degree depending upon the varying values of the signaling potentials or currents employed. The compound to be thus reduced or converted preferably, although not necessarily, is disposed in a suitable vehicle as a thin adherent coating or film applied as a pigment or lacquer to a conducting base material which for practical purposes may be considered as permanent and uninfluenced by the electrical currents or potentials, and which functions as one electrode surface for the entire record coating.

An object of the invention is an electrosensitive recording blank in which the foregoing disadvan-

tages of the prior art methods are obviated, and which produces sharp definition of the recorded image and various gradations and tonal values, with a relatively small expenditure of electrical marking energy, and in which marking may proceed at a high rate of speed and the marking energy confined to sharply defined areas beneath the recording stylus at any given instant during the scanning operation.

Another object is an improved recording blank embodying a marking compound which is generally light in color to provide a desired light background for the blank, and which readily is reduced or converted to a black or dark colored compound by the application thereto of electrical marking potentials or currents to produce the desired recording effects, and without requiring a metathetical reaction between two different compounds.

A further object of the invention is a recording blank of the character disclosed which is dry and capable of recording in the absence of moisture, and is substantially unaffected by ordinary conditions of humidity, temperature and heat, and in which complete recording may be effected with a blank in the same dry state as when it was made.

Other objects and advantages of the invention will be apparent from the following detailed description, taken in connection with the accompanying drawings, in which:

Fig. 1 illustrates diagrammatically a facsimile system embodying transmitting and recording means, the said system being of the type embodying a receiver in which a telegraphic blank embodying the present invention is adapted to be used; and

Fig. 2 is a perspective view of one form of receiving blank embodying the present invention.

Referring to Fig. 1 of the drawings, there is shown a transmitter T comprising a rotatable metallic cylinder **12** supported by a driving shaft **13** which is journaled in a suitable manner in the frame members **14** and **15**. During transmission of signals, the cylinder is rotated in the direction indicated by the arrow by suitable means such as the motor **16**. The latter may conveniently be of the alternating current synchronous type and is connected by a driving pulley **17** and the belt **18** to the driven pulley **19** secured for rotation with the shaft **13**. Means are provided, as shown, to prevent slippage of the belt on the pulleys.

Transmission is effected by the apparatus illustrated in Fig. 1 in a well known manner, such as described in my Patents No. 2,229,091, issued January 21, 1941, and No. 2,251,742, issued August 5, 1941. Briefly, a scanning electrode or stylus **22**, whose point bears on the surface of a blank *b* bearing conductive characters, is supported by a traveling carriage **23** adapted for longitudinal movement. The stylus **22** is caused to traverse the cylinder in a longitudinal direction by means of the rotatable threaded shaft **24**, and therefore the stylus point will describe a spiral path as it moves over the surface of the transmitting blank and thus produce a scanning action.

The method of obtaining the scanning movement described above is well known, as are various other methods of scanning a given field, and likewise the action of the receiver R which is to be briefly described and which forms no part of the present invention, is well known. The transmitting apparatus T and the receiving apparatus R may include transmitting and receiving amplifiers A_1 and A_2 respectively, which are interconnected by an available communication circuit L. If desired, the transmitted signals may have a carrier frequency component introduced by the transformer **26** which is connected in series with the lead **29** from the transmitting drum **12**.

At the receiving end the recording may be accomplished by any apparatus suitable for the purpose. It is to be especially noted that a telegraphic blank produced in accordance with the present invention enables the receiving device to be of an extremely simple nature. The receiver R illustrated by Fig. 1 shows one arrangement for recording upon a recording web or blank *w* and comprises a rotatable cylinder **31** of substantially the same diameter as the cylinder of the transmitter T. The cylinder **31** is rotated in synchronism with the transmitting cylinder **12** in any suitable manner, as by means of an alternating current synchronous motor **32** or other kind of motor which is kept in step with the transmitting motor **16** by any known method of obtaining synchronism. The receiving blank, which is of the kind embodying the present invention, is secured to the cylinder **31** in any suitable manner so that it may be traversed by the point of the scanning recording stylus **33**. The stylus **33** is secured to a carriage **34** mounted on a threaded shaft **35** which is rotated with the cylinder **31**. The threaded shaft in combination with the rotation of the cylinder produces the scanning action of the stylus **33**. The incoming signals are repeated and amplified in the amplifier A2 in a manner well known in the art to translate the signals into suitable current impulses of the received image.

It will be understood that instead of the receiver just described, any other known receiver of a like nature and suitable for the purpose may be used. Also, it is to be noted that the only essential of a suitable receiver is that it shall possess an electrode or stylus similar to the stylus **33** which is capable of applying marking potentials to selected elemental areas of the message blank to cause passage of a marking current through the blank in accordance with incoming signals.

A message blank *w* embodying the invention in its simplest form is shown in Fig. 2 of the drawings wherein reference numeral **36** represents a sheet of fibrous material such as paper, and applied to the surface of the paper is an adhesive coating or film **37** which comprises a marking substance embodying the principles of the present invention.

In accordance with the instant invention, I have discovered that a large class of substantially water-insoluble organic sulphur bearing compounds of metals is especially suitable for use as the marking coating or film. These compounds, for example, comprise thio-oxalates, thiolates or mercaptides, thiolacetates or thio-glycolates, and thiocarbamides, of metals such as, for example, copper, silver, mercury and lead, and are in general characterized by originally being white or light in color, thus providing a desirable light-colored background for the recording blank, and when marking potentials or currents are applied to or passed through a coating of such compounds in selected elemental areas of the recording blank, the compounds in just those areas are reduced or converted to sulphides of the metals. These sulphides, being black or dark in color, serve to delineate the recorded subject matter, whether it be pictures, writing, drawings, or other subject matter, in sharp distinct contrast with the light colored background of the blank.

Moreover, especially sharp definition of the

picture or other subject matter is obtained, and the values of the marking potentials or currents necessary to effect the reaction may be relatively small. Apparently this is because, in this class of metallic salts, the passage of electrical currents through a coating comprising such compounds causes a reduction or conversion of the compounds by elimination of a portion of the molecule. The amount of current thus required is less than that which would be necessary to effect disintegration and removal of those portions of the coating on which marking is desired to be effected, since the action involves only a partial decomposition of the molecules of the marking material. Moreover, the marking may be effected at a higher rate since it is not necessary to effect reaction between a plurality of different compounds by metathesis, as in the case of certain wet electrolytic blanks or pyro-recording blanks heretofore known in the prior art, and also due to the fact that the organic compounds disclosed herein are more readily converted by the action of electric currents than are inorganic compounds. The resulting sulphides produced are insoluble and permanent in character, and usually are either black or dark colored in appearance.

Preferably, although not necessarily, the foregoing compounds of copper, silver, mercury and lead are employed. Of these compounds, the thio-glycolates of copper, silver and lead, the mercaptides of copper, silver, lead and mercury, the thiooxalates of mercury, and the copper, silver and mercury compounds of thiocarbamide have been found especially suitable, since they are all easily formed and may readily be applied to the recording paper, and are converted to black distinct sulphides of these metals upon the application of relatively small signaling potentials to the selected elemental areas of the recording blanks coated or impregnated with such compounds. Moreover, these compounds provide a very light and pleasing background against which the recorded subject matter sharply stands out, since they are either white or light yellow in color prior to their conversion by the application of the signaling potentials. Those compounds which are light yellow in appearance may be used to simulate the ordinary telegraph blank which usually is of this color, and the white compounds may advantageously be employed for transmitting pictures, photographs and similar subject matter, although the particular compound employed for a particular service will in general be a matter of choice.

The compounds of silver are not as stable as the others, and, under certain circumstances show some tendency to decompose or become darkened if exposed to direct rays of strong light, and therefore greater care must be taken prior to a recording operation. On the other hand, this characteristic of the silver salts may be desirable for certain purposes, such as to provide a self-effacing message blank in which, after the message has been perused by the recipient, the blank may be subjected to a light of sufficient intensity to obliterate the record and thus give a desired secrecy.

Similar compounds of metals other than those specifically set forth hereinbefore may be employed, providing the other sulphur-bearing compounds of such metals or other metals are convertible or reducible to the sulphides of the corresponding metals by the passage of electrical signaling currents through a coating thereof, or

by the application of electrical signaling potentials to such coating, although for economic considerations the foregoing metallic compounds specifically mentioned are preferred. There are, however, hundreds of organic sulphur-bearing compounds, many of which are capable of forming light-colored, water-insoluble compounds with metals, which compounds are convertible to the sulphides of the metals in accordance with the present invention.

The body **36** of the recording blank may be made conducting by being impregnated with a suitable electrolyte such, for example, as salts of sodium, potassium and ammonium, particularly their iodides, sulpho-cyanides, bromides, chlorides, nitrates and sulphates; metanitrobenzene sulphonic acid; or other electrolytes disclosed in my Patents No. 2,229,091, issued January 21, 1941, No. 2,251,742, issued August 5, 1941, No. 2,181,533, issued November 28, 1939, and No. 2,283,558, issued May 19, 1942. Preferably the electrolyte employed is dissolved or suspended in a suitable non-aqueous solvent or vehicle, such as triethylene glycol, diethylene glycol, propylene glycol, or butylene glycol, disclosed in the aforesaid Patent No. 2,229,091, or in solid aliphatic or aromatic alcohols or other suitable solid oxygen containing solvent, such as disclosed in the aforesaid Patent No. 2,283,558; or the body of the blank may have incorporated therein finely divided carbon or metallic powders of silver, aluminum, copper, brass, etc., which particles are homogeneously disposed throughout the sheet to render the same conducting. The particles of carbon or metal may be incorporated in the pulp from which the paper is made so that the paper is inherently a relatively good conductor of electricity, and therefore will be suitable for use by merely applying the marking coating to its surface.

If the paper layer **36** of the blank is of a kind which is not inherently conductive, it may be desirable to first apply the film or coating of the marking substance to its surface and thereafter to impregnate the back of the paper with one of the electrolytic solutions above referred to. In either case the conductive base immediately beneath the coating provides a relatively good conducting path directly through the recording blank from the point of the scanning stylus to the recording cylinder beneath the blank, and prevents dispersion of substantial amounts of marking current in and around the area of the blank beneath the stylus at any given instant so that the electrical effects are concentrated in just the elemental area being scanned by the stylus, and thus spraying effects or other undesirable effects on the coating at this point of the blank are eliminated, and exceedingly sharp and fine definition is obtainable.

If desired, the paper layer may be impregnated with an electrolyte such as ammonium nitrate, ammonium sulphate, sodium nitrate and nickel sulphate which will cause the blank to become conductive when it is used in a moist atmosphere, generally in the manner disclosed in the Kline and Engler Patent No. 2,225,247, issued December 17, 1940.

Inasmuch as the material in the coating to be reduced or converted represents the load of the electric current, the resistance of the recording material should be concentrated in that region. In order to provide a permanent record, the marking material or pigment may be suspended in a vehicle or binder of cellulose derivative lacquers, hydrocarbon resins, shellac dissolved in alcohol,

ester gums, natural varnish gums, polyvinyl resins, etc., and suitable solvents, such as ester solvents, viz., ethyl, butyl and amyl acetates, or butyl lactate and "cellosolve," or hydrocarbon solvents, such as isopropyl and ethyl alcohol. The vehicles and binders may also include oils such as linseed, tung, perilla, fish and soya bean. Thinners may comprise turpentine, spirits and esters, such as butyl acetate or butyl lactate, and suitable gums and resins which may be used are natural varnish gums such as kauri, dammar and cumar, and synthetic resins.

The filler or marking compound such as above referred to, is preferably uniformly distributed in finely divided form throughout the binder. The resistance characteristics of the entire mixture may be adjusted either by controlling the resistance characteristics of the binder itself or the filler, although in practice the resistance characteristics of the binder are not easily controlled since such binders ordinarily are insulators when dry. By controlling the fineness of the grains of the filler and the dispersion of this material throughout the binder, it is possible to control the electrical breakdown characteristics of the entire coating within reasonable limits. This coating preferably is applied as a surface covering to the base material and forms therewith a unitary record blank. Inasmuch as the electrical breakdown strength of the entire coating is to be maintained at a uniform value with the variations in reduction or conversion of the marking material being controlled by the intensity of the signaling currents or potentials, the thickness of the coating should be maintained at a substantially constant value throughout the useful area of the record. While the base material itself should have an electrical resistance low in comparison to the resistance of the marking coating which inherently is high, the resistance of the base material may have a substantial value and may vary within a considerable range of values.

The marking substance may conveniently be applied to the surface of the blank as an ink or pigment which is formed by powdering the substance and grinding this powder with a linseed oil or other suitable vehicle to a suitable consistency for application to the surface of the blank by a printing operation, or by grinding in a lacquer or other binder vehicle. It is within the scope of the invention to mix a plurality of selected substances from the class herein disclosed in formulating the ink or other coating mixture. In some cases it may be desirable to incorporate a trace of drier to aid oxidation of the vehicle when in ink form, the powdered marking substance being substantially unaffected in any way by the inclusion of a drier. Resinates, linoleates of lead, cobalt, manganese, etc., are standard driers and may be used when a drier is considered desirable or necessary.

In order to facilitate finer definition of the recorded subject matter, and to enable the lower marking potentials and current values to be employed, the marking substance when used as a coating or film is applied as a very thin film, the surface layer preferably being of the order of .00008 to .00015 of an inch. As above stated, the white or light colored sulphur bearing salts are reduced or converted, by the application thereto or passage therethrough of the signaling potentials or currents, to colored metal sulphides, this change in color at the points to which the signaling energy is applied, providing a sharp contrast

with the unchanged portions of the coating which have not been affected by the signaling potentials or currents.

The thickness of the coating should be just sufficient to mask the base material or supply a good background for the recorded subject matter. The potential applied to the coating may be just below the marking value so that superimposed signal potentials will provide the differential necessary for effective operation. The character of potential appears to be immaterial and recording may be effected either with direct or alternating currents including frequencies ranging into the carrier spectrum.

Instead of applying a coating to a conducting blank in the manner aforesaid, for certain purposes it may be sufficient to impregnate the recording blank with the marking substance together with the electrolyte or conducting substance, or these compounds may be mixed with the paper pulp during the manufacture of the paper or other material prior to formation of the web of which the blank is composed, although the sharp definition obtainable with the coated form will not in general be obtainable where the blank has thus been impregnated. Such a blank will be suitable where relatively coarse recording is sufficient, or where still lower power input levels are desired.

Combinations of the foregoing types of materials may be employed, if desired, and two or more coatings of the substances may be employed to provide better covering power which is especially desirable in the case of carbon bearing paper or a blank which is relatively dark in color. It is also possible to add other substances to the marking substances to give them greater covering power or increase the opacity thereof, if desired, such for example as a small amount of titanium dioxide or other pigment which in combination with the marking substance gives the desired covering effect.

It will be appreciated that other compounds may be employed in whole or in part in addition to those specifically mentioned as illustrative examples, which other compounds will be recognized by those skilled in the art as being equivalents for the purpose of the invention, and I therefore do not wish to be limited except as indicated by the scope of the appended claims.

What is claimed is:

1. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said recording medium comprising a sulphur-containing organic chemical compound of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

2. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said

recording medium comprising a sulphur-containing organic chemical compound of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and initially is light in color and has the property of being convertible by partial decomposition to a dark-colored sulphide of the metal uppon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

3. An electrosensitive recording blank comprising an electrically conductive layer having a recording medium in intimate contact therewith for producing marking effects in selectable elemental areas of the recording surface of the blank upon application of an electrical signaling potential to said areas, said recording medium comprising a sulphur-containing organic chemical compound of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

4. An electrosensitive recording blank comprising an electrically conductive layer having a recording medium in intimate contact therewith for producing marking effects in selectable elemental areas of the recording surface of the blank upon application of an electrical signaling potential to said areas, said recording medium comprising a sulphur-containing organic chemical compound of a metal, for example, copper, silver, mercury and lead, in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

5. An electrosensitive recording blank comprising an electrically conductive layer and a superficial coating of a recording medium directly disposed over said conductive layer as a thin adherent film for producing marking effects in selectable elemental areas of the recording surface of the blank upon application of an electrical signaling potential to said areas, said recording medium comprising a sulphur-containing organic chemical compound of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluable in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the the background of the recording surface of the blank.

6. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said recording medium comprising a mercaptide of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being

convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

7. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said recording medium comprising a thio-glycolate of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

8. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said recording medium comprising a thiocarbamide of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

9. An electrosensitive recording blank comprising a sheet having in intimate contact therewith, over the recording surface of the blank, a coating of a recording medium for producing marking effects in selectable elemental areas of said recording surface upon application of an electrical signaling potential to said areas, said recording medium comprising a thio-oxalate of a metal in an amount sufficient to produce said marking effects, which compound is substantially insoluble in water and has the property of being convertible by partial decomposition to a sulphide of the metal upon application of an electrical potential to said compound, thereby to form a colored mark contrasting with the background of the recording surface of the blank.

BERNARD L. KLINE.

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