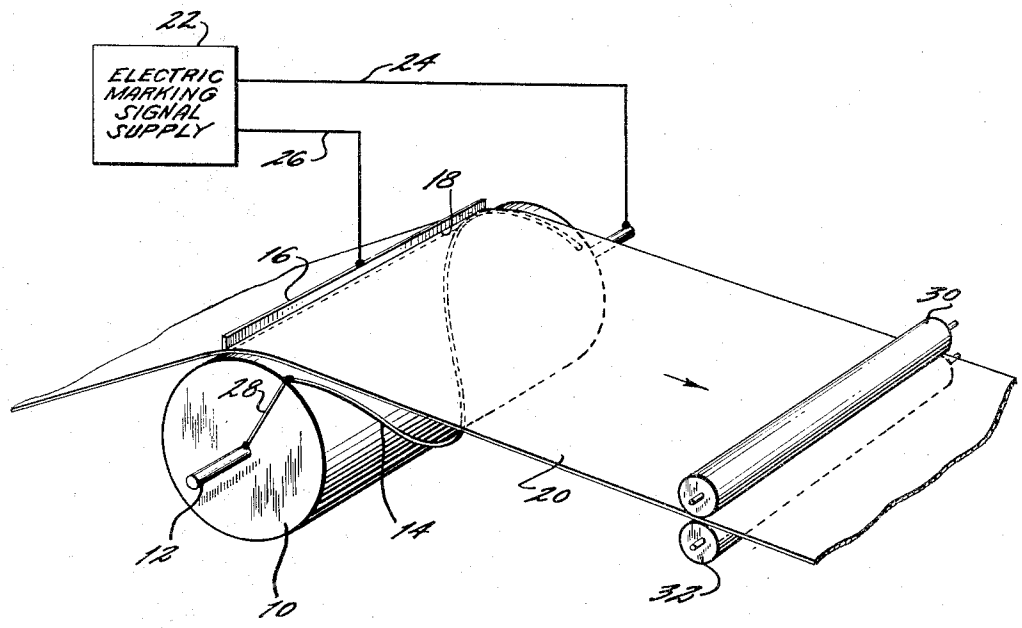
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METHOD OF MARKING

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METHOD OF MARKING

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This invention relates to improved methods of marking a carrier support sheet, to improved solutions for impregnating a sheet to be marked, and to improved impregnated sheets thus produced. More particularly, the invention relates to methods of marking a carrier support sheet, either by the passage of an electric current through portions of the sheet that are to be marked or by application of heat to these portions. The electrolytic type of marking is of particular value in connection with facsimile or telautograph systems where images are transmitted between distant points in the form of electrical signals and reproduced, when received, by causing the electrical signals to effect marking corresponding to the image.

Up to the present time, facsimile systems have been severely handicapped by the restrictions imposed in the marking step. One difficulty is the length of time required for producing a mark. A paper sheet may, for example, be impregnated with chemicals that go through a localized color change in response to electrolytic treatment, but this treatment is of finite duration if the marks are to have acceptable definition. In addition, the reproduced image should have good resolution which requires the size of its individual component marks to be reduced as much as possible. This multiplies the total number of individual marks that form the entire image and correspondingly lengthens the total marking time.

Considerable work has been done in an effort to increase marking speeds, but such increases are invariably accompanied by difficulties. By way of example, the copending patent application, Serial No. 39,549, filed July 19, 1948, now Patent No. 2,636,848, April 28, 1953, describes a marking technique that is highly practical for commercial use at linear marking speeds of about 150 inches per second, and which, for certain purposes, can be used at speeds up to 600 linear inches per second. However, the sensitizing mixture that enables these speeds has a useful life of only about one day when in solution, and for any appreciable storage life must be divided into at least two parts, one of which is carefully isolated from the other as well as from atmospheric moisture.

At least in some instances, previously used processes which provide high marking speeds use sensitizing ingredients so ready to react as to be too unstable for simple storage. The problem of handling chemicals and solutions accordingly reaches a magnitude sufficient to severely limit the usefulness of the systems.

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It is a principal object of the present invention to provide an improved marking technique having a high marking speed but using only relatively stable chemicals.

Another object of the present invention is to provide an improved marking technique using a sensitized carrier support which is not susceptible to premature mark production or discoloration upon storage.

An additional object of the present invention is to provide an improved marking method, sensitizing mixture, and sensitized carrier support, which develop marks by producing gas bubbles that effect substantially permanent changes in opacity of the carrier support.

Another object of the present invention is to provide an improved marking technique in which a carrier support is impregnated with a sensitizing mixture which is affected by electrolytic treatment to produce a substantial change in carrier opacity by generating gas within the carrier without appreciably tending to neutralize the electrolytically induced effect, thereby achieving efficient marking.

Still another object of the present invention is to provide an improved method of marking a carrier support sheet by localized application of heat.

The above as well as still further objects of the invention will be more readily understood from the following description of exemplifications thereof, reference being made to the accompanying drawings wherein the figure is a diagrammatic illustration of one form of an apparatus for carrying out the essential features of an electrolytic marking technique embodying the invention.

There will now be described in detail a preferred form of one modification of the present invention.

ELECTROLYTIC MARKING METHOD

According to the present invention, a carrier support to be electrolytically marked is impregnated with a mixture of chemicals that responds to a change in acidity (pH) by generating gas bubbles within the carrier. The gas bubbles so affect the carrier that its opacity is substantially permanently changed locally and these changes are clearly visible. By arranging that the gas generation does not tend to neutralize the pH change appreciably, a distinct mark is developed, even with a relatively slight amount of electrolytic action, so that high marking speeds and efficiencies can be attained. The gas is generated by providing a mixture of a nitrite with a material such as a sulfamate, which mixture is quite

stable to wet or dry storage in alkaline or neutral condition. When the pH of the wet mixture is shifted to the acid side, the nitrite reacts to liberate free nitrogen. Substantially no acidity is neutralized when the nitrite reacts with the sulfamate, so that a copious evolution of gas follows a very slight increase in acidity.

If desired, the sensitizing mixture containing nitrite and sulfamate can include a water-soluble salt of a metal such as barium, strontium, calcium or lead, that forms a water-insoluble sulfate. Since the generation of gas by this mixture is accompanied by the conversion of sulfamate ions to sulfate ions, any barium present, for example, will at once precipitate as barium sulfate. This heightens the increase in opacity produced by the gas bubble action on at least partially light-transmitting carriers such as transparent regenerated cellulose ("cellophane") or ordinary paper.

As one example of how to practice the invention, a sensitizing solution of the following composition is prepared:

Example I

	Parts by weight
Water	200
Sodium sulfamate ($NaSO_3NH_2$)	12
Sodium nitrite ($NaNO_2$)	7

The ratio of nitrite to sulfamate may be varied considerably without rendering the solution inoperative. However, the weights given above are in accordance with molar proportions required for the reaction to go to completion and a departure therefrom merely results in a waste of that proportion of the ingredient present in excess. Also, the more dilute the solution, the less efficient is the step of impregnating the carrier support. Besides sodium nitrite, any other alkali metal nitrite, such as potassium nitrite or lithium nitrite, may preferably be used. In a similar manner, it is preferred to use any alkali metal sulfamate.

The carrier support to which markings are to be applied is then impregnated with the sensitizing solution and subjected to electrolytic treatment at those localized portions where marks are desired. The carrier support may, for example, be sized or coated white paper, glassine paper, or regenerated cellulose of the type commonly known as "cellophane" of the water-wettable variety.

The figure shows one convenient technique for effecting the electrolytic treatment, using a conventional facsimile scanning device. A cylindrical drum **10** is mounted for rotation on a shaft **12** and carries a helically disposed electrically conductive wire **14** secured to its cylindrical surface and projecting outwardly therefrom. An electrically conductive bar **16** has an elongated linear edge **18** held in preferably parallel relation with respect to the outer surface of drum **10**. The bar **16** is also biased toward the helix; that is, the longitudinal axis of the bar is preferably parallel to the axis of rotation of the drum. The carrier support **20**, which is to be marked, is passed between the helix **14** and the bar edge **18**, and pulled through at the desired linear velocity by pinch rollers **30** and **32** while the drum **10** is revolved at a suitable speed. The electric signals that produce the desired markings are supplied from a source **22**, which may be a conventional facsimile receiver, by means of conductors **24** and **26**, and are passed as electric currents between the helix and the bar. The moving helix may have its electrical connection supplied through the shaft **12** to which it may be electrically connected by the link **28** or through the drum **10**, itself, where the drum is electrically conductive. A conventional contact brush (not shown) is used to complete the circuit to the rotating shaft. The details of the signal supply **22** as well as the synchronization of the marking signals with the drum rotation and the pinch roll actuation are more completely explained in the book Radio Facsimile, volume I, edited by A. N. Goldsmith and others, and copyrighted 1938 by RCA Institutes, Inc., especially on pages 76–79, 132, 133, 184–192, and 322–327.

During the rotation of the drum, successive minute portions of the helix are brought into opposed relation with successive portions of the bar edge **18**. This is done in such manner that successive minute portions of the sensitized moist carrier became electrolytic paths for the passage of current between the bar and helix. For each revolution of the drum **10** these minute carrier portions are successive portions of a line extending across the scanned portion of the carrier width. Successive drum revolutions scan other lines parallel to the first and these lines are successively placed along the carrier support such that all of the lines taken together form a raster or picture area.

The electrical signals delivered by the source **22** are in the form of direct current pulses that vary in potential in accordance with the intensity of the marks to be made at each minute area of the carrier support **20**. In general, the greater the intensity of the mark desired, the higher the potential of the current pulse which should be used.

With the sensitizing mixture of the above example, marks are produced at the anode of the minute electrolytic cell formed by the helix **14**, the opposed portion of bar **16** and the intervening carrier support. At this anode, which may be either the helix or the bar, the passage of direct electric current causes an increase in acidity. Although nitrite and sulfamate ions (NO_2— and SO_3NH_2—, respectively) are present in the solution in addition to sodium ions (Na^+), the presence of water contributes hydrogen and hydroxyl ions (H^+ and OH^-, respectively) in a definite ratio depending upon the acidity of the solution. The hydroxyl ions are preferentially discharged at the anode during the passage of current, and these ions can be considered as the medium by which the current is at least partially carried through the minute electrolytic cell. The discharge of hydroxyl ions leaves, adjacent the anode, a superabundance of hydrogen ions, the effect of which is to increase the local acidity.

In this condition, the reactions, taken as a whole, appear to result in the following:

$$NO_2^- + SO_3NH_2^- \rightarrow N_2 + SO_4^= + H_2O$$

The nitrogen (N_2) is liberated as tiny gas bubbles and leaves a characteristic white mark in the paper. The mark is substantially completely opaque and appears to be the result of a permanent disturbance of the carrier fibers or structure by the copiously evolved bubbles. The mark is clearly visible in ordinary glue-sized white paper, such paper being translucent at least to some degree. The mark becomes an integral part of the carrier and persists after drying. Its permanence appears to be that of the carrier, itself.

By reason of the relative opacity of the mark, it can be readily reproduced by photographic or diazotype processes or projected onto a screen,

using the marked carrier as a copying "transparency" or lantern slide. Where a highly transparent carrier is used, glassine paper or water-wettable regenerated cellulose, for example, the white marks stand out with maximum contrast. With an ordinary white paper carrier, the contrast of the marks diminishes with the reduction in the extent of sizing or coating. Filter paper which is completely unsized and uncoated can be used to produce marks of lowest contrast.

The marking technique of the invention can also be used with other marking machines for electrolyzing the carrier, or the marks may be made by hand, as by placing the sensitized carrier on a conductive plate connected to the negative terminal of a source of direct current, and moving over the carrier a conductive stylus connected to the positive terminal of this source. The stylus can be manipulated as a pencil to effect white markings.

The potential used to pass the marking current is subject to wide variations. As little as 5 volts is enough, but to increase the speed with which the marks are applied higher voltages can be used, limited only by the conductivity of the sensitizing solution. Using less than about 100 volts potential, the marks can be made with very good definition at a linear rate of up to about 160 inches per second. Higher speeds can also be used with still higher voltages. In general, higher voltages provide markings having more contrast in relation to the background.

The markings do not appear to change the tensile strength or any of the physical characteristics of the carrier significantly other than its transparency. Marked carriers appear to be just as stable toward storage as the carrier, itself. The sensitizing ingredients are also highly stable, both when impregnated in the carrier or when mixed dry or in solution. The sensitization retains its full efficacy after a year's storage and does not appreciably accelerate the ageing of the carrier, either before or after marking.

A feature of the invention is the fact that any premature reaction of the sensitizing chemicals, as a result of ageing, for example, does not discolor or prematurely mark the carrier. Although some slow decomposition of the chemicals may take place, no color formation can take place, there being no color-forming materials present. A slow liberation of gas that may accompany ageing is of no effect in leaving a mark, apparently, because gas in such small amounts can be given off by the carrier without disturbing its physical structure.

For preventing the obliteration of marks by later markings that may be inadvertently made, the marked carrier can be readily desensitized, as by merely washing out the sensitizing ingredients. These ingredients are easily soluble in water. For added simplicity, the desensitizing is effected just after the marking, when the carrier is still moist and the solute washes out very rapidly.

The amount of sensitizing material used per unit carrier surface is subject to wide variation. As little as 0.1 gram or as much as 2 grams of solute per square foot is effective. Larger concentrations are difficult to retain in the moistened sheet by reason of run-off with water that drains from the sheet. Smaller concentrations produce marks of somewhat reduced contrast.

Another feature of the invention is that the generation of gas bubbles for the marking does

not involve any change in acidity that would counteract the acidity increase which causes the gas generation. This is shown by the fact that the above equation indicating the chemical action involved does not include the consumption or liberation of hydrogen or hydroxyl ions. In other words, the hydrogen ions added to produce marking are not used up in the marking. The marking can, therefore, be extreme in intensity even though caused by an exceedingly slight pH shift of temporary nature.

The marking intensity and efficiency can be increased by adding to the sensitizing ingredients a material that reacts with the sulfate ions ($SO_4^=$) formed by the marking reaction, to increase the visibility of the mark. This may be accomplished by adding to the sensitizing mixture a soluble salt of a metal that forms an insoluble sulfate. Any of the soluble salts of barium, calcium, strontium, or lead, for example, may be used for this purpose. The insoluble sulfate will form whenever the marking takes place. These salts do not precipitate out in the presence of sulfamate ions. The slow decomposition of sulfamate which normally takes place causes the sulfate-producing mixture to show some amount of premature whitening upon extended storage. Decomposition of sulfamate also tends to reduce the contrast of marks made on carriers that are not desensitized after marking takes place since the formation of insoluble sulfates gradually increases the opacity of the carriers.

An example of a sensitizing solution which contains a component for producing an insoluble sulfate is as follows:

Example II

	Parts by weight
Water	200
Barium chloride	32.5
Sodium sulfamate	16
Sodium nitrite	9.3

The above solution is used to impregnate a sheet of carrier support material in a manner similar to that described in connection with Example I and the marking process is carried out electrolytically as previously described.

According to another modification of the present invention, the sensitizing mixture may also include an amine. Water soluble aliphatic amines make effective neutralizing agents for keeping the sensitizing solution neutral or slightly alkaline during storage, as well as for neutralizing sulfamic acid, to prepare the solution with all or most of the sulfamate in the form of amine sulfamate. It is desired to maintain the solution within a pH range of about 7 to about 10.5 during storage.

Water soluble primary aliphatic amines also react with the nitrite in acid solutions to generate nitrogen so that the amount of sulfamate can be reduced when this type of amine is used. The following are examples of suitable primary amines:

Monoethanolamine
2-amino-2-methyl-1-propanol
2-amino-1-butanol
Tris (hydroxymethyl) aminomethane
2-amino-2-methyl-1:3-propanediol
N-aminoethyl-ethanolamine
Ethylenediamine
Diethylenetriamine
Triethylenetetramine
Tetraethylenepentamine
Propylenediamine

The following are examples of sensitizing solutions including a primary aliphatic amine.

Example III

	Parts by weight
Water	200
Sulfamic acid	9.7
Ethylene diamine (69.1% solution)	5
Sodium nitrite	7

Example IV

	Parts by weight
Water	200
Sulfamic acid	9.7
Monoethanolamine	6.8
Sodium nitrite	7

The above solutions are utilized to impregnate sheets of carrier support material as previously described and marking is accomplished in the same manner heretofore explained.

METHOD OF MARKING USING HEAT

Primary, secondary and tertiary amines make the sensitized carrier sensitive to heat in addition to acids. Thus, the application of hot printers' type or a heated flatiron or stylus will cause the carrier so sensitized to become white at the heated zone. Apparently, the amine salts are readily decomposed by the heating in the presence of a nitrite to liberate nitrogen gas bubbles that have the same opacifying effect as the acid-liberated nitrogen.

In addition to the primary aliphatic amines previously listed, secondary and tertiary amines, of which the following are examples, have also been found suitable for sensitiing the carrier to heat:

Diethanolamine
Triethanolamine
Dibutylamine
Triethylamine
Diisopropanolamine

Alicyclic amines, of which morpholine is one example, have also been found suitable for use in compositions used in the heat marking method.

These amines do not react with nitrites to liberate nitrogen, however, so that their function is solely that of neutralizing part of the sulfamic acid.

In order to prepare a carrier sheet for marking by local application of heat, the sheet is preferably impregnated with a solution containing the various ingredients in about the same proportions by weight as given in Examples III and IV used to illustrate the modification of the process directed to electrolytic marking. The concentrations of the ingredients can also be varied as previously explained.

There have thus been described improved methods of marking a carrier support sheet, which methods include the use of a sensitizing material which liberates a gas when a shift in pH occurs sufficient to render the sensitizing material at least slightly acid. Liberation of the gas within the carrier sheet causes a change in opacity which is visible to the unaided eye. The carrier support sheet should be, at least, translucent and may be transparent. The sheet may either be of fibrous material, such as paper, or of film-forming material, such as regenerated cellulose. For automatic recording, an electrolytic method is preferred wherein pulses of direct current are passed through successive minute portions of the carrier sheet. However, the invention also includes use of sensitizing materials readily decomposed by heat to liberate a gas. Heat may, therefore, also be used as the agent for causing the marks to appear on the carrier sheet wherever desired.

I claim as my invention:

1. In a method of producing marks electrolytically, the steps of: impregnating a carrier support consisting of a porous sheet of material selected from the class consisting of paper and organic film-forming materials, with an aqueous solution having a pH within the range of substantially neutral to about 10.5 and containing nitrite ions and sulfamate ions; and electrolytically treating the impregnated support to render it at least temporarily acid at desired zones to cause the nitrite and sulfamate ions to react and generate gas bubbles within the support for imparting substantially permanently visible changes in opacity to said zones.

2. The method of claim 1 in which the solution is alkaline and the materials in solution include substances giving rise to ions of at least one metal of the class consisting of barium, calcium, strontium, and lead.

3. A marking medium comprising a carrier support consisting of a porous sheet of material selected from the class consisting of paper and organic film-forming materials, said sheet being impregnated with a composition comprising a water-soluble sulfamate and a water-soluble metal nitrite.

4. A medium according to claim 3 in which said sheet is composed of regenerated cellulose.

5. A medium according to claim 3 in which said sulfamate is an alkali metal sulfamate and said nitrite is an alkali metal nitrite.

6. A marking medium according to claim 3 in which said sulfamate and said nitrite are present in substantially molar proportions.

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