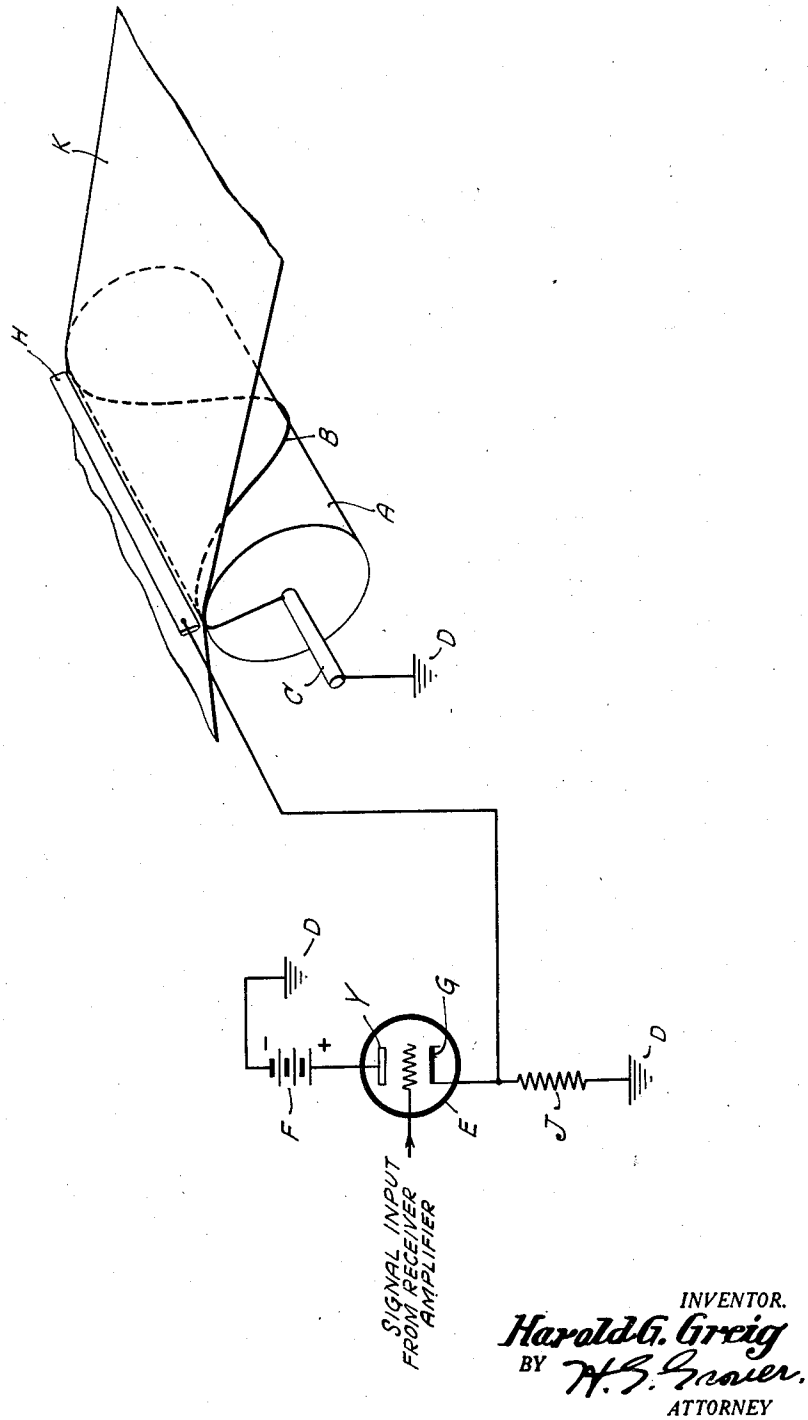
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ELECTROLYTIC RECORDING

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ELECTROLYTIC RECORDING

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1

The present invention relates to electrolytic facsimile recording and particularly to alkaline compositions designed to produce azo dyes by electrolysis and processes for using such compositions whereby recordings stable to light and storage are obtained.

Solomon in his U. S. P. 2,306,471 discloses a number of methods of producing colored records by the electrolytic method. The best of the methods disclosed by Solomon from a practical standpoint is that which may be termed the electrolytic diazotization and coupling method. This procedure involves the utilization of a fibrous carrier which is impregnated with an alkaline solution of a diazotizable amine, an ionizable nitrite, an electrolyte, and an azo dye coupling component. When the carrier in the form of a traveling web or band is subjected to electrolysis in the usual facsimile recording apparatus, the acid liberated at the anode converts the ionizable nitrite into nitrous acid which in turn diazotizes the amine with the formation of a diazonium compound. The diazonium compound then reacts with the azo coupling component with the formation of what is probably an azo dyestuff. While this method has many advantages over the previously known method, employing an electromagnetically controlled printer bar, particularly as regards the speed at which the records are made and the wear on the printer bar, it nevertheless presents problems from the standpoint of the stability of the records obtained on the one hand and the stability of the damp, pretreated carrier on the other hand.

Both the records obtained by this method and the damp carrier pre-treated with the sensitizing or recording solution have a very marked tendency to darken. There are several factors which contribute to this darkening action. In the recordings which are dried with the sensitizing chemicals still in the carrier, prolonged exposure to light causes a darkening of the dye intermediates with the result that the contrast between the recorded color and the background is materially reduced. Difficulties are accordingly presented in the reproduction of the records. A further darkening also takes place during the storage of the records in the files. On the other hand, it is noted that after the carrier has been pre-treated with the sensitizing or recording solution and is then stored in a damp state ready for recording, a discoloration of the carrier ensues with an attendant loss in ability of the same to form color upon being subjected to the electrolyzing current. While these effects appear to be attributable to actions independent of each other, nevertheless they very materially reduce the efficiency of the process in commercial application.

An improvement over the method of Solomon

2

discussed above is described in my copending application Serial No. 558,717, filed October 14, 1944, now Patent 2,459,521, granted January 18, 1949. The method described in said copending application proposes to substitute a diazoamino compound for the diazotizable amine and ionizable nitrite of the Solomon method. It is found that when employing the method of my aforesaid copending application, a material improvement in stability of the records is obtained. However, even this method leaves something to be desired in so far as the stability of the records is concerned.

It has now been ascertained that the disadvantages or lack of stability in the prior procedures can be markedly avoided if there be added to the recording solutions a small quantity of an aliphatic amine or a salt thereof. It is of course manifest that records possessing optimum contrast are those which are obtained on a white background. If, however, the background suffers a color change as it always does according to my experience, then it is preferable that this be yellow, since highest contrast is afforded with a yellow background than with a background of any other color. It has been my observation that the usual darkening of the background in prior methods goes from pink to bluish red. By utilizing the aliphatic amines, however, the background change to pink is greatly retarded and the tendency for the background when darkening to change to yellow is greatly enhanced. In fact, it has been found that when the aliphatic amines are used with, say, diacetoacetyl diamine as a coupler, the life of the yellow stage is increased by a factor of 3 to 4.

It is accordingly an object of the present invention to provide an alkaline composition for the electrolytic production of facsimile records having improved stability to light and storage.

It is a further object of the present invention to provide an alkaline composition for electrolytic recording containing a diazotizable amine, an ionizable nitrite and a coupling component which yields records upon electrolysis having improved stability to light and storage.

It is a further object of the present invention to provide an alkaline composition for the preparation of facsimile records containing a diazoamino compound and a coupling component which yields records having improved stability to light and storage.

A further object of the present invention are compositions for electrolytic facsimile recording containing a source of diazonium ions, a coupling component and an aliphatic amine or a salt thereof.

A further object of the present invention is the preparation of facsimile records by subjecting to electrolysis an alkaline composition

containing a source of diazonium ions, a coupling component, and an aliphatic amine.

A further object of the present invention are carriers, storage stable when in a damp condition and which have been pretreated with an alkaline solution containing a source of diazonium ions, an azo dye coupling component and an aliphatic amine or a salt thereof.

Other and further important objects of the invention will become apparent as the description proceeds.

The essential components of the compositions contemplated by the present invention are a source of diazonium ions, an azo dye coupling component, a water-soluble inorganic salt as the electrolyte, an aliphatic amine or a salt thereof, and an alkali. The diazonium ions may be supplied either by a diazotizable amine and a water soluble metal nitrite or by a diazoamino compound. In other words, the diazonium ions which react with the coupling component originate from the diazotizable amine and nitrite on the one hand, or the diazoamino compound on the other hand, and accordingly the term "source of diazonium ions" as used in the claims should be so construed. In either case, the acidity generated at the anode during electrolysis leads to a diazonium compound capable of directly coupling with the azo dye coupling component.

Suitable diazotizable amines are: naphthionic acid and its water soluble salts, such as sodium naphthionate and the like,

Benzidine-3.3'-disulfonic acid
Benzidine-2.2'-disulfonic acid
Anthranilic acid
4-amino-benzoic acid
Metanilic acid
Sulfanilic acid
p-Amino-benzophenone
p-Phenylenediamine
2.5-diaminobenzene sulfonic acid
o-Tolidine-2.2'-disulfonic acid
4.4'-diaminostilbene-2.2-disulfonic acid
J acid
2-naphthylamine-5.7-disulfonic acid
Gamma acid
Chicago acid
2.6-diaminopyridine

If it be desired to employ these amines in the form of their diazoamino compounds, they may be first diazotized or tetrazotized and then reacted with an amine which is difficult of coupling and which may be aliphatic, such as ethanolamine, diethanolamine, sarcosine, diisopropylamine, dimethylamine, diethylamine, methyl mannamine and the like, or heterocyclic such as α-carboxy-pyrrolidine, α-1-α-2-dicarboxy-pyrrolidine, tetra-hydroquinoline, carbazole and the like. Examples of diazoamino compounds are:

1 mol of diazotized naphthionic acid + 1 mol of diethanolamine
1 mol of diazotized naphthionic acid + 2 mols of diethanolamine
1 mol of tetrazotized benzidine-3.3'-disulfonic acid + 2 mols of diethanolamine
1 mol of diazotized naphthionic acid + 1 mol of carbazole-2-sulfonic acid and the like

Reference is here made to my copending application Serial No. 558,717, which contains a more comprehensive disclosure of the diazoamino compounds which may be employed according to the present invention.

The diazotizable amine utilized in the recording solution or the diazoamino compound thereof is preferably employed in a quantity of about .03 to .15 gram mol per liter of the recording solution, amounts which in turn yield .03 to .15 gram mol of diazonium salt. If the diazotizable amine is utilized as such, a metal nitrite must be present and it is recommended that the same be employed in a quantity of about .06 to .15 gram mol per liter of the recording solution. The metal nitrite is water soluble and is preferably an alkali metal nitrite such as sodium nitrite, potassium nitrite and the like.

The electrolyte is a water soluble, inorganic salt such as sodium chloride, sodium bromide, potassium bromide, potassium chloride, lithium chloride, potassium sulfate, sodium sulfate and the like. Of these, the sodium chloride gives the best results and its use is accordingly preferred. The electrolyte is generally employed in a quantity of .25 to 1 gram mol per liter of the recording solution, although larger or smaller quantities may be used depending upon the other ingredients of the solution.

Any of the common azo dye coupling components is suitable for my purpose, but I prefer to utilize those which are soluble in aqueous alkaline solutions having a pH up to 11. These compounds are generally employed in an amount ranging from .01 to .06 gram mol per liter of the recording solution. As examples of coupling components which may be utilized, reference is made to

Chromotropic acid
Benzoyl H acid
Benzoyl-p-amino benzoyl H acid
Acetyl-p-amino benzoyl H acid
Toluyl H acid
and the like;
Resorcinal
Salicylaldehyde
Phloroglucinol
Schaeffer's acid
F salt
Chicago acid
Benzoyl J acid
Gamma acid
Chloro H acid
1-p-sulfophenyl-3-carboxy-5-pyrazolone
diacetoacetylethylenediamine
2.6-diaminopyridine
and the like.

The stabilizing effect which is the purpose of the present invention is general for the class of aliphatic amines which are soluble in aqueous alkaline solutions and the salts of said amines. However, for practical reasons it is inadvisable to utilize amines which are either normally gaseous or readily volatilized since such amines evaporate during the electrolytic process as a consequence of which their stabilizing effect is lost. It is therefore preferable, particularly when using alkyl amines as subsequently noted, to employ such amines as contain from 3 to 6 carbon atoms since within this range the alkyl amines do not tend to evaporate from the carrier.

Suitable aliphatic amines for my purpose are the alkylamines containing from 3 to 6 carbon atoms, such as propylamine, butylamine, amylamine, hexylamine and the like, alkylene polyamines such as ethylene diamine, propylene diamine, butylene diamine, pentamethylenediamine, diethylenetriamine, triethylene triamine, triethylenetetramine and the like, and alkylolamines such as monoethanolamine, diethanol-

amine, triethanolamine, aminoethyl ethanolamine, and the like. All of these amines are soluble in aqueous alkaline solutions and in addition are not readily volatilized during the electrolytic recording procedure.

As stated, the amines may also be used in the form of their salts, the salt-forming acid being either inorganic or organic. It appears that the salts when present in the alkaline solution dissociate, liberating the free amines so that the salts function in the same way as the amines per se. The use of the salts has the advantage that they may be more readily used in dry compositions and can be added in much larger amounts without the necessity of adjusting the pH of the solution.

Suitable inorganic acids for neutralizing the amines to form the salts thereof are hydrochloric acid, sulfuric acid, phosphoric acid, boric acid and the like. Suitable organic acids are acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid and the like. It is preferred to use the organic acids and particularly the polybasic organic acids since they appear to contribute to the stabilizing effect produced by the amines. In this connection particular reference is made to oxalic acid, the potassium salt of which is known to increase the life of damp stored pre-treated paper.

The quantity of the acid employed may vary from that giving partial neutralization to that giving complete neutralization. For instance, if a diamine be employed, the mono salt of the diamine or the di-salt of the same may be utilized.

The quantity of the amine or its salt which has been found to be effective ranges from about .02 to about .05 gram mol per liter of the recording solution. While stabilization is effected with greater amounts of the amine than that given, the degree of stabilization does not justify the use of the added quantities of the amine. If the quantity of the amine be depreciated below that given, some stabilization is obtained but the degree does not represent the optimum. Accordingly, while quantities of amine or the salts thereof other than those given may be employed, while obtaining stabilization, it is recommended that for best results the proportions be in the range provided.

The solutions made up of the above ingredients must contain an alkali to provide a pH which will preclude premature diazotization and coupling of the diazotizable amine and coupling component or premature splitting of the diazoamino compound and coupling with the coupling component. The amount of the alkali is such as to provide a pH ranging from about 9 to 11. To this end there may be added to the solution a water soluble alkali such as sodium hydroxide, potassium hydroxide, potassium carbonate and the like.

The solvent for the various ingredients is preferably water, although water containing another ionizable solvent may be employed. As such ionizable solvent there may be mentioned methyl alcohol, ethyl alcohol, ethylene glycol and the like.

Various other adjuncts may be added to the composition to improve the shades of the records and to facilitate the impregnation of the paper by the recording solution. Compounds in the first category are aliphatic thioamides such as thiourea, thiosinamine, thiocarbamic acid and the like. These compounds are generally employed in an amount ranging from .02 to .0526 gram mol per liter of solution.

Compounds in the second category are substances which are known as wetting agents. As examples of such compounds may be mentioned alkylated napthalene sulfonic acids, such as butyl naphthalene sulfonic acid and the like, sulfonated benzene reacted with chlorinated kerosene, N-stearoyl sarcosine, N-stearoyl glycine, oleyl polyglycol ether, palmitic acid monoethanolamide, dioctyl sodium sulfosuccinate, sulfanated, polyalkoxylated aryl compounds and the product said to have the formula $C_4H_9CH(C_2H_5)CH_2SO_4Na$. (See page 130, volume 35, Journal of Industrial and Engineering Chemistry.) The quantity of the wetting agent used will vary depending upon the particular recording material, the nature of the wetting agent and the like, but generally will range from about .1 to .5 per cent by volume of the recording solution.

The carrier or material which is impregnated with the recording solution and upon which the color is to be recorded may be any fibrous impregnatable material such as paper, cloth, fabric and the like. Rosin sizing in the paper should be avoided since it has the effect of causing darkening of the background of the records on storage. Resins produced from melamine and formaldehyde give good wet strength to the paper and their use is recommended.

The amines employed in preparing the recording solutions may be incorporated in the compositions in different ways. For instance, the amines or their salts are added directly to the recording solutions. On the other hand, the amines or their salts may be added to dry mixes of the chemicals, which are then dissolved in water. As a further alternative, one may employ the amines or their salts to pre-treat the paper before the paper is subjected to the action of the recording solution proper.

The stabilizing effect obtained by the ultilization of the amines and their salts is greatly in excess of that which was to be expected from the substitution of these products for the inorganic bases and salts normally used in facsimile recording solutions. It is not known, nor can it be definitely ascertained, to what the added stability is attributable. There are several theories which may help to arrive at an understanding of this matter, though it is to be understood that such theories are not to be considered as imposing any limitation upon the scope of the present invention.

It is usually the practice in compounding recording solutions of the type here in question, to utilize diazotizable amines and coupling components which contain sulfonic acid groups to increase their water solubility. The amines, as stated, are capable of forming salts. It is possible that salt formation between the sulfonic acid groups in the dye-forming intermediates used in the recording solutions and the amines, contribute to the increase in stability especially to the action of light and to oxidation. Thus it has been ascertained that the amine salts of aromatic sulfonic acids darken less readily than the corresponding alkali metal salts when subjected to the action of air, moisture and heat.

On the other hand, the most used carrier for the recording solution is paper. The dye intermediates which are used to make up the recording solutions generally possess substituent groups capable of reacting with the cellulose in the paper. The amines are likewise capable of reacting with cellulose. It is therefore conceivable that the amines may react with the cellulose

in preference to the substituent groups in the dye intermediates, as a consequence of which they block or retard a reaction between the intermediates and the cellulose. This competing action may be merely a physical absorption of the organic materials on the paper. In either case, the result would be the same and could account for the increase in the storage life of paper pre-treated with the recording solutions to which the amines or their salts have been added. In any event, it is manifest that the involved situation is quite complex, which explains why the particular effect of the amines has not been capable of ascertainment.

An apparatus by which the invention may be effected is diagrammatically disclosed in the accompanying drawing.

ON THE DRAWING

Referring to the drawing, it will be seen that the apparatus comprises a drum A mounted on a drive shaft C. The drum is provided with a helix B which is made of a conducting material and is connected in any appropriate manner, such as through the drive shaft C to ground D.

The signals representative of the image to be recorded are applied on the grid of an output amplifier tube E, the anode Y of which is connected to a positive source of voltage F and the cathode G of which is connected to the printer bar H. By this arrangement, output signals from the tube are taken across the cathode output resistor J, one end of which is connected to the cathode G and the other to ground D. The carrier K which is a traveling web or band of paper or fabric, moves intermediate the printer bar H and the drum A. The carrier K is impregnated with an electrolytic solution prepared as in Example I.

When current flows through the printer bar to the ground through the carrier K and the helix B, the benzidine-3.3'-disulfonic acid is tetrazotized and coupling ensues between the resulting diazonium compound and the coupling components with the formation of a dye. The dye will appear in a concentration depending upon the impulses to which the printer bar is responsive.

The helix is the cathode or negative element of the cell and is usually formed of beryllium-copper alloy, stainless steel or platinum. The printer bar, on the other hand, constitutes the anode element and is usually formed of platinum, platinum-iridium or stellite. The quantity of dye which is produced by the current passing between these elements is in proportion to the current flow and the time it is flowing and is determined by coulombs per square inch. The current flow is generally so set that a maximum depth of recording is represented by full current from the tube. Lower values of current give half tones. While the color formed is proportional to the current flowing, this proportionality is not necessarily linear.

It will be evident that in the process effected with this apparatus the electrolytic cell is a very small space in the interstices of the carrier lying between the positive electrode or printer bar and the negative electrode or helix wire at the point where they cross. During recording, these electrodes mechanically scan the carrier at a very high rate so that the time of current flow for any one point of contact may be considerably under 1/10,000 of a second depending upon the recording rate. The voltage across the electrodes may vary widely and even have a reversal of polarity at the minimum value. It can be increased to 200 or 300 volts for maximum current flow when full color is being recorded.

The current density under these conditions may also vary considerably although it has a minimum value for faint color formation. This minimum is termed the threshold value and varies with the composition of the solution used. High alkalinity or readily oxidized organic intermediates and the like increase this threshold value or minimum current necessary for faint color formation. The primary requisite is that the current produce a high enough concentration of hydrogen ions at the surface of the positive electrode to overcome the initial alkalinity of the wet carrier and allow for nitrous acid formation and diazotization of the diazotizable amine. The upper limit of the current density is determined by either that density at which the color formed is burned out or by that density at which the carrier structure is ruptured or burned, whichever density be the lower. Inasmuch as these are variables which depend upon the carrier used, the strength of color desired, and the like, but nevertheless may be readily ascertained by a person skilled in the art, it is deemed unnecessary to specifically state voltages, current densities and the like for any particular set of conditions.

The invention is further illustrated by the following examples but it is to be understood that the invention is not restricted thereto.

Example I

	Gram mol
Benzidine-3.3'-disulfonic acid	.03
Benzoyl H acid	.013
Diacetoacetyl ethylenediamine	.035
Thiourea	.053
Diethylene triamine neutralized with o-phosphoric acid	.04
Sodium nitrite	.139
Sodium chloride are dissolved in a liter of water	.5

the sodium nitrite being withheld until the pH of the solution has been adjusted to pH 10 with sodium hydroxide. Paper impregnated with this solution may be stored while damp for a considerable period of time, for instance, 60 days, without any noticeable darkening. If paper be impregnated with a composition prepared with the same ingredients as above, but while omitting the salt of diethylene triamine, the paper has a storage life of only two to three weeks. The paper when utilized in the apparatus described above yields facsimile records which are a very dark blue-purple approaching black, on a pale yellow background. The records retain their original high contrast even after being subjected to the action of light or after being stored for a considerable period.

Example II

	Gram mol
Sodium naphthionate	.03
Chromotropic acid	.02
Sodium chloride	.35
Ethylenediamine which has been neutralized with o-phosphoric acid	.04

are dissolved in a liter of water. Sodium hydroxide is then added until the pH is approximately 10. .07 gram mol of sodium nitrite is then dissolved in the solution. This solution is then used in the same way as in Example I to produce

bright blue-purple records on a white background.

Example III

	Gram mol
Benzidine-3.3'-disulfonic acid	.03
Benzoyl H acid	.013
o-Phosphoric salt of monoethanolamine	.04
Sodium chloride	.5

are dissolved in a liter of water. Sodium hydroxide is then incorporated in the solution to adjust the pH to 10. .07 gram mol of sodium nitrite is dissolved in the solution, and paper is impregnated with the resulting composition. When employed as in Example I, bright blue records on a pale yellow background having high stability to light and storage are obtained.

Example IV

The procedure is the same as in Example I excepting that the diethylene triamine salt is replaced by .04 gram mol of monophosphoric acid salt of aminoethylethanolamine. Paper treated with the resulting solution has a considerably longer damp storage life than paper treated with the same solution but free from the aminoethylethanolamine. When subjected to the action of an electrolyzing current in the apparatus described above, it yields dark purple records on a pale yellow background.

Example V

The procedure is the same as in Example II excepting that the ethylenediamine salt is replaced by .04 gram mol of ethylene diamine itself.

Example VI

The procedure is the same as that of Example II excepting that the ethylenediamine salt is replaced by .04 gram mol of propylamine.

Example VII

.5 gram mol of sodium naphthionate is dissolved in approximately 750 cc. of water to which sufficient sodium hydroxide is added to make the solution alkaline to brilliant yellow test paper.

.5 gram mol of sodium nitrite is then added and the solution is run under rapid agitation at a temperature of 5 to 10° C. into a solution of 140 cc. of 38% hydrochloric acid and 750 cc. of water and ice. Diazotization is complete almost as soon as the solution is added and the diazonium compound, which is quite insoluble, precipitates out as a thick, creamy slurry. Stirring is continued for one hour to obtain the product in a form in which it is more easily filtered. The filter cake obtained upon filtration is reslurried in approximately 500 cc. of water until a smooth paste is secured. This paste is added slowly at 10 to 15° C. over a two-hour period with rapid agitation to a solution of 125 cc. of diethanolamine in 250 cc. of water while maintaining a temperature of 10 to 15° C. in an ice bath to minimize decomposition.

The reaction is complete when all the diazonium compound has been added. The resulting solution is amber in color and may stain paper with a reddish tint. It must be alkaline when tested with brilliant yellow test solution.

2 grams of sodium hydrosulfite are added and the solution stirred for one hour at room temperature to clear away the red-staining impurities. 20 grams of activated charcoal are incorporated and the temperature raised to 50 to 55° C. for ½ hour for the purpose of further clarifying the solution and to remove basic impurities. The solution is then filtered and the volume is adjusted to 1000 cc.

A recording solution is then prepared by dissolving .03 gram mol per liter of the monosodium salt of chromotropic acid in 500 to 700 cc. of water. 8 grams of sodium carbonate are then added to render the solution alkaline to test with brilliant yellow test solution.

.06 gram mol of the above described diazoamino compound

30 grams of sodium chloride

.04 gram mol of ethylenediamine, and

.5 gram of a sulfonated benzene which has been alkylated with chlorinated kerosene are then added and when the solution is complete, the same is filtered and diluted to a liter. The final solution is adjusted to a pH of 10 by the addition of approximately 20 cc. of 2½ N sodium hydroxide solution.

Paper impregnated with this solution and used in the apparatus described above yields dark blue to purple records on a white background which are stable to light and storage.

I claim:

1. The process of producing colored image records on only one side of a fibrous carrier by the electrolytic facsimile recording method, said records having an improved stability to light and storage, which comprises subjecting to the action of an electrolytic facsimile recording current a travelling fibrous carrier impregnated with an alkaline solution containing as its essential components a source of diazonium ions, an azo dye coupling component in a sufficient quantity to react with the diazonium ions when formed to produce an azo dye, a water soluble inorganic salt as the electrolyte in an amount to insure the passage of the electrolytic recording current and a small amount of an aliphatic nitrogenous compound soluble in aqueous alkaline solutions selected from the class consisting of alkylamines containing from 3 to 6 carbon atoms, alkylene polyamines, alkylolamines and the salts of such amines, said aliphatic nitrogenous compound operating to increase the stability of the records to light and storage.

2. The process as defined in claim 1 wherein the amine is an alkylolamine.

3. The process as defined in claim 1 wherein the amine is an alkylene polyamine.

4. The process of producing colored image records on only one side of a fibrous carrier by the electrolytic facsimile recording method, said records having improved stability to light and storage, which comprises subjecting to the action of an electrolytic facsimile recording current of travelling fibrous carrier impregnated with an alkaline solution containing as its essential components a diazotizable amine, a sufficient quantity of a water soluble metal nitrite to produce the nitrite ions necessary for diazotization of said amine under the influence of the electrolytic recording current, a water soluble inorganic salt as the electrolyte in an amount to insure passage of the electrolytic recording current, an azo dye coupling component to react with said diazonium ions when formed to produce an azo dye and a small amount of an aliphatic nitrogenous compound soluble in aqueous alkaline solutions selected from the class consisting of alkylamines containing from 3 to 6 carbon atoms, alkylene polyamines, alkylolamines and the salts of such amines, said aliphatic nitrogenous compound op-

erating to increase the stability of the records to light and storage.

5. The process as defined in claim 1 wherein the source of diazonium ions is a diazoamino compound.

6. The process as defined in claim 1 wherein said aliphatic compound is present in an amount of from about .02 to about .05 gram mol per liter of said alkaline solution.

7. The process of producing colored image records on only one side of a fibrous carrier by the electrolytic facsimile recording method, said records having an improved stability to light and storage, which comprises subjecting to the action of an electrolytic facsimile recording current a travelling fibrous carrier impregnated with an alkaline solution containing as its essential components a diazoamino compound capable of yielding diazonium ions under the influence of said electrolytic recording current, a water soluble inorganic salt as the electrolyte in an amount to insure the passage of the electrolytic recording current, an azo dye coupling component in a sufficient quantity to react with said diazonium ions when formed to produce an azo dye and about .02 to .05 gram mol per liter of said alkaline solution of an aliphatic nitrogenous compound soluble in aqueous alkaline solutions selected from the class consisting of alkylamines containing from 3 to 6 carbon atoms, alkylene polyamines, alkylolamines and the salts of said amines, said aliphatic nitrogenous compound operating to increase the stability of the records to light and storage.

8. The process as defined in claim 1 wherein said alkaline solution contains per liter a source of diazonium ions capable of yielding from about .03 to .15 gram mol of diazonium salt, from .25 to 1 gram mol of said water soluble inorganic salt as the electrolyte, from .01 to .06 gram mol of said azo dye coupling component, and from about .02 to .05 gram mol of said aliphatic nitrogenous compound.

9. The process as defined in claim 4 wherein said diazotizable amine is benzidine 3:3'-disulfonic acid, said nitrite is sodium nitrite, said coupling component is a mixture of benzoyl H-acid and diacetoacetyl ethylenediamine, said water soluble inorganic salt is sodium chloride, and said aliphatic nitrogenous compound is diethylene triamine neutralized with o-phosphoric acid.

10. The process of producing colored image records on only one side of a paper carrier by the electrolytic facsimile recording method, said records having an improved stability to light and storage, which comprises subjecting to the action of an electrolytic facsimile recording current a travelling carrier of paper impregnated with an aqueous solution consisting of .03 gram mol of benzidine-3,3'-disulfonic acid as the diazotizable amine, .013 gram mol of benzoyl H acid and .035 gram mol of diacetoacetyl ethylenediamine as the coupling component, .053 gram mol of thiourea, .139 gram mol of sodium nitrite, .5 gram mol of sodium chloride, and .04 gram mol of diethylene triamine neutralized with o-phosphoric acid, said solution containing sufficient sodium hydroxide to provide a pH of approximately 10, said diethylene triamine neutralized with o-phosphoric acid operating to increase the stability of the records to light and storage.

11. The process as defined in claim 4 wherein the diazotizable amine is sodium naphthionate, the coupling component is chromotropic acid, the water soluble inorganic salt is sodium chloride, the water soluble metal nitrite is sodium nitrite, and the aliphatic nitrogenous compound is the diphosphoric acid salt of ethylene diamine.

12. The process of producing colored image records on only one side of a fibrous carrier by the electrolytic facsimile recording method which comprises subjecting to the action of an electrolytic recording current a travelling fibrous carrier impregnated with an alkaline solution containing as the essential components per liter of said solution .03 gram mol of sodium naphthionate as the diazotizable amine, .03 gram mol of chromotropic acid as the coupling component, .35 gram mol of sodium chloride as the electrolyte, .07 gram mol of sodium nitrite and .04 gram mol of the diphosphoric acid salt of ethylene diamine, the solution having a pH of approximately 10, said diphosphoric acid salt of ethylene diamine operating to increase the stability of the records to light and storage.

13. The process as defined in claim 1 wherein said source of diazonium ions is diazotized sodium naphthionate stabilized by diethanolamine, the coupling component is chromotropic acid, the electrolyte is sodium chloride, and the aliphatic nitrogenous compound is ethylene diamine.

14. A fibrous sheet material for the formation of colored image records thereon by the electrolytic facsimile recording method, said records having an improved stability to light and storage, said sheet material carrying a composition containing as its essential components a diazotizable amine, a quantity of an ionizable nitrite sufficient to effect diazotization of said amine, a water soluble inorganic salt as the electrolyte in an amount sufficient to facilitate the passage of the electrolyzing current, an azo dye coupling component in a quantity sufficient to react with said diazonium compound when formed to yield an azo dye, an aliphatic nitrogenous compound soluble in aqueous alkaline solutions and selected from the class consisting of alkylamines containing from 3 to 6 carbon atoms, alkylene polyamines, alkylolamines and the salts thereof, and a quantity of an alkali sufficient to give a pH on the alkaline side to thereby prevent premature diazotization of said diazotizable amine, said aliphatic nitrogenous compound acting to increase the stability of the records to light and storage.

15. The article as defined in claim 14 wherein the aliphatic nitrogenous compound is an alkylene polyamine.

16. The article as defined in claim 14 wherein the aliphatic nitrogenous compound is the diphosphoric acid salt of ethylene diamine.

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2,078,388	Kern	Apr. 27, 1937
2 138,572	Etzelmiller	Nov. 29, 1938
2,232,405	Schmelzer	Feb. 18, 1941
2,306,471	Solomon	Dec. 29, 1942
2,419,296	Solomon	Apr. 22, 1947
2,421,367	Solomon	May 27, 1947