

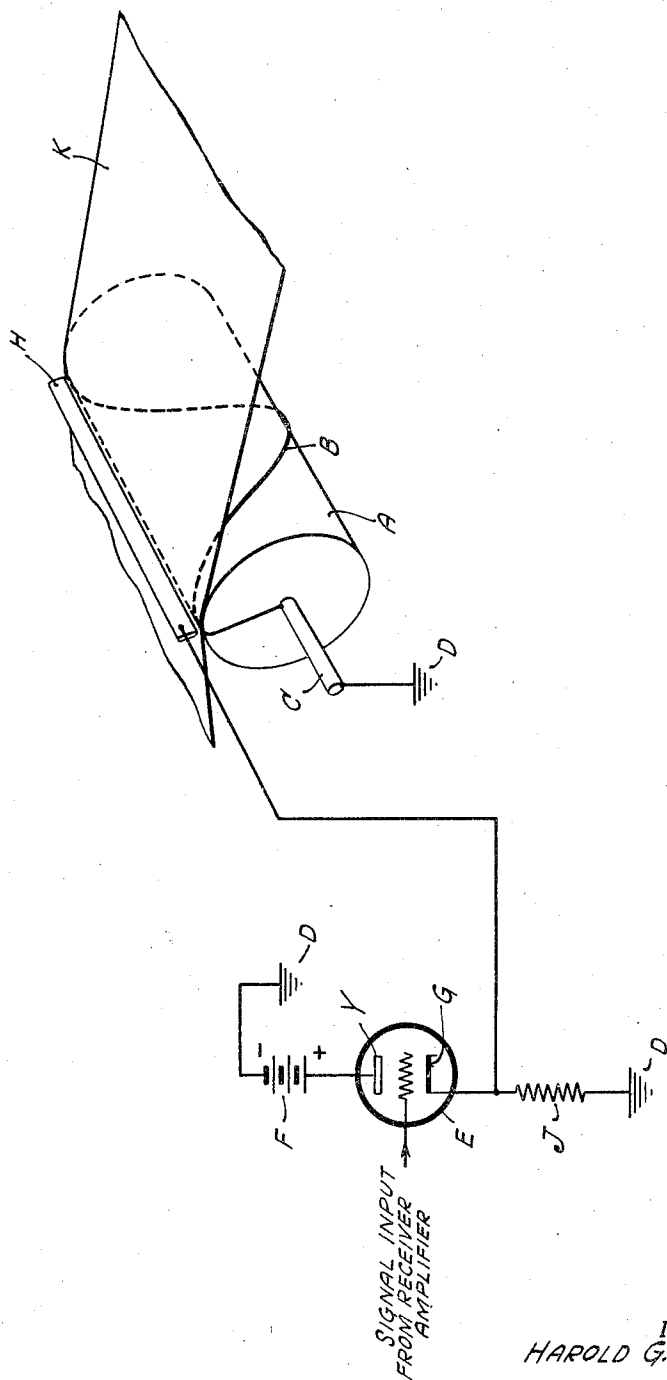
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H. G. GREIG

2,451,331

ELECTROLYTIC RECORDING

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ELECTROLYTIC RECORDING

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The present invention relates to the electrolytic production of colored records and particularly to the use in such a method of compositions which are designed to give on a light background dark blue gray color images which simulate black in color.

Solomon in his U. S. P. 2,306,471 discloses various 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. In this procedure, a traveling web or band of fibrous material which has been impregnated with a diazotizable amine, an ionizable nitrite, an electrolyte and a coupling component is subjected to electrolysis with the formation of a diazonium compound at the anode which subsequently couples with the coupling component to produce what is probably an azo dyestuff. While this method has many advantages over the previously known method involving the utilization of an electromagnetically controlled printer bar, particularly from the standpoint of the speed at which the records are made and the wear on the printer bar, it nevertheless presents the difficulty of selecting diazotizable amines and coupling components which when chemically united give color images approaching black on a light background. Many of the diazotizable amines and azo dye coupling components which have been proposed in the past give dark color images but these are either too blue, purple or red in color. On the other hand, others which have been selected yield dark colors but with a colored background so that there is insufficient contrast from a practical standpoint in transmission of the record. While many attempts have been made to select components which when diazotized and coupled produce black records on a light background, to the best of my knowledge such attempts have to the present time met with consistent failure.

I have now found that it is possible by the electrolytic diazotization and coupling method to produce dark images on a stabilized light background if there be employed as the diazotizable amine a particular aryl diamine disulfonic acid and as the coupling component a mixture of a particular naphthol sulfonic acid on the one hand and a particular compound containing a reactive methylene group on the other hand. I have further ascertained that it is possible while using such components to vary the color of the recorded image through all shades ranging from bright blue to bright yellow. Another and very important observation which I have made is that the compound which contains a reactive methylene

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group and which serves in part as the coupling component also has a decided stabilizing effect upon the background of the records obtained.

It is accordingly an object of the present invention to provide a composition for the production of colored records by electrolytic diazotization and coupling which insures the formation of colored images simulating black in color on a light background.

It is a further object of the present invention to provide a method for producing electrolytic records in which the color images formed simulate black in color and are produced on a light background.

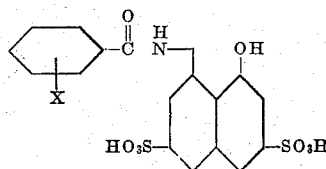
It is a further object of the present invention to provide for the production of colored records by electrolytic diazotization and coupling while using a specific diazotizable amine and specific coupling components and to vary the shade of the recorded color image from blue to yellow while adjusting the proportions of the diazotizable amine and of the coupling components.

It is a further object of the present invention to employ a nitrogen containing organic compound for increasing the darkness of the image of the records.

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

The particular diazotizable amine contemplated by the present invention is benzidine-3,3'-disulfonic acid. No other diazotizable amine has been found which will function in the desired relationship to yield the black appearing records on a light background required herein. As a matter of fact, if benzidine monosulfonic acid appears in the composition even as an impurity, it affects the stability of the solution by forming paper staining reaction products. Furthermore, such compound if present shifts the shade of the recorded color towards purple. Even the isomeric benzidine-2,2'-disulfonic acid when present as an impurity causes a shift in the shade of the record towards purple. The employment of benzidine-3,3'-disulfonic acid as the diazotizable amine is accordingly critical to the invention.

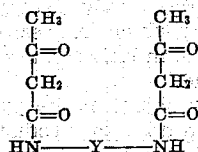
The naphthol sulfonic acid coupling component which is employed is a benzoyl H acid having the following constitution:



in which X is hydrogen, an acylamino group such as acetylamino, propionylamino, benzoyl-amino, furoylamino and the like, alkyl such as methyl, ethyl, propyl, butyl, octyl and the like, alkoxy such as methoxy, ethoxy, propoxy, butoxy and the like, halogen such as chlorine, bromine and the like, and aryloxy such as phenoxy and the like.

Where X is a substituent group, it may be attached at any position ortho-, meta-, or para- to the amide linkage in the 8-position of the naphthol ring. Examples of suitable compounds are benzoyl H acid, benzoyl-p-amino benzoyl H acid, acetyl-p-amino benzoyl H acid, benzoyl m-amino-benzoyl H acid, toluoyl H acid, m-methoxy-benzoyl H acid, p-phenoxy-benzoyl H acid, p-ethyl-benzoyl H acid, m-butyl-benzoyl H acid, p-chloro-benzoyl H acid, and the like.

The other coupling compound containing the reactive methylene group is a diacetoacetyl alkylene polyamine in which the alkylene chain may be interrupted by imino. Such compounds have the following structural formula:



in which Y is an alkylene radical or such a radical interrupted by an imino group. Examples of such compounds are diacetoacetyl ethylene diamine, diacetoacetyl propylene diamine, diacetoacetyl butylene diamine, diacetoacetyl diethylene triamine, diacetoacetyl triethylene tetramine and the like.

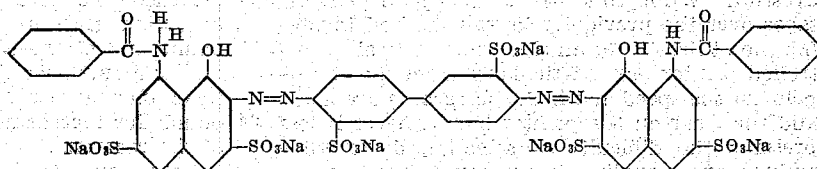
Compounds other than those in the above class and which contain a reactive methylene group have been tested but for the most part the results obtained therefrom are negative in character. Theoretically, mono-aceto-acetyl-p-phenylene diamine should give a more pronounced change in shade towards black than the diacetoacetyl alkylene polyamines. Unfortunately, however, the solubility of this compound does not permit a sufficient quantity of the same to remain in solution to produce the desired black shade. While it may be employed in admixture with the diacetoacetyl alkylene polyamine (say, in amounts ranging from .10 to .25 gram mol of the former

to 1 gram mol of the latter) to produce a black record, such record shows a greater tendency to darken in the background upon file storage.

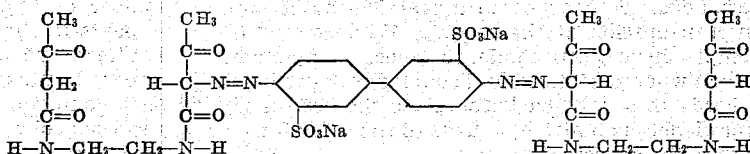
The hue or color of the records is dependent to a large extent upon the proportions of the components forming the dyestuff of the images thereof and this is particularly true as regards the coupling components. The benzidine-3,3'-disulfonic acid is used in the ratio of about .02 to .036 gram mol per liter with the proportions of the coupling components as subsequently stated has relatively little effect on the color of the image records. If the amount be decreased below .02 gram mol per liter, the recorded color has a strength which is below that required for practical recording solutions. Nevertheless, legible recordings can still be made at concentrations below said limit of .02 gram mol per liter. If the quantity of the benzidine 3,3'-disulfonic acid be increased above the upper limit of .036 gram mol, the stability of the background suffers, although here again, legible recordings can be made.

My investigations have established that with an amount of the diacetoacetyl amine in the ratio stated, the desired black images on a light background can be obtained while using the benzoyl H acid or its derivatives in an amount of .0094 to .022 gram mol per liter and the diacetoacetyl alkylene polyamine in an amount of .0292 to .05 gram mol per liter.

If the recording solution be made up with the benzidine-3,3'-disulfonic acid with only a benzoyl H acid as the coupling component, the product which will be obtained, assuming the coupler to be benzoyl H acid, will have the following probable formula:

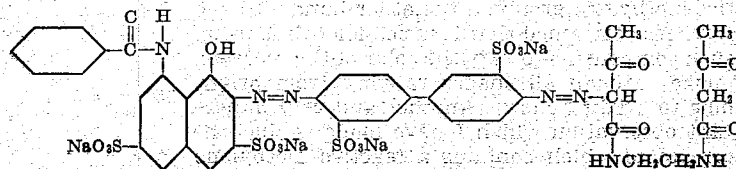


This dyestuff gives a bright blue record on a yellow tinted background. If, on the other hand, the recording solution is made up with the benzidine-3,3'-disulfonic acid and with, for example, diacetoacetyl ethylene diamine as the only coupling component, the dyestuff which is obtained has the following probable formula:



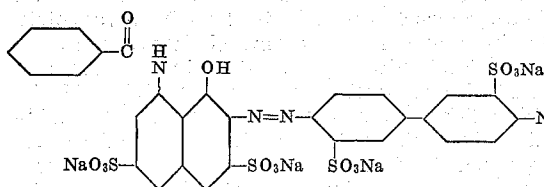
lene polyamines. Unfortunately, however, the solubility of this compound does not permit a sufficient quantity of the same to remain in solution to produce the desired black shade. While it may be employed in admixture with the diacetoacetyl alkylene polyamine (say, in amounts ranging from .10 to .25 gram mol of the former

This dyestuff gives a bright yellow record. If, however, the recording solution be made up with benzidine-3,3'-disulfonic acid and a mixture of the benzoyl H acid and the diacetoacetyl ethylene diamine, particularly in the proportions stated, a product will be obtained which will contain a dyestuff having either the following formula:



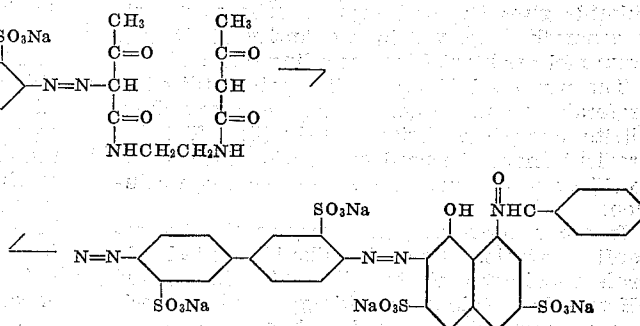
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or a longer chained structure as represented by the following formula:



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the record obtained is bright yellow. On the other hand, if there be employed .0303 gram mol



It appears that when the two coupling components are employed, a mixture of dyestuffs ensues in which, however, there is probably present the product of Formula III or IV. Where the proportions are selected as indicated, such product is the major ingredient in which case the desired blue-gray records are formed. For instance, the recorded color obtained when using a mixture of coupling components in said ratio is a gray on white on a washed copy and such color under ultraviolet light appears as a bright red on white. The recorded color on unwashed copy, however, is more nearly black on a light yellow background and under ultraviolet light appears to be a strong black on a yellow background. This difference in color between the washed and the unwashed records indicates that two or more colors are formed during the electrolytic step. It is to be pointed out, however, that there is no indication of the presence of a product of Formula I or of II as these appear blue and bright yellow respectively when viewed under ultraviolet light. Despite the fact that a mixture of dyes appears to be formed, it is surprising that the mixture does not show up as a two-tone effect in recording a picture where a gradation in the density of the color is necessary.

It is apparent from what has been said above about the proportions of the coupling components that by having present an excess of the benzoyl H acid or its derivative over the ratios given, the recorded color will be shifted towards the blue end of the spectrum. Conversely, if there be an excess of the diacetoacetyl ethylene diamine present, the recorded color will be shifted towards the yellow region of the spectrum. By a modification of the expressed ratios, it is as a matter of fact possible to obtain recorded colors ranging from bright blue through dark blue, blue-gray (almost black), brown, orange brown and bright yellow. While the main purpose of the present invention is to utilize the aforementioned diazotizable amine and mixture of the coupling components in a ratio assuring the formation of a record simulating black in color, nevertheless it is to be understood that the invention in its broadest aspects also contemplates the utilization of mixtures of the aforesaid coupling components in ratios which will lead to a recorded color other than black.

An indication of the results which ensue when departing from the aforesaid ratio of coupling components may be gathered from the following information. If, for instance, there be employed .0231 gram mol per liter of the benzidine-3,3'-disulfonic acid with .008 gram mol per liter of the benzoyl H acid compound and .073 gram mol per liter of the diacetoacetyl alkylene polyamine,

per liter of the benzoyl H acid compound, .025 gram mol per liter of diacetoacetyl alkylene polyamine with .0214 gram mol per liter of the benzidine-3,3'-disulfonic acid, the record obtained is a pleasing blue in color. These proportions therefore give a general indication of the variations in color which may be obtained within the range of hues previously mentioned.

The importance of the observation that the invention contemplates other proportions of coupling components than those stated is more forcibly brought home by the fact that the diacetoacetyl alkylene polyamine exerts a dual function in the composition. Thus not only does this component react with the diazotized benzidine-3,3'-disulfonic acid in forming the colored record but it also has the surprising capability of exerting a very strong stabilizing effect which retards the background darkening attributable to the benzoyl H acid. This effect is produced even when the diacetoacetyl alkylene polyamine is employed in quantities outside of the ranges serving to produce the blue-gray, simulating black colors.

Another feature of the invention, which is of prime significance, is the finding that the darkness of the color may be considerably improved if there be present in the recording solution a quantity of an aliphatic compound containing a thio amide group in which the nitrogen atom of the amide is disubstituted by hydrogen. Suitable examples of compounds within this category are thiourea, thiosinamine, thiocarbamic acid and the like. These compounds due to the presence of the NH_2 group therein have the ability to form salts with the sulfonic acid groups in the diazotizable amine and the coupling components. On the other hand, it is an accepted fact that the grouping =C=S present in the aforesaid compounds is a very strong chromophoric group. It has not been ascertained whether the darkening of the color resulting from the utilization of these compounds is attributable either to salt formation or to the presence of the chromophoric group or both. However, despite the theory involved, the fact remains that the use of these compounds definitely effects darkening of color and hence they are desirable adjuncts in the recording composition. The quantity of the compounds which are to be used should range from about .02 to .0526 gram mol per liter of solution.

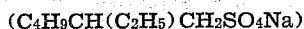
The other essential components of the composition are an electrolyte to facilitate the passage of the electrolyzing current, and a water-soluble metal nitrite to furnish the ions necessary for diazotizing the benzidine-3,3'-disulfonic acid. Preferably the electrolyte is a water-soluble neutral inorganic salt such as sodium chloride, so-

dium bromide, potassium bromide, potassium chloride, lithium chloride, potassium sulfate, sodium sulfate, and the like. Of these, the sodium chloride gives the best results. The electrolyte is generally employed in a quantity of .25 to 1 gram mol per liter of the recording solution.

The water-soluble metallic nitrite utilized is preferably an alkali metal nitrite, such as sodium nitrite, potassium nitrite, and the like. This ingredient should be used in a ratio of about .06 to .15 gram mol per liter of the recording solution.

In order to obtain satisfactory results, the recording solution should be alkaline and should preferably have a pH from 9 to 11. The desired pH may be obtained by adding to the composition a water-soluble alkali such as sodium hydroxide, potassium hydroxide, potassium carbonate and the like. If the pH of the recording solution be too low, the solution has a decreased stability on storage.

If when the solution is prepared it is found that it is difficult to wet the recording material, a wetting agent may be incorporated in the solution. For this purpose there may be employed alkylated naphthalene sulfonic acids such as butyl naphthalene sulfonic acid and the like, sulfonated benzene which has been reacted with chlorinated kerosene, N-stearoyl sarcosine, N-stearoyl glycine, stearic acid monoglyceride, oleyl polyglycol ether, stearyl polyglycol ether, stearic acid polyglycol, of polyglycerol ester, lauric acid monoglycol ester, palmitic acid monoethanol amide, dioctyl sodium sulfo succinate, the product sold under the trade name "Triton 812" which is understood to be a sulfonated, polyalkoxylated aryl compound; the product sold under the trade name "Tergitol Penetrant" which is understood to have the formula



and the like. 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% by volume of the recording solution.

The carrier or material which is to be 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. If paper be the carrier material, there are certain factors which must be borne in mind in selecting the paper. Thus rosin sizing has the effect of causing darkening of the background of the records on storage and should therefore be kept to a minimum. Resins produced from melamine and formaldehyde give good wet strength to the paper although they may cause a shift of the shade of recorded color towards blue. This may be compensated for however by increasing the quantity of the diacetoacetyl alkylene polyamine in the recording solution.

The recording solutions may be prepared by slurring the benzidine-3,3'-disulfonic acid and the benzoyl H acid or its derivative in about a liter of water, preferably with mechanical stirring. The temperature of the water is generally maintained at 25 to 30° C. When the slurry has become uniform, sodium hydroxide is added to effect complete solution of the intermediates at a pH of 10. If at this point any residue remains because of impurities in the intermediates, the mixture should be filtered to remove said

impurities. The clear solution is adjusted to a pH of about 10.2 at this point while utilizing dilute hydrochloric acid if the pH be too high. At this stage the remaining chemicals are added, preferably in the order given in the examples, with stirring until solution is complete. If the pH at this stage be too low, alkali should be added to bring it up to that desired. Acid cannot be added to decrease the pH inasmuch as premature diazotization and discoloration of the receiver will result. The solution thus obtained may be utilized immediately or it may be placed in a stoppered receptacle and stored until ready for use.

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 above.

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 benzidine-3,3'-disulfonic acid. 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

A recording solution is prepared by the method previously indicated from .03 gram mol of benzidine-3,3'-disulfonic acid, .0104 gram mol of benzoyl H acid, .88 gram mol of sodium hydroxide (2.5 N solution), .39 gram mol of sodium chloride, .035 gram mol of diacetoacetyl ethylene diamine, .0526 gram mol of thiourea, .139 gram mol of sodium nitrite and a liter of water. Paper is impregnated with this solution and the so impregnated paper is passed through the apparatus described above. There is thus obtained a dark record on a light background which is storage stable.

Example II

The composition is the same as in Example I except that there is added to the composition .5 gram per liter of the wetting agent obtained by condensing benzene sulfonic acid with chlorinated kerosene.

Example III

The procedure is the same as in Example I excepting that there is employed .0273 gram mol of benzidine-3,3'-disulfonic acid, .0094 gram mol of benzoyl H acid and .05 gram mol of diacetoacetyl ethylene diamine.

Example IV

The procedure is the same as in Example I excepting that there is employed .025 gram mol of benzidine-3,3'-disulfonic acid, .022 gram mol of benzoyl H acid and .0292 gram mol of diacetoacetyl ethylene diamine.

In each of the above examples, the recorded color is a sufficiently dark one to give good contrast on a yellow tinted background.

Example V

The procedure is the same as in Example I excepting that the benzoyl H acid is replaced by an equivalent amount of benzoyl-p-amino-benzoyl H acid.

Example VI

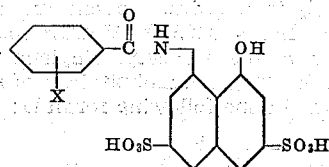
The procedure is the same as in Example I excepting that the diacetoacetyl ethylene diamine is replaced by an equivalent amount of diacetoacetyl propylene diamine.

Example VII

The procedure is the same as in Example I excepting that the diacetoacetyl ethylene diamine is replaced by an equivalent amount of diacetoacetyl diethylene triamine.

I claim:

1. A process of producing colored image records simulating black on a light background on a traveling carrier which comprises treating the carrier with an alkaline solution containing as its essential components benzidine-3,3'-disulfonic acid in an amount ranging from .02 to .036 gram mol per liter of solution, an alkali metal nitrite in a sufficient amount to effect tetrazotization of the benzidine-3,3'-disulfonic acid, a neutral electrolyte in a sufficient quantity to facilitate the passage of the electrolyzing current, and as coupling components .0292 to .05 gram mol per liter of solution of a diacetoacetyl alkylene polyamine and .0094 to .020 gram mol per liter of solution of a compound of the following formula:

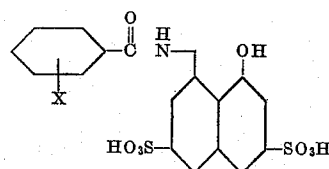


in which X is selected from the class consisting of hydrogen, acylamino, alkoxy, alkyl, halogen and aryloxy, and subjecting the treated carrier to the action of an electrolytic recording current.

2. The process as defined in claim 1 in which the solution includes an aliphatic thioamide for the purpose of increasing the darkness of the recorded color.

3. The process as defined in claim 1 in which the solution includes a wetting agent for facilitating the application of the solution to the carrier.

4. The process of producing colored images on a traveling carrier, said images having a blue-gray color simulating black on a light background, which comprises treating the carrier with an alkaline solution containing as its essential components and per liter of solution .020 to .036 gram mol of benzidine-3,3'-disulfonic acid, from .0094 to .020 gram mol of a compound of the following formula:



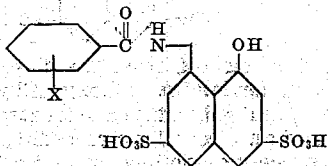
in which X is selected from the class consisting of hydrogen, acylamino, alkoxy, alkyl, halogen and aryloxy, from .0292 to .050 gram mol of a diacetoacetyl alkylene polyamine, from .25 to 1 gram mol of a water-soluble neutral electrolyte, and from .06 to .15 gram mol of sodium nitrite, and subjecting the so-treated carrier to the action of an electrolytic recording current.

5. The process as defined in claim 4 in which there is present in the solution from .02 to .0526 gram mol of an aliphatic compound containing a thioamide group.

6. The process as defined in claim 4 in which there is present in the solution from .02 to .0526 gram mol of thiourea.

7. The process of producing colored images on a traveling carrier in which the images are a blue-gray simulating black on a light background which comprises treating the carrier with an aqueous solution containing as its essential components and per liter of solution .0273 gram mol of benzidine-3,3'-disulfonic acid, .0095 gram mol of benzoyl H acid, .05 gram mol of diacetoacetyl ethylene diamine, .39 gram mol of sodium chloride, .139 gram mol of sodium nitrite, and .0526 gram mol of thiourea and sufficient sodium hydroxide to give a pH of 9 to 11, and subjecting the treated carrier to the action of an electrolytic recording current.

8. A fibrous sheet material for the electrolytic formation thereon of azo dye records simulating black on a light background, said sheet material being treated with an aqueous alkaline solution containing as its essential components benzidine-3,3'-disulfonic acid in an amount ranging from .02 to .036 gram mol per liter of solution, a water-soluble metallic nitrite in a sufficient amount to effect tetrazotization of said benzidine-3,3'-disulfonic acid, a neutral electrolyte in an amount sufficient to facilitate the passage of the electrolytic recording current and as the coupling components .0292 to .05 gram mol per liter of solution of diacetoacetyl alkylene polyamine and .0094 to .020 gram mol per liter of solution of a compound of the following formula:

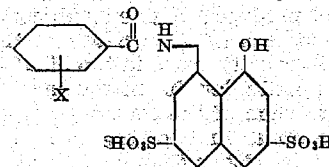


in which X is selected from the class consisting of hydrogen, acylamino, alkoxy, alkyl, halogen and aryloxy.

9. A fibrous sheet material as defined in claim 8 in which there is present in the solution an aliphatic compound containing a thioamide group.

10. The fibrous sheet material as defined in claim 8 in which the solution contains a wetting agent.

11. A fibrous sheet material treated with an aqueous solution capable of electrolytically yielding thereon colored records simulating black on a light background and containing as its essential components and per liter of aqueous solution .02 to .036 gram mol of benzidine-3,3'-disulfonic acid, .0094 to .022 gram mol of a compound of the following formula:



in which X is selected from the class consisting of hydrogen, acylamino, alkoxy, alkyl, halogen and aryloxy, .029 to .05 gram mol of a diacetoacetyl alkylene polyamine, .25 to 1 gram mol of a neutral water-soluble electrolyte, .06 to .15 gram mol of an alkali metal nitrite and sufficient of an alkali to give the solution a pH of 9 to 11.

12. A fibrous sheet material treated with an aqueous solution capable of electrolytically yielding thereon colored records simulating black on a light background and containing as its essential components and per liter of water, .0273 gram mol of benzidine-3,3'-disulfonic acid, .0094 gram mol of benzoyl H acid, .05 gram mol of diacetoacetyl ethylene diamine, .39 gram mol of sodium chloride, .139 gram mol of sodium nitrite, .0526 gram mol of thiourea, and sufficient sodium hydroxide to give the solution a pH of from 9 to 11.

HAROLD GREY GREIG.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,306,471	Solomon	Dec. 29, 1942