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FIBROUS SHEET MATERIAL FOR THE ELECTROLYTIC FORMATION OF AN AZO DYE-STUFF THEREON

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This invention relates to the art of electrolytic dye production. More particularly, it pertains to the production of azo and other dyes, embracing among its features novelty as to procedure, composition, and article of manufacture. In a preferred adaptation, it includes the production of dyes of the aforementioned type in connection with the art of facsimile recording. The fundamentals of the present disclosure are set forth in the copending application Serial No. 178,743, now U. S. P. 2,306,471 included herein by reference, of which earlier application the present application is a continuation-in-part.

In the aforesaid copending application, there are disclosed applicant's general methods of electrolytic dye formation designed particularly for electrolytic recording, for example, facsimile recording. These methods can be generally classified as, (I) electrolytic coupling, in which azo dye formation is secured by first preparing a diazonium compound and subjecting a solution of the diazonium compound together with a suitable coupling compound to an electric current; (II) electrolytic diazotization, in which a solution containing amine, nitrite, and a coupling compound is subjected to an electric current to electrolytically form a diazonium compound and secure the formation of an azo dye by the coupling of the diazonium compound with the coupling compound during the action of the electric current, after its action, or both during and after; and (III) electrolytic oxidation, in which dyes are formed by electrolytically oxidizing chemicals that react to produce dyes, either exclusively or conjointly with method (II).

Thus, various different types of facsimile receivers are used at the present time, and in substantially all of them pictures, printed matter, or other characters are produced on a recording sheet of paper in response to variations in electrical current which are received from the transmitter station. In one type the reproduction of the character or indicia is through the use of carbon paper and the transfer of the carbon to the record paper is accomplished by means of an electromagnetically controlled printer bar. In such a device the recording paper and carbon paper are placed in the facsimile receiver and are moved forward at rates which are necessarily slow because of mechanical inertia limitations, while line increments of the material being received are reproduced through the application of varying degrees of pressure to the printer bar, in order that varying amounts of the carbon will be transferred from the carbon paper to the recording paper. Such a device for facsimile recording is shown in the patent to Charles J. Young, Reissue #20,152, October 27, 1936.

In another type, a light sensitive recording paper is used and the amount of light permitted

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to strike the paper is controlled in accordance with the electrical variations transmitted by the facsimile transmitting device. In this type some developing or fixing process generally follows.

In still another type a stream of hot air is directed against a heat responsive recording paper, the intensity of the heat or the amount of hot air being controlled in response to the energy transmitted by the facsimile transmitting device. Another type uses a jet of ink or some colored fluid, the jet being permitted to strike, or prevented from striking, the recording paper according to the series of signals received from the transmitting device. The patent to Richard H. Ranger, #1,770,493, of July 15, 1930, shows, for example, devices wherein jets of hot air or ink are used for facsimile recording.

In the facsimile receiving or recording systems referred to above, the production of half tones and shades such as occur in the reproduction of pictures, is somewhat difficult, since, for instance, in the carbon paper method, the transfer of the carbon to the recording paper is somewhat critical in response to the pressure applied to the printer bar. Furthermore, the use of hot air or ink jets is not entirely satisfactory since such systems are difficult to control and to maintain in proper operation.

The present invention may be generally characterized as directed to dye formation, in which electrolytic action plays an essential part, and is particularly applicable to the electrolytic diazotization method (II) above while utilizing heterocyclic amines for forming the diazonium compound.

It is an object of the invention to overcome the difficulties and limitations of the prior art procedures noted hereinabove.

It is another object of the present invention to obtain diazonium compounds by the action of an electric current on mixtures or solutions containing diazotizable heterocyclic amines and nitrites.

It is a further object to provide mixtures or solutions containing diazotizable heterocyclic amines and nitrites which are adapted to electrolytically react for the purpose of producing diazonium compounds.

Another object of the invention is to provide solutions or, where feasible, mixtures, of appropriate reagents comprising a diazotizable heterocyclic amine and an ionizable nitrite which are adapted for electrolytic reaction to produce a diazonium compound, and to form azo dyes from such diazonium compound by reaction with a coupling reagent present in said mixture or solution.

An added object of the invention is a supporting material or carrier treated with azo dye forming chemical reagents including a diazotiz-

able heterocyclic amine which will react suitably when subjected to electrolytic treatment, said carrier as a result of its chemical treatment being electrolytically conductive.

A still further object of the invention is to provide a supporting surface or carrier which is saturated or impregnated with a diazotizable heterocyclic amine and an ionizable nitrite, which is advantageously adapted for production in situ of a diazonium compound when subjected to an electric current.

An additional object of the invention is to provide a supporting surface saturated or impregnated with a diazotizable heterocyclic amine, an ionizable nitrite, a coupling reagent, an electrolyte, said supporting surface being thereby adapted for electrolytic facsimile recording through azo dye formation.

Another object of the invention is to provide suitable procedures for preparing the compositions and articles of manufacture hereinabove referred to.

Other objects, features and advantages of the invention will be apparent from the following detailed description.

In the present invention, it is proposed to produce the picture or printed matter on the recording paper in the form of a dye, the amount of such dye deposited being a function of the amount of current caused to flow through the recording paper. When the image is thus formed, for example, by applicant's electrolytic azo dye formation, the pressure of the printer bar can be maintained constant and the amount of current which is passed through increments of the paper simply varied in accordance with the light and dark portions present on the picture or printed matter being scanned at the facsimile transmitter. When dyes are so formed by electrolytic action, the varying half tone shades may be produced by merely regulating the amount of the current which is caused to flow through the recording paper.

The principle of operation of the present invention depends on the fact that when an electric current flows through a mildly alkaline solution containing a suitable diazotizable heterocyclic amine and a source of nitrite ions a diazonium compound is formed at the acid or positive electrode termed the anode. Said diazonium compound is capable of coupling with an azo dye coupling component to produce an azo dye. Said operation employs as essential components the following:

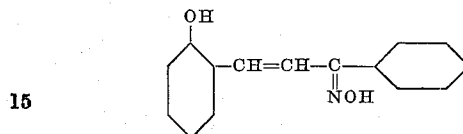
- (a) A heterocyclic amine, desirably a primary amine.
- (b) A nitrite.
- (c) An alkali.
- (d) A coupling compound.
- (e) An electrolyte.
- (f) Water or other solvent in which electrolytes ionize.

Among the amines which may be utilized are heterocyclic amines with a nuclear attached primary amino group such as the amino quinolines, amino pyridines and amino pyrimidines such as 2,6-diamino pyridine. The presence of a sulphonate group tends to enhance the stability of the background of the carrier towards light although the dye may, in some cases, manifest somewhat less fastness to washing.

The following coupling compounds may be utilized for forming the azo dyestuffs electrolytically while utilizing the aforementioned diazotizable heterocyclic amines.

Benzene compounds

- Resorcinol
- 4-chlororesorcinol
- 2-nitroresorcinol
- Salicylaldehyde
- Salicylaldoxime
- 5-chlorosalicylaldehyde
- 5-chlorosalicylaldoxime
- Orthohydroxybenzalacetophenone
- Orthohydroxybenzalacetophenoneoxime



- Resorcyllaldehyde
- Resorcyllaldoxime
- Resorcylic acid
- Parahydroxyacetophenone
- Parahydroxypropiophenone
- Resacetophenone
- Resacetophenoneoxime
- Phloroglucinol
- Metaaminophenol
- Acetoacetanilide
- Isonitrosoacetoacetanilide
- Isonitrosoacetoacetanilideoxime
- Acetoacetanilideoxime
- Acetoacetanilide hydrazone
- 2-chloroacetoacetanilide
- 2-chloro-isonitrosoacetoacetanilide
- 2,5-dichloroacetoacetanilide
- 2,5-dichloro-isonitrosoacetanilide
- Acetoacetanilide-parasulphonic acid
- Acetoacetanilide oxime parasulphonic acid
- 1-metaaminophenyl-3-carboxy-5-pyrazolone
- Hydroxylamine with No. 112
- Acetoacetanilide hydrazone parasulphonic acid
- Orthophenylenediamine
- Metaphenylenediamine
- Paraphenylenediamine
- Chloroparaphenylenediaminedihydrochloride
- 2,5-diaminobenzenesulphonic acid dihydrochloride
- Diacetoacetyl-paraphenylenediamine
- Diisonitrosodiaceoacetyl-paraphenylenediamine
- Diacetoacetyl-paraphenylenediaminedioxime
- 2,4-diaminotoluene
- 2,5-diaminotoluenedihydrochloride
- 2,4-diaminoanisole dihydrochloride
- 2,5-diaminoanisole dihydrochloride
- Triaminotoluenetrihydrochloride
- 4,4'-dihydroxybenzophenone
- 4,4'-dihydroxybenzophenoneoxime
- Metadiethylaminophenol
- Metadigallic acid (tannic acid)

Naphthalene compounds

- Alpha naphthol
- Alpha hydroxynaphthoic acid
- Schaeffer's alphanaphtholsulphonic salt
- Neville and Winther's acid
- L acid
- N-phenyl peri acid
- R.G acid
- Andresen's acid
- Schoellkopf's acid
- Oxy Koch acid
- Beta naphthol
- Beta hydroxynaphthoic acid
- Naphthanil OA
- Schaeffer's acid
- F⁻ salt

Bayer's or Crocein salt
 Disodium R salt
 Disodium G salt
 Naphthoresorcinol
 1,5-dihydroxynaphthalene
 1,7-dihydroxynaphthalene-4-sulphonic acid
 Dioxy S acid
 Nigrotic acid
 Yellow acid
 Red acid
 A acid
 Chromotropic salt or acid
 2,7-dihydroxynaphthalene
 Phenyl J acid
 Benzoyl J acid
 Di J acid urea
 J acid Imide
 J acid
 M acid
 Gamma acid
 Phenyl gamma acid
 S acid
 Chicago or 2S acid
 Monosodium H salt
 Chloro H acid
 Phenyl H acid
 Acetyl H acid
 K acid
 2R acid (oxyamino)
 R acid (oxyamino)

Miscellaneous compounds

8-hydroxyquinoline
 8-hydroxyquinoline-5-sulphonic acid
 Barbituric acid
 Violuric acid
 Hydroxylamine with 179
 Thiobarbituric acid
 Thiovioluric acid
 1-phenyl-3-methyl-5-pyrazolone
 1-parasulphophenyl-3-methyl-5-pyrazolone
 Hydroxylamine with 185
 1-parasulphophenyl-3-carboxy-5-pyrazolone
 2,6-diaminopyridine
 Diacetoacetylenediamine
 Monoisonitrosodiaceoacetylenediamine
 Diisonitrosodiaceoacetylenediamine
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Relative to the proportioning of the ingredients, as a general rule by way of estimate and not restriction, approximately 0.03 gram molecular weights (0.015 for diamines) of amine and of a mono-valent nitrite per liter of solution produce quite satisfactory results. Usually 0.025 gram molecular weights or mols of amine are used per liter of solution for paper that is treated at the recorder—that is, for paper which is subjected to the diazotizable solution substantially at the time that the recording is made.

A comparatively wide range of nitrites are available, the requisite being an ionizable compound, desirably a metallic nitrite. Whereas the examples in the present disclosure may largely involve the use of sodium nitrite, it should be clear that this compound is referred to merely as illustrative of a convenient material which may be utilized in the diazotization procedure. While sodium provides entirely satisfactory results, the same may be said of potassium nitrite as well as many other metallic nitrites. In view of the fact

that neutral or alkaline solutions of sodium nitrite are comparatively stable, this reagent is particularly desirable in predetermined recording solutions prepared for storage over a substantial period prior to usage. It has been found that excess nitrite does not impair the background permanence of electrolytic diazotization recordings and is in fact beneficial because it causes a greater percentage of the amine to be diazotized, and consequently permits a decrease in the concentration of amine with no loss in color intensity. Concentrations of 0.025 and 0.05 gram molecular weights of amine and of nitrite, respectively, per 1000 cc. of solution, usually give excellent results.

Similarly, a substantial latitude in choice of alkaline reagent is available, but for purposes of illustration herein, recourse is had to sodium hydroxide. The usual content of sodium hydroxide may be characterized as that required to neutralize all strongly acid groups in the amines and coupling compounds, as well as that providing a slight excess (usually 20 cc. of normal NaOH per liter or recording solution).

Where the alkalinity pertains to the recording solution and is not particularly critical, simple expedients for its approximate evaluation are available in the form of the so-called Beckman instrument or other commercial devices. Similarly, a small piece of La Motte "Oleo Red B" pH test paper may be immersed in the facsimile recording solution for a few seconds. The alkalinity is satisfactory if the paper turns orange-brown, insufficient if yellow or orange-yellow, and excessive if red. It should be noted that insufficient alkalinity is more harmful than excessive, since it impairs the background permanence; on the other hand, a stronger signal in the form of electrical impulse is required from the amplifier, and half tones are impaired, when the solution is excessively alkaline.

As a general matter, the color intensity at full electric current depends on the alkalinity and the amount of diazonium compound formed. The deepest color is usually formed at a pH of 7.5 to 9 which is not alkaline enough for good background permanence. At a pH of 6 to 7.5, hydroxy coupling is too slow in some cases, and premature non-electrolytic diazotization discolors the paper in others. At the compromise pH range of 9 to 11.5, the color intensity is not sacrificed unduly in order to gain in background permanence.

Insofar as the diazotizable composition and the treated carrier, such as paper, are concerned, they may be stored a considerable period of time if the solution is moderately strongly alkaline. A pH range of 7.5 to 12.5 is applicable, although best results are obtained within the range of 10.0 and 11.5. As the pH drops, the stability decreases, the tendency of the background to darken on standing increases, and the sensitivity of the reaction increases.

In lieu of sodium hydroxide, other strong bases may be used, as illustrated by potassium hydroxide, barium hydroxide, or a quaternary ammonium hydroxide. On a weight basis, the amount of alkali used may vary from 0.01 to 0.12 gram molecular weights per liter of solution, depending upon the original acidity or alkalinity of the other ingredients, and is adjusted to the predetermined pH of the finished solution, which, as above suggested, may desirably be within the range of 10.0 to 11.5.

Concerning the coupling compounds, hereinabove they are desirably soluble in a mildly alka-

line salt solution and preferably subject to the same oxidation limitations as discussed above in connection with the amines. Aromatic compounds with hydroxy, amino or active methylene groups ortho or para to unsubstituted positions in the ring will usually couple. Sulphonic groups have the same effect as in amines. Resorcinol, phloroglucinol, the naphthols and their sulphonic acids, 8-hydroxy quinoline, and some amino naphthol sulphonic acids have given good results. Some amino naphthol sulphonic acids (for example, gamma, H, J, S and 2S acids) may either diazotize or couple. Good recordings may thus be obtained, using the same chemical for both diazotization and coupling. However, most amino naphthol sulphonic acids give recordings that require washing in order to prevent the backgrounds from darkening during storage.

Chromotropic salt is considered the best all-round coupling compound, giving darker colors than any of the others having reasonably permanent white backgrounds. The acetoacetyl amino compounds, their oximes and hydrazones, and the isoxazolones and pyrazolones derived from them, give yellow or orange colors, the oximes and hydrazones being most effective. When added to facsimile recording solutions containing chromotropic salt, these yellow or orange couplers improve the color, giving brownish-purple shades that are more pleasing in appearance than the purple obtained with chromotropic salt alone. The ratio of chromotropic salt to oxime or hydrazone is usually three gram-molecules to one.

The coupling compounds may be utilized individually or in admixture, particularly desirable results being obtainable from the use of a plurality of coupling compounds, as indicated in an example hereinbelow.

The amount of coupling compound utilized may vary between 0.01 to 0.02 gram molecular weights, although more may be utilized without harm. Usually approximately 0.015 gram molecular weights of coupling compound per liter of solution provides excellent results, and a greater amount rarely shows any improvement in recorded color intensity.

The coupling compound may be of the type which reacts in alkaline medium or in acid medium, although the former is preferable. It is interesting to note that some amino compounds may function as coupling agents regardless of the pH, and many diazotizable primary amines serve in the dual function of amine and coupling compound. Under alkaline conditions, the hydroxy-coupling rate of reaction is generally so much greater than the amino coupling rate that substantially little or no amino coupling takes place in alkaline solution when both amino and hydroxy groups are present.

As for the electrolyte (e), NaCl is quite satisfactory, but there is no intent to be limited to the use of this salt. Other strong water soluble, inorganic salt electrolytes such as NaBr, KBr, KCl, LiCl, BaCl₂, CaCl₂, MgCl₂, K₂SO₄, Na₂SO₄, MgSO₄, etc., may be substituted for sodium chloride. Some dye intermediates are more soluble in potassium chloride solutions, in which cases the substitution is made. Lithium chloride has been found to retard the time of paper drying, but the same result is cheaper and more effectively obtained by the use of wetting agents. An additional electrolyte which has provided excellent recordings, while at the same time obviating the corrosive effect of nascent chlorine, is sodium sulphamate, NaOSO₂NH₂.

The amount of electrolyte required is not critical. Low concentrations require more electric current, while excessively high concentrations may cause partial precipitation of the dye intermediates. About two-thirds of a mol (a mol equals one gram molecular weight) of total electrolyte per liter of solution is fully adequate. For convenience in making the sodium ion correction to the Beckman pH meter readings, a total sodium ion concentration of 0.64 mol is used. The total sodium present in all the other ingredients is subtracted from 0.64, the remainder representing the amount of sodium chloride to be added.

Where NaCl is utilized, it has been found that the total concentration of sodium ions equal to 1.0 gram molecular weights per liter is quite effective, although good recordings have been obtained in some cases with as low as 0.1 and as high as 3.0 gram molecular weights of sodium per liter.

Substitution of sodium oxalate for part of the sodium chloride retards the background darkening of damp pretreated paper, although the electric current requirements are increased, and the halftone response is somewhat impaired. Oxalates have little effect on the background permanence of recordings exposed to light after drying, and their use is advisable primarily with damp treated paper.

It is, of course, apparent that water functions as a very desirable and effective vehicle within which the diazotization and azo dye formation are carried out. However, various non-aqueous neutral solvents that permit electrolytes to ionize may be substituted for all or a part of the water. If approximately half the water is replaced by alcohols or glycols, the freezing point of the solution is lowered to such an extent that recorders may be operated outdoors in winter.

Ethyl, methyl and isopropyl alcohols evaporate more rapidly than water, so that the paper dries too quickly in summer; in winter the added speed is desirable. Normal propyl alcohol dries at approximately the same rate as water, and may be used both summer and winter; the tendency of the propanol-water-salt mixture to separate into two liquid phases is eliminated by replacing ten per cent of the propanol with ethylene glycol. Larger amounts of the glycols are unsatisfactory, as their low volatility causes the recordings to be permanently limp and moist.

Some solvents, notably Cellosolve, methyl Cellosolve, and most denatured ethyl alcohols, gradually react with the alkali in the recording solution, which eventually becomes acid (unless more alkali is occasionally added), whereupon diazotization and coupling begin, causing paper treated with the solution to become discolored. Normal propyl alcohol and ethylene glycol do not reduce the alkalinity.

It will be noted that auxiliary chemicals are of substantial usage, and contribute materially to the control of the diazotization, dye formation, and recording generally. Such substances as oxalates, antifreeze solvents, hydroxylamine and hydrazine may be considered either as auxiliary chemical or as replacements for part of the essential chemicals.

An important role may be attached to the use of auxiliary chemicals in connection with the dye formation, and particularly where facsimile recording is concerned. These substances contribute materially to the control of the diazotization, dye formation, and recording generally.

Urea, thiourea, and, to a still greater extent, dicyandiamidine have been found to improve the color intensity. About 1 to 2 mols of either of these compounds per mol of amine are used. This effect is more apparent when combined with that due to excess nitrite. If a sulphate or hydrochloride of these bases is used, sufficient caustic soda or other alkali must be added to liberate the free base, in order to maintain the proper pH range.

Providing a desirable function in connection with recordings, wetting agents may be utilized in the treatment of the carrier, such as paper. Many of such wetting agents and their general field of usage as well as chemical characteristics are set forth in the Journal of Industrial and Engineering Chemistry, volume 31, June 1939, pages 66-69. Wetting agents which have been found quite effective are those sold under the trade name "Triton 812" and "Triton 720," which are understood to be sulfonated, polyalkoxylated aryl compounds, and "Aerosol OT," which is dioctyl sodium sulfo succinate.

The rate of penetration of the dye forming solution into the carrier or supporting material, such as paper, is most rapid at high alkalinity and low surface tension of the solution, as well as at high atmospheric humidity. It is in this connection that wetting agents have been found highly effective in reducing the surface tension sufficiently for adequate wetting to occur in a brief interval of paper submersion time, desirably approximately six seconds, regardless of the humidity and alkalinity prevailing. As an example of the quantity of wetting agent, 0.8 gram of wetting agent solids per liter of solution have been found to afford adequate wetting when the paper is immersed; where the paper is supplied with the dye forming solution through the expedient of contact with a wet roller on one side alone, approximately 1.5 grams of wetting agent per liter of solution may be essential.

The desirability of resort to wetting agents in the recording solutions is emphasized by the fact that without the same it has been necessary to submerge the paper for at least two minutes to insure adequate wetting on dry days. The use of pretreated paper, i. e., paper treated with recording solution prior to its utilization in the recording apparatus, has heretofore proven impractical for the electrolytic treatment when subjected to moistening by water in the absence of a wetting agent. Differently stated, the wetting agent causes the water to penetrate pretreated paper more rapidly than the solution penetrates untreated paper. Moreover, an additional function of the wetting agent is to cause the recording solution on the surface of the paper to continue penetration until saturation occurs, where excess liquid is available on the paper surface. At that time, any remaining excess of liquid is subject to removal in accordance with any conventional expedient, such as by resort to a doctor blade or to a preheater.

An undue amount of liquid on the paper may function to cause blurring at the instant of printing. Where the interval between paper wetting and facsimile printing is comparatively long, the tendency is for the paper to become partially dry, causing streaking and paper scuffing when the printing is applied. The wetting agents, under these circumstances, serve to retard the rate of drying at this stage of the operation. Glycols and other high boiling solvents also retard drying at room temperature and improve wetting, but

they are not as effective as wetting agents, thereby necessitating much greater concentrations. If the damp paper, after being subjected to recording, is passed over a hot roller for the purpose of drying and ironing it, the glycols require a greater extent of heating, since at higher temperatures they are more effective than wetting agents as drying retardants. Wetting agents similarly are advantageous in the case of pretreated damp paper which is stored in a moisture-proof container, to be later positioned in a slotted container at the point of unrolling at the recorder.

The color intensity at full electric current is affected by the alkalinity and the amount of diazonium compound formed. The deepest color is usually obtained at a pH of 7.5 to 9, which may not be sufficiently alkaline for optimum background permanence. At a pH of 6 to 7.5, hydroxy coupling is too slow in many cases, and premature non-electrolytic diazotization may discolor the paper in other cases. By resort to the compromise pH range of 9 to 11.5, the color intensity is not materially sacrificed, and at the same time background permanence is attained.

The effect of urea, thiourea and dicyandiamidine as reagents for improving color intensity has been amply treated, hereinabove.

An additional element which materially affects color intensity is the amount of diazonium compound formed electrolytically. It will be appreciated, in this respect, that the halftones of photographs are reproduced by variations in color intensity caused by variations in signal strength. The extent of diazonium compound formation, and therefore color intensity, assumes the characteristics of a linear function of the current flow, except at very low currents where the color intensity drops sharply due to the so-called threshold value effect. In view thereof, reducing agents as well as high alkalinity serve to detract from the light tones. This threshold effect may be compensated by resort to color-deepening chemicals, illustrated by urea, thiourea, and dicyandiamidine, which improve the halftone characteristics by accentuating the light tones.

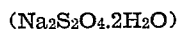
Other substances which tend to deepen the color or improve background permanency are barium and calcium chlorides which may be substituted in part, or entirely, for sodium chloride as the electrolyte. Such substitution may, however, not be without its shortcomings in view of the possibility that the solubility of the dye chemicals may be lowered and on occasion objectionable sludges may be formed.

Through the choice of primary amines and coupling compounds used a great variety of colors may be obtained, although orange, red and purple shades predominate. In general, the orange dyes give recordings whose backgrounds are more permanent without washing than the reds, purples or blues. Furthermore, it has been found that alpha-naphthalene compounds generally give darker colors, but with less permanent backgrounds, than the corresponding beta compounds.

On the question of background permanence, some amines and coupling compounds, in some cases those having two or more amino or hydroxy groups on the same benzene or naphthalene ring, may manifest an undue tendency to air oxidation; in view thereof, it may be desirable as a general expedient to wash recordings made through the use of such reagents within a few hours after such recordings in order to prevent excessive background darkening on storage. Taken as a whole,

the remaining amines and coupling compounds give satisfactory recordings which retain their white backgrounds, or at least do not darken sufficiently to impair their legibility and utility when stored several years in a file or holder.

As previously suggested, various chemicals function to retard background darkening, among which are the glycols; these substances are used in the proportion of approximately 100 cc. per liter of solution. In some cases, they reduce darkening due to the slow reaction during storage, but are not as effective with respect to darkening which results from light exposure. Reducing agents, such as sodium hydrosulphite



and acetaldehyde sodium bisulphite



tend to retard the darkening action of light, but may not preclude slow darkening. Quantities varying from 0.002 to 0.01 mol per liter have been utilized with effective results within the scope indicated. The reducing agents specified are merely illustrative, since other reducing agents have a similar effect. Such other reagents are tartrates, formates, sulphites, thiosulphites, other hydrosulphites than sodium, mentioned above, etc.

The effect of alkalinity upon background darkening has already been recited, and the same applies to the optimum range of pH between 9.5 and 11.0, especially where sodium chloride is used as the electrolyte. Higher pH may cause weakening and decomposition of the paper, while lower pH may result in partial oxidation and partial self-diazotization of the amines. The pH of the paper before treatment with the solution is known to effect the final alkalinity of the treated paper; therefore, if an acid paper is used, the alkalinity of the solution should be increased to compensate therefor.

Complex cyanides of iron, chromium, or other metals, in some instances improve the fastness of the dye to washing and deepen the shade, or even alter the dye color. Noteworthy is the fact that dyes are on the whole distinctly faster to washing than the intermediates from which they are formed; as a result of this, washing may be resorted to for removing unused chemicals from the unrecorded areas, thereby leaving the dyes intact, corresponding to the subject of transmittal. As a general rule, recordings intended to be washed should preferably be made at a pH range of 8.0 to 10.0 within the broader range of 9 to 11.5; in this way advantage is taken of the greater color strength and increased fastness during such pH range. Urea, thiourea, and dicyandiamidine increase the fastness to washing. Thus these compounds serve the dual function of improving color strength as well as color fastness.

The minimum current which is required to produce a faint color is referred to as the threshold value. Before diazotization can take place, the initial alkalinity of the wet paper must be overcome. If reducing agents are present they are oxidized by part of the current, leaving less for acidification and diazotization. Thus the reducing agents referred to hereinabove show this threshold value effect. With neutral solutions or in the absence of reducing agents, small stray currents cause streaks and spots of color on unrecorded areas, thereby detracting from the appearance of the recordings and in some cases seriously interfering with the legibility of the small type.

The application of a constant negative potential to the printing mechanism has an effect analogous to that of high alkalinity in preventing streaks due to stray currents, since the positive facsimile signals must overcome this negative voltage before color appears. This expedient is, however, not without some difficulties in the way of an increased rate of corrosion of the negative electrode, and in the case of certain metals produces a pale negative recording on the back of the paper. It may also tend to eliminate the lighter shades in reproduction of photographs.

Illustrative of desirable embodiments of the invention, the following examples are presented:

Example 1

Name and Use	Mols per Liter	Grams per 250 Liters
<i>Pre-Mixed Ingredients</i>		
Benzidine-3,3'-disulphonic Acid (amine).....	.015	1,634.5.
Acetoacetanilide (coupler).....	.002	88.5.
Schaeffer's Salt (coupler).....	.003	231.0.
Chromotropic Salt (coupler).....	.010	1,248.7.
Sodium Hydrosulphite (auxiliary).....	.003	157.5.
Urea (auxiliary).....	.010	150.2.
Sodium Chloride (electrolyte).....	.450	6,576.1.
<i>Separate Mixture</i>		
Sodium Hydroxide (alkali).....	.061	626.6 or 6.10 liters.
Sodium Nitrite (nitrite).....	.060	1,035.2 or 3.00 liters.
"Triton 720" (wetting agent).....	.08%	750 cc.

Example 2

Name	Mols per liter	Grams per Liter
<i>Pre-Mixed Ingredients</i>		
Benzidine-3,3'-disulphonic Acid.....	.015	6,538.
Chromotropic Salt.....	.015	6,000.
Barbituric Acid.....	.004	0.512.
Sodium Hydrosulphite.....	.0028	0.583.
Dicyandiamidine Sulphate.....	.0010	0.316.
Thiourea.....	.0010	0.076.
Sodium Carbonate.....	.030	3,721.
Sodium Chloride.....	.300	17,536.
<i>Separate Mixture</i>		
Sodium Hydroxide.....	2.5 Normal.....	.050 Cc.
Sodium Nitrite.....	5.0 Molal.....	.074 20.0

It will be noted in the above examples that while the ingredients in each instance are separated into two groups, this is primarily indicative of a desirable expedient for packaging or storing the reagents prior to usage. However, considering the compositions from the standpoint of their substantive content, they comprise the reagents specified in both groups.

As illustrative of the preparation of the composition of Example 1, the proper amounts of each of the pre-mixed ingredients are weighed, and all are thoroughly mixed mechanically. A convenient method utilizes an inclined rotating drum containing pebbles or metal balls to break up any lumps in the chemicals. The mixture may be stored in bulk or packaged in small packages each containing the required quantity for a quart, liter, gallon, or other desired volume of recording solution.

Since measuring liquids is much more convenient than weighing solids, it is advisable to use concentrated stock solutions of sodium hydroxide and sodium nitrite instead of the corresponding solids. Approximately 2.5 normal sodium hy-

dioxide (102 grams per liter) and 5.0 normal sodium nitrite (345 grams per liter) are adequate. The wetting agent is already in liquid form.

Irrespective of the predetermined coloration to be obtained, dependent upon the reagents utilized, the supporting material, such as the paper, after having been appropriately treated with the reagents, is passed through the facsimile recorder in wet or moist condition. A desirable facsimile recorder which may be utilized is the bar-helix type, the bar serving as the anode and the helix providing the cathode. However, it is apparent that the performance of the recording is not restricted to the use of any particular type of apparatus.

Upon contact with the printing electrodes of the recorder, the diazonium compound is formed, which couples with the coupling component present. As previously indicated, the operation is not restricted to the use of any particular recording device, and may be adapted to any of those known to the prior art. Desirably, the treated or sensitized paper is fed continuously from a roll; where the paper has not been sensitized, it is initially fed from the roll through the appropriate immersion bath from impregnation with the dye intermediates and auxiliary compounds, the excess immersion solution removed, and the paper passed directly to the recorder.

The reference to paper as the supporting material or carrier has been recited solely by way of illustration. Substantially any fibrous material capable of being dyed by an azo compound is within contemplation, including such materials as fabric, cloth, and other types of cellulosic sheets, regenerated or otherwise. Quite desirable results have been obtained with an all-rag sheet, surface-sized with glue-formaldehyde in order to impart adequate wet strength. Similarly, good results have been obtained with partially parchmented wood pulp paper. In the case of papers which are too highly sized, wetting agents are satisfactorily employed to facilitate quick penetration of the solution; from 0.5 to 1.5 grams of wetting agent solids per liter of recording solution is usually sufficient for this purpose. Among the effects produced are more rapid solution penetration into the paper and slower drying after leaving the treating bath.

Most all-sulphite papers are too weak when wet to be used on electrolytic bar-and-helix facsimile recorders. When treated with urea-formaldehyde resins, sulphite paper increases in wet strength to the point where it becomes usable, although the tendency of formaldehyde to combine with the amine before diazotization weakens the recorded color. If a sulphite with a fairly high initial wet strength is used, a moderate treatment gives adequate strength without excessive color-weakening. The treatment is preferably applied to the unsized paper.

Effective results may be obtained by combining formaldehyde and urea with the recording solution which has been freshly prepared, when glycols are also included to stabilize the initial resins formed. However, such solutions are not particularly stable when retained in storage for several days, since a substantial proportion of the amine content is consumed, thereby resulting in a decrease in recorded color intensity. Freshly prepared solutions of this type utilized in obtaining dry pretreated paper (paper which has been treated with the reagent solution and dried preliminary to its utilization as a recording sheet) may "set" the resin, and the dry storage condi-

tions serve to prevent or minimize the relatively slow chemical reaction between the formaldehyde resin and the amine.

After subjecting the sheet to electrolytic treatment, especially where facsimile recording is involved, the carrier in a dry state is desirably kept in a folder protected from exposure to light. Although there may be a slight decoloration of the background after several hours' exposure to daylight, this does not seriously affect the utility of the article. Washing the freshly recorded sheets thoroughly with water at the most only slightly weakens the coloring of the dye which has been formed; at the same time, such washing substantially improves the permanence of the background.

Under preferred conditions of operation, the recording paper, after having passed through the facsimile receiver with the azo dye formed thereon corresponding to the subject-matter scanned at the transmitter, the supporting paper may be subjected to a fixing bath for the purpose of rendering the dye more permanent in nature and/or to aid in the preservation of the white or neutral characteristic of the background. Pursuant to such fixation, the paper is then desirably washed, as above indicated, to remove any chemicals which remain in the undiazotized portions of the paper in order to thereby minimize any tendency toward gradual fading of the color produced or darkening of the background when the recorded copy is exposed to light and/or air.

In preparing the various reagent solutions for utilization to saturate or impregnate the supporting material, certain precautions and details of procedure may be advisable, dependent upon the particular circumstances involved. Thus, where all the ingredients of a solution are neutral or alkaline upon their being dissolved in water, they may all be dissolved together. The sodium and potassium salts of amino- or hydroxy-naphthalene sulphonic acids fall in this class. Where the amines, coupling compounds, or other ingredients are free acids as distinguished from sodium or potassium salts, it is necessary to omit the sodium nitrite from the solution until all the acidic compounds have been dissolved by the excess alkali required to give the proper final alkalinity. Failure to observe this precaution results in the formation of diazonium compounds in the acidic zone adjacent to each dissolving crystal of the acidic compounds, with subsequent coupling and dye formation when the diazonium compound has reached the alkaline zone. Such solutions discolor any paper that is treated with them.

On storage, the solutions may tend to darken because of auto-oxidation of some of the ingredients, especially if exposed to light in clear bottles and to air in partly emptied bottles; sometimes this oxidation causes the formation of sediment, even though the solution was originally filtered. Nevertheless, good recordings have been obtained with some year-old solutions, at a slight sacrifice in background permanence. Solutions that have become dark on standing may be restored to their original color (amber, clear brown, or red) by the addition of small amounts of sodium hydrosulphite.

Where the reagents are retained in their solid form, all or part of them may be packed in glass bottles, waterproof fiber or tin cans, or any other suitable containers, so that the user merely dissolves the contents of one or two containers in water, mixes the two solutions if two containers

are needed, and adds more water until the required volume of solution is reached. In those cases where impurities in the water or in the chemicals cause sediment to form, the solution may either be filtered, or allowed to stand several hours to permit the precipitate to settle, so that the clear liquid may be decanted.

By separating the rest of the ingredients (in the containers for dry solids) by layers of salt (which constitutes the greater part of the volume of dry ingredients), any tendency for slow chemical reactions between the ingredients during dry storage is avoided, since salt is inert with respect to the other ingredients. In case any of the dry solids cake in the container, they may be rinsed into the solution with water.

In packaging the reagents in admixture and in their dry state, precautions similar to those above suggested are essential; thus, it is necessary to omit the sodium nitrite from packages wherein the reagents manifest free acidity. After the dry reagents are dissolved and the appropriate content of alkali has been added, the nitrite may then be supplied. In this manner, premature dye formation is avoided.

As a convenient expedient, large batches of all of the dry materials other than sodium hydroxide and sodium nitrite, may be mixed thoroughly and subsequently stored indefinitely. Recording solutions are prepared from such mixtures by dissolving weighed or measured amounts of the dry mixture in water containing a weighed or measured amount of sodium hydroxide, and subsequently adding the proper quantity of sodium nitrite, more water to the required volume, and wetting agent if needed. Sediment is removed either by filtration, decantation after settling, or by a combination of both methods.

In preparing the carrier material, illustrated by paper, for electrolytic facsimile recording, alternative procedures are available. These may be listed as involving the following three methods: (a) chemical treatment of paper at the recorder, (b) damp pre-treated paper requiring no treatment at the recorder, and (c) dry pre-treated paper requiring treatment with water at the recorder.

Considering the recorder-treated paper, the untreated paper is fed through an immersion bath or over wet rollers, where it becomes saturated with a solution of the recording chemicals. After removal of excess solution by doctor blades, and of excess moisture, by natural evaporation or by a heated roller, the wet paper passes through the facsimile recording mechanism. This method has been the one most commonly used in this laboratory, as it is more convenient experimentally, since both recording and paper treatment are combined in one operation. It has the advantage of lower cost for chemicals and paper due to elimination of pretreating costs, and is excellent for use in commercial high speed recording where properly instructed operators give the recorders frequent attention. It may not be entirely suitable for home reception of facsimile broadcasting, since it involves the handling in the home of chemicals which require an element of care and precaution to avoid spilling, discoloring of furniture and clothes.

With respect to the damp pre-treated paper (b), the treating and recording operation may be separated, the paper being treated and rewound while still wet, and delivered in sealed moisture-proof containers to the recorders. When required for use, the wet roll of paper is transferred to a

slotted container in a recorder, from which it is fed to the printing mechanism. This method imposes less strain on the paper than any other wet electrolytic recording method, as the damp paper does not stretch or wrinkle between the slot and the printing point. Consequently much weaker paper may be used. Quick starting with intermittent operation, a desirable feature in telegraph offices, is easily accomplished by manually pulling out the paper for a distance equal to that between the container slot and the printing point. The inclusion of wetting agents in the treating solution eliminates excessive drying of the paper between the container slot and the printing point during normal operation.

The shelf life of damp treated paper varies with the chemicals used and with the alkalinity; usually, the interval within which it should be utilized extends for slightly less than three months from the time that the paper has been prepared. Refrigeration, even with dry ice, does not harm either the chemicals or the paper and desirably functions to increase the shelf life. A temperature just above the freezing point of water has shown indications of providing the best results, and avoids the necessity for thawing the paper before use.

Both metal foil wrappers and tin cans with or without internal coating have been utilized for packaging damp pretreated paper in the case of the cans, a tendency toward rusting is manifested, and for this reason the metal foil is preferable. Tin foil gives better results than either lead or aluminum foil, but it is believed that the moisture retention may not be as effective as in the case of a sealed metal can. The acidity of asphalt-laminated paper causes discoloration of the outer layers of the pre-treated paper. Preferred results may be obtainable by use of a metal foil wrapper on the treated roll of paper, together with a waxed fiber can, desirably with a screw top that is waxed after being closed.

It is not intended to be restricted to any special procedure with respect to the application of the reagents to the paper prior to winding the same for storage. The immersion time may be comparatively short in view of the fact that penetration continues even after the roll is rewound, and with rapid paper travel sufficient solution adheres to the surface to insure adequate penetration afterward. As an advantageous expedient, the reagents may be supplied by rollers, coating one side of the paper with the dye intermediates and the other with the electrolyte, distributing the other ingredients between the two solutions utilized. In this way, salt insoluble intermediates may be used, extending the color range. This method of application may improve the characteristic of background permanence, since any tendency toward darkening will be manifested only on one side of the sheet, thereby providing a lighter background especially where the paper carrier is semi-translucent.

In the case of dry pre-treated paper, the paper is supplied with the chemicals from a solution and dried before being rewound into rolls. The application of water or other suitable liquid at the recorder is all that is essential to render the paper susceptible to recording. This obviates the paper storage problem, since rolls of dry pre-treated paper retain their white backgrounds very satisfactorily, in some cases the background being unaffected for as much as three years.

Where wetting agents are resorted to in the

treating solution, the rate of penetration of water into dry pretreated paper becomes more rapid than that of solution into untreated paper. Proper spreaders should be utilized to remove paper wrinkles formed as a result of stretching after water is applied, unless the distance from the wetting roller or trough to the printing point is great enough for the paper to flatten out.

For dry pre-treated paper, the treating solution is desirably more highly concentrated than in the case of recorder-treated paper. A wetting agent concentration of 1.5 grams per liter of solution is desirable if water is applied only to one side of the paper by means of a roller, in order to attain penetration through the paper to the other side. Doubling the dye chemicals (0.05, 0.10 and 0.03 mol per liter of solution of amine, nitrite, and coupling compound instead of the 0.025, 0.05, and 0.015 mol usually used for recorder-treated paper) greatly increases the contrast and color intensity of recordings on dry pre-treated paper, as distinguished from the case of recorder-treated paper where substantial increase in concentration may provide only a slight beneficial effect. The electrolyte concentration of approximately two-thirds of a mol per liter of solution, which is used for recorder-treated paper, similarly is quite satisfactory for dry pre-treated paper.

The packaging problem is much simpler than with wet pre-treated paper. An acid-free wrapper in contact with the paper, with an outer asphalt-laminated moisture-proof paper is adequate for storage purposes.

As in the case of preparing the damp paper, it may be advantageous to coat part of the ingredients on one side of the paper and the remainder on the other, in order to improve background permanence and permit the use of mutually insoluble ingredients. The problem of large scale production of treating paper remains to be solved.

Another, or dry electric method, involves the use of paper that is electrically conductive when dry and is also coated with dry chemicals which undergo a color change upon being subjected to an electric current.

In accordance with the above description, it will be apparent that sheets of the carrier material may be impregnated with one or more of the various ingredients and solutions within the purview of the invention, and then permitted to dry. When the carrier is dry, it is essentially non-conducting and is not in proper condition to be operated upon by the passage of electric current. To utilize the same, it may be humidified or dampened by any appropriate means, such as by steam or water vapor, in order to increase the conductivity thereof and render it utilizable in the facsimile receiving machine. By so preparing the sheets of chemically treated paper in a dry form as separate rolls, it is possible to use this treated or sensitized paper by merely subjecting the same to an appropriate degree of moisture in order that the current may pass therethrough and accordingly cause a dye to appear thereon, corresponding with the electric impulses from a transmitting source.

As pointed out hereinabove, the details of the facsimile recorder from a structural standpoint do not constitute an element of the present invention. Substantially any facsimile recorder available wherein its functioning is dependent upon electrical impulses emanating from a transmitting source, passing through a conductive carrier material provided with ingredients

adapted for diazotization and coupling to produce an azo dye coloration, will satisfy the apparatus requirements of the present invention. The nature of the electrodes, however, may be of interest, although it is not contemplated that they should be of the type which enter into the compositions of the dyes formed during electrolytic diazotization. Among the contact electrodes which have been utilized are stainless steel, tungsten, molybdenum, platinum, and platinum-iridium. In general, the hard, inert metals such as platinum-iridium and the stellites provide the best results as recording anodes. Non-magnetic stainless steels similarly give good results, but the colors differ from that produced by the platinum or stellite, and may be less attractive in appearance, possibly attributable to collateral reactions involving the iron. Stellite, according to Hackh's Chemical Dictionary, third edition (1944), is an alloy of steel with cobalt and 10 to 50 per cent chromium and/or tungsten, used for high-speed tools and instruments. Ordinary steels which are strongly attracted by magnets do not permit any diazotization reaction, but, on occasion, they produce a moderately pale green recording which is believed to result from oxidation of the intermediates. In the case of alloy electrodes, the percentage of azo color resulting from diazotization appears to increase as the magnetic characteristics of the alloy decrease. By way of explanation as a plausible hypothesis, it may be that the magnetic metals create a strong magnetic field when the current passes, and this magnetic field orients the electrically charged ions in such directions and in such manner that they preclude the possibility of diazotization.

Copper alloys and electrodes generally made from copper or nickel tend to inhibit electrolytic diazotization recording and are, therefore, as a general matter not satisfactory for use as recording anodes, although they give excellent results as cathodes. In this category is the beryllium-copper alloy.

Tungsten generally provides satisfactory recordings, but it manifests a tendency to build up a non-conductive coating, thereby requiring more signal current for effective recording as well as the occasional necessity for reversing the current during a brief interval in order to remove the coating.

The tendency is for the cathode to indicate substantially less electrolytic wear than the anode, since it is attacked only by nascent hydrogen and by increased alkalinity at the time of current flow. With a bar-helix type of recorder, the cathode is desirably in wire form, and the principal wear is due to abrasion which gradually renders the wire flat. The beryllium-copper cathode necessitates more frequent replacement than the anode when the latter is either platinum-iridium or stellite. A cathode helix wire of stellite may out-last several stellite or platinum-iridium anode printer bars.

It will be apparent from the foregoing that the use of compositions within the scope of the present disclosure enables the production of dyes and pigments by subjecting solutions or mixtures of chemicals to electric current. Such dyes or pigments may be obtained in the form of a paste, powder, or as a liquid solution, and subsequently adapted for use as coloring paints, inks, etc., or for dyeing various materials. It is within the contemplation of the invention to produce such dyes or pigments by intermittent or continuous reaction. Materials such as clothing, piece goods,

yarn, paper, and generally any fibrous material susceptible to dyes, and particularly azo dyes, fall within the purview of the present disclosure. They may be treated by immersion in a container filled with a solution of predetermined ingredients and subsequently subjecting such solution to the flow of an electric current in order that the dye may be fixed in or on the materials immersed therein; thus, the dye application may be in the form of a surface coating or a dyeing within the fibrous structure. Definitely contemplated is the formation of the dye in situ.

As a significant feature of the invention, the preparation of a carrier surface or material in a manner to render it subject to diazotization and azo dye formation upon the passing of a current therethrough, as in facsimile recording, is described herein. In accordance with the present disclosure, a uniform color concentration, dependent upon the electrical impulses which motivate the electrolytic action, as for example, the current which passes to the facsimile recorder from a transmitting source, is attained. Moreover, the invention enables a regulation and control of the reaction in a manner to prevent premature dye formation, and this is particularly applicable to facsimile recording, since it makes possible a precision commensurate with the vastly increased rate of recordation which is possible by an effective electrolytic reaction. Many other advantages are similarly attributable to the invention as will be apparent from a consideration of the above description of the many details and ramifications which have been presented.

While I have described my invention in accordance with preferred embodiments as to compositions, articles of manufacture, and procedure, it is apparent that many variations and modifications both as to procedural details, compositions of matter, and articles of manufacture may be made without departing from the scope of equivalents within the purview and spirit of the invention.

The term "facsimile" as used herein is intended to involve not only the reproduction on the recording material of a pre-existing subject, for example a photograph which is scanned and reproduced in accordance with the impulses emanating from the scanning operation, but also embraces the recording of subject matter in the process of creation or formation without a physically preexisting subject. As illustrative of this latter category would be the recording of simply a mental preconception, for example a pattern or design, either of a single color and shades thereof, or multicolors, which is recorded in accordance with an appropriate manual or automatic variation of the electric impulses delivered to the electrodes. Similarly in this category is intended the recording of an arbitrary or haphazard design, pattern or other subject, for example one secured by haphazardly or arbitrarily varying electric impulses delivered to the electrode by punching keys on a master keyboard having suitable electrical connections, by manually or automatically varying resistance, or the like.

What is claimed is:

1. A fibrous sheet material for the electrolytic formation of an azo dyestuff thereon carrying a dyestuff-forming composition comprising a diazotizable heterocyclic amine selected from the class consisting of aminoquinolines, aminopyridines and aminopyrimidines, a sufficient quantity

of an ionizable nitrite to produce the nitrite ions necessary for diazotization of said amine under the influence of the electrolyzing current, a water-soluble, inorganic salt as the electrolyte in an amount to insure passage of the electrolyzing current, a sufficient quantity of an azo dye coupling component to couple with the diazonium compound when formed to produce an azo dye and a quantity of alkali sufficient to impart to said composition a pH on the alkaline side to thereby preclude diazonium salt formation until the fibrous sheet material is subjected to the action of the electrolyzing current.

2. The article as defined in claim 1 wherein the heterocyclic amine is an amino pyridine.

3. The article as defined in claim 1 wherein the heterocyclic amine is 2,6-diaminopyridine.

4. The article as defined in claim 1 wherein the coupling component is a compound having an active methylene group.

5. The article as defined in claim 1 wherein the coupling component is a phenol.

6. The article as defined in claim 1 wherein the composition contains a wetting agent to facilitate the application of the composition to the fibrous sheet material.

7. The article as defined in claim 1 in which the composition contains a compound to improve the color intensity of the azo dyes, said compound being selected from the class consisting of urea, thiourea and dicyandiamidine.

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Administratrix of the Estate of Myer Solomon, Deceased.

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