Patented May 27, 1947

2,421,367

UNITED STATES PATENT OFFICE

2,421,367

FIBROUS SHEET MATERIAL FOR THE ELECTROLYTIC FORMATION OF AZO DYES THEREON

Myer Solomon, deceased, late of Westmont, N. J., by Nellie W. Solomon, administratrix, Princeton, N. J., assignor to Radio Corporation of America, a corporation of Delaware

No Drawing. Application October 24, 1942, Serial No. 463,218

5 Claims. (Cl. 204—2)

1

The present invention relates to fibrous sheet material for the electrolytic production of azo dyes thereon by electrolytic diazotization and coupling and more particularly to fibrous sheet material bearing a composition comprising a sulfonated diazotizable aromatic amine, a metallic nitrite and an azo dye coupling component such that when the sheet material is subjected to the action of an electrolyzing current, azo dyestuffs result. The present application is a continuation-in-part of copending application Serial No. 178,743, now U. S. P. 2,306,471.

The preparation of azo dyes on a traveling carrier by the electrolytic diazotization and coupling method is disclosed in aforesaid application, now U. S. P 2,306,471. This method has been found to be particularly suitable for the preparation of facsimile records. The present invention contemplates the employment of a fibrous sheet material carrying a composition in which the diazotizable aromatic amine is sulfonated. It has been found that such amines when containing a sulfonic acid group give an increased stability of the background of the facsimile record towards light.

It is accordingly an object of the present invention to provide fibrous sheet material for the preparation of azo dyes thereon by electrolytic diazotization and coupling of a diazotizable sulfonated aromatic amine with a coupling component.

A further object of the present invention is fibrous sheet material for the electrolytic production of an azo dye thereon carrying a composition containing as its essential components a diazotizable sulfonated aromatic amine, a coupling component, a metallic nitrite, an alkali, and an electrolyte.

It is a further object of the present invention to provide fibrous sheet material for the production of azo dyes thereon by subjecting the fibrous sheet material to the action of an electrolyzing current while carrying a composition containing as its essential components a diazotizable sulfonated aromatic amine, an azo dye coupling component, a metallic nitrite, an electrolyte, and a sufficient quantity of an alkali to preclude premature diazotization of the diazotizable amine.

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

2

Various different types of facsimile receivers are used at the present time, and in all of them pictures, printed matter, or other characters are produced on a sheet of paper in response to variations in electrical currents 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 relatively slow rates 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 the present invention, it is proposed to produce the picture or printed matter on the recording paper in the form of an azo dye by subjecting the recording paper to the action of the electrolyzing current while carrying a composition containing a diazotizable sulfonated aromatic amine, an azo dye coupling component, an ionizable nitrite, an electrolyte and an alkali. The amount of dye deposited is a function of the amount of current caused to flow through the recording paper. When the image is so formed, the pressure of the printer bar is maintained constant and the amount of current which is passed through increments of the paper is 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, 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 involves the diazotization of the diazotizable sulfonated aromatic amine carried by the fibrous sheet material as the result of the acidity generated at the anode. The diazonium compound thus formed then reacts with the azo-dye coupling component to produce the azo dye.

Where the fibrous sheet material is utilized in facsimile recording, the dye will be formed in consonance with the electrical impulses to which the fibrous sheet material is subjected. The electric current to which the fibrous sheet material is subjected is carried through the cell by virtue of the electrolyte, which raises the conductivity of the cell constituted by the anode, cathode and the fibrous sheet material. The ionizable nitrite present of course provides the necessary nitrite ions to effect diazotization of the amine under the influence of the acidity generated at the anode. The alkali present is of importance since it serves the function of maintaining the ingredients in the status quo, i. e., prevents premature diazotization until the fibrous sheet material is subjected to the electrolyzing current.

As is evident, provision is made for the presence in the composition carried by the fibrous sheet material of the azo coupling component. Where such compounds are present in the reacting mixture, azo dyes are formed under conditions appropriate to the reaction of the coupling reagent with the diazonium compound. Thus, where mixtures containing diazotizable sulfonated aromatic amines, nitrites, and coupling compounds are diazotized electrolytically, and the coupling compound is of the acid reacting type, coupling will occur substantially spontaneously within an extremely brief interval after passage of the current which results in the provision of an acid zone adjacent the anode.

While an acid zone prevails adjacent the anode, it is believed that the zone attendant the cathode tends to increase in alkalinity as a result of the current passing through the cell. Therefore, the tendency of the solution within the cell as a whole is to retain its original alkalinity despite the presence of hydrogen ions produced at the anode, probably due to the phenomenon of ionic migration. Accordingly, where the coupling reagent is of the desirable type which reacts in an alkaline medium, the diazonium salt will be produced adjacent the anode, because of the aforementioned acidity prevailing at that point; in view of the retention of alkalinity by the solution, this diazonium salt will couple with the alkaline coupling reagent at any point removed from the anode where alkalinity prevails, to form the predetermined dye product. As a general rule, coupling compounds that react in alkaline solution have been found to yield preferable results, because acid coupling compounds must be sufficiently reactive for coupling to be completed before the original alkalinity is restored.

The ingredients utilized in accordance with the preferred embodiment of the invention, and especially in its adaptation to facsimile recording, comprise the following:

(*a*) A diazotizable sulfonated aromatic amine, desirably a primary amine.

(*b*) A nitrite.

(*c*) An alkali.

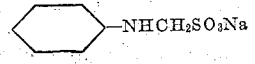
(*d*) A coupling compound.

(*e*) An electrolyte.

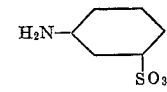
(*f*) Water or other solvent in which electrolytes ionize.

Examples of diazotizable sulfonated aromatic amines contemplated herein are:

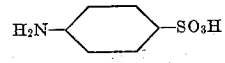
Monoamino benzene compounds



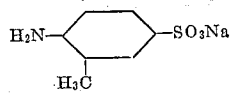
Aniline omega-sulphonic acid



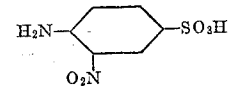
Metanilic acid



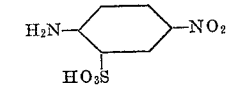
Sulphanilic acid



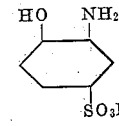
2-aminotoluene-5-sodium sulphonate



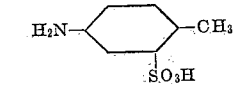
Orthonitroaniline-parasulphonic acid



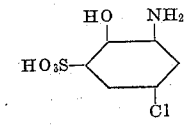
Paranitroaniline-orthosulphonic acid



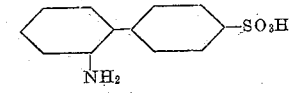
Orthoaminophenol-parasulphonic acid



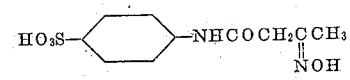
4-aminotoluene-2-sulphonic acid



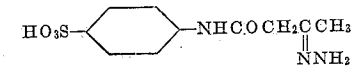
2-amino-4-chlorophenol-6-sulphonic acid



Orthoaminodiphenyl parasulphonic acid (2-amino-4'-sulfodiphenyl)



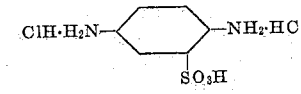
Acetoacetanilide oxime parasulphonic acid



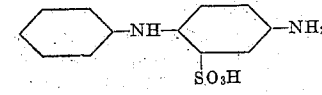
Acetoacetanilide hydrazone parasulphonic acid

Polyamino benzene compounds

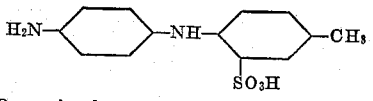
(1) All amino groups on the same benzene ring:



2,5-diaminobenzene-sulphonic acid dihydrochloride (1-sulfo-2,5-diamino-benzene-dihydrochloride)

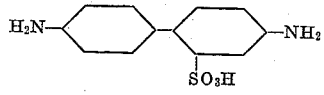


Paraaminodiphenylamine-sulphonic acid (2-sulfo-4-amino-diphenylamine)

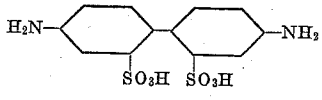


Paraaminophenylparatolylaminosulphonic acid
(4-amino-2'-sulfo-4'-methyl-diphenylamine)

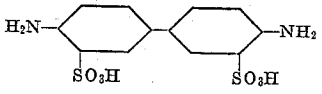
(2) At least two amino groups on different benzene rings:



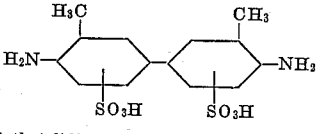
Benzidinemonosulphonic acid (benzidine-2-sulfonic acid)



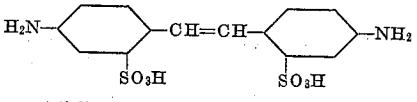
Benzidine-2,2'-disulphonic acid



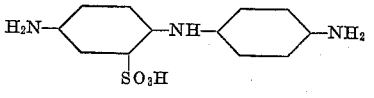
Benzidine-3,3'-disulphonic acid



Orthotolidine-2,2'- or -6,6'-disulphonic acid



4,4'-diaminostilbene-2,2'-disulphonic acid



4,4'-diaminodiphenylamine-sulphonic acid
(2-sulfo-4,4'-diaminodiphenylamine)

Relative to the proportioning of the ingredients, as a general rule by way of estimate and not limitation, about 0.03 gram molecular weights (0.015 for diamines) of amine and of sodium nitrite per liter of solution gives quite satisfactory results.

Relative to the nitrite, a wide range is available, the requisite being an ionizable compound, desirably a metallic nitrite. For purposes of the present disclosure, consideration is directed to the use of sodium nitrite, but it will be clear that there is no intent to be restricted to this desirable compound essential to the diazotization.

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 of 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. 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.

With respect to the coupling compound, it may desirably be soluble in a mildly alkaline salt solution, and is subject to the same oxidation limitations as discussed in connection with 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 remains the best all-round coupling compound, giving darker colors than any of the others having reasonably permanent white backgrounds. The acetoacetylamino 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. However, particularly desirable results have been obtained from the use of a plurality of coupling compounds, as illustrated by those listed in the examples presented hereinbelow.

The amount of coupling compound used usually varies from 0.01 to 0.02 gram molecular weights, although more may be used without harm.

As for the electrolyte (*e*), NaCl is quite satisfactory, but there is no intent to be limited to the use of this salt. Other water soluble inorganic salts such as NaBr, KBr, KCl, LiCl, $BaCl_2$, $CaCl_2$, $MgCl_2$, K_2SO_4, Na_2SO_4, $MgSO_4$, etc., may be substituted for sodium chloride.

Where NaCl is utilized, it has been found that

the total concentration of sodium ions equal to 1.0 gram molecular weight 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.

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.

In addition to sulfonated ether (see page 69, vol. 31, of Journal of Industrial and Engineering Chemistry, January, 1939) as a wetting agent, additional wetting agents function satisfactorily with respect to the treatment of the carrier, exemplified by paper. Dioctyl ester sodium sulfosuccinic acid (page 126, vol. 35, of Journal of Industrial and Engineering Chemistry) obtainable in either solid or solution form has been utilized with practical results, although it is probably not as effective as the first named agent. Similarly desirable as a wetting agent has been found to be a sodium salt of aryl alkyl polyether sulfonate (page 130, vol. 35, of Journal of Industrial and Engineering Chemistry) which occurs in the form of a white emulsion.

Illustrative of desirable and effective embodiments of the invention, the following examples which utilize an aromatic amino compound having two benzene rings, and containing a nuclear sulphonate group, are presented:

Example 1

Name and Use	Mols per Liter	Grams per 250 Liters
Pre-Mixed Ingredients		
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
Separate Mixture		
Sodium Hydroxide (alkali)	.061	620.6 or 6.10 liters.
Sodium Nitrite (nitrite)	.060	1035.2 or 3.00 liters.
Sodium salt of aryl alkyl polyether sulfanate (wetting agent).	.80%	750 cc.

Example 2

Name	Mols per Liter	Grams per Liter
Pre-Mixed Ingredients		
Benzidine-3,3'-disulphonic Acid	.015	6. 538
Chromotropic Salt	.015	6. 000
Barbituric Acid	.004	0. 512
Sodium Hydrosulphite	.0028	0. 588
Dicyandiamidine Sulphate	.0010	0. 316
Thiourea	.0010	0. 076
Sodium Carbonate	.030	3. 721
Sodium Chloride	.300	17. 536
Separate Mixture		
Sodium Hydroxide, 2.5 Normal	.050	20.0 cc.
Sodium Nitrite, 5.0 Molal	.074	14.8 cc.

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

The composition adapted for electrolytic diazotizing and coupling is prepared by dissolving the pre-mixed chemicals and sodium hydroxide

in approximately three-fourths the required water, adding sodium nitrite and the remaining water, and filtering or decanting to remove sediment. The wetting agent may be added at any time during or after the preparation, and varies in amount with operating conditions, although it is not critical.

The following table is indicative of expedient amounts of each component utilizable in a recording solution, based upon the two different unit volumes, namely, the quart and the liter:

Total Volume of Recording Solution	Pre-mixed Ingredients		Sodium Hydroxide (2.50 Normal) cc.	Sodium Nitrite (5.0 Normal) cc.
	grams	cc.		
1 quart	38.181	32.50	23.091	11.356
1 liter	40.346	34.34	24.400	12.000

Wetting agent—0.0 to 3 cc. of 25% solution per liter of recording solution.

In preparing the compounds of Example 2, the ingredients of the pre-mixed portion, containing all of the reagents except sodium hydroxide and sodium nitrite, may be mixed and ground together dry and stored in bulk. At the time that the reacting composition is prepared, the sodium hydroxide and sodium nitrite are added in appropriate proportion. A desirable pH for the composition when the respective portions have been admixed is between 10.75 and 11.0.

As a convenient procedure in the preparation of recording solutions, 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.

The carrier or material which is to be impregnated or saturated with the reagents, and upon which the dye is to be formed in situ or the facsimile is intended for recordation, may be fabric, paper, cloth, or similar fibrous substances.

By the use of compositions within the scope of the present disclosure, it is possible to produce dyes and pigments by subjecting solutions or mixtures of chemicals to an electric current. Such dyes or pigments may then be collected in a paste, powder or liquid form and subsequently used for coloring paints, inks, etc. or for dyeing various materials. Also, materials such as clothing, piece goods, yarn, etc. may be dyed by immersing such material in a container which has been filled with the solutions and subsequently subjecting the entire mixture to the flow of an electric current in order that the dyes may be fixed in the materials so immersed. This method produces a uniform coloring of the material, particularly when some agitation is present during the time that the electrical current is applied to the solution.

Briefly stated, electrolytic facsimile recording may be accomplished by either of the following three methods of paper treatment and handling: (*a*) chemical treatment of paper at the recorder, (*b*) damp pretreated paper requiring no treatment at the recorder, and (*c*) dry pretreated paper requiring treatment with water at the recorder. The claims accordingly contemplate the fibrous sheet material prepared by any of these expedients.

It is to be understood that sheets of paper or similar material may be impregnated with one or another of the various solutions and the paper permitted to be subsequently dried. When the paper is dry it is relatively non-conducting and is not in a proper condition to be operated upon by the passage of electric current. The paper may then be humidified or dampened by any appropriate means, such as by steam or water vapor, for instance, in order to increase the conductivity thereof and the paper may then be placed in the facsimile receiving machine for use. By so preparing separate sheets of paper or separate rolls of paper it is possible to use the sensitized paper by merely subjecting the same to a certain degree of moisture in order that the current may pass therethrough and accordingly cause a dye to appear on the paper.

While the invention has been described in accordance with preferred embodiments, 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 as defined in the following claims.

What is claimed is:

1. A fibrous sheet material for the electrolytic formation of azo dyes thereon carrying a composition comprising a diazotizable sulfonated aromatic amine, a quantity of an ionizable nitrite sufficient to effect diazotization of said amine, a water-soluble inorganic salt as the electrolyte in an amount sufficient to facilitate the passage of the electrolyzing current, an azo dye coupling component in a quantity sufficient to react with said diazonium compound when formed to yield an azo dye, and a quantity of an alkali sufficient to give a pH on the alkaline side to thereby prevent premature diazotization of said diazotizable amine.

2. The article as defined in claim 1 wherein the sulfonated aromatic amine is a sulfonated polyamino compound of the benzene series.

3. The article as defined in claim 1 wherein the sulfonated aromatic amine is a sulfonated polyamino compound of the benzene series and wherein the azo dye coupling component is a phenol.

4. The article as defined in claim 1 in which the composition includes a wetting agent to facilitate the application of the composition to the fibrous sheet material.

5. The article as defined in claim 1 wherein the sulfonated aromatic amine is benzidine 3.3'-disulfonic acid and the azo dye coupling component is a mixture of acetoacetanilide, Schaeffer's salt and chromotropic salt.

NELLIE W. SOLOMON.
Administratrix of the Estate of Myer Solomon, Deceased.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
168,465	Edison	Oct. 5, 1875
761,310	Loeb	Mar. 31, 1905
1,333,700	Bloom	Mar. 16, 1920

(Other references on following page)

UNITED STATES PATENTS

Number	Name	Date
1,844,199	Bicknell et al.	Feb. 9, 1932
1,970,539	Bausch	Aug. 21, 1934
2,038,486	Glas	Apr. 21, 1936
2,306,471	Solomon	Dec. 29, 1942
1,457,235	Stusser	May 29, 1923
2,075,022	Crossley et al.	Mar. 30, 1937
2,217,478	Crossley et al.	Aug. 16, 1928
2,173,141	Talmey	Sept. 19, 1939

Number	Name	Date
2,181,533	Kline et al.	Nov. 28, 1939
2,229,091	Kline	Jan. 21, 1941
2,080,209	Kappeler	May 11, 1937

OTHER REFERENCES

The Aromatic Diazo—Compounds and Their Technical Applications by K. H. Saunders, published by Edward Arnold and Co. 1936, London. Page 2. (Copy in Div. 43.)