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3,153,592

COMPLEX SALT DIAZOTYPE PHOTOPRINTING MATERIALS

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The present invention relates to the production of diazotype photoprinting materials. More particularly, the subject invention is directed to improve diazotype photoprinting compositions which are developed under the influence of heat.

In diazotype photoprinting processes, a suitable base such as paper is treated with a solution of two dye components. One of the components is a diazo compound which is sensitive to light, and the other component is an azo coupling compound. The coupling compound is capable of reacting under proper conditions with the diazo component to form a dye. In making a print, the treated base is exposed to light under a translucent original or master. In those areas of the base which are reached by the light, the diazo compound is at least partially destroyed. In those areas that are beneath opaque lines or designs, on the other hand, the diazo compound is not affected by the light. The print is developed by reacting the retained diazo compound with the coupler to form a highly colored azo dyestuff in precise duplication of the original.

Diazotype reproduction processes are classified as either moist processes or dry processes. In a moist process the base is coated with a diazo compound which is exposed to light under a pattern. Thereafter, color development is brought about by contacting the latent diazo image with a solution of a coupling compound and aqueous alkali. In the dry process the light sensitive layer contains both the diazo compound and a coupler together with acids and various other stabilizing substances. After the treated base has been exposed to light the print is formed by the use of hot aqueous ammonia fumes.

Each of the above systems has serious disadvantages. The principal objection to the dry process is that it requires the use of ammonia fumes. Because of the pungent and corrosive nature of the fumes it is necessary to provide special venting devices before the process can be used to any great extent. Although the moist process does not require the use of ammonia fumes it has the disadvantage that the developing solution must be mixed frequently because it is susceptible to oxidation. Furthermore, the evaporation of water from the developer causes crystallization to occur and often leaves a sticky mass on the developing machine.

Many attempts have been made to provide practical two-component thermographic diazotype reproduction materials which can be used in place of systems requiring developing solutions and/or alkaline vapors. Until very recently, these efforts for the most part were unsuccessful. Difficulties arose because of the dual need to prevent premature reaction between the diazo compound and the coupling component and to cause a rapid reaction between the components at the desired time. In the first heat developable systems, satisfactory shelf life was

only accomplished at the expense of print quality. Stabilizing methods such as placing the coupler within a gelatin coating and dusting powdered coupler on the diazo coated paper prevented precoupling but also resulted in the development of faint and weak reproductions.

More recently, a heat developable diazotype system has been developed which is feasible from a commercial standpoint. In this system a layer containing an intimate mixture of a diazo compound, an azo coupling component, and an alkali generating compound is formed on a suitable base. A solution of the various materials is brushed or otherwise applied to the base. Following the removal of volatiles from the liquid coat, the paper, cloth, plastic, etc., is ready for photoprinting. A description of a preferred heat developable process is disclosed in a copending application Serial No. 5,688, which was filed on February 1, 1960. The disclosure of application Serial No. 5,688 is incorporated in the present specification by reference.

Even though the most recent heat developable processes provide commercially acceptable results, there is still room for improvement both as to the shelf life of the coated materials and as to the color density of the resultant reproduction.

It is an object of the present invention to provide improved diazotype photoprinting materials and methods.

Another object of the invention is to provide heat developable diazotype photoprinting materials which have an excellent shelf life.

A further object of the invention is to provide stable diazotype photoprinting materials which produce permanent prints of excellent quality.

A still further object is to provide diazotype photoprinting materials and methods which produce prints having excellent color density.

Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the present invention comprises the discovery that improved diazotype photoprinting compositions can be prepared by using a complex salt in place of a diazo compound and a coupler compound. Such compounds, which will be described more fully below, undergo molecular rearrangement to form an azoic dye. The physical attachment of the diazo compound and the coupler in the present invention produces a greatly accelerated dye forming reaction when the copy paper is heat treated.

In our process, a stable salt of a diazo compound and a sulfonic acid coupler is formed in such a way that when a coating containing the complex and an alkaline generating material such as urea is heated, the complex need only undergo a molecular rearrangement to produce the azoic dye. It is essential that an acid stabilizer also be present in the dye-forming composition. Preferably, this stabilizer is a noncoupling sulfonic acid stabilizer. The diazo-sulfonic acid coupler complex can be formed and then applied to a base material in the coating solution, or the complex can be formed in situ. In the latter case, a complex of a diazo compound and a noncoupling sulfonic acid, such as m-benzene disulfonic acid, is formed. This complex is then applied in solution to a base material along with a coupling sulfonic acid. When the complex and the coupler are dissolved in the solution, the

diazo ionizes to form a diazonium ion. Upon drying of the coating on a sheet of paper or the like the less soluble complex of the diazo and the coupler is primarily formed.

In practicing the invention, a suitable base is coated with a solution containing a diazo compound-sulfonic acid coupler complex, an acid stabilizer, and an alkaline generating compound such as urea. As an alternative, the coating solution contains a diazo compound-noncoupling sulfonic acid complex, a coupling sulfonic acid, and an alkaline generating agent. Thereafter, the volatile constituents of the solution are removed. In either of the above alternatives the coating will consist of a diazo compound-coupling sulfonic acid complex, an acid stabilizer (preferably a noncoupling sulfonic acid), and an alkali generating material. The treated base is exposed to the action of ultraviolet rays through the master to be copied. The rays destroy or otherwise inactivate the print-forming components in all areas of the coated material which are not protected by the lines or designs of the original. The print is formed by heating the exposed base above the temperature required to decompose urea or another alkaline generating compound. The ammonia that is generated causes a sudden molecular rearrangement of the complex to form an azoic dye. Alternatively, the print may be made by applying infrared radiation to the original while the original is in contact with the reproduction material. In this manner the design or letter areas of the original are heated above the temperature at which the urea decomposes. The heat thus generated is transmitted to the reproduction paper whereupon ammonia produces an alkaline reaction which causes an intramolecular rearrangement of te complex. The resulting print is a precise positive copy of the original. Subsequently, the nondeveloped portions of the coated base can be treated with ultraviolet rays to destroy the diazo compound.

Examples of diazo compounds which can be used to produce the diazo-coupling sulfonic acid complex include the following:

p-Amino-N,N-dimethylaniline
p-Amino-N,N-diethylaniline
p-Amino-N,N-dipropylaniline
p-Amino-N-ethyl-N-propylaniline
p-Amino-N-ethylaniline-N-propyl
p-Amino-N-ethyl-N-β-hydroxyethylaniline
p-Amino-N-methyl-N-β-hydroxyethylaniline
p-Amino-N,N-di-β-hydroxyethylaniline
p-Amino-m-ethoxy-N,N-diethylaniline
p-Amino-N-ethylotoluidine
p-Amino-N-ethyl-m-toluidine
p-Amino-N,N-diethyl-m-toluidine
p-Amino-N-ethyl-N-hydroxyethyl-m-toluidine
p-Amino-N-ethyl-N-benzylaniline
p-Amino-N-ethyl-N-β-hydroxyethyl-m-toludine
N-p-Amino-phenylmorpholine
N-(2,5-diethoxy-4-aminophenyl)-morpholine
p-Amino-diphenylamine
3-Aminocarbazole and the like

As was indicated above, an acid stabilizing agent should be added to the composition. These agents include such acids as malonic, gluconic, cyanoacetic, maleic, tartaric, citric, diglycolic, oxalic, acetic, and malic acids, and anhydrides of such acids, e.g., the lactones. Reference to such acids is intended to include the equivalent anhydrides. It is preferred that noncoupling aromatic sulfonic acids such as m-benzenedisulfonic acid be used as the stabilizing agent. The use of such aromatic sulfonic acids as stabilizers is described in copending application Serial No. 67,289 which was filed on November 4, 1960. The disclosure of said copending application is incorporated in the present specification by reference. Metal sulfates such as cadmium sulfate, zinc sulfate, nickel sulfate, cobalt sulfate, aluminum sulfate, magnesium sulfate, and ceric ammonium sulfate can also be added to

the composition. The use of such sulfates in heat developable processes is described in copending application Serial No. 156,260 which was filed on December 1, 1961. The disclosure of this copending application is also incorporated in the present specification by reference.

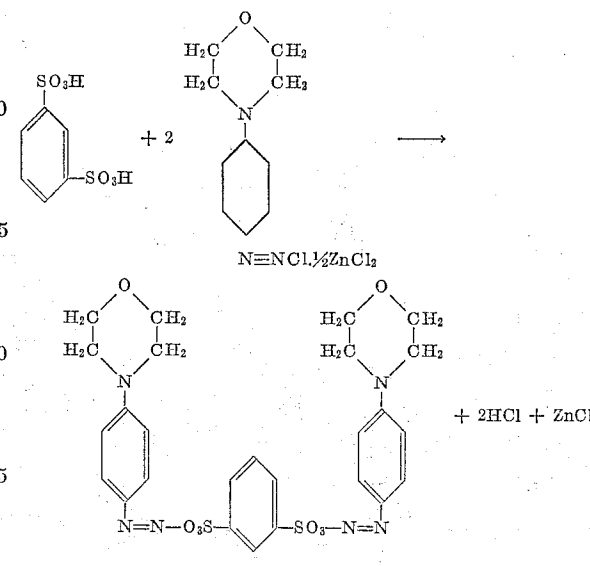
The following examples illustrate suitable methods of preparing the diazo-sulfonic acid coupler complexes of the subject invention.

Example I

This example discloses a method for preparing the complex of p-diazophenylmorpholine and 2,3-dihydroxynaphthalene-6-sulfonic acid. To 1 liter of H_2O held at approximately 30° C. is added 2.5 ml. of 37% HCl, 10 g. of citric acid, and 40 g. of p-diazophenylmorpholine zinc chloride salt. The mixture is stirred until the diazo is completely dissolved. Twenty (20) g. of Nuchar is added to the solution and the solution is stirred for twenty minutes. After the Nuchar has been filtered out, the filtrate is poured into a clean beaker equipped with a stirrer. Fifty (50) g. of 2,3-dihydroxynaphthalene-6-sulfonic acid sodium salt is then added to the filtrate. After the sodium salt dissolves the solution is seeded with a pinch of complex which has previously been prepared. The mixture is allowed to stand overnight whereupon the product is filtered off with a coarse filter and dried at 45° C.

Example II

This example disclose the preparation of the complex of m-benzenedisulfonic acid (a noncoupling sulfonic acid) and p-diazophenylmorpholine. The diazo and the acid are dissolved in a minimum amount of water. A ratio of two equivalents of diazo to one equivalent of acid is maintained. The temperature is kept at about 35° C. and the solution is protected from light. Five (5) g. portions of diazo are added to the acid. The first portion should be dissolved before adding the second portion. When no more diazo will go into the solution, the solution is cooled to a temperature of about 5° C. The product is then filtered off with a coarse filter. The reaction is as follows:



Example III

This example shows the preparation of a complex of 4-diazo-2,5-dibutoxy-N-benzoylaniline and 2,3-dihydroxy-

naphthalene-6-sulfonic acid. In the order given, 6 g. of tartaric acid, 10 ml. of 37% HCl, and 11.4 g. of 4-diazo-2,5-dibutoxy-N-benzoylaniline zinc chloride salt are dissolved in 585 ml. H_2O at 35° C. After the chemicals have been dissolved, 5 g. of charcoal is added and the solution is stirred for 30 minutes and filtered. A solution containing 9 g. of 2,3-dihydroxynaphthalene-6-sodium sulfonate and 225 ml. of H_2O is added dropwise (approximately one drop per second) to the previously prepared solution. The resultant product is then filtered and dried.

Example IV

This example illustrates a suitable composition which can be used in preparing the subject heat developable papers. The composition included the following materials:

Water	ml	100
Urea	g	27
Thiourea	g	1
MBDA [1]	g	2.03–2.89
2,3-dihydroxynaphthalene-6-sulfonic acid sodium salt	g	10
Complex salt of N-p-diazophenylmorpholine and m-benzenedisulfonic acid	g	2.27–4.54

[1] m-Benzenedisulfonic acid.

In this instance, the complex consisted of the diazo and a noncoupling sulfonic acid. In solution, however, the diazo ionized into a diazonium ion and after being applied to sheet paper the less soluble complex of the diazo and 2,3-dihydroxynaphthalene-6-sulfonic acid was primarily formed. The composition was applied to standard commercial diazo process paper at the rate of about 30 g. of the complex per 1,000 square feet. An original and the reproduction paper were placed in face-to-back contact with each other and conducted through the focal zone of an infrared beam. The materials travelled through the focal zone at a rate of about 1 to 2 inches per second and reached temperatures of about 205 to 220° C. By this process a black line reproduction was obtained having good color and shelf life.

Example V

In this test, the following formulations were applied to standard reproduction paper in the manner described above in connection with Example IV. Once again, the paper was developed by the use of an infrared beam. In each instance, a reproduction was obtained having good color and shelf life characteristics.

	1	2	3	4	5	6
Water, ml	100	100	100	100	100	100
Urea, g	27	20	10	10	20	20
Thiourea, g	1	1	1	1	1	1
MBDA [1], g	2.89	2	2	2	2	2
Complex salt of N-p-diazophenyl-morpholine and MBDA, g	2.27	4	4	2	2	2
2,3-dihydroxy-naphthalene-6-sulfonic acid, g	10	10	10	10	10	10
Cyanamide (50%), g	------	20	20	20	20	10

[1] m-Benzenedisulfonic acid.

Water	ml	100
Urea	g	45
Zinc sulfate	g	8
2,3-dihydroxynaphthalene-6,8-disulfonic acid	g	12.3
Complex salt of N-p-diazophenylmorpholine and MBDA	g	4
Thiourea	g	1
Saponin	g	0.3

Water	g	14,000
Urea	g	3,000
Thiourea	g	400
Sulfamic acid	g	1,000
Guanidine carbonate	g	400
2,3-dihydroxynaphthalene-6,8-disulfonic acid	g	6,000
Resorcinol	g	1,000
X99	g	100
Complex salt of N-p-diazophenylmorpholine and MBDA	g	1,000
Complex salt of N-p-diazophenylmorpholine and 2,3-dihydroxynaphthalene sulfonic acid sodium salt	g	400
Water	ml	100
MBDA	g	1.5
Urea	g	50
Complex of N-p-diazophenylmorpholine and 2,3-dihydroxynaphthalene-6,8-disulfonic acid	g	2.8
Cadmium sulfate	g	15

	1	2
Water, ml	100	100
Urea, g	40	40
MBDA, g	------	1
Malonic acid, g	2.3	------
2,3-dihydroxynaphthalene-6,8-disulfonic acid sodium salt, g	6	6
Complex of p-diazo-ml-diethylaniline and 2,3-dihydroxynaphthalene-6,8-disulfonic acid, g	2.8	2.8
Water, g	100	100
Malonic acid, g	1	1
Urea, g	20	40
Complex of N-4-diazo-2,5-diethoxy-phenylmorpholine and 2,3-dihydroxynaphthalene-6-sulfonic acid, g	5	5

	1	2	3	4	5
Water, ml	100	100	100	100	100
Urea, g	20	20	20	15	20
Thiourea, g	1	1	3	3	2
MBDA, g	3	4	3	3	3
2,3-dihydroxynaphthalene-6-sulfonic acid, g	5.5	5.5	2	4	3.8
Complex salt of N-p-diazo-phenyl-morpholine and 2,3-dihydroxy-naphthalene-6-sulfonic acid, g	6.86	6.86	6	4	6.4
Acetoacetanilide, g	3	5	5	------	4

	1	2	3	4
Water, ml	100	100	100	100
MBDA, g	2.5	1.5	------	------
Urea, g	21.5	21.5	21.5	21.5
2,3-dihydroxynaphthalene-6-sulfonic acid, g	2	2	2	2
Complex salt of N-p-diazophenylmorpholine and 2,3-dihydroxynaphthalene-6-sulfonic acid, g	3	3	3	3
Sulfamic acid, g	------	------	2	3

	1	2	3	4	5
Water, ml	100	100	100	100	100
2,3-dihydroxynaphthalene-6-sulfonic acid sodium salt, g	2	2	2	2	2
Urea, g	21.5	25	21.5	21.5	21.5
Thiourea, g	1	1	1	1	1
Complex salt of N-p-diazophenyl-morpholine and 2,3-dihydroxynaphthalene-6-sulfonic acid, g	3	3	3	3	3
Sulfamic acid, g	5	5	3	3	3
Boric acid, g	------	------	2	------	------
Citric Acid, g	------	------	------	2	------
Tartaric acid, g	------	------	------	------	2

Preferred compounds which produce an alkaline reaction when heated are those which yield ammonia by decomposition or dissociation. The compounds include urea and its derivatives such as guanidine, alkyl substituted urea, and alkyl substituted guanidines, said alkyl groups containing from 1 to 4 carbon atoms. Specific urea derivatives would include methyl urea, ethyl urea, propyl urea, and butyl urea, and hydroxy ureas such as hydroxy methyl urea and hydroxy ethyl urea. It is

often advantageous to use a plurality of such compounds, such as mixtures of urea and guanidine, and urea and tetramethyl guanidine.

Organic nitrogen base salts which produce an alkaline reaction when heated may be employed, particularly salts of amines with volatile or decomposable acids such as acetic acid, malonic acid, gluconic acid, and other heat fugitive acids. Amino-paraffins and especially hydroxylated derivatives thereof or amino alcohols are preferred, particularly those having low volatility, substantial alkalinity, and no odor, and which are resistant to oxidation. Examples of such amines are tri-(hydroxymethyl)-aminomethane, 2-amino-2-methyl-1,3-propanediol, ethanolamine, diethanolamine, and ethyl diethanolamine. The aforementioned guanidines are also basic, and their basicity may provide or contribute to the necessary alkaline reaction, with or without decomposition thereof to produce ammonia. Other compounds which are contemplated include the ammonium salts of weak acids, such as ammonium gluconate, ammonium acetate, ammonium carbonate, ammonium diglycolate, and ammonium oleate. The compounds containing the ammonium ion presently are not preferred as the materials produced therewith tend to have a reduced shelf life.

Paper, cloth, plastic sheet materials, plastic impregnated materials, and metal bodies all may be employed as the base material in the direct printing process, provided that the material is not so heat-conductive as to interfere with the process. The reproduction material for use in the reflex process requires that the base be capable of transmitting the heat-producing radiations, and conducting the heat from the original to the sensitive layer.

Various drafting and print-making papers are suitable, as are regenerated cellulose, synthetic plastic and other such sheet materials capable of transmitting the radiation without substantial absorption thereof.

The diazo-sulfonic acid coupler complex, the acid stabilizer, the alkali generator, and the other constituents of the coating composition are applied to the base in solution by one of the conventional coating methods. The materials are preferably dissolved in water, and the one-phase liquid coat is dried by evaporation to a residual moisture content of preferably less than about 5%. A volatile organic solvent may also be employed, although such is not ordinarily necessary and therefore is not preferred due to the increased cost and normal disadvantages attendant upon such use. It is necessary that the solvent be one which can be removed substantially completely in the drying process, so as not to have an adverse effect on the shelf life.

The diazo compound is preferably employed in a proportion of about 1 to 10% by weight on the basis of the water or other solvent content of the sensitizer composition. The composition is applied to the base at standard rates of application, for example, application to diazo process paper is made at the rate of about 10 to 50 grams of diazo compound per one thousand square feet.

The coupling component is employed in a proportion preferably at least sufficient to constitute a stoichiometric amount with respect to the diazo compound, and preferably in substantial excess. Thus, about 2 to 15 equivalents of coupler per equivalent of diazo compound is preferred in most cases.

The quantity of alkaline reacting material employed should be sufficient to elevate the pH of the sensitized layer to that required for coupling, and this quantity will likewise depend upon the characteristics of the material and of the other substances in the sensitive layer. It has been found, for example, that compounds of the type of urea may be employed in a weight ratio to diazo compound of about 3–10:1. The proportion of an amino alcohol while varying with its basicity and molecular weight, will frequently be in the range of about 0.5–10 parts by weight to 1 part of diazo compound. Other compounds may be employed at rates corresponding thereto on the basis of the ammonia evolved or the resulting pH change.

The conditions of time and temperature for developing the image are selected for the system employed to produce the necessary alkaline reaction without undesirable decomposition of the diazo compound. The results are generally advantageous when the sensitive layer is subjected to a relatively high temperature of about 150° C. to 220° C. for a short time, ranging from a few seconds to about a minute. While rapid development is preferred, the materials can be heated for a longer period of time at a lower temperature. As an example, the temperatures reached in the sensitive layers in the examples which follow were about 205° C. to 220° C. for a period of about six to fifteen seconds. These rates are very advantageous and enable a number of copies to be made in a short period of time. As was indicated above, the use of the diazo-sulfonic acid coupler complex substantially increases the development speed of the composition.

Satisfactory temperatures may be provided in the sensitive layer in a number of ways. Thus, the primary source of the necessary heat may be a quartz lamp used in conjunction with an elliptical reflector so as to provide an intense zone of near infrared and infrared light. The lamp may produce a color temperature of about 2750° K. with about 1500 watts. The reflector ellipse dimensions may be 0.750 inch for the minor axis and 0.845 inch for the major axis. The tungsten element of the lamp is located at one focus of the ellipse, and the surface of the original or master at the other.

The duplicating machine may be allowed to operate without cooling the parts, so that part of the heat increment is supplied by the parts such as the rollers or conveyor means, or the heat produced by absorption of the radiations may be supplemented in another manner. If the background diazo compound is first decomposed in the direct process the latent image produced thereby may be developed if desired by contact with a heated surface.

As has been indicated above, the essential components of the subject composition include (1) a diazo compound, (2) a coupling sulfonic acid, (3) an alkaline producing compound, and (4) an acid stabilizer. It is preferred that the acid stabilizer be an organic sulfonic acid stabilizer of the type decribed in application Serial No. 67,289 which was filed on November 4, 1960. Any aromatic compound which is capable of coupling and which contains at least one sulfonic acid group can be used as the coupler in preparing the subject complex. Coupling naphthol sulfonic acids are of particular interest. Amino naphthol sulfonic acids can also be used, although these materials tend to become discolored on storage.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. Reproduction material which comprises: a supported layer of a visibly heat-sensitive composition, said composition comprising a mixture of the complex salt reaction product of a diazonium salt and a coupling aromatic sulfonic acid, an acid stabilizer, said stabilizer being free of azo coupling groups, and an organic nitrogen base producing an alkaline reaction when heated, said composition being free of any substantial precoupling.

2. A process for graphically reproducing an original which comprises: placing the original to be reproduced in superimposed relationship with a supported layer of a visibly heat-sensitive composition, said composition comprising the complex salt reaction product of a diazonium salt and a coupling aromatic sulfonic acid, an acid stabilizer, said stabilizer being free of azo coupling groups, and an organic nitrogen base which produces an alkaline reaction when heated, irradiating said superimposed original to render the diazo compound incapable of coupling in

the areas not protected by the characters of said original, and thereafter heating said supported layer of said visibly heat-sensitive composition whereby said complex salt undergoes an intramolecular rearrangement to form an azo dye, and whereby said original is visibly reproduced.

3. A process as in claim 2 wherein said compound which produces an alkaline reaction when heated is urea.

4. A process for graphically reproducing an original which comprises: placing an original having preferential radiation-absorbing areas in contact with a supported layer of a visibly heat-sensitive composition, said composition comprising the complex salt reaction product of a diazonium salt and a coupling aromatic sulfonic acid, an acid stabilizer, said stabilizer being free of azo coupling groups, and an organic nitrogen base which produces an alkaline reaction when heated, and irradiating said original with heat producing radiations to effect an intramolecular rearrangement of said complex salt in the areas of said supported layer registering with said radiation-absorbing areas of said original, whereby said original is visibly reproduced.

5. A process as in claim 4 wherein said compound which produces an alkaline reaction when heated is urea.

6. Reproduction material which comprises: a supported layer of a visibly heat-sensitive composition, said composition comprising a mixture of the complex salt of p-diazophenylmorpholine and 2,3-dihydroxynaphthalene-6-sulfonic acid, an acid stabilizer, said stabilizer being free of azo coupling groups, and urea, said composition being free of any substantial precoupling.

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UNITED STATES PATENT OFFICE

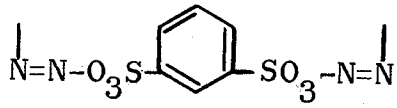
CERTIFICATE OF CORRECTION

Patent No. 3,153,592 October 20, 1964

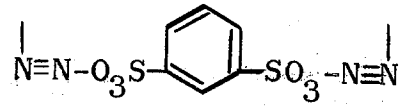
Robert J. Klimkowski et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 44, for "p-Amino-N-ethylaniline-N-propyl" read -- p-Amino-N-ethylaniline --; line 49, for "p-Amino-N-ethylotoluidine" read -- p-Amino-N-ethyl-o-toluidine --; column 4, lines 56 to 68, for that portion of the formula reading:



read



column 5, in the table, first column, line 10 thereof, for "Cyanamide (50%)-------g" read -- Cyanamide (50%)-------ml --; column 6, in the table, second column, line 4 thereof, for "2.3" read -- 2.5 --; same table, first column, line 7 thereof, for "-ml-" read -- -NN- --; same column 6, same table, first column, line 9 thereof, for "Water-------g" read -- Water-------ml --.

Signed and sealed this 30th day of March 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

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Commissioner of Patents