March 9, 1965 V. TULAGIN ETAL 3,172,827

PERMANENT REPRODUCTIONS

Filed April 18, 1960

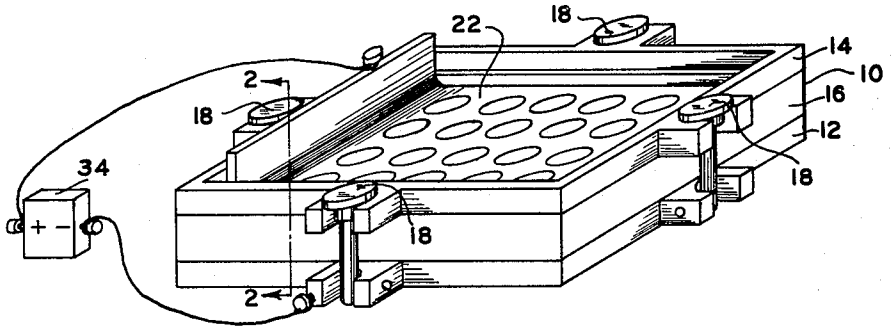


FIG. 1

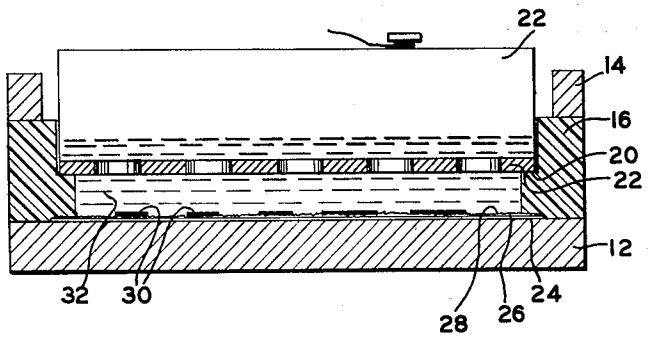


FIG. 2

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3,172,827

PERMANENT REPRODUCTIONS

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Filed Apr. 18, 1960, Ser. No. 23,017
4 Claims. (Cl. 204—18)

This invention relates to new and useful permanent reproductions and their method of preparation by selectively depositing a basic nitrogen containing compound on the surface of a photoconductor.

A method for making visible reproductions electrolytically is described in the application of Johnson and Neher, Ser. No. 575,070, filed March 30, 1956, now U.S. Patent 3,010,883. The Johnson and Neher application discloses the prepartion of light sensitive sheet material from a conductive backing and a photoconductor which is also useful in the practice of this invention.

An object of this invention is to disclose a method of selectively depositing basic nitrogen containing organic compounds on the surface of a photoconductor thereby producing reproductions in a fast and efficient manner.

Another object of this invention is to disclose a process for preparing colored reproductions by electrophotography. Full colored reproductions are prepared by successively applying substractive primary colors to the surface of the dye-sensitized photoconductor. The method of making colored reproductions from subtractive primaries is described in J. S. Friedmen's "A History of Color Photography," American Photographic Publishing Company, Boston, Mass. (1944).

It has now been discovered that permanent reproductions may be made on the surface of a dye-sensitized photoconductor uniformly bonded to an electrically conductive carrier by selectively depositing a basic nitrogen containing organic compound which is soluble in the presence of an acid and substantially insoluble in water at a pH above 7 by neutralizing the solution with the electrons which are released at the photoconductor-cathode when an electric current passes through the water solution of the basic nitrogen containing organic compound and the conducting areas of the photoconductor-cathode. The photoconductor surface is first exposed to a light source in the selected areas to render the photoconductor conductive in the exposed areas. The photoconductor surface is then contacted with an acid-water solution of the basic nitrogen containing organic compound. An electrical current is then passed through the water solution and the conducting areas of the photoconductor-cathode to neturalize the acid solution at the conducting areas with the electrons which are released at the photoconductor-cathode. In this manner the basic nitrogen containing compound is insolubilized and deposited on the photoconductor at the exposed areas.

The term "dye-sensitized" indicates that the photoconductor has been treated with an organic dyestuff so that radiant energy is absorbed by the dye on the surface of the photoconductor and the energy is transferred to the photoconductor thereby making the photoconductor conductive.

This process may be employed in various ways to prepare permanent photographic reproductions. The preferred method of course is to directly deposit a basic nitrogen containing organic dyestuff directly on the photoconductor. If the basic nitrogen containing organic compound is colorless it may then be dyed or colored in a subsequent step to produce a negative image, or the deposited compound may serve as a protective coating on the surface of the photoconductor and the unprotected areas dyed or modified chemically in some manner, such as by etching away the photoconductor with an acid or solvent. Likewise the compound deposited on the surface of the photoconductor may sufficiently modify the wetting characteristics of the photoconductive sheet. In this manner the two areas will have a differential repellency or attraction to water or oil. The varying of the surface wetting characteristics of the photoconductive sheet is particularly suitable for the production of lithographic plates where the photoconductor is rendered hydrophobic by the deposited compound.

Broadly speaking, the structural formula of the basic nitrogen containing organic compound to be deposited from an aqueous solution in accordance with the teachings of this invention corresponds to the formula

$$M—[NH(CH_2)_{n+1}]_{m-1}NR'(CH_2)_{p+1}NR''_2$$

where M is an organic radical, R' and R'' are hydrogen or an alkyl radical containing up to 18 carbon atoms, m is an integer of less than 4, p is an integer of less than 6 and n is an integer of less than 6. A preferred class of compounds are those that contain an alkyl radical of at least 6 carbon atoms (preferably 10). Especially preferred because of their solubility characteristics are compounds where R' is an alkyl radical of at least 6 carbon atoms (preferably 10) and the R'' radicals are alkyl radicals containing less than 6 carbon atoms. The long chain alkyl radical may also be present in the radical M, as in the case of the amino-polyamides described but is preferably one or more of the R constituents. The preferred class of dyestuffs falling within the above general formula is where M is an organic radical containing a chromogenic nucleus. Illustrative chromogenic nuclei are represented by the following general classes of dyestuffs:

Azo	Quinacridone
Anthraquinone	Thioindigo
Anthrapyridone	Xanthene
Phthalocyanine	

Non-chromogenic basic nitrogen-containing organic compounds corresponding to the above formula are best illustrated by polyamides derived from polybasic acids, particularly polymeric fat acids, such as dimerized linoleic acid, and polyamines containing unreacted amine groupings as evidenced by their high amine members. These compounds may be employed in the production of pigmented images of non-basic nitrogen containing organic compounds.

In the utilization of non-chromogenic basic nitrogen containing organic compounds colorless images may be prepared or the colorless basic nitrogen containing organic compound may be deposited in the presence of colloidal organic or inorganic pigments. For instance, a reaction product of dimerized linoleic acid and an excess of a polyethylenamine having an amine number of about 100 is dissolved in ethanol and acetic acid as a one percent solution. This solution may then be neutralized at the photoconductor-cathode and thereby a colorless insoluble solid is deposited on the surface of the photoconductor. If the solution is mixed with colloidal titanium dioxide, neutralization and deposition of this dispersion results in the producton of white images. If the photoconductor-cathode is some color other than white, the titanium dioxide may be deposited as the white portions of an image. In this manner, a direct positive image is formed.

Carbon black images may be formed by mixing colloidal carbon in the solution. Using this type of dispersion black images are prepared which are completely resistant to the action of light and most atmospheric conditions. As such, they represent one of the most permanent photographic elements attainable.

These basic nitrogen containing organic compounds

are dissolved in water by the formation of a salt with an acid moiety. Suitable organic acids include formic acid, acetic acid, lactic acid, levulinic acid and the like. Suitable inorganic acids include hydrochloric acid, nitric acid, sulfuric acid and the like. The final pH of these solutions is in the range of pH 2 to 7 (preferably 4.5 to 7). These aqueous solutions which are substantially free of positive ions other than those containing the basic nitrogen-containing organic compound are employed at solution concentrations of 0.1 to 5% by weight.

In the drawings, FIGURE 1 is a perspective view of developing apparatus useful in the practice of this invention and FIGURE 2 is a cross-sectional view of FIGURE 1 along section lines 2—2.

Developer tray 10 is composed of a base plate 12, which also serves as an electrode, top clamping frame member 14, and an intermediate open frame member 16 forming upstanding walls around the base plate periphery. Frame member 14 and base plate 12 have cooperating, releasable clamping means 18, which draw these members toward one another when engaged to render the tray 10 water tight.

The open frame member 16 is composed of a nonconductor such as polyethylene, polytetrafluoroethylene or polytrifluorochloroethylene and is provided with a ledge 20 for supporting electrode 22 such that an electrical current passing to electrode 22 from the base plate-electrode 12 passes through a photoconductor sheet 24 which is interposed between the open frame member 16 and the base plate 12. This photoconductor sheet 24 is composed of an electrically conductive carrier 26 which is placed in intimate contact with the base plate 12 and photoconductor particles 28.

In order to selectively deposit images 30 on the photoconductor sheet 24, a solution 32 is placed in the developer tray 10, electrode 22 is connected to the positive terminal of the direct current power source 34 and the base plate 12 is attached to the negative terminal of the power supply 34. When arranged in this manner the electrical current passes through solution 32 and the photoconductive areas of the photoconductive sheet 24 resulting in image deposits 30 on the cathode-photoconductor surface. In order to graphically show the photoconductor particles 28 and the image deposit 30, they have been represented in FIGURE 2 in exaggerated size.

A step-wise procedure for producing an image in accordance with the teachings of this invention is as follows:

(1) The negative electrode from a direct current power supply 34 is attached to the metal base plate thereby making electrical contact with the conductive backing of the photoconductor sheet 24. (2) The photoconductor sheet 24 in the developing tray 10 is exposed to light in selected areas such as by focusing and projecting a photographic negative on the photoconductor sheet 24 through a light projector. (3) The electrode 22 is placed on the ledge 20 and connected to the positive terminal of the direct current power supply 34. (4) The solution 32 is added to the tray. (5) The electrical current is turned on so as to effect the electrolytic development. (6) The solution is poured off and the photoconductor sheet is thoroughly washed with water. After suitable dark adaptation additional images may be put on the photoconductor sheet by repeating the above procedure. An especially useful method for dark adaptation of the photoconductor sheet is to place it in contact with water heated to at least 100° F. which may be accomplished simultaneously with the washing by employing the hot water as the wash water.

Full color reproductions may be obtained by carrying out the above procedure three times with monochromatic light. For example, a color negative is placed in a projector equipped with a photoflood lamp and a red filter is interposed between the photoflood lamp and the photoconductor sheet, preferably between the color negative and the photoflood lamp, thereby exposing the photoconductor sheet selectively to red light. A cyan image is then developed on the photoconductor using a cyan dye. The photoconductive paper is then washed with warm water (heated to at least 100° F.) and dried with a stream of air. The developing tray is then returned to the enlarger and a green filter is interposed between the light source and the photoconductor sheet. After the photoconductor has been exposed selectively to the green light, the above process is repeated using a magenta dye. This procedure is repeated again to produce a yellow image on those areas selectively exposed through a blue filter. In this manner a full "true-to-life" color picture is obtained by electrophotography.

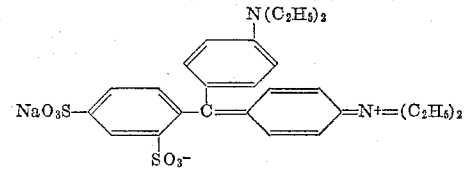
Generally speaking, the light intensity of the projected image, time of exposure which may be from 0.1 second to sixty seconds, and period of electrolytic development which may be from 1 to 30 seconds at a voltage of from 5 to 150 volts are varied in accordance with quality of the image required or desired and the relative effectiveness of the photoconductor surface.

PREPARATION OF PHOTOCONDUCTOR SHEET

(A) A Waring Blendor mixer is employed to thoroughly blend the following ingredients over a period of 15 minutes:

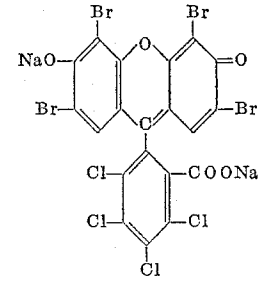
	G.
Methyl-isobutyl ketone	139
Zinc oxide (USP 12) having a particle size of less than 40 microns	252
Binder [30% toluene solution of butadiene (30 parts by weight) and styrene (70 parts by weight) copolymer]	210

Sensitizing dyes are then added to the blend as 0.5% methanol solutions in order to dye-sensitize the photoconductor sheet as follows:



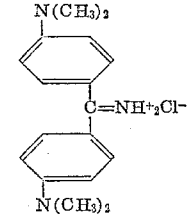
50 cc.

Acid Blue 1*



20 cc.

Acid Red 92*



5 cc.

Basic Yellow 2*

*"Color Index," 2d ed., Chorley & Pickersgill Ltd., Leeds (1956).

After being blended for an additional five minutes and filtered through a coarse "sintered glass" filter, the blend

is coated with a doctor blade coater onto an aluminum sheet (3 mil) to a wet thickness of .006 inch.

When dry and fully dark adapted, this sheet is used to produce reproductions and had high response spectral bands at 460–465 mu, 560 mu and 660 mu.

(B) Zinc oxide, USP 12 (34.4 parts by weight); a binder (29.6 parts by weight), Pliolite S–7, a product of the Goodyear Tire and Rubber Company, Akron, Ohio; and acetone (11.8 parts by weight) were mixed in a ball mill for 8 hours until a smooth dispersion was obtained. This dispersion, diluted with ethyl acetate (23 parts by weight), was mixed with 0.5% methanol dye-sensitizer solutions of "Phosphine R" (2 parts), a product of the General Dyestuff Corporation, and "Xylene Cyanol FF" (0.6 part), a product of British Drug Houses Ltd. The resulting mixture was filtered through a 325 mesh screen and coated at a wet thickness of .007" on a 3 mil aluminum backing. After being dried in a stream of warm dry air and dark adapted by storage in the absence of light for 24 hours, the resulting photoconductor sheet could be used to prepare reproductions in accordance with the teachings of this invention.

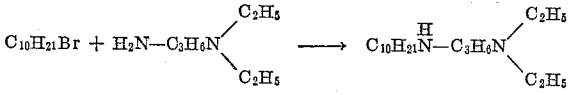
Because of their flexibility, durability, and resistance to crease formation, photoconductor sheet backings prepared by vapor deposition of a metal, such as aluminum, on a paper or plastic backing are especially useful. Polyethylene terephthalate films (5 mil) are preferred.

DYESTUFF PREPARATION

Dyes employed in preparing the colored reproductions in accordance with the teachings of this invention are new and useful compositions of matter. Illustrative preparations of preferred dyes and their intermediates are as follows:

Intermediate preparations:

(I) *Preparation of N-decyl-N',N'-diethyl-1,3-propanediamine*



In a five-liter, three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser and dropping funnel was placed N,N-diethyl-1,3-propanediamine (1950 g., 15 moles). The amine was heated to 125° C. and 1-bromodecane (1106 g., 5 moles) was added with stirring at a rate sufficient to maintain the exothermic reaction at about 130–140° C. The reaction mixture was stirred for an additional hour at a temperature of 125–135° C., then cooled to room temperature. Sodium methoxide (250 g., 5 moles) was added to neutralize the hydrobromic acid formed. Upon cooling to room temperature a solid separated which was removed by filtration and washed with petroleum ether. Unreacted amine and solvent were removed by distillation.

N-decyl-N',N'-diethyl-1,3-propanediamine (1080 g.) having a boiling point of 130° C. at 1 mm. pressure was then collected by vacuum distillation.

(II) *Preparation of N-(2-cyanoethyl)-N-decyl-N',N'-diethyl-1,3-propanediamine*

In a two-liter, one-necked flask with thermometer well were placed acrylonitrile (250 g., 4.70 moles) and N-decyl-N',N'-diethyl-1,3-propanediamine (1013 g., 3.76 moles). The flask was fitted with a reflux condenser and heated on a mantle to gentle reflux. The mixture was heated three days at a temperature not exceeding 110° C.

Unreacted acrylonitrile was removed at reduced pressure and 1206 grams of unpurified N-(2-cyanoethyl)-N-decyl-N',N'-diethyl-1,3-propanediamine were recovered.

(III) *Preparation of N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine*

In a three-liter, three-necked flask equipped with stirrer, reflux condenser and dropping funnel were placed lithium aluminum hydride (114 g., 3.00 moles) and diethyl ether (750 ml.) in an atmosphere of dry nitrogen. After a 15 minute period of refluxing and stirring, N-(2-cyanoethyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (969 g., 3.00 moles) was added slowly so as to produce only moderate reflux. The reaction mixture was stirred and refluxed for 5 hours after all the nitrile had been added and allowed to stand overnight under dry nitrogen. Excess hydride was decomposed by the addition of ethyl acetate (264 g., 3.00 moles) slowly so as to produce a gentle reflux. The resulting mixture was hydrolyzed by the cautious addition of water (270 g., 15.0 moles) accompanied by external cooling and the addition of ether to facilitate stirring. The solution was filtered to remove insoluble inorganic salts, distilled through a 15-inch Vigreux column, and redistilled to produce N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (499 g.) having a boiling range of 160° C./1.2 mm. Hg to 170° C./0.9 mm. Hg.

(IV) *Preparation of N^1-(3-diethylaminopropyl)-N^1-decylsulfanilamide*

A solution of N-decyl-N',N'-diethyl-1,3-propanediamine (135 g., 0.5 mole) in 100 ml. of benzene was treated with p-acetylaminobenzenesulfonyl chloride (120 g., 0.5 mole). The resulting homogeneous solution was stirred for 1 hour. After removing the solvent, the residue was treated with 200 ml. of water and 100 ml. of concentrated hydrochloric acid. This mixture was heated on a steam bath for six hours. N^1-(3-diethylaminopropyl)-N^1-decylsulfanilamide which separated as an oil was precipitated by the addition of an excess of alkali.

YELLOW DYE PREPARATIONS

(A) *Preparation of alpha, alpha'-bis-[4-(N-(3-diethylaminopropyl)-N-decyl)sulfamylphenylazo] - 4,4'-bi-o-acetoacetotoluidide*

N^1-(3-diethylaminopropyl)-N^1-decylsulfanilamide (80 g., 0.2 mole) was dissolved in 75 ml. of glacial acetic acid, and diluted with 100 ml. of water. This solution was poured into a mixture of ice (500 g.) and concentrated hydrochloric acid (75 ml.). The resulting solution was then diazotized by the rapid addition of 5 N sodium nitrite solution (40 ml.). Additional ice was added to keep the mixture cold and the solution treated rapidly while stirring with a solution consisting of 34 g. (0.09 mole) of "Naphtol AS-G Supra," a product of General Aniline & Film Corp., dissolved in 750 ml. of dimethylformamide and 150 ml. of pyridine. More ice and water were added to insure good cooling and stirring. After one-half hour the dye was completely precipitated by the addition of concentrated ammonium hydroxide (300 ml.) and the product collected by filtration. The resulting yellow dye was washed with water and ethanol and was then crystallized from a mixture of dimethylformamide and ethanol.

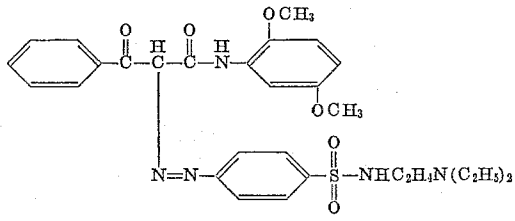
(The diazo from N'-(3-diethylaminopropyl)-N'-decylsulfanilamide was also reacted with the coupler N-(2-naphthyl)-3-hydroxy-2-naphthamide to produce a reddish dye and with various salicylamides to produce yellow dyes.)

(B) *Preparation of alpha,alpha'-bis[4-(4-decyl-8-ethyl-4,8-diazadecyl)sulfamylphenylazo] - 4,4' - bi-o-acetoacetotoluidide*

Alpha, alpha' - bis[4-(4-decyl-8-ethyl-4,8-diazadecyl)-sulfamylphenylazo]-4,4'-bi-o-acetoacetotoluidide was pre-

pared by reacting the diazo prepared from N^1-(4-decyl-8-ethyl-4,8-diazadecyl)sulfanilamide with Naphthol AS-G in a manner similar to Preparation A above.

(C) *Preparation of alpha-[4-(2-diethylaminoethyl)-sulfamylphenylazo]-2',5'-dimethoxybenzoylacetanilide*



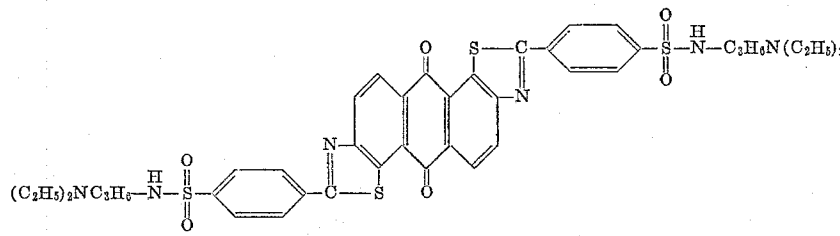
This yellow dye was prepared in the same manner as Preparation A above using N^1-(2-diethylaminoethyl)sulfanilamide and a coupler prepared by an ester-amide interchange reaction between ethyl benzoylacetate and 2,5-dimethoxyaniline as the intermediates.

A solution of 45 g. (0.22 mole) of isophthalyl chloride in 500 ml. of xylene was heated to near reflux and 1-aminoanthraquinone (23 g., 0.1 mole) was added slowly while stirring. The mixture was heated at reflux until the evolution of hydrogen chloride ceased. The hot mixture was then treated with decolorizing carbon and filtered. After the filtrate was cooled in ice, a solid was collected, washed with xylene and recrystallized from fresh xylene.

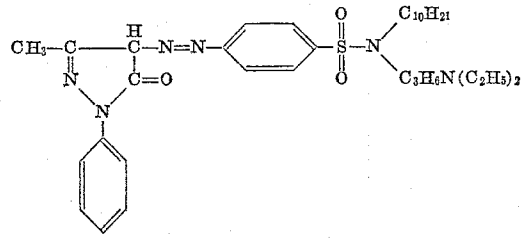
The recrystallized product was added slowly to a solution of N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (22 g., 0.067 mole) in 50 ml. of toluene. After being heated on a steam bath for one hour, the reaction product was precipitated with 300 ml. of ligroin, collected and dried. The crude product was then dissolved in hot ethanol and filtered. Upon dilution with water, a yellow dye precipitated from the filtrate which was collected and dried.

The corresponding terephthalyl derivative was prepared in a similar manner.

(F) *Preparation of 2,8-bis[4-(3-diethylaminopropyl)-sulfamylphenyl] - dithiazo[5,4-a]-[5,4-h]-6,12-anthraquinone*

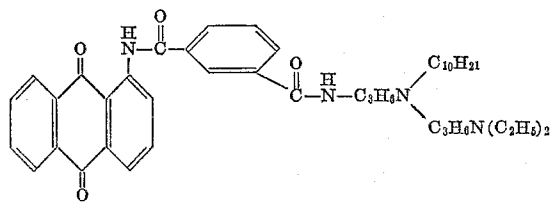


(D) *Preparation of 4-[4-(N-(3-diethylaminopropyl)-N-decyl)sulfamylphenylazo]-3-methyl-1-phenyl - 5 - pyrazolone*



A solution of the diazo (0.05 mole) prepared as shown in Preparation A above was added rapidly with stirring to a solution of 3-methyl-1-phenyl-5-pyrazolone (9 g., 0.05 mole) in a mixture of 100 ml. dimethylformamide and 100 ml. pyridine. Ice was added and after one-half hour the yellow dye was precipitated with ammonium hydroxide and then washed with water, filtered and dried.

(E) *Preparation of N-(4-decyl-8-ethyl-4,8-diazadecyl)-N'-(1-anthraquinonyl)isophthalamide*

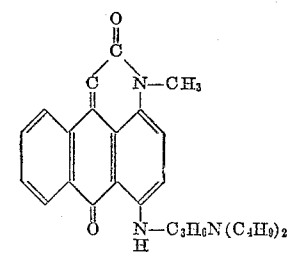


Algol Yellow GC, a product of General Aniline & Film Corp., was purified by water and acetone extraction. Ten grams of the dried material were added to chlorosulfonic acid (50 ml.). The mixture was then heated and stirred at 135–140° C. for 2 hours. The reaction mixture was then cooled and poured onto ice. A yellow green solid was collected by filtration and washed with water and dried.

Two grams of the yellow green solid were dissolved in N,N-diethyl-1,3-propanediamine (10 g.). This solution was diluted with water and a large excess of ammonium hydroxide added. The precipitated product was collected, washed with water and then extracted with methanol.

MAGENTA DYES

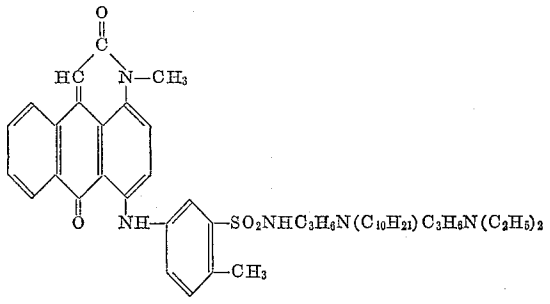
(G) *Preparation of 1'-methyl-4-(3-dibutylaminopropylamino)anthrapyridone*



1'-methyl-4-bromoanthrapyridone (10 g.) and N,N-dibutyl-1,3-propanediamine (20 ml.) were heated at 160–180° C. to yield a deep magenta colored solution. The reaction mixture was diluted with toluene, cooled and a solid product collected, which was transformed to a gum by triturating with ammonium hydroxide. After mixing the gum with concentrated hydrochloric acid and diluting the mixture with acetone, 1'-methyl-4-(3-dibutylaminopropylamino)anthrapyridone was obtained as a crystalline solid.

4-toluidino)anthrapyridone (7.0 g., 0.0151 mole). The reaction mixture was stirred and heated on the steam cone for one hour and allowed to stand at room temperature for 16 hours. The reaction mixture was then mixed with water (500 ml.), made basic with concentrated ammonium hydroxide, and filtered. The collected solid was washed with water and with petroleum ether and dried at reduced pressure to yield 1'-methyl-4-[3-(4-decyl-8-ethyl - 4,8 - diazadecylsulfamyl)-4-toluidino]anthrapyridone (8.4 g.).

(H) *Preparation of 1'-methyl-4[3(4-decyl-8-ethyl-4,8-diazadecylsulfamyl)-4-toluidino]anthrapyridone*

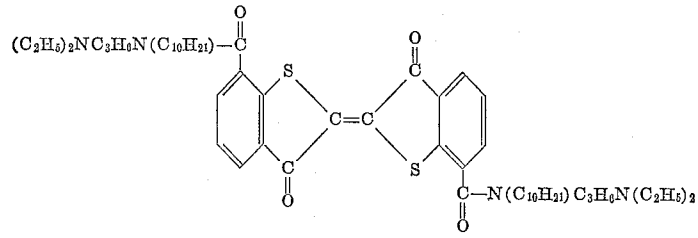


Alizarine Rubinol R–CF (200 g.), a product of the General Dyestuff Company, was mixed with water (2 liters) and heated on a steam bath. The mixture was made strongly acidic with concentrated hydrochloric acid and stirred and heated until the solid turned dark red. The mixture was filtered and the solid was washed with water. After dispersing the solid in a dilute sodium chloride solution (1 liter) the mixture was made basic with sodium carbonate, heated on a steam bath, and filtered. The purified product was dried at reduced pressure at 100° C. for 24 hours.

Phosphorus oxychloride (250 ml.) was added with cooling to the finely powdered purified Alizarine Rubinol R-CF (46.8 g., 0.1 mole). To this mixture was added with cooling phosphorus pentachloride (46 g., 0.22 mole). The mixture was then stirred at room temperature for one and one-half hours. The reaction mixture was filtered through a sintered glass funnel. The filter cake was stirred vigorously into ice to hydrolyze excess phosphorus halides. This mixture was filtered and the solid was washed with cold water. The damp cake was stirred into hot nitrobenzene (500 ml.) and dry magnesium sulfate was added to help remove water. After removal of the water, the mixture was filtered through a sintered glass funnel. Upon standing overnight at room temperature crystals of 1' - methyl - 4 - (3-chlorosulfonyl-4-toluidino)anthrapyridone were formed and removed from the filtrate by filtration, washed with heptane and twice with petroleum ether.

To a mixture of N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (10 g., 0.0306 mole) and pyridine (50 ml.) was added 1'-methyl-4-(3-chlorosulfonyl-

(I) *Preparation of N,N'-bis(3-diethylaminopropyl)-N,N'-didecylthioindigo-7,7'-dicarboxamide*



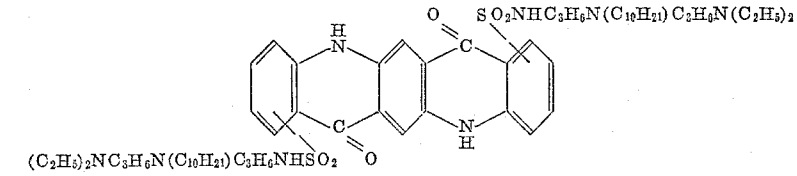
3-hydroxythionaphthene-7-carboxylic acid was prepared from phenyl-1-thioglycollic-2-carboxylic acid by the method described in British Patent 360,349.

3-hydroxythionaphthene-7-carboxylic acid (0.3 mole) was dissolved in water (1 liter) containing sodium carbonate monohydrate (40 g., 0.32 mole). To this was added with stirring a solution of potassium ferricyanide (218 g., 0.66 mole) in water (700 ml.). An additional amount of sodium carbonate monohydrate (40 g., 0.32 mole) was added to keep the mixture alkaline. The mixture was stirred about one and one-half hours and filtered. The filter cake was mixed with water (700 ml.), and the resulting mixture was made strongly acid with concentrated hydrochloric acid and filtered. The solid collected was washed with dilute hydrochloric acid, and acetone, and dried under vacuum at 75° C. to produce thioindigo-7,7'-dicarboxylic acid (38 g.).

To a mixture of phosphorus pentachloride (12 g., 0.057 mole) and phosphorus oxychloride (70 ml.) was added thioindigo-7,7'-dicarboxylic acid (10 g., 0.026 mole). This was heated slowly to 90–95° C. on the steam bath with stirring, and maintained at that temperature for 5 hours. The red solid obtained by filtering the reaction mixture was washed with benzene, filtered, washed with benzene, and washed with petroleum ether to produce thioindigo-7,7'-dicarbonyl chloride (10 g.).

To a mixture of N-decyl-N',N'-diethyl-1,3-propanediamine (2.9 g., 0.011 mole) and benzene (80 ml.) was added thioindigo-7,7'-dicarbonylchloride (2.1 g., 0.005 mole). The mixture was stirred and refluxed about 5 hours. The solvent was removed at reduced pressure. The residue was dissolved in water (400 ml.) with vigorous agitation, and this solution was made alkaline with ammonium hydroxide solution. A small amount of saturated sodium chloride solution was added to agglomerate the dye, and the mixture was filtered. The solid N,N'-bis - (3 - diethylaminopropyl)-N,N'-didecylthioindigo-7,7'-dicarboxamide was washed twice with water in which it became increasingly soluble and dried to produce an ultimate yield of 4 grams.

(J) *Preparation of X,X'-bis(4-decyl-8-ethyl-4,8-diazadecylsulfamyl)quinacridone*

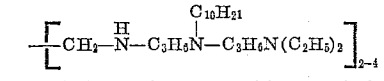


In a 2-liter, 3-necked flask equipped with stirrer, thermometer, and gas outlet tube connected to a calcium chloride-filled drying tube and cooled in an ice bath was placed chlorosulfonic acid (1.00 liter, 15.2 moles). Quinacridone (100 g., 0.32 mole), which had been dried in a vacuum oven at 90° C. was added so that the temperature of the reaction mixture did not exceed 20° C. The mixture was stirred at room temperature for 4 days at which time the reaction mixture was divided into 2 portions. Each portion was added slowly with stirring to acetone (2.5 liters) which was cooled in an ice bath so that the temperature did not exceed 25° C. The resulting mixture was filtered. The solid was washed with acetone and petroleum ether and dried to yield 136 grams of quinacridone-X,X'-disulfonyl chloride.

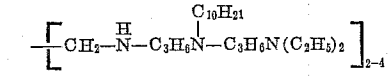
In a one-liter, three necked flask with stirrer and condenser was placed N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (100 g., 0.306 mole) and pyridine (650 ml.). To this was added with stirring quinacridone-X,X'-disulfonyl chloride (77 g., 0.152 mole). This mixture was stirred and heated on the steam bath for 24 hours. The reaction mixture was poured with stirring into water (1 liter), and concentrated ammonium hydroxide (100 ml., 1.5 moles) was added. The resulting mixture was stirred and digested, then filtered. The filter cake was washed with water, digested and filtered. The solid product was washed with acetone, digested and filtered. The resulting filter cake was washed twice with acetone and dried at reduced pressure to produce a yield of 110 grams of the magenta dye, X,X'-bis(4-decyl-8-ethyl-4,8-diazadecylsulfamyl)quinacridone, whose color purity was improved by trituration with warm N,N-dimethylformamide.

CYAN DYES

(K) *Preparation of copper phthalocyanine*

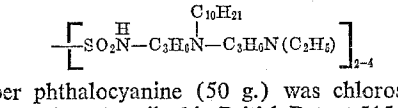


Copper phthalocyanine was chloromethylated in the manner described in British Patent 586,341. The tetrachloromethyl derivative thus obtained (4 g., 0.005 mole) was added to a solution of N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (15 g., 0.05 mole) in 50 ml. of dimethylformamide. The mixture was stirred at reflux for one hour and then allowed to cool. The precipitated solid was collected, and washed with dimethylformamide and ethanol and suspended in ethanol. The product was converted to the hydrochloride by the addition of an excess of concentrated hydrochloric acid to an ethanol suspension and the hydrochloride of copper phthalocyanine

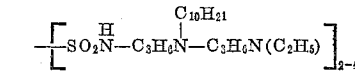


was collected by filtration, washed with acetone and dried.

(L) *Preparation of copper phthalocyanine*



Copper phthalocyanine (50 g.) was chlorosulfonated by the procedure described in British Patent 515,637. The damp cake of the tetrasulfonyl chloride was stirred vigorously with a mixture of ice and N-(3-aminopropyl)-N-decyl-N',N'-diethyl-1,3-propanediamine (130 g., 0.4 mole). After one hour the reaction mixture was poured with stirring into 500 ml. of water containing 200 ml. of concentrated hydrochloric acid. The precipitated hydrochloride of copper phthalocyanine



was collected, washed with cold water and dried.

SOLUTION PREPARATIONS

The basic nitrogen containing compounds, such as are illustrated by Preparations A to L above, are dissolved in water in the presence of an acid. The solution concentration and acid employed may vary. Preferably, the compounds are dissolved as the acetate or hydrochloride salts in 0.5 to 2% aqueous solution. Illustrative solutions of the compounds shown in Preparations A to L which may be used to form colored deposits on a photoconductor sheet are as follows:

(*a*) *Cyan solution.*—The cyan dye (40 g.) from Preparation L was triturated with 200 ml. of hot absolue ethanol and gradually diluted with 150 ml. of water. The resulting homogeneous solution was poured rapidly with vigorous stirring into 1500 ml. of water. The solution was filtered and made up to 2 liters with water.

(*b*) *Magneta solution.*—The magenta dye (4 g.) from Preparation J was mixed with ethanol (40 ml.), glacial acetic acid (0.58 ml.) and water (360 ml.) with constant heating and stirring until the mixture was homogeneous.

(*c*) *Yellow solution.*—The yellow dye (16 g.) in the form of the terephthalyl derivative from Preparation E was dissolved in absolute ethanol (80 ml.) and concentrated hydrochloric acid (2.8 ml.) and was diluted to 800 ml. with water.

A colorless solution suitable for use in the process of this invention was prepared as follows:

The polyamide reaction product of polymeric fat acids and a polyamine having unreacted amine groups, "Versamid 100," a product of General Mills, Inc. (27.5 g.), was boiled gently with 110 ml. of absolute ethanol until dissolved. A solution of 1.8 ml. of concentrated hydrochloric acid in 100 ml. of water was added and the solution diluted to 1350 ml. with water.

Solutions especially useful for the deposition of dye images by electrophotography are obtained by mixing this colorless solution with a dye solution. For instance, 50 g. portions of this colorless solution in admixture with 100 g. portions of solutions (*a*), (*b*) and (*c*) were found to be especially useful for the production of colored images. This colorless stock solution can, of course, also be deposited by itself or in admixture with other pigments. For instance, white images are obtained by using the solution in admixture with dispered titanium dioxide in the following developmental procedure. Black images are obtained using dispersed carbon particles in this solution.

The procedure employed to prepare reproductions by the deposition of the basic nitrogen-containing organic compounds, including the various dyestuffs shown in Preparations A to L and the colorless amine-containing

polyamides, on the surface of a zinc oxide photoconductor sheet prepared as described was as follows:

(1) The negative electrode from a direct current power supply was attached to the metal base of a developer tray as illustrated in FIGURES 1 and 2 of the drawings thereby making electrical contact with the aluminum backing of the photoconductor sheet.

(2) The photoconductor sheet retained in the developer tray was exposed to a light source in the selected areas by projecting an image on the photoconductor sheet with the projector having a low *f* stop projection range and a 500 watt tungsten projection lamp as the light source, thereby rendering select areas conductive. Relative humidity of the atmosphere in the work area should be less than 40 percent.

(3) An electrode attached to the positive terminal was placed in the developer tray and the various solutions were added to the tray.

(4) After a total lapse of time of about 20 seconds after exposure, a 30 volt electrical current was then passed through the photoconductor at the conductive areas for a period of 10 seconds.

(5) The solution was removed from the developer tray and the photoconductor sheet was thoroughly washed with water.

(6) If the photoconductor sheet was to be re-exposed, it was placed in contact with water heated to 140° F. for a period of at least 20 seconds to restore it to a dark adapted state and the sheet was then dried by placing it under a stream of air.

By this procedure colored images were selectively deposited on the exposed interface of the photoconductor sheet using solutions of the dyestuffs shown in Preparations A to L. A preferred combination of solutions for preparing a "true-to-life" colored reproduction are solutions (*a*), (*b*), and (*c*) above whereby the yellow dye (solution (*c*)) is deposited first, the magneta dye (solution (*b*)) is deposited second, and the cyan dye (solution (*a*)) is deposited third.

We claim:

1. A method for selectively depositing a basic nitrogen-containing organic compound which is water soluble in the presence of an acid and substantially insoluble in water at a pH above 7 on the surface of a photoconductor bonded to an electrically conductive carrier which comprises exposing said photoconductor to a light source in the selected areas thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of said basic nitrogen-containing organic compound having a substituent group of the general structural formula

$$-[NH(CH_2)_{n+1}]_{m-1}NR'(CH_2)_{p+1}NR''_2$$

where R′ and R″ are selected from the group consisting of hydrogen and alkyl radicals containing up to 18 carbon atoms, *m* is an integer less than 4, *p* is an integer less than 6, and *n* is an integer less than 6, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting areas with the electrons which are released at the photoconductor-cathode, and depositing the insolubilized compound on the photoconductor at the exposed areas.

2. A method for selectively depositing a basic nitrogen-containing organic compound which is water soluble in the presence of an acid and substantially insoluble in water at a pH above 7 on the surface of a photoconductor bonded to an electrically conductive carrier which comprises exposing said photoconductor to a light source in the selected areas thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of said basic nitrogen-containing organic compound having a substituent group of the general structural formula

$$-[NH(CH_2)_{n+1}]_{m-1}NR'(CH_2)_{p+1}NR''_2$$

where R′ and R″ are selected from the group consisting of hydrogen and alkyl radicals containing up to 18 carbon atoms and at least one R is an alkyl radical containing at least 6 carbon atoms, *m* is an integer less than 4, *p* is an integer less than 6, and *n* is an integer less than 6, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting areas with the electrons which are released at the photoconductive-cathode, and depositing the insolubilized compound on the photoconductor at the exposed areas.

3. A method for selectively depositing a basic nitrogen-containing organic compound which is water soluble in the presence of an acid and substantially insoluble in water at a pH above 7 on the surface of a photoconductor bonded to an electrically conductive carrier which comprises exposing said photoconductor to a light source in the selected areas thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of said basic nitrogen-containing organic compound having a substituent group of the general structural formula

$$-[NH(CH_2)_{n+1}]_{m-1}NR'(CH_2)_{p+1}NR''_2$$

where R′ is an alkyl radical containing at least 6 carbon atoms, R″ is an alkyl radical containing less than 6 carbon atoms, *m* is an integer less than 4, *p* is an integer less than 6, and *n* is an integer less than 6, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting areas with the electrons which are released at the photoconductor-cathode, and depositing the insolubilized compound on the photoconductor at the exposed areas.

4. A method for preparing a multi-colored reproduction by selectively depositing colored basic nitrogen-containing organic compounds which are water soluble in the presence of an acid and substantially insoluble in water at a pH above 7 on the surface of a photoconductor bonded to an electrically conductive carrier which comprises exposing said photoconductor to a monochromatic image from a light-image of a colored subject thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of a basic nitrogen-containing organic compound, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting areas with the electrons which are released at the photoconductor-cathode, depositing the insolubilized compound on the photoconductor at the exposed areas, desensitizing the photoconductor to remove any latent image and to restore the photoconductor to its dark adapted state, exposing said photoconductor to a second monochromatic image from a light-image of said colored subject thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of a second basic nitrogen-containing organic compound, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting areas with the electrons which are released at the photoconductor-cathode, depositing the insolubilized compound on the photoconductor at the exposed areas, desensitizing the photoconductor to remove any latent image and to restore the photoconductor to its dark adapted state, exposing said photoconductor to the third monochromatic image from a light-image of said colored subject thereby rendering the exposed areas electrically conductive, contacting the exposed areas with an acid solution of a third basic nitrogen-containing organic compound, passing an electrical current through the water solution and the conducting areas of the photoconductor-cathode thereby neutralizing the acid solution at the conducting

areas with the electrons which are released at the photoconductor-cathode, and depositing the insolubilized compound on the photoconductor at the exposed areas, the basic nitrogen-containing compound in each instance having a substituent group of the general structural formula

$$\text{-}NH(CH_2)_{n+1}]_{m-1}NR'(CH_2)_{p+1}NR''_2$$

where R' and R'' are selected from the group consisting of hydrogen and alkyl radicals containing up to 18 carbon atoms *m* is an integer less than 4, *p* is an integer less than 6, and *n* is an integer less than 6.

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