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DIAZO PRINT PROCESS

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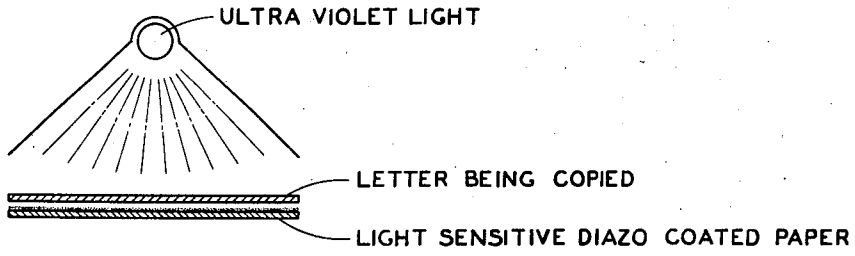


FIG. 1

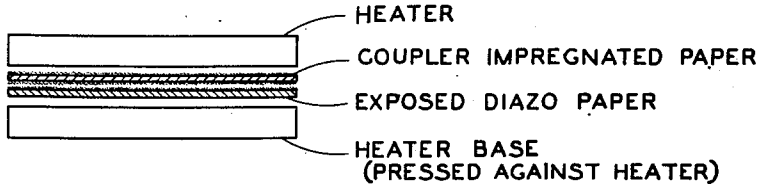


FIG. 2

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DIAZO PRINT PROCESS

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This invention relates to the production of prints from light sensitive diazo materials.

The process of making positive prints of drawings, letters, photographs, etc. by the use of light sensitive diazo compounds is well known. Two general methods are in extensive commercial use.

The first of these processes involves the use of a paper which supports a light sensitive layer containing both a diazo compound and a coupler, together with acids and other stabilizing substances designed to prevent thermal decomposition of the diazo as well as premature coupling between the diazo and coupler. Following exposure of the layer to light under a pattern such as a letter, color development is brought about by exposing the paper to hot aqueous ammonia fumes at a temperature of about 180° F. Since both the diazo and coupler are intimately mixed in the same layer, it is clear that severe restrictions are placed on the choice of the diazo coupler pair if premature coupling is to be avoided. Precoupling frequently takes place after relatively short storage periods with the result that the background areas are no longer white but badly discolored. The principal objection to this process, however, is the use of ammonia fumes which are impractical for use in such places as metropolitan office buildings. Machines designed to handle ammonia are relatively expensive because of the necessity for making them corrosion resistant. Furthermore, they often require the installation of expensive venting and exhaust equipment for the removal of ammonia fumes.

The second type of diazotype process which is in extensive use involves a paper coated with a diazo and a stabilizing substance, but not containing a coupler. Following exposure to light, development is brought about by coating the latent diazo image with a solution of a coupling compound in aqueous alkali. While this process eliminates the use of ammonia development, several difficulties are introduced which more than compensate for the advantages gained. The handling of corrosive solutions is difficult and hazardous. The choice of a suitable diazo and a coupler is limited. The developing solutions which contain alkali discolor on standing, weaken the fiber and discolor the background of the paper. The dye formed by the diazo and coupler must be exceedingly wash-fast, since it is formed under wet conditions favorable to bleeding. Other disadvantages include the need for drying the wet print and the difficulties incurred in changing from one color to another involving time consuming cleaning of the developing apparatus.

A number of heat developing systems have been proposed which involve the formation of a dye by the action of heat or both heat and moisture on the sensitive layer and in which ammonia or wet development are not involved. In such systems, the diazo component used is

usually of the fast coupling or wet development type and when in contact with a coupler, premature coupling difficulties are encountered. Attempts to prevent precoupling include the separation of the diazo and coupler, as by dusting powdered coupler onto a diazo coated paper, but under conditions of moderate to high humidity, precoupling may still occur. This operation is not only a time consuming operation since the excess of powdered coupler has to be brushed off, but it results also in pictures of non-uniform dye intensity.

It has also been proposed to incorporate the coupler in a gelatin coating which is placed in contact with the exposed paper which contains the diazo compound. Coupling under these conditions is obviously very slow and leads only to very faint images. If the gel is heated to accelerate coupling, offset occurs and the gel transfers to the diazo paper while some of the diazo is adsorbed by the gel. The print obtained is messy and the gelatin coating containing the coupler cannot be re-used.

It has also been proposed to incorporate the coupler and the diazonium compound on the opposite side of a sheet of paper. This procedure does not prevent precoupling since the two ingredients ultimately diffuse and migrate until they are intermingled.

It has further been suggested to use aryl diazosulfonates which do not couple with azo components in the presence of alkali such as ammonia but only couple when heated. These materials show some tendency to precouple at room temperatures, which becomes even more pronounced when the materials are stored at the relatively high temperatures and humidities of the summer months.

Still another process utilizes a diazo type paper without coupler which is exposed and then subjected to vapors of aromatic amines such as naphthylamine at ordinary or elevated temperatures.

This latter system suffers from many disadvantages as follows:

(1) The aromatic amines which have to be volatile, are exceedingly toxic materials. They cause eczema when contacted with the skin and may cause malignancies in susceptible individuals after prolonged exposure to their vapors.

(2) They have a pronounced and unpleasant odor.

(3) They are undesirable as coupling components because they cause a bad background color on standing for a few days.

(4) The time of development required is far beyond any practical duration for a diazo development process, i. e., about ten minutes.

(5) A distinct shift in the shade by the dye formed from the amino coupler occurs on standing or handling.

(6) The selection of colors obtainable with this process is limited and the spectral quality of colors obtained is poor.

It is, therefore, an object of the present invention to provide a process for making diazo prints without resorting to the use of ammonia vapors or volatile aromatic amines.

It is a further object of the present invention to provide a process for making prints from light sensitive diazo materials without the use of alkaline processing.

It is a further object of the present invention to provide a process for making prints from light sensitive diazo materials which are not subject to precoupling of the diazo with a coupler.

It is a further object of the present invention to provide

a process for making multicolored prints from light sensitive diazo materials.

These and other objects are attained by the process of this invention which comprises exposing a material sensitized by means of a light sensitive diazo compound to actinic light under a pattern; subsequently contacting the exposed material with a fibrous, absorbent carrier material impregnated with a coupler capable of thermal transfer or vapor distillation, and heating the two materials while in direct contiguous contact with each other in the presence of vapor. The coupler may be selected from the group consisting of such phenols, naphthols, and compounds containing a reactive methylene group which are free of primary amino groups.

We have found that the thermal transfer development takes place at temperatures between 140° C. and 225° C. and preferably between 160° C. and 190° C. At these temperatures, the layers containing the light sensitive diazo compounds can be essentially completely developed within a fraction of a minute in the absence of ammonia, dilute alkali or volatile aromatic amines.

The light sensitive diazo compounds preferably used with the present invention are those which we shall describe as "fast" or rapidly coupling diazos including those which are found useful in the "wet" process of diazo development. The following are illustrations of suitable diazo compounds. All of them are derivatives of p-phenylenediamines which are mono- or di-substituted on one of the two amino groups while the primary amino group is converted into a diazo group.

4-benzoylamido-2,5-diethoxybenzene diazonium chloride
4-benzoylamido-2-chloro - 5 - methoxybenzene diazonium chloride
4-benzoylamido-2,5-dimethoxybenzene diazonium chloride
3-chloro-4-diethylaminobenzene diazonium chloride
4-benzoylamido-2-methoxy-5-methylbenzene diazonium chloride
4-(N-ethyl-N-benzyl)aminobenzene diazonium chloride
4-phenylaminobenzene diazonium sulfate
2-methoxy - 4 - phenylaminobenzene diazonium chloride (2'-methoxy-4-diazodiphenylamine chloride)
4-(4'-methoxyphenyl)aminobenzene diazonium chloride (4-diazo-4'-methoxydiphenylamine chloride)

These diazo compounds are used in the form of their stabilized salts as exemplified by the 4-diphenylamino diazonium sulfate or in the form of their zinc chloride or boron trifluoride double salts. These diazonium salts are employed in concentrations ranging from 1.5% to 10% based on the volume of the coating solutions. They may be used alone or as mixtures.

The diazo compounds are coated in the usual manner upon a suitable support or carrier. Suitable carriers for the diazo solutions include not only various types of paper such as ordinary wood pulp paper, rag type paper or document paper but also textiles including fabrics made from cotton, cellulose acetate, batiste regenerated cellulose of the xanthate or viscose type, rayon, balloon cloth, knitted rayon jersey, mixed cotton and rayon, silk or other fibrous, absorbent woven or felted materials which can be impregnated with the diazo solutions.

The coating solutions are neutral or contain preferably a stabilizing amount of an acid such as citric, tartaric, boric, sulfo salicyclic, phosphoric or 1,3,5-naphthalene trisulfonic acid in concentrations ranging from 1.5 to 7.5 percent based on the volume of the coating solution. The coating solutions further contain an anti-oxident such as urea, thiourea, allyl isothiocyanate and the like, in concentrations ranging from 2.5 to 15 percent. These anti-oxidizing agents improve the whiteness of the burned out areas and increase the brightness and the density of the developed dyes.

The couplers used include those azo components which are substantially non-volatile at temperatures below 100° C. but are capable of thermal transfer or diffusion or distillation in the presence of vapor particularly superheated steam but are otherwise non-volatile at temperatures between 140° C. and 225° C. excluding couplers which contain, in addition to the phenolic or reactive methylene group, an amino group. Aromatic amines are not suitable because they tend to darken in color when exposed to air. Inasmuch as an excess of aromatic amines will always accumulate in the white areas of the print, this gradual darkening of the amine leads to a darkening of the background upon aging. Couplers containing saltlike groups such as the alkali salts of sulfonic acid groups cannot be used because they do not undergo thermal transfer. The components may be incorporated in the absorbent support such as cloth, felt, paper, blotting paper, saturation paper or newsprint by padding, impregnating or coating the support with a solution of the coupler in a volatile solvent, for instance, water, dimethyl formamide or an aliphatic alcohol such as ethanol, n-propanol, isopropanol, isobutyl alcohol or tert.-alcohol.

The carrier can also contain a small amount of a neutral hydroxyl-containing liquid boiling between 100° C. and 235° C., for instance, water, a higher boiling alcohol, e. g., n-hexyl alcohol, n-heptyl alcohol, 3-heptanol, 4-heptanol and 2-octanol or a glycol, e. g., ethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol and 2,3-butane diol which provides upon heating, the vapor for the distillation of the coupler. The amounts used are at least equal and do not exceed by more than a factor of five, the amount of coupler employed in the coating solution.

Where water is employed as the neutral hydroxyl-containing liquid, the moisture is provided by the presence of a humectant or hygroscopic agent capable of retaining a small amount of water in the carrier after drying in air at room temperature or at moderately elevated temperatures. Suitable humectants include glycerol, diethylene glycol (2,2'-oxydiethanol) and the higher polyalkylene glycols, hexitols such as sorbitol, apple honey derived from the sugar mixtures of cider, acetamide, sodium sulfate, potassium acetate and the like. Although the carrier containing the coupler is air dry and appears dry to the touch, it contains an amount of moisture commensurate to the ability of the humectant to retain or store water at room temperatures and to give it off at temperatures between 140° C. and 225° C. The amount of water expandable upon heating will vary with the hygroscopic properties of the humectant and relatively higher or lower amounts of humectants have to be used depending on the amount of water made available by the humectant. In general, the weight of the humectant is at least equal and does not exceed by more than a factor of five, the amount of coupler employed in the coating solution.

The absorbent carrier impregnated with the coupler can be re-used to make more than a hundred prints. If a humectant be used, it re-absorbs moisture within a short time. However, if the impregnated coupler carrier is to be used for printing in rapid succession or if no humectant be used, it becomes necessary to accelerate the re-absorption of the vapor providing liquid by placing the carrier briefly in an atmosphere saturated with vapors of said liquid. A further increase in rapid printing speed can be achieved by contacting during the heat printing step, the coupler material with a blotting paper or felt moistened with said liquid. If moist heat, for instance, super-heated steam is used in the developing process, the humectant may be omitted from the developing carrier.

The useful couplers may be selected from the group consisting of phenols, naphthols in which the phenolic hydroxyl group is the only coupling directing group and compounds containing a reactive methylene group, such as set forth in "The Aromatic Diazo Compounds and

Their Technical Applications" by K. H. Saunders. The following list illustrates the various shades obtained with different couplers using 4-benzoylamido-2,5-diethoxybenzene diazonium chloride.

Coupler	Shade
Phloroglucinol	Black.
Resorcinol	Brown.
2,3-Dihydroxy naphthalene	Purplish Blue.
1-Phenyl-3-methyl pyrazolone	Orange.
3-Methyl pyrazolone	Orange Red.
β-Naphthol	Purplish Red.
Acetoacetanilide	Golden Yellow.
o-Acetoacetanisidide	Lemon Yellow.
Dimethyldihydroresorcinol	Orange Red.
α-Resorcylic acid	Brown.
4,4'-Biresorcinol	Brown.
p-Carboxyacetoacetanilide	Yellow.
1-Phenyl-3-carboxypyrazolone-5	Pale Red.
3-Carbmethoxy-2-naphthol	Tan.

Thus, it is seen that a large number of couplers, which are not dependent upon a basic amine group for activity, can be used to produce prints of good density, in a variety of colors having white backgrounds.

The following examples serve to illustrate our invention but the invention is not limited thereto.

Example I

Twenty one pound paper is coated with a solution containing 2 parts of 2,5-diethoxy-4-benzoylaminobenzene diazonium chloride zinc chloride double salt, 5 parts of citric acid and 100 parts of water. After drying, and exposure under ultraviolet light through an original, the image is developed by heating for 36 seconds at 165° C. in direct contact with a sheet of newsprint previously padded with an alcoholic solution containing 5 parts of phloroglucinol and 20 parts of glycerine and air dried. The developed image was a deep black of good visual density and light fastness and its background was pure white.

Example II

Example I was repeated except that 10 parts of 2,3-dihydroxy naphthalene was used in place of the phloroglucinol and that the citric acid was omitted from the diazo paper. A deep blue shade was obtained indicating that acid is not essential in the diazo paper.

Example III

Example II was repeated except that the blotting paper was padded with an isopropanol solution of 10% resorcinol and 20% glycerol. A brown print was obtained.

The time of best treatment will vary depending upon the temperature used and other factors and in the temperature range of 140° C. to 220° C., times of from 6 to 60 seconds have given good prints. For most compounds, a temperature of 165° C. for 30 seconds is preferable.

Various supplementary materials may be included in the diazo paper. The addition of 0.1% saponin or equivalent amounts of a synthetic surfactant to the diazo coating formulation improves the evenness of the coating. The addition of glycerol or ethylene glycol to the diazo paper reduces brittleness and improves the light sensitivity of the diazo prints in certain cases.

Example IV

A cotton cloth was padded with an aqueous solution having the following composition:

Zinc chloride double salt of 4-benzoylamido-2-methoxy-5-methylbenzene diazonium chloride	gms.	50
Citric acid	gms.	2
Thiourea	gms.	17
Water to make	liter	1

The padded material was dried in the dark at 50° C. and then exposed through a transparency with ultraviolet light. Simultaneously, a blotting paper was impregnated with the following solution:

Acetoacetanilide	gms.	100
Glycerol	gms.	200
Ethanol	gms.	100
Water to make	liter	1

The impregnated paper was dried at a temperature of 50° C. and then placed in contact with the exposed diazo containing cotton strip. Heat was supplied by means of a metal plate heated to 170° C. After 30 seconds, the plate was removed. A brilliant yellow picture of high density and good wash fastness was obtained on the cotton cloth.

Example V

A sheet of silk was padded with a solution having the following composition:

4-phenylamino-2-methoxybenzene diazonium sulfate	gms.	30
Thiourea	gms.	50
Citric acid	gms.	10
Water to make	liter	1

The silk sheet was dried in the dark at a temperature of 50° C. and exposed under a pattern.

A newsprint was coated with a solution having the following composition:

3-methyl pyrazolone	gms.	100
Glycerol	gms.	20
Dimethyl formamide	mls.	100
Water to make	liter	1

A strip of the dried newsprint was folded over to cover both sides of the exposed silk material. The sandwich was heated from both sides with two metal plates having a temperature of 165° C. The necessary steam was provided by placing moistened filter paper between the newsprint and the heating plates.

An orange red print was obtained after 20 seconds.

Example VI

Example I was repeated with the exception that the glycerine was replaced by an equal number of parts of n-hexanol which provided the vapor for the transfer of the coupling component.

Example VII

A strip of the diazo padded silk material prepared as described in Example V was exposed with ultraviolet light under a transparency. Half of the strip was covered with a sheet of the coupling paper of Example IV, the other half of the strip was covered with a sheet of the coupling paper of Example II. After heating the side which was covered by the coupler papers for 40 seconds with a metal plate, a picture was obtained which was partly yellow and partly blue.

It will be evident from the preceding examples that the present process is unique in permitting the production of multicolored diazo prints. The paper containing couplers may not only be cut into strips and placed side by side with strips of paper containing other couplers in contact with the diazo paper, but the different coupler papers may also be cut into fanciful patterns, for instance, those representing flowers of different colors. Alternatively, colors may be superimposed upon each other by treatment in separate steps with various couplers or by placing two absorbent papers containing two different couplers on the opposite sides of the diazo coated paper or textile.

The invention is further illustrated by the accompanying drawing. Figure 1 shows the first step of the process wherein a letter, transparency or other pattern is placed over a light sensitive diazo layer and actinic light such as ultraviolet light passed through the pattern. Figure 2

shows the exposed diazo layer in contact with a paper impregnated with a coupler and subjected to heat.

Our improved diazo print process has a number of advantages over the prior art processes. Ammonia is entirely eliminated so that the necessity for disposing of these diasagreeable and corrosive fumes is eliminated. The use of volatile amines is avoided and this is advantageous because of their disagreeable odor, high toxicity and carcinogenic action as well as the bad background discoloration caused by amines. There is no necessity for choosing diazo coupler pairs having stability towards precoupling since the diazo and coupler are separated in our process and there is no possibility of precoupling, thus allowing the use of paper having substantially longer shelf life. Also an increased variety of colors including multicolored prints is possible. The process affords flexibility and ease of operation over the wet developing diazo systems, including the ease of changing from one coupler to another, the fact that the paper does not require drying after development and the lack of necessity for handling unstable, caustic and corrosive liquids.

This application is a continuation in part of our application Serial Number 86,562, filed April 9, 1949, now abandoned.

We claim:

1. The process of preparing diazo prints from a material sensitized by means of a light sensitive diazo compound which comprises exposing said material to actinic light under a pattern, then contacting the exposed material with an absorbent layer containing a coupler capable of thermal transfer and selected from the group consisting of phenols, naphthols, and compounds containing a reactive methylene group, said coupler being free from primary amino groups, and heating said material at a temperature between 140° C. and 225° C. while in contact with said coupler containing layer in the presence of steam.

2. The process of preparing diazo prints from a material sensitized by means of a light sensitive diazo compound which comprises exposing said material to actinic light under a pattern, then contacting the exposed material with an air dry, absorbent, fibrous layer containing a coupler which is non-volatile at temperatures below 100° C., but capable of thermal transfer in the presence of super-heated steam and selected from the group consisting of phenols, naphthols, and compounds containing a reactive methylene group, said coupler being free from primary amino groups, and heating said material while in contact with said coupler containing layer in the presence of steam at a temperature between 140° C. and 225° C.

3. The process of preparing diazo prints from a material sensitized by means of a light sensitive diazo compound which comprises exposing said material to actinic light under a pattern, then contacting the exposed material with an air dry, fibrous, absorbent layer containing a coupler which is non-volatile at temperatures below 100° C. but capable of steam-distilling in the presence of super-heated steam and selected from the group consisting of phenols, naphthols, and compounds containing a reactive methylene group said couples being free from primary amino groups, and heating said material while in contact with said coupler containing layer in the presence of steam heated to a temperature between 160° C. and 190 C.

4. The process of preparing diazo prints from a material sensitized by means of a light sensitive diazo compound which comprises exposing said material to actinic light under a pattern, then contacting the exposed material with an air dry, fibrous, absorbent layer containing, in addition to a humectant, a coupler incapable of distilling at a temperature below 100° C. but capable of distilling in the presence of super-heated steam and selected from the group consisting of phenols, naphthols, and compounds containing a reactive methylene group, said coupler being free from primary amino groups, and heating said material to a temperature between 140° C. and 225° C. while in contact with said coupler containing layer in the presence of super-heated steam as provided by the water stored by the humectant at room temperatures and given off at the temperature of heating during printing.

5. The process of claim 1 wherein the coupler containing, absorbent layer is paper.

6. The process of claim 1 wherein the diazo layer contains thiourea.

7. The process of claim 1 wherein the absorbent layer contains a humectant in an amount in the range of 1 to 5 parts by weight per part of coupler.

8. The process of claim 4 wherein the absorbent layer is newsprint and the humectant is glycerol.

9. The process of claim 1 wherein the coupler is phloroglucinol.

10. The process of claim 1 wherein the coupler is 2,3-dihydroxynaphthalene.

11. The process of claim 1 wherein the coupler is resorcinol.

12. The process of claim 1 wherein the coupler is acetoacetanilide.

13. The process of claim 1 wherein the coupler is 3-methyl pyrazolone.

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