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PRINTING PROCESS WHEREIN AN ALKALINE SUBSTANCE PASSING THROUGH STENCIL OPENINGS EFFECTS COUPLING OF AN AZO DYE IN SITU

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This invention relates to printing and more particularly to printing by means of diazo compounds, and is a continuation-in-part of our U. S. application Ser. No. 63,224, filed December 2, 1948, now abandoned.

The azo dyes are a well defined group containing the chromophor—N=N—. The chromogen of azo dyestuffs with which we are concerned comprises at least one aryl radical with one or more chromophor groups attached to it. The mono azo dyes are generally prepared by joining two components of which the first is called the diazo component, and the second, usually a phenol, an amine, or an active methylene compound, is called the coupling component. The diazo component and the coupling component are caused to react to form a dye.

Use of the coupling action of diazo compounds to form dyes has been made in the printing art. In this process a light sensitive diazo compound, and a coupling agent, together with various stabilizing agents are coated on a support and dried. The paper is exposed through a printed pattern to light for several seconds and then to moist ammonia gas. The ammonia "develops" the dye by neutralizing the stabilizing acids present with the diazo and coupler components, i. e. it allows the diazo compound to couple to form a reproduction of the pattern. The pattern is faithfully reproduced since the light falling generally on the printed pattern passes only through those portions of the pattern not opaque to light and destroys the diazonium salt with liberation of nitrogen so that it is no longer capable of coupling.

The process of printing described above does, however, have several limitations for specialized uses. It is, for instance, quite slow, taking several seconds to complete a reproduction. Other conventional printing processes such as those requiring the use of ink associated with stencils have the difficulty that the stencils must be carefully cleaned before storage.

It is an object of the present invention to prepare mixtures of a diazo component and a coupling component that will serve to give a reproduction substantially instantly.

It is another object to provide a method of reproduction with the aid of a membrane, certain areas only of which are permeable to vapor or liquids.

Another object is to prepare reproductions that require little, if any, cleaning operations prior to storage.

Still another object is to print sharp images.

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These, and other objects, which will be apparent, may be preferably accomplished by first preparing an application of a diazo component and a dye-coupling component on a surface to be printed. Acid sufficient to stabilize a mixture of the diazo and coupler components on the base to be printed is included with the coating. The image is developed by an alkali which is placed on the treated surface in a predetermined pattern, and is "fixed" by destroying the unreacted diazo component. This may be done by the use of light, heat, or chemicals.

The preferred alkali in our process is ammonia gas inasmuch as it permits reproduction which is better in several respects than that obtained by other variations in the process. A principal advantage of employing a gas is that if a gas is placed through a stencil a sharp reproduction is produced almost instantly, while if a liquid is passed through a stencil there is a certain amount of spreading of the fluid due to capillary action of fibers in proximity to the liquid, and therefore some indistinctness about the edges develops. Another advantage in the use of a gas is that the quantity need not be so critically controlled as in the case with a liquid. These factors are of more significance in some cases than in others.

In the practice of this invention the diazo component may be any diazo compound which, when coupled, will yield a colored dye. The dye formed may be fixed by the action of light, heat or chemicals. The fixing process serves to destroy the activity of any of the diazo component remaining uncoupled after the process is completed. By so fixing, unwanted dye will not be subsequently formed in the background by any alkalinity which was present in the paper or which subsequently reached the paper or surface. The fixing is necessary since no amount of acid material will permanently prevent eventual coupling.

The diazo component may be any light sensitive diazo compound. The three preferred diazo compounds are:

1 diazo-2 oxy naphthylene-4 sulfonate

p-Diethyl amino benzene diazonium chloride·$ZnCl_2$

4-benzoylamino-2-5-diethoxy benzene diazonium chloride.

Of the many diazo components the following are typical examples of useful compounds:

Para-chlorobenzene-sulfonate of 4-diazo-1-cyclohexylaniline

Para-chlorobenzene-sulfonate of 4-diazo-2-methoxy-1-cyclohexylamino benzene

Tin chloride double salt of 4-N-methylcyclohexylamino benzene diazonium chloride
p-Acetamino benzene diazonium chloride
4-dimethylamino benzene diazonium chloride
3-methyl 4-diethyl amino benzene diazonium chloride
4-morpholino benzene diazonium chloride
4-piperidyl 2-5-diethoxy benzene diazonium chloride
1-dimethyl amino naphthalene-4 diazonium chloride
4-phenyl amino diazo benzene diazonium chloride

The preferred coupling components are:

Phloroglucinol
Resorcinol
2-naphthol

Other coupling agents include:

1-naphthol-4,7-disulfonic acid
1,8-dihydroxynaphthalene-3,6-disulfonic acid
2,3-dihydroxynaphthalene
2-naphthol-3,6-disulphonic acid
Acetoacetanilide and its substitution products
Phenylmethylpyrazazolone and its substitution products
Anilides of 2-hydroxy-3-naphthoic acid, e. g. the anilide, and 3-methyl-anilide.

The alkaline component is preferably a vapor such as ammonia gas, or methyl amine. Other alkaline agents which also may be used include aqueous solutions of ammonia, alkali metal hydroxides, alkali metal carbonates, and alkaline earth alkalies.

The acidic materials used are preferably non-volatile or not readily volatile materials such as tartaric, boric, acetic, maleic, citric, ammonium sulfate, aluminum sulfate, and sodium acid sulfate.

The proportions of diazo component to coupler are well known and are not a part of this invention. It is customary to include an excess of the coupler component to insure the presence of sufficient coupler for any dye component that may be present.

The amount of a given acid present to insure stabilization in the preferred process is, to some extent, dependent upon the particular diazo compound stabilized. It is a fact that the reaction of diazo compound with a coupler may be retarded by preventing the hydrolysis of the diazo compound as by the addition of an acid. Normally, sufficient acid is added to lower the pH to a point where the coupling action is prevented for long periods of time. For some purposes, we prefer to use only sufficient acidic material to prevent immediate coupling or to prevent coupling on the surface to be printed for a few hours. The speed of the neutralization process is thereby increased, but more importantly less alkali need be added thus requiring less time when reproduction is carried out by means of a stencil. The desired speed of contact for reproduction is usually between 0.001 and 1 second contact time, and these speeds are easily attainable by the process herein described.

The exact concentration of acid desirable is dependent partially upon the support being used. Many ordinary types of paper for instance appear to accelerate dye formation in the absence of sufficient acid, probably because of the alkalinity of the paper.

After the image is fixed, the print may not be color stable due to a difference in pH between the alkali developed image and the acid treated paper. That is, many of the diazo dyes, to some extent at least, change color with changing pH. Thus it is best to subject the acid surface to an alkali treatment after the fixing step to insure a permanent color, or adjust the pH of the original sensitizing solution so that it is harmless.

Example I

The surface of a type-impressed stencil is placed in close contact with the outside surface of a perforated 10'' diameter metal drum, to the inside surface of which is fastened a wad of cotton saturated with concentrated aqueous ammonia. A sensitizing solution of the composition presented below is applied to the paper which is to receive the image. While still moist, the paper is rolled against the stencil at the rate of about 250 linear feet per minute, pressure being exerted upon the paper over the area of contact, which should be about 1 linear inch of the sensitized paper at any given instant. A purple image of the openings of the stencil is immediately developed. The remaining uncoupled diazo component is destroyed by holding the developed paper under a No. 1 photoflood lamp for 5 seconds at a distance of four inches.

The composition of the sensitizing solution is as follows:

$ZnCl_2$ double salt of 4-diethylamino diazo benzene	gm.	2.0
Phloroglucinol	gm.	0.25
Tartaric acid	gm.	0.4
Sodium acid sulfate	gm.	0.5
Water	ml.	100

Example II

Example I is repeated except that the remaining uncoupled diazo component is destroyed by passing the image containing surface of the unfinished paper over a metal surface maintained at about 500° F. The time of contact between any one point of paper and the heated surface should be about 2 seconds.

Example III

Example I is repeated except that the remaining uncoupled diazo component is destroyed by applying the following solution by kissroll:

Acetic acid (glacial)	ml.	5
Water	ml.	90
Stannous chloride	grams.	5

Example IV

An image of the openings of a cut stencil is formed by passing an "ink" consisting of a thickened 10 per cent solution of sodium carbonate through the openings of the stencil onto a paper surface. Development of a green image occurs when the sheet is subsequently treated by kissroll with a solution prepared as follows:

p-Diazo-diphenyl amine sulfate	gm.	1
2-hydroxy-3-naphthoic acid-o-toluidide	gm.	0.25
Tartaric acid	gm.	0.5
Water	ml.	50
Acetone	ml.	50

Destruction of the undeveloped diazo compound by exposure for two minutes to a Hanovia type 7420 ultraviolet light serves to "fix" the image by destruction of the unexposed diazo component. The final dry image is violet.

Example V

Paper is pretreated with a solution prepared as follows:

$ZnCl_2$ double salt of 4-diethyl amino diazo benzene	gm.	2
Tartaric acid	gm.	0.5
Water	ml.	100

The paper is brought into contact with a cut stencil through which is passed an ink consisting of a thickened 10 per cent solution of sodium carbonate to form the potential image. Subsequent treatment of the paper with a 0.25 per cent solution of phloroglucinol develops a deep purple image. The remaining uncoupled diazo component is destroyed by exposure to moderately bright direct sunlight for 1 minute.

Example VI

Example V is repeated with the exception that the paper is pretreated with the following solution:

Phloroglucinol	gm.	0.25
Tartaric acid	gm.	5.0
Water	ml.	100

After passing the sodium carbonate ink through the stencil, the paper is treated with a 2 per cent solution of $ZnCl_2$ double salt of 4-diethyl amino diazo benzene. Destruction of the uncoupled image is accomplished by simply leaving the paper exposed to ordinary daylight for 8 hours. The increased acid over that used in Example V prevents coupling of the undeveloped diazo compound for this extended period.

In the practice of the invention it is advisable that the image accepting surface be distinctly moist, thereby considerably increasing the speed. Under such conditions the image is produced in only a fraction of a second, whereas when ammonia gas is passed through a stencil onto a dry coating of the diazo component, the coupler component and acid, the time required is several times as long. It has been found, however, that when reproduction is made on paper the added moisture tends to curl the paper. The use of a non-swelling agent for cellulose fibers such as a water-alcohol mixture helps to eliminate objectionable curl when printing a paper, and is therefore advised. On the other hand it may be necessary in the case of highly sized or wax coated papers to add a wetting agent in order to secure even distribution of the components over the surface to be printed. Such a procedure would not induce curl where "spot" sensitization is employed—a feature of this process. By spot sensitization is meant coating over a limited area of the sheet on which printing is to take place. Further speed may be obtained where necessary when ammonia gas is passed through a stencil by applying pressure, although satisfactory speeds may be obtained without resort to this alternative.

In the practice of this invention either light sensitive and/or heat-sensitive diazo compounds may be employed. Many of the diazo compounds are quite light sensitive and relatively heat insensitive; these may be fixed by ultraviolet light or in fact ordinary daylight in a very short period. Other diazo compounds are quite heat sensitive and may be fixed rapidly by heat, as with an infra red lamp. Preferably both ultraviolet and infra-red radiations are to be used in conjunction since together they fix the reproduction more rapidly than either alone. Reducing chemicals, such as stannous chloride, may be employed, if desired, to remove unreacted diazo compound, although this procedure is not recommended due to the incidental development of phenyl hydrazine.

In the preparation of the coating materials stabilizers and sensitizers well known in the art may be added if desired. These include such materials as thiourea to prevent the darkening of the background due to oxidation of the couplers.

It is readily apparent that by the use of the above process rapid reproductions may be accomplished. In order to illustrate the process of the invention still further the following commercial use is described.

Magazines, house organs, papers, and so forth, are frequently mailed to an address which may be applied by a stencil. Since these stencils become coated with a difficultly removable ink during use, their storage and reuse is normally somewhat of a problem. In the preferred process, herewith described, no such cleaning and storing problem exists.

When a continuous strip of stenciled addresses is to be used to address envelopes, the strip is placed in an automatic feed mechanism capable of advancing address areas singly and in rapid succession; the envelopes to be addressed are placed in another automatic feed mechanism. In operation, as each envelope is advanced, it is coated by kissroll in a given small area with the sensitizing solution noted in Example I above. Immediately after this spot-sensitization, the stencil feed mechanism advances a stenciled address and places it in position over the slightly damp, sensitized area of the envelope. The stencil surface and paper are pressed into intimate contact and automatically advanced into and out of the ammonia chamber, stencil side toward the ammonia. Contact is maintained for about $\frac{1}{40}$ second to develop a deep purple image. During each exposure, another envelope is being sensitized, ready for repetition of the above process.

After the image is developed upon the envelope, the remaining, undeveloped diazo material is destroyed by exposure to a No. 1 Photoflood lamp for five seconds at a distance of four inches, to prevent darkening of the background. The stencil strip, meanwhile, is taken up for subsequent filing and reuse.

In the above process, the sensitizing solution is applied by kissroll. Other methods of application such as spraying, sponging, etc., may be employed as alternative if desired. It is also noted that the stencils are supplied in a continuous strip. Any alternative methods in which the addresses are singly framed or mounted in a way which would permit the use of an automatic feed mechanism might be used.

In the above discussion reference has been made to passing an alkali, and particularly ammonia, through a stencil. It will be readily appreciated that the stencil need not be one which is permeable to light; there need be only a differential resistance to transfer through the stencil at predetermined points.

While the process of the invention is most advantageously practiced, for most purposes by passing ammonia gas through a stencil onto a moist, sensitized surface, other modifications of our process are possible.

The alkaline material may be applied to the sensitized support as by off-set, type, or by other printing means. In the case of ammonia it may be projected through the end of a tube onto a sensitized support.

The essential part of the application of alkali

is that it be placed upon the support in a differential manner, to form a predetermined pattern. The differential quantity of alkali brings out variation in intensity of color and variation between color and no color.

A further modification or extension of our process includes the use of two or more dyes designed to complement one another to reproduce color. For example, by proper and known procedure a colored image may be broken down into the primary color images, and half tone stencils or printing plates made of these images. It is also known that suitable diazo-coupler systems yield the primary colors as well as colors complementary to them. Multicolored printing then consists in developing the various colors separately with alkali and fixing after each operation. In any case the alkali is applied in a predetermined pattern upon the support thus producing, by the coupling of the dye components, the predetermined image. The unreacted diazo component is then destroyed by light and/or other suitable means so that disturbing background color will not subsequently develop. Care must be taken that coupling previously employed does not interfere with subsequent dye systems.

The support commonly employed is of course paper. Other types of support include fabric such as cotton cloth, leather, wood, walls, etc. Any support, in fact, on which the dye components may be placed and stabilized is subject to the operation of the process herein described.

The above examples are given as illustrations only, and any modifications within the skill of the art are intended to be included within the appended claims.

In the practice of our invention it has been observed that after contact with alkali, the image, while appearing instantly, does not always reach its full intensity until perhaps several seconds after exposure to ammonia vapor. The time of development may be decreased considerably by insuring the amount of moisture, and by heat. It has been observed, for instance, that the rate of coupling increases rapidly with increasing temperature. Thus when it is desired to fix an image immediately after exposure to alkali, heat alone or heat as well as light could be employed to advantage.

We claim:

1. A process of printing which comprises applying to a support a diazo compound capable of yielding a dye when coupled, and a coupler for the diazo compound the reaction of said compounds being inhibited by acid, and an acid, said acid being present in an amount at least sufficient to prevent immediate coupling of the diazo compound, exposing the support through a stencil to sufficient alkali to cause coupling of alkalized diazo component and said coupler, and fixing the uncoupled compound.

2. The process according to claim 1 wherein the alkalization takes place in the presence of moisture.

3. The process according to claim 2 wherein the alkali is ammonia gas.

4. The process according to claim 2 wherein the alkali is sodium carbonate.

5. A process of printing which comprises applying to a paper sheet with a light sensitive diazo compound capable of yielding a dye when coupled, a coupler for the diazo compound the reaction of said compounds being inhibited by acid, and an acid, said acid being present in an amount sufficient to prevent immediate coupling of the diazo compound, exposing the paper sheet through a stencil to sufficient ammonia to cause coupling of exposed diazo compound, and fixing the uncoupled compound, said paper being moist at the time of contact with the ammonia.

6. A process of printing which comprises applying to a paper sheet a light sensitive diazo compound capable of yielding a dye when coupled, a coupler for the diazo compound the reaction of said compounds being inhibited by acid, and an acid, said acid being present in an amount sufficient to prevent immediate coupling of the diazo compound, exposing the paper sheet through a stencil to sufficient alkali solution to cause coupling of exposed diazo compound, and fixing the uncoupled compound.

7. A process of printing which comprises applying to a paper sheet a heat sensitive diazo compound capable of yielding a dye when coupled, a coupler for the diazo compound the reaction of said compounds being inhibited by acid, and an acid, said acid being present in an amount sufficient to prevent immediate coupling of the diazo compound, exposing the paper sheet through a stencil to sufficient alkali solution to cause coupling of exposed diazo compound, and fixing with heat the uncoupled compound.

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