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3,578,452  
**DEVELOPING COMPOSITIONS FOR  
 DIAZOTYPE MATERIALS**

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No Drawing. Continuation-in-part of application Ser. No. 440,752, Mar. 18, 1965. This application Sept. 12, 1968, Ser. No. 759,503

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U.S. Cl. 96-49

8 Claims 10

**ABSTRACT OF THE DISCLOSURE**

Diazotype developing compositions comprising a liquid organic amine such as morpholine, alkylmorpholine, piperidine, alkylpiperidine, or an amine of the formula 15



wherein R<sub>1</sub> is hydroxyalkyl, cycloalkyl or aralkyl dissolved in a polyhydric alcohol, a glycol ether or a monohydric alcohol containing at least six carbon atoms with water in an amount not greater than the weight of the organic solvent. 20 25

**REFERENCE TO CO-PENDING APPLICATION**

This application is a continuation-in-part of my co-pending application Ser. No. 440,752, filed Mar. 18, 1965. 30

**SUMMARY OF THE INVENTION**

This invention relates to compositions for developing diazotype materials. More particularly, it relates to concentrated amine solutions for the development of two-component diazotype materials by the application of controlled amounts of such solutions to produce a finished dry copy directly after said development. 35

Diazo reproduction processes based on light-sensitive diazonium compounds and their ability to form azo dyes with a coupling component under proper pH conditions are generally well known. The various techniques for carrying out the development include the moist or semi-moist process, the dry or ammonia process, and more recently the thermal process. The diazo copying materials adapted for the moist process are referred to as one-component materials since they contain only the light-sensitive compounds and the coupling component is provided in a separate buffered developing solution and applied at the time of development. Diazotype materials developed in an atmosphere of water vapor and ammonia gas are generally referred to as two-component materials since they contain both the diazonium salt and the coupling component stabilized against premature coupling in an acidic medium. In the thermal systems heat is employed to release the alkaline agents which are coated on the copy material along with the diazonium salt and the coupler. Each of these systems provides a successful copying process but not without certain disadvantages that limit their utility which would otherwise permit diazo copying to enjoy more widespread application as a reproduction medium. 40 45 50 55

Two-component materials have found wide use in the reproduction of engineering drawings. The process of 60 65

developing with ammonia gas and water vapor is fast and essentially dry. Ammonia vapor readily penetrates into the exposed copy sheet surface and permeates the light-sensitive coating containing acid stabilizers, shifting the pH of the coating to the alkaline side. Any excess of ammonia enhances the rate of the reaction and volatilizes from the copy sheet without leaving a residue. One of the major objections to the use of ammonia in developing diazotype materials is the strong odor of ammonia in the copying area as well as the tendency for the odor to linger on the copies themselves. Installation of ammonia reproduction machines requires venting of the equipment to the outdoors to remove the toxic vapors. This limits the installation of the equipment to sites where the venting may be conveniently accomplished. The equipment is further complicated by the need for a gas developing chamber to contain the ammonia gas and water vapor and the other appurtenances required for feeding the developing ingredients to the chamber. The equipment, understandably, is not well suited for office installations. 5 10 15 20

The one-component systems have effectively eliminated the odor problem by applying liquid developers directly to the copy sheet. Reproduction equipment for use with the one-component type papers requires heating elements to dry the copy sheet after development. 25

Thermal systems, while offering the advantages of dry copying without the presence of undesirable odors, suffer in that the copying materials themselves may lack stability. The machines are objectionable because of the amount of heat given off into the surrounding work area. 30

Attempts have been made to simplify the processing of diazotype materials, particularly the two-component types, by using alkaline liquids applied directly to the latent image bearing surface. These prior attempts to eliminate the complexities of gaseous development have been unsuccessful for the following reasons: 35

(1) In general, the use of dilute alkaline solutions produced prints of rather low image density when compared to development with ammonia.

(2) The application of large quantities of dilute alkaline solution did not appreciably improve image density and rendered the sheet moist so that it required a drying step before it could be used.

(3) Alkaline developer solutions formulated with non-volatile inorganic salts, such as disclosed in U.S. Pat. 1,841,653, required an inordinately long time to develop into a print having suitable image density.

(4) The dye shade of the azo dye images obtained with conventional two-component diazotype materials developed with inorganic salts deviated from the hues obtained with ammonia. The off-shade images in some instances were weaker, giving prints of poor contrast.

(5) Developer solutions containing high concentrations of inorganic salts resulted in crystals of these salts forming on the various rollers causing streaked, uneven development. Such concentrated solutions also tended to leave a residue of the salt on the copy causing a more rapid discoloration of the print background.

Attempts to control the fluid application by adapting the techniques well-known for developing the one-component diazotype materials such as disclosed in U.S. Pat. 2,241,104 to the development of two-component diazotype papers using alkaline liquids resulted in applying too much fluid. These prior techniques rely, in the main, on first applying an excess amount of developer solution to 60 65

the copy surface, which excess is then squeegeed off. The use of grooved roller systems generally required some form of drying of the copy after development.

In summation, it can be said that prior attempts to simplify development of diazotype materials, and in particular the development of two-component copy papers, were unable to match the dry conditions of ammonia and the speed with which the latent image is developed. The processes were by no means dry in the sense that the copy sheet still required some form of drying and, finally, the quality of the reproduction was lacking in uniformity and image density by comparison to the quality obtained with ammonia development.

It is a general object of this invention to provide improved compositions for developing two-component diazotype materials that produce high quality prints rapidly which emerge essentially dry after development and ready for use.

Another object of this invention is to provide novel compositions for developing two-component diazotype materials which supply controlled amounts of an amine to a developing region so that the diazo print is rapidly developed, emerging from the developing region in a condition that is dry to the touch.

Another object of this invention is to provide improved compositions for developing two-component diazotype materials which are concentrated solutions of aliphatic or similar amines capable of giving consistently high quality diazo prints.

Other objects and advantages will be apparent to those skilled in the art after having reference to the following detailed description.

To secure the advantages of the known techniques of development of diazotype materials, particularly the two-component type, but to avoid the limitations thereof, new liquid developers have been prepared which produce a dry copy directly from the developing step. Development is accomplished by supplying controlled amounts of a concentrated developer solution, preferably comprising an aliphatic amine in a specified solvent, to a developing region and then passing an exposed diazotype paper through the developing region. At the developing region the controlled small amount of developer liquid is applied directly to the surface bearing the latent diazo image to effectively develop the azo dye image and produce prints which emerge dry, odor free and ready for use.

When referring to a controlled amount of liquid hereinafter, it will be understood to mean amounts not in excess of 3.0 grams of developer solution per square meter of the image-bearing surface and preferably in the range of from about 0.5 gram to 2.0 grams per square meter. Surprisingly, small quantities of developer liquid applied over the entire area uniformly as the copy passes through the developing region immediately develop the latent image into a readable azo dye image.

Within the developing region the limited quantity of developer liquid is applied under pressure, thus being spread out uniformly over its entire surface in a layer having a thickness of about 1 micron, which is sufficient to cause rapid image development. The azo dye image is found to develop evenly and uniformly everywhere across the copy area, indicating the effectiveness of the method. A visible, readable image begins to form instantaneously as the copy emerges from the developing region and rapidly increases in density, attaining its maximum image density well within one minute and usually within 15 seconds. Understandably, the rate at which maximum density is reached will depend in part on the couplers and diazonium compounds used in making the copy sheets.

The condition of the sheet described as being dry may be defined as being dry to the touch as soon as it emerges from the developing region. No further drying is required and the copy may be used immediately. The copies are free of any objectionable odors. They are flat lying, free

of curl, cockles or other irregularities that are normally attendant upon paper surfaces to which liquids have been applied. Further, the copies are not limp due to the presence of excess moisture that would prevent them from being filed, folded or handled by the automatic stacking devices of copying equipment. The emerging copies may be written upon with pen or pencil and otherwise handled.

Giving consideration to the subject of developing two-component diazotype materials in general, it is understood that the reaction is a two-step process, namely:

(1) Increasing the pH of the environment in which the diazo salt and coupling component are found to the level where the coupling action can take place, and

(2) The coupling reaction between the coupling component and the diazonium salt.

It is the first reaction to which this invention is directed. The second reaction or coupling proceeds at a rate determined solely by the particular reactants once the proper pH has been provided.

In any practical developing process the developer must penetrate the surface of the sheet and neutralize the acid uniformly and evenly. It will be appreciated that incomplete neutralization in certain areas will leave the diazonium salt uncoupled and result in an irregularly developed copy. Accordingly, it is critical that the alkaline liquid developer be applied over the entire surface uniformly so as to achieve an even and uniform treatment. The developer liquid must react rapidly with the acid component; it should not discolor the print background; and it should not be absorbed into the body of copy material but remain only at the surface thereof. The composition of the developer liquid will be considered further in greater detail hereinafter.

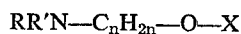
The developer composition must be such that it can rapidly react with the acid component in the diazo coating, shifting the pH to the level where the coupling reaction can proceed. The developer should remain stable during storage and use in the apparatus and not undergo degradation due to oxidation caused by atmospheric exposure. The background area of developed prints should not appreciably discolor upon aging so as to reduce print contrast. The image dye lines should correspond to the hues obtainable with ammonia and not be off shade. The concentration of the various ingredients in the composition should not vary due to evaporation at ordinary temperatures or the absorption of water from the atmosphere. The developer should, of course, not have an objectionable odor, be non-toxic, and simple to handle and use.

In the instant invention it is critical that small amounts of the developer having the proper amine concentration be capable of being spread uniformly and evenly over the entire copy area.

Developer compositions which meet the aforescribed requirements comprise from 20% to 80% by weight of a liquid amine component such as an aliphatic amine, the preferred range being from 40% to 80% by weight. The amine component may be a compound having the general formula:



wherein  $\text{R}_1$  is alkanol (hydroxyalkyl), cycloalkyl or aralkyl, and  $\text{R}_2$  and  $\text{R}_3$  are hydrogen, alkyl, alkanol (hydroxyalkyl), cycloalkyl or aralkyl. Heterocyclic amines such as morpholine and piperidine and N-alkyl derivatives of morpholine and piperidine can also be used as the amine component. Preferred are the alkanolamines of the general formula



wherein R and R' are the same or different alkyl or hydroxyalkyl substituents or are hydrogen, X is hydrogen,

5

lower alkyl or lower hydroxyalkyl, and  $n$  is an integer from 2 to 4, inclusive.

The amine is diluted with a solvent selected from polyhydric alcohols, glycol ethers, and monohydric alcohols containing at least 6 carbon atoms. The solvent may be present in amounts ranging from 20–80% by weight of the formulation, the preferred range being 40%–60%. The operable pH range of the developer solutions prepared in accordance with this invention is 10 to 14.

The following amines have been eminently successful in the practice of the method: ethanolamine, isopropanolamine, 2-(2-aminoethoxy)ethanol, triethanolamine, diethanolamine, 2-amino-2-methyl-1-propanol, N-methylethanolamine, N,N-dimethylethanolamine, hexylamine, cyclohexylamine, N-aminoethylethanolamine, alkyl substituted morpholine and piperidine; but the heterocyclic amines are somewhat less desirable because they have a detectable odor or they tend to adversely affect the dye shade.

The solvent or diluent is essential in providing greater latitude in the amount of developer liquid that may be applied within the specified range and still provide the optimum amount of amine. The solvent or diluent also aids in the spreadability and wetting out of the developer across the area to which it is applied.

The solvent or diluent may be a polyhydric alcohol selected from the following:

hexylene glycol  
diethylene glycol  
triethylene glycol  
trimethylene glycol  
ethylene glycol  
propylene glycol  
butylene glycol  
dipropylene glycol  
glycerol

and glycol ethers such as:

ethylene glycol monoethyl ether  
diethylene glycol monoethyl ether  
4-methoxy-4-methyl-pentanol-2  
ethylene glycol monomethyl ether  
ethylene glycol monobutyl ether

or a higher mono-functional alcohol such as:

2-ethylhexanol  
cyclohexanol  
isooctyl alcohol  
hexanol

It has been found advantageous to use the polyhydric alcohols which are completely compatible with the aliphatic amines and do not adversely affect the print quality. Also, polyhydric alcohols such as, for example, hexylene glycol, and glycol ethers enhance the spreadability of the developer liquid. To some extent the formulation of the diluent depends on the type of equipment employed. Thus, it may be desirable to decrease the viscosity by adding water, a mono-functional alcohol, or mixtures thereof. The amount of water should not be greater than the weight of the organic solvent, and preferably from 25% to 50% of the weight of the latter.

In general, most of the commercially available two-component papers can be used successfully with the process and developers of this invention. The quality of the final print and the rapidity with which the print develops will depend in part on the coupling component and diazonium salt that is used. Examples of such diazo compounds which are used are the diazonium salts obtained by the diazotization of the following amines:

p-amino-N,N-diethylaniline  
p-amino-N-ethylaniline  
p-amino-N-ethyl-N-hydroxyethylaniline  
p-amino-N-methyl-N-hydroxyethylaniline  
p-amino-N,N-di- $\beta$ -hydroxyethylaniline

6

p-amino-m-ethoxy-N,N-diethylaniline  
p-amino-N-ethyl-o-toluidine  
p-amino-N-ethyl-m-toluidine  
p-amino-N,N-diethyl-m-toluidine  
p-amino-N-ethyl-N- $\beta$ -hydroxyethyl-m-toluidine  
N-p-aminophenylmorpholine  
1-amino-2,5-diethoxy-4-morpholinobenzene

Examples of couplers that can be used are resorcinol, acetoacetanilide, 4-chlororesorcinol, diresorcinol, diacetoacetylenediamine, aminoethylethanolamine amide of 3-hydroxy-2-naphthoic acid, and 2,3-dihydroxy-6-naphthalene sulfonic acid (sodium salt).

It will be appreciated that certain of the many two-component diazotype materials commercially available will give better density and faster development than others when used in accordance with the instant invention. However, it can be stated that most two-component papers will give acceptable copies.

The following examples of developer solutions which may be employed in accordance with this invention are given for the purposes of illustrating preferred embodiments of the invention. It will be understood, however, that this invention is not limited to these illustrative embodiments of developer solutions useful in practicing this invention. All percentages are shown as percent by weight unless otherwise specified.

#### EXAMPLE I

A diazotype paper was prepared with the following two-component sensitizing solution:

Water—600 cc.	
Diethylene glycol—40 cc.	
Citric acid—20 grams	
Zinc chloride—50 grams	
Isopropyl alcohol—10 cc.	
	Grams
2,3-dihydroxynaphthalene-6-sulfonic acid (sodium salt)	40
p-Diazo-N,N-diethylaniline zinc chloride	15
Thiourea	30
Water to make 1000 cc.	

The formulation was coated on a suitable paper such as a direct process sulphite stock, 20 lb. basis weight (17" x 22"—500), in an amount of about 15 grams per square meter.

The sensitized paper was exposed to an actinic radiation pattern such as by contact exposure through a transparent or translucent original.

A developer composition was prepared by combining the following ingredients expressed in percent by weight in a mixing vessel at room temperature and stirring until thoroughly mixed:

	Percent
Monoethanolamine	60
Hexylene glycol	20
Water	20

The mixture had a pH of 12.7. It was charged into a trough and the above exposed diazo paper was passed through the developing zone at about 30 ft./min. which resulted in applying 1.1 grams of the developer solution per square meter of the latent image bearing surface.

A study of the density of the azo dye image measured at various time intervals after going through the processing steps of the instant invention showed the following:

	Density units
15 sec.	1.07
30 sec.	1.11
60 sec.	1.13
2 min.	1.15
5 min.	1.15
Ammonia developed	1.18

7

The above values represent an average of several readings taken on the image using a standard reflectance densitometer and the values are reflectance density units with the instrument calibrated against a magnesium oxide block.

The copy was immediately readable upon emerging from the last processing step. Moderate amounts of heat applied at the time of development such as by warming the developer solution or heating the emerging copy will accelerate the azo dye image formation. In the case of black line prints this may be desirable. However, it should be pointed out that use of heat is optional and not necessary to the successful operation of the process. The copy was dry to the touch, measuring less than 10% in moisture content; it could be handled, written upon with ink or pencil, folded or filed, as required. An examination of the copy after it was aged for a period of several weeks showed no undue discoloration of the background, that is, it was comparable in all respects to diazotype prints processed by known conventional developing techniques.

## EXAMPLE II

A developer of the following formulation was prepared:

	Percent
Monoethanolamine .....	60
Diethylene glycol .....	25
Water .....	15

An exposed two-component diazotype material, such as described in Example I, was processed in accordance with the procedure of Example I. A measurement of the amount of developer applied to the image revealed that from 1.1 to 1.2 grams of developer were applied per square meter of latent image bearing surface. A visible-readable azo dye image was immediately observed as the copy sheet emerged from the last processing step which, after 15 seconds, had a density of about 1.13 units measured on a standard reflectance densitometer. The copy was dry and ready for use.

## EXAMPLE III

The following formulations represent various developing solution of this invention in addition to those described in the previous examples. In all cases the developer formulations produced diazo prints of the quality described in the previous examples.

## Formula A

	Percent
2-(2-aminoethoxy)ethanol .....	40
Hexylene glycol .....	25
Diethylene glycol .....	10
Water .....	25

pH 12.3.

## Formula B

	Percent
2-(2-aminoethoxy)ethanol .....	50
(Diglycolamine) diethylene glycol .....	25
Water .....	25

pH 12.5.

## Formula C

	Percent
Diethanolamine .....	40
Diethyleneglycol .....	30
4-methoxy-4-methyl-pentanol-2 .....	20
Water .....	10

pH 11.7.

## Formula D

	Percent
Morpholine .....	5
Monoethanolamine .....	10
Dimethylethanolamine .....	5
4-methoxy-4-methyl-2-pentanol .....	20
Ethylene glycol monomethyl ether .....	10
Hexylene glycol .....	25
Water .....	25

pH 11.9.

8

## Formula E

	Percent
Monoethanolamine .....	50
N-methylethanolamine .....	10
Triethanolamine .....	10
Ethylene glycol monomethyl ether .....	10
Water .....	20

pH 12.2.

## Formula F

	Percent
Monoethanolamine .....	40
Ethylene glycol .....	30
Glycerol .....	10
Water .....	20

pH 12.4.

## Formula G

	Percent
Monoethanolamine .....	40
Tetraethylene glycol .....	30
Water .....	30

pH 12.8.

## Formula H

	Percent
Diethylene triamine .....	50
Hexylene glycol .....	25
Water .....	25

pH 12.9.

## Formula I

	Percent
Hexylamine .....	50
Hexylene glycol .....	25
Water .....	25

pH 12.6.

## Formula J

	Percent
Cyclohexylamine .....	50
Diethylene glycol .....	25
Water .....	25

pH 13.1.

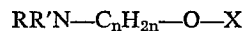
In all of the foregoing formulas the developers were extremely stable. While the developers did experience some evaporation under low humidity conditions, it was found that their consistency remained essentially unchanged. No appreciable change was noted in their effectiveness as alkaline compounds when exposed to air for long periods of time under ordinary conditions of use. The materials were found safe to handle and could be stored in containers for long periods of time without any adverse effect.

When water is present in the compositions, all or part of it can be replaced by a volatile water-miscible organic solvent such as a lower alcohol or ketone having a boiling point not greater than about 125° C.

In the foregoing description there have been presented in detail the method and various compositions useful in developing two-component diazotype materials which are intended to be exemplary without limiting the method or the composition contemplated by the instant invention as defined in the claims.

I claim:

1. A developer composition for developing two-component diazotype materials bearing latent images consisting essentially of from 20% to 80% by weight of a liquid organic amine dissolved in a compound selected from polyhydric alcohol, a glycol ether or a monohydric alcohol containing six carbon atoms, said amine having the formula:



wherein R and R' are the same or different alkyl or hydroxy alkyl radicals or hydrogen, X is hydrogen, alkyl or hydroxy alkyl, and n is an integer from 2 to 4, inclusive, and said composition has a pH value in the range of 10 to 14.0.

9

2. A developer composition as defined by claim 1 wherein the amine is an ethanolamine.

3. A developer composition as defined by claim 1 wherein the amine is an isopropanolamine.

4. A developer composition as defined by claim 1 wherein the amine is 2-(2-aminoethoxy)ethanol. 5

5. A developer composition as defined by claim 1 wherein the organic solvent is an ethylene glycol ether.

6. A developer composition as defined by claim 1 wherein the organic solvent is cyclohexanol.

7. A developer composition as defined by claim 1 wherein the organic solvent is diethyleneglycol mono-ethylether. 10

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8. A developer composition as defined by claim 1 wherein the organic solvent is hexylene glycol.

## References Cited

## UNITED STATES PATENTS

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2,308,058	1/1943	Crowley et al. ....	96—49

NORMAN G. TORCHIN, Primary Examiner

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,578,452

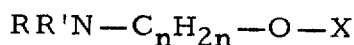
Dated May 11, 1971

Inventor KONRAD PARKER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The words "at least" should appear in Claim 1, at column 8, line 67, before "six carbon atoms", so that the entire claim correctly reads as follows:

1. A developer composition for developing two-component diazotype materials bearing latent images consisting essentially of from 20% to 80% by weight of a liquid organic amine dissolved in a compound selected from polyhydric alcohol, a glycol ether or a monohydric alcohol containing at least six carbon atoms, said amine having the formula:



wherein R and R' are the same or different alkyl or hydroxy alkyl radicals or hydrogen, X is hydrogen, alkyl or hydroxy alkyl, and n is an integer from 2 to 4, inclusive, and said composition has a pH value in the range of 10 to 14.0.

Signed and sealed this 29th day of August 1972.

(SEAL)  
Attest:

EDWARD M. FLETCHER, JR.  
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Commissioner of Patents