

PATENT SPECIFICATION

1,143,703

NO DRAWINGS.

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Int. Cl.:—G 03 c 5/34.

COMPLETE SPECIFICATION.

Diazotype Development Materials.

We, ADDRESSOGRAPH-MULTIGRAPH CORPORATION, of 1800 West Central Road, Mount Prospect, Illinois, United States of America, a Corporation organised under the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for developing diazotype materials and their use. More particularly, it relates to compositions for the development of two-component diazotype materials.

Diazotype 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 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 contained along with the diazonium salt and

the coupler on the copy material. 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.

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

The one-component systems have effectively eliminated the odor problem by applying liquid developers directly to the copy sheet. Reproduction equipment for use

[Price 4s. 6d.]

Price 25s

with the one-component type papers requires the use of heating elements in order to dry the copy sheet after development.

5 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.

10 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:

- 20 1. In general, the use of dilute alkaline solutions produced prints of rather low image density when compared to development with ammonia.
- 25 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.
- 30 3. Alkaline developer solutions formulated with non-volatile inorganic salts, such as disclosed in British Patent Specification No. 295,993, required an inordinately long time to develop into a print having suitable image density.
- 35 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.
- 40 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.
- 50

In the Applicants co-pending Application No. 10800/66 (Serial No. 1,143,702), from which this present Application is divided, there is described and claimed a method of developing a latent image-bearing two-component diazotype material in which an alkaline developer liquid is applied to the latent image in an amount not exceeding 3 grams per square metre to produce a visible, readable image on the two-component diazotype material instantaneously. As the copy emerges from the developing region of a developer apparatus for example

the apparatus described in U.K. Patent Application No. 10800/66 (Serial No. 1,143,702), it is completely developed. There does occur an increase in density with time after emergence from the developing region with the copy attaining a maximum density within one minute and usually within 15 seconds upon the application of the developing solution of this invention. Understandably, the range at which maximum density is reached will depend in part upon the couplers and diazonium compounds comprising the sensitizing formula used in preparing the copy sheets.

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 diazonium 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.

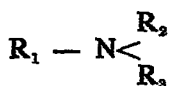
It is the first reaction to which this invention is directed. The second reaction or coupling proceeds at a rate determined solely by the particular reactants once the proper pH has been provided.

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 diazo 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 liquid must react rapidly with the acid component; it should not discolour the print background; and it should not be absorbed into the body of copy material but remain only at the surface thereof. This presents the problem of applying just the right amount of fluid to accomplish development without excessively wetting or saturating the sheet. The composition of the developer liquid will be considered further in greater detail hereinafter.

Giving pause to consider the nature of the surface of the copy sheet coated with a solution containing a light sensitive diazonium salt, a coupler, and an acid component, it has been found that the chemicals in the sensitizing solution are deposited on the individual random cellulose fibre structure at the paper surface and, in the case of films, absorbed into the treated or prepared portion of the surface. For the liquid developer to be effective, it must

penetrate and completely wet out the random fibre structure of the treated film surface.

- The invention provides developer compositions for developing a latent image bearing two-component diazotype material comprising 20% to 80% (by weight) of a liquid organic amine dissolved in as diluent a polyhydric alcohol, a glycol ether, or a monohydric alcohol containing at least six carbon atoms, said diluent containing water in an amount equal to from 0% to 200% (preferably 0 to 100%) of the weight of the organic solvent, said amine being morpholine, piperidine, alkyl-substituted morpholine, alkyl-substituted piperidine, or an amine of the formula



- wherein R_1 is hydrogen, alkyl or hydroxyalkyl; R_2 is cycloalkyl, hydroxyalkyl or hydroxyalkoxyalkyl; and R_3 is hydrogen hydroxyalkyl or alkyl containing at least six carbon atoms.

- The diluent may be present in amounts ranging from 40% to 60%. The operable pH range of the developer solutions prepared in accordance with this invention is within 10 to 14.

- The following amines have been eminently successful in the practice of the method: monoethanolamine; isopropanolamine; 2-(2-aminoethoxy) ethanol; triethanolamine; diethanolamine; 2-amino-2-methyl-1-propanol; N-methyl-ethanolamine; dimethylethanolamine; hexylamine; cyclohexylamine; 2-(2-aminoethoxy) ethanol. Other amines have demonstrated the ability to develop the diazo print such as N-aminoethyl-ethanolamine; alkyl substituted morpholine and piperidine; but are somewhat less desirable because they have a detectable odour or they tend to adversely affect the dye shade.

- The use of a diluent provides a greater latitude for the amount of developer liquid that may be applied within the specified range and still provide the optimum amount of amine. The use of a diluent also aids in the spreadability and wetting out of the developer across the area to which it is applied.

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

- hexylene glycol
diethylene glycol
polyethylene glycol
trimethylene glycol
ethylene glycol
propylene glycol
dipropylene glycol
glycerine

and glycol-ethers such as:

ethylene glycol monoethyl ether
("Cellosolve")
diethylene glycol monoethyl ether 65
butyl "Cellosolve"
(The word "Cellosolve" is a Registered Trade Mark)

or a mono-functional alcohol such as:

4-methoxy-4 methyl-pentanol-2 70
(Pentoxol)
2-ethyl hexanol
cyclohexanol
isooctyl alcohol
hexanol 75

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 monohydric alcohol, or mixtures thereof. The diluent may be a mixture of equal parts of water, polyhydric alcohol and a glycol ether. 90

In general, most of the commercially available two-component papers can be used successfully with the developers of this invention. The quality of the final print and the rapidity with which the print develops will depend in part of 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: 100

p-amino-N, N-diethylaniline
p-amino-N -ethylaniline
p-amino-N -ethyl-N-hydroxyethylaniline
p-amino-N -methyl-N-hydroxyethylaniline 105
p-amino-N, N-di- β -hydroxyethylaniline
p-amino-N, -ethyl-*o*-toluidine
p-amino-N -ethyl-*m*-toluidine
p-amino-N, N-diethyl-*m*-toluidine
p-amino-N-ethyl-N-(β -hydroxyethyl)-*m*-toluidine 110
N-*p*-aminophenylmorpholine
1-amino-2,5-diethoxy-4-morpholinobenzene

Examples of couplers that may be used are resorcinol, acetoacetanilide, 4-chlororesorcinol, diresorcinol, diacetoacetylene-diamine, aminoethylethanolamine amide of 3-hydroxy-2-naphthoic acid, 2,3 dihydroxy- 115

6-naphthalene sulfonic acid (sodium salt).

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 c.c.
diethylene glycol	...	...	40 c.c.
citric acid	...	...	20 grams
zinc chloride	...	...	50 grams
isopropyl alcohol	...	...	10 c.c.
2,3-dihydroxy naphthalene, 6-sulfonic acid (sodium salt)	...	...	40 grams
p-diazo-N,N-diethylaniline	...	...	15 grams
zinc chloride	...	...	30 grams
thiourea	...	...	1000 c.c.
water to make	...	...	1000 c.c.

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 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:

monoethanolamine	...	...	60%
hexylene glycol	...	...	20%
water	...	...	20%

The mixture had a pH of 12.7. It was charged into the trough and the above exposed diazo paper was passed through the developing zone at 9.1 meters/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 showed the following:

	15 sec.	30 sec.	60 sec.	2 min.	5 min.	Ammonia Developed
	1.07	1.11	1.13	1.15	1.15	1.18

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 the 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 discolouration of the background, that is, it was comparable in all respects to diazo-type prints processed by known conventional developing techniques.

EXAMPLE II

2-(2-aminoethoxy) ethanol	...	...	40%
hexylene glycol	...	...	25%
diethylene glycol	...	...	10%
water	...	...	25%
pH 12.3	...	...	...

EXAMPLE III

diethanolamine	...	...	40%
diethyleneglycol	...	...	30%
4-methoxy-4 methyl-pentanol-2	...	...	20%
water	...	...	10%
pH 11.7	...	...	...

EXAMPLE IV

morpholine	...	...	5%
monoethanolamine	...	...	10%
dimethyl ethanolamine	...	...	5%
Pentoxol solvent	...	...	20%
Cellosolve (a Registered Trade Mark)	...	...	10%
hexylene glycol	...	...	25%
water	...	...	25%
pH 11.9	...	...	...

EXAMPLE V

monoethanolamine	...	...	50%
N-methylethanolamine	...	...	10%
triethanolamine	...	...	10%
methyl Cellosolve	...	...	10%
water	...	...	20%
pH 12.2	...	...	...

EXAMPLE VI

monoethanolamine	...	...	40%
ethylene glycol	...	...	30%
glycerine	...	...	10%
water	...	...	20%
pH 12.4	...	...	...

EXAMPLE VII

monoethanolamine	40%
tetraethylene glycol	30%
water	30%

pH 12.8

EXAMPLE VIII

diethylene triamine	50%
hexylene glycol	25%
water	25%

pH 12.9

EXAMPLE IX

cyclohexylamine	50%
diethylene glycol	25%
water	25%

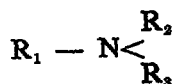
pH 13.1

In all the foregoing examples 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 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.

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

WHAT WE CLAIM IS:—

1. A developer composition for developing a latent image bearing two-component diazotype material comprising 20% to 80% (by weight) of a liquid organic amine dissolved in as diluent a polyhydric alcohol, a glycol ether, or a monohydric alcohol containing at least six carbon atoms, said diluent containing water in an amount equal to from 0% to 200% of the weight of the organic solvent, said amine being morpholine, piperidine, or an amine of the formula



wherein R_1 is a hydrogen, alkyl or hydroxyalkyl; R_2 is cycloalkyl, hydroxyalkyl or hydroxyalkoxyalkyl; and R_3 is hydrogen, hydroxyalkyl or alkyl containing at least six carbon atoms.

2. A developer as claimed in claim 1 containing water in an amount of from 0 to 100% of the weight of the organic solvent.

3. A developer as claimed in claim 1 or 2, in which said amine is monoethanolamine.

4. The developer as claimed in claim 1 or 2, wherein said amine is 2-(2-aminoethoxy) ethanol.

5. The developer as claimed in claim 1 or 2 wherein said amine is methylethanolamine.

6. The developer as claimed in claim 1 or 2 wherein said amine is dimethylethanolamine.

7. The developer as claimed in claim 1 or 2 wherein said amine is isopropanol amine.

8. The developer as claimed in claim 1 or 2 wherein said amine is triethanolamine.

9. The developer as claimed in claim 1 or 2, wherein said amine is diethanolamine.

10. The developer as claimed in claim 1 or 2, wherein said amine is 2-amino-2-methyl-1-propanol.

11. The developer as claimed in claim 1 or 2, wherein said amine is hexylamine.

12. The developer as claimed in claim 1 or 2, wherein said amine is cyclohexylamine.

13. The developer as claimed in claim 1 or 2, wherein said amine is N-aminoethyl-ethanolamine.

14. The developer as claimed in any preceding claim wherein said diluent is a mixture of equal parts of water and a polyhydric alcohol.

15. The developer as claimed in any preceding claim wherein said diluent is a mixture of equal parts of water, polyhydric alcohol and a glycol-ether.

16. The developer as claimed in any preceding claim wherein said diluent is hexylene glycol.

17. The developer as claimed in any preceding claim containing from 40% to 60% of diluent.

18. A developer as claimed in any preceding claim having the formula:

50%	aliphatic amine
25%	polyhydric alcohol
25%	water

19. A developer composition as claimed in claim 1 substantially as herein described.

20. A developer composition substantially as described in Example I to IX.

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EXAMPLE VII

monoethanolamine	...	...	40%
tetraethylene glycol	...	...	30%
water	...	...	30%
pH	12.8		

EXAMPLE VIII

diethylene triamine	...	...	50%
hexylene glycol	...	...	25%
water	...	...	25%
pH	12.9		

EXAMPLE IX

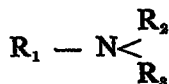
cyclohexylamine	...	...	50%
diethylene glycol	...	...	25%
water	...	...	25%
pH	13.1		

In all the foregoing examples 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 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.

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wherein R_1 is a hydrogen, alkyl or hydroxyalkyl; R_2 is cycloalkyl, hydroxyalkyl or hydroxyalkoxyalkyl; and R_3 is hydrogen, hydroxyalkyl or alkyl containing at least six carbon atoms.

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25%	water

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