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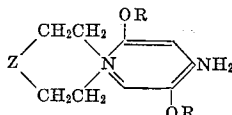
ONE-COMPONENT DIAZOTYPES

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ABSTRACT OF THE DISCLOSURE

One-component diazotype photoprinting material and sensitizing compositions therefor, comprising acetamide or formamide and a diazonium salt derived from an N-benzyl - N - alkyl-p-phenylenediamine or of a 4-morpholino- or 4 - thiomorpholino - 2,5 - dialkoxyaniline in which the alkoxy groups have 3 to 5 carbon atoms.

This invention relates to light-sensitive one-component diazotype printing materials having fast printing speeds and being capable of yielding prints having dye images of high density wherein said light-sensitive one-component diazotype comprises an amide selected from the group consisting of formamide and acetamide. More particularly this invention relates to one-component diazotype printing materials having fast printing speeds and being capable of yielding prints having dye images of high density wherein said light-sensitive one-component diazotype comprises a diazonium salt of at least one amine selected from the group consisting of N-benzyl-N-alkyl-p-phenylenediamine and



wherein Z is a divalent radical selected from the group consisting of —O—, —S—,



and —CH₂— and R is an alkyl group of from 3 to 5 carbon atoms.

There has been a continuous demand for faster printing light-sensitive diazotype materials which yield prints having dye images of high density and good contrast. The diazotype process in commercial use is a bleach-out positive process which generally utilizes equipment that performs successively the two operations of exposure and development by transporting the print material with the same speed through separate exposure and development chambers. In order to achieve the maximum possible output, these printers are usually operated at, or near, their maximum speed. In general, the maximum speed of these printers has been determined by the light-sensitivity and concentration of the light-sensitive diazonium compound. For example, if one uses a given diazo of a certain ultraviolet light sensitivity, a reduction in concentration of the diazo will permit one to achieve faster printing. This is due, of course, to the fact that there is less diazo to burn out in the non-image areas and less diazo to couple in the image areas. However, it is equally evident that the increase in printing and development speed is obtained at the sacrifice of azo dye density in the image produced by subsequent development. As diazonium compounds of greater light-sensitivity have become available, there has been a decided tendency when operating the printing machines at, or near, their maximum speed, for incomplete development of the diazonium compound in the developing chamber. This is a severe problem since the undecomposed diazonium compound in the image

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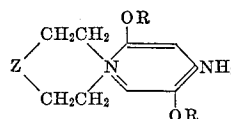
areas has a tendency to bleach out thereby destroying the contrast between image and non-image areas. Essentially the same problem has been experienced with both the dry (two-component diazotypes) and semi-wet (one-component diazotype) processes.

Various suggestions have been made such as to increase the size of the developing chamber and/or run the print through the developing chamber a second time. However, these suggestions have not been very practical.

U.S.P. 2,727,820 proposed to solve this problem in the processing of two-component diazotypes by incorporating carboxamides into the sensitizer. The carboxamides, which are stated to be effective when they comprise from 10 to 50 percent by weight of the aqueous sensitizer composition (preferably 25 to 35 percent by weight), apparently promote and speed up the rate of development of two-component diazotypes. However, the relatively high concentration of carboxamide employed is economically unattractive. Attempts to improve the processing of one-component diazotypes in the same manner has been unsuccessful. For some unknown reason diazonium compounds in one-component diazotypes tend to decompose when prepared with the concentration of carboxamide recommended in U.S.P. 2,727,820. This decomposition leads to loss of background contrast. Further, there is a tendency for the carboxamides when used in the high concentration required in U.S.P. 2,727,820 in one-component diazotypes to leach out of the diazotype paper into the developing bath and contaminate said bath. This contamination tends to lead to undesirable variations in dye coloration in the image areas.

The object of this invention is to provide one-component diazotypes of enhanced dye density and brightness which can be processed completely at relatively high speeds on conventional one-component diazotype prints without loss of maximum dye density.

The objects of my invention can be accomplished by employing certain highly light-sensitive and fast coupling diazonium compounds in conjunction with either acetamide or formamide. The diazonium compounds useful in my invention comprise the diazonium salts of N-benzyl-N-alkyl-p-phenylenediamine and



wherein Z is a divalent radical selected from the group consisting of —O—, —S—,



and —CH₂— and R is propyl, butyl or amyl. I have now found that the coupling speed and dye density of the one-component diazotypes based on these diazonium compounds can be enhanced with relatively small concentrations of acetamide and/or formamide. At the concentration of acetamide and/or formamide useful in my invention there is no tendency for the diazonium compounds of my invention to decompose prematurely in one-component diazotypes. Likewise there is virtually no contamination of the developing bath. In general the acetamide and/or formamide can comprise from about 1 to 10% by weight of the aqueous sensitizing composition or from about .5 to 15 parts by weight per part by weight of light-sensitive diazonium compound.

In somewhat greater detail the diazonium compounds useful in my invention are the diazotization products of:

N-benzyl-N-methyl-p-phenylenediamine
 N-benzyl-N-ethyl-p-phenylenediamine
 N-benzyl-N-propyl-p-phenylenediamine
 N-benzyl-N-butyl-p-phenylenediamine
 2,5-dibutoxy-4-morpholinoaniline
 2,5-dibutoxy-4-thiomorpholinoaniline
 2,5-dibutoxy-4-piperazinoaniline
 2,5-dibutoxy-4-piperidinoaniline
 2,5-dipropoxy-4-morpholinoaniline
 2,5-diamyloxy-4-morpholinoaniline

These compounds are preferably stabilized in the form of their salts with zinc chloride, tin chloride, cadmium chloride and the like.

Azo coupling components which are incorporated in the developing bath of this invention are for example

2-(m-hydroxyphenoxy)ethanol
 2,3-dihydroxynaphthalene
 1,8-dihydroxynaphthalene
 Phloroglucinol
 Resorcinol
 Octylresorcinol
 Alpha-resorcyamid
 3-methyl-1-phenyl-5-pyrazolone
 Acetoacetanilide
 H-acid
 2,3-dihydroxynaphthalene-6-sulfonic acid
 2,5-xylenol
 2-methyl resorcinol

Acid stabilizers such as citric acid, tartaric acid, boric acid, acetic acid and similar acid reacting compounds are used to prevent premature coupling of the diazonium salt and azo coupling component.

In addition to the foregoing materials there can also be included reagents commonly employed in diazotype photoprinting materials, as for example, intensifiers such as ammonium sulfate, zinc chloride or nickel sulfate; stabilizing agents such as thiourea, or thiosinamine; accelerators such as 1-allyl-3-beta-hydroxyethyl-thiourea or 1-allyl-thiourea; hygroscopic agents such as glycol or glycerin; and wetting agents such as saponin, lauryl sulfate, keryl benzene sulfonate or oleyl-N-methyltaurine.

The components of the sensitizing composition are preferably incorporated in a single solution or suspension and applied in a single coating step to the base. The latter can be paper, or film such as regenerated cellulose, cellulose acetate or other plastic films.

The material coated in accordance with this invention is developed after exposure under an opaque pattern on a translucent background, by passing the exposed copy through the developing bath containing coupler or couplers.

The following examples are merely illustrative and should not be construed as limiting the scope of this invention. In the examples that follow, parts and percentages are by weight unless otherwise indicated:

EXAMPLE I

Paper base material was coated uniformly with the following sensitizing composition:

	Parts by weight
Tartaric acid	0.3
Aluminum sulfate	0.3
Thiourea	0.3
Acetamide	9.0
Sodium 2,7-naphthalene disulfonate	1.0
4-N-ethyl-N-benzylaminobenzene diazonium chlorozincate	0.7
Granular POCl ₃ inhibited corn starch	10
Silica	2
Polyvinyl acetate emulsion	4
Water	100

The paper was dried, exposed to light under a translucent original containing opaque image areas and de-

veloped by passing the exposed sheet through the following fresh alkaline developing solution using a commercially available developing machine at the correct printing speed:

	Parts by weight
Borax	50
Sodium carbonate	20
Thiourea	10
Phloroglucinol	8
Resorcinol	6
Sodium salt of isopropyl-naphthalene sulfonic acid	2
Water	1000

A black dye was formed which had greater density and brightness than a print made in the same manner except acetamide was omitted from the sensitizing formula. Ninety percent of the maximum available dye density was formed using the sensitizer containing acetamide as opposed to 80 percent of the maximum dye density when acetamide was omitted.

EXAMPLE II

Paper base material was coated uniformly with the following sensitizing composition:

	Parts by weight
Tartaric acid	0.3
Aluminum sulfate	0.3
Thiourea	0.3
Acetamide	5.0
Sodium 2,7-naphthalene disulfonate	1.0
4-N-ethyl-N-benzylaminobenzene diazonium chlorozincate	0.7
Granular POCl ₃ inhibited corn starch	10
Silica	2
Polyvinyl acetate emulsion	4
Water	100

The paper was dried, exposed to light under a translucent original containing opaque image areas and developed by passing the exposed sheet through the following fresh alkaline developing solution using a commercially available developing machine at the correct printing speed:

	Parts by weight
Borax	50
Sodium carbonate	20
Thiourea	10
Phloroglucinol	8
Resorcinol	6
Sodium salt of isopropyl-naphthalene sulfonic acid	2
Water	1000

A black dye was formed which had greater density and brightness than a print made in the same manner except acetamide was omitted from the sensitizing formula. Eighty-five percent of the maximum available dye was formed using the sensitizer containing acetamide.

EXAMPLE III

Paper base material was coated uniformly with the following sensitizing composition:

	Parts by weight
Tartaric acid	0.3
Aluminum sulfate	0.3
Thiourea	0.3
Formamide	5.0
Sodium 2,7-naphthalene disulfonate	1.0
4-N-ethyl-N-benzylaminobenzene diazonium chlorozincate	0.7
Granular POCl ₃ inhibited corn starch	10
Silica	2
Polyvinyl acetate emulsion	4
Water	100

The paper was dried and exposed to light under a translucent original containing opaque image areas. Develop-

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ment was obtained by passing the exposed sheet through the following alkaline solution:

	Parts by weight
Borax -----	50
Sodium carbonate -----	20
Thiourea -----	10
Phloroglucinol -----	8
Resorcinol -----	6
Sodium salt of isopropyl-naphthalenesulfonic acid --	2
Water -----	1000

A black dye was formed which had greater density and brightness than a print made in the same manner except formamide was omitted from the sensitizing formula.

EXAMPLE IV

Paper base material was coated uniformly with the following sensitizing composition:

	Parts by weight
Tartaric acid -----	0.3
Aluminum sulfate -----	0.3
Thiourea -----	0.3
Acetamide -----	5.0
Sodium 2,7-naphthalene disulfonate -----	1.0
2,5 - dibutoxy - 4 - morpholinobenzenediazonium chlorozincate -----	0.7
Granular POCl ₃ inhibited corn starch -----	10
Silica -----	2
Polyvinyl acetate emulsion -----	4
Water -----	100

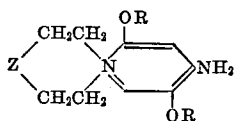
The paper was dried, exposed to light under a translucent original containing opaque image areas and developed by passing the exposed sheet through the following fresh alkaline developing solution using a commercially available developing machine at the correct printing speed:

	Parts by weight
Borax -----	50
Sodium carbonate -----	20
Thiourea -----	10
Phloroglucinol -----	8
Resorcinol -----	6
Sodium salt of isopropyl-naphthalenesulfonic acid --	2
Water -----	1000

A black dye was formed which had greater density and brightness than a print made in the same manner except acetamide was omitted from the sensitizing formula. Eighty-nine percent of the maximum available dye was formed using the sensitizer containing acetamide. Ninety-four percent of the maximum available dye was formed by increasing the acetamide concentration from 5 to 9 parts.

Variations and modifications can be made in the procedures, compositions and materials herein described without departing from the scope or spirit of this invention. I claim:

1. A sensitizing composition for one-component diazo-type material characterized by fast printing speeds and being capable of yielding prints having dye images of high density comprising water, an amide selected from the group consisting of formamide and acetamide and a diazonium salt formed by diazotizing the primary amino group of the compounds selected from the group consisting of N-benzyl-N-alkyl-p-phenylenediamine and



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wherein Z is a divalent radical selected from the group consisting of —O—, —S—,



and —CH₂—, R is an alkyl group of 3–5 carbon atoms and said amide comprises from about 1 to 10% by weight of said sensitizing composition, said composition excludes an azo-coupling component.

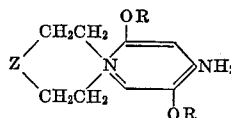
2. The composition of claim 1 wherein said amide comprises acetamide.

3. The composition of claim 1 wherein said amide comprises formamide.

4. The composition of claim 1 wherein said diazonium salt comprises a diazotized salt of N-benzyl-N-ethyl-p-phenylenediamine.

5. The composition of claim 1 wherein said diazonium salt comprises a diazotized salt of 2,5-dibutoxy-4-morpholinoaniline.

6. One-component diazo-type photoprinting material characterized by having fast printing speeds and being capable of yielding prints having dye images of high density comprising a base having on a surface thereof a light-sensitive layer comprising an amide selected from the group consisting of acetamide and formamide and a diazonium salt formed by diazotizing the primary amino group of the compounds selected from the group consisting of N-benzyl-N-alkyl-p-phenylenediamine and



wherein Z is a divalent radical selected from the group consisting of —O—, —S—,



and —CH₂— and R is an alkyl group of 3–5 carbon atoms and said amide comprises from about 1 to 10% by weight of the aqueous sensitizing formulation for said layer, said layer excludes an azo-coupling component.

7. The article of claim 5 wherein said amide comprises acetamide.

8. The article of claim 6 wherein said amide comprises formamide.

9. The article of claim 6 wherein said diazonium salt comprises a diazotized salt of N-benzyl-N-ethyl-p-phenylenediamine.

10. The article of claim 6 wherein said diazonium salt comprises a diazotized salt of 2,5-dibutoxy-4-morpholinoaniline.

References Cited

UNITED STATES PATENTS

2,727,820	4/1952	Botkin et al. -----	96—91 XR
2,822,272	2/1958	Kosalek et al. -----	96—75 XR
2,840,472	6/1958	Sus et al. -----	96—75
3,028,240	4/1962	Werner et al. -----	96—91
3,255,007	6/1966	Kosar -----	96—49
3,255,011	7/1966	Welch -----	96—75

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