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54 **Diazo type compositions and materials.**

57 The use of soluble methylol compounds from primary or secondary amines or ammonia with formaldehyde in diazo types improves solution compatibility and prevents coupler migration upon storage of diazo type materials. The methylol compounds may be reacted with couplers separately or added to the coating preparations.

DIAZOTYPE COMPOSITIONS AND MATERIALSBACKGROUND OF THE INVENTIONField of the Invention

The invention relates to diazotypy and more particularly relates to improved diazotype compositions, materials and diazonium compound couplers used therein.

Brief Description of the Prior Art

The diazotype reproduction process is well known to the art and is described in great detail in "Light Sensitive Systems" by Jaromir Kosar, John Wiley & Sons, Inc., N.Y. 1965, and in "Reproduction Coating" by E. Jahoda, 4th Edition, Andrews Paper & Chemical Co., Inc., Port Washington, New York.

In general, diazotype reproduction prints are obtained by an imagewise exposure of a light-sensitive diazo material to ultraviolet light followed by development of the exposed diazotype material. There are several different methods available to develop the latent image imposed on the light-sensitive diazo material by the light exposure including ammonia development, amine development, thermal development and moist (liquid) development.

The light-sensitive diazo material generally comprises a light-sensitive diazo composition affixed to a support base such as paper or film such as polyethylene terephthalate film, cellulose acetate, or a polymeric resin coated, base support. The light-sensitive diazonium may comprise a light-sensitive diazonium salt compound in

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admixture with diazo enhancing compounds. Upon exposure of the light-sensitive diazonium compound to ultraviolet light through a translucent original having opaque image portions, the unmasked portions of the diazonium salt are decomposed by the ultraviolet radiation whereas the masked portions are left undecomposed. The latent image created by the image-wise exposure may then be developed by the methods described above.

In the so-called "dry development" process, the light-sensitive diazo composition will contain, in addition to the light-sensitive diazonium salt, an azo coupling agent or color former and an acidic coupling inhibitor. Development of the latent azo dye image is accomplished by placing the exposed diazo material in an alkaline atmosphere which neutralizes the acidic inhibitor, allowing the undecomposed diazonium salt and coupler to react to form an azo dye.. The latent image is thereby developed.

It is of great importance in the dry development processes that print development be obtained rapidly and that a minimum of premature development and other deterioration of diazotype materials occur during the time between their manufacture and their use, a period which may be of 6 months length or more.

Unfortunately, most diazo compounds have low stability and tend to decompose quickly. The coupling reaction of a diazo composition containing a coupler unavoidably begins

and continues at a very slow rate, immediately after the manufacture of the diazotype materials (i.e., precoupling). Consequently, their shelf life is very limited unless efficient stabilizers are added to delay or block such reactions.

Stabilizers for diazotype materials have several drawbacks. For example, they tend to slow the desired coupling reaction during development when it is supposed to occur rapidly. They also may adversely influence the developed image appearance by reducing brilliance and shifting color shades. Many stabilizers are not compatible with diazo coating solutions because they rapidly form insoluble salts or complexes with diazo compounds or couplers.

Azo dye couplers are organic compounds with active methylene groups or aromatic hydroxyl groups, and they may or may not also have carboxylic or sulfonic groups, the use of low molecular weight couplers and various phenol or resorcinol derivative types of couplers often produce desirable print dyes, but they tend to migrate from the diazotype composition layer during storage of the diazotype materials. Mono and dihydroxy naphthalene types of couplers do not migrate but are poorly soluble in acidic solutions. Their mono and disulfonated derivatives are mostly water and acid soluble but the better their solubility, the more they tend to migrate upon storage. From the diazotype material the migration of couplers results in a substantial loss of print dye when coupling is initiated during development.

Moreover, the print dye color changes substantially if the diazotype composition contains a mixture of couplers with different migration tendencies. Thus, a freshly produced blackline diazotype composition may develop to a deep black dye and grey half tones, but after a month of storage, the same material will develop to flat dyes of brown or blue color depending upon which coupler tended to migrate more.

Azo dye couplers of larger molecular weight tend not to migrate, but they are often poorly soluble and have solution compatibility problems with diazoniums or commonly used stabilizers. They will not go in solution and may precipitate with one of the other diazonium composition components.

It is an objective of this invention to overcome the above problems and to provide for diazo coating compositions to be more consistent in the development of print colors regarding shade and print dye density even after prolonged periods of storage. The invention also provides diazo coating preparations with improved solution compatibility. For example, it has been found that blackline diazotype compositions of the invention containing as a blue coupling component 2,7-dihydroxynaphthalene-3,6-disulfonic acid sodium salt, upon aging, did not exhibit the usual print color shift towards brown, due to migration of the highly water-soluble coupler. Similarly, no color shift towards blue occurred with easily migrating brown couplers such as chlororesorcinol or yellow couplers such as cyanoacet

morpholide in the compositions of the invention.

U. S. Patent 2,531,485 teaches the addition of secondary amines to diazotype compositions containing sulfonated hydroxynaphthalenes as couplers for improving print dye water fastness. However, such additions do not stop migration of the coupler upon storage of the diazotype material prior to printing the azo dye development.

Mannich bases of alkyl phenols have been disclosed in U. S. Patents 2,946,684 and 3,139,341, as couplers with high actinic opacity of the azo dyes they form in diazotypes.

Improved water solubility through formation of Mannich bases has been disclosed for 2-hydroxy-naphthoic amides in U. S. Patent 3,433,960, and for 1-hydroxy-4-alkoxy-naphthalenes 8-sulfonamides in U. S. Patent 3,664,840.

However, none of these disclosures reveal or are concerned with coupler migration of highly water-soluble couplers and inhibition of migration through conversion of such couplers into their Mannich bases.

SUMMARY OF THE INVENTION

The invention comprises a diazotype sensitizing composition, prepared with;

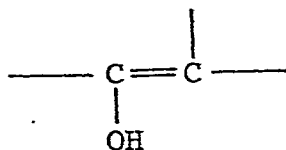
- (a) a diazonium compound; and
- (b) a coupling agent which comprises the reaction mixture obtained upon reaction of

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- (i) a compound capable of coupling the diazonium compound (a) and having an enolic moiety selected from the group consisting of an aromatic compound of six carbon atoms, substituted with at least 2 hydroxy groups and having at least 3 hydrogen atoms in the ring thereof, an N-mono-substituted acetacetamide, an N-di-substituted acetoacetamide, an N-mono-substituted cyanoacetamide and an N-di-substituted cyanoacetamide; and
- (ii) formaldehyde; with
- (iii) a compound selected from the group consisting of a primary organic amine, a secondary organic amine, and ammonia;
- under Mannich reaction conditions.

The invention also comprises the use of the diazo sensitizing compositions of the invention in diazo materials and diazo reproduction processes.

The term "enolic moiety" as used through the specification and claims means a multivalent unit of the formula:-



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DETAILED DESCRIPTION OF THE PREFERRED
EMBODIMENTS OF THE INVENTION

5 The present invention comprises the use of a new azo dye coupler, in an otherwise conventional diazo sensitizing composition.

As is well known in the art, conventional diazo sensitizing compositions for the two-component diazotype process comprise at least one light-sensitive diazonium compound, at least one azo coupler and acidic stabilizers
10 which are desirable to obtain a diazotype copy. Additional components for such diazo compositions may include, for example:

1. development accelerators such as glycerol, polypropylene glycol, urea and the like to minimize the
15 necessary ammonia or amine concentration in the developing environment;

2. antioxidants such as thiourea and the like to stabilize diazotype prints against discoloration under daylight exposure;

20 3. contrast controlling compounds; and

4. solubilizers such as caffeine which improve the compatibility of the various components in the sensitizing solution.

Sometimes such components fulfill more than one of
25 these functions.

Acid stabilizers generally employed are well known as are methods of their preparation. Representative of such acid stabilizers are citric acid, tartaric acid, boric acid, mixtures thereof and the like or inorganic acid salts such as zinc sulfate, aluminum sulfate, zinc chloride and the like.

In the diazotype coating compositions of the present invention, any of the conventionally employed compounds described above may be used, with any of the known light-sensitive diazonium compounds. Such diazonium compounds and the method of their preparation are well known in the art. Representative of such diazonium compounds are:

1. Derivatives of 1-diazo-4-amino benzene with or without alkyl, oxyalkyl or halogen substitutions in the benzene ring and with alkyl or dialkyl or acyl or acyl-alkyl or aryl substitution on the amino nitrogen or with the amino nitrogen forming a member of a heterocyclic ring with or without a second hetero atom of oxygen or nitrogen.

2. Derivatives of 1-diazo-4-alkylaryl mercapto benzene with or without substitution in the benzene ring.

3. Derivatives of 1-diazo-4-phenyl benzene with and without substitution in the phenyl and in the benzene rings.

The prior art diazonium compounds employed in preparing light-sensitive diazo materials are generally used in the form of their acidic salts such as the zinc chloride,

cadmium chloride, stannic chloride, sulfate and borofluoride salts. The acid salt derivatives are generally more stable than the parent diazonium compounds, which will often decompose spontaneously under ambient conditions. Typical examples without limiting their scope are stabilized salts of:

- 1 diazo-4-dimethylamino benzene
- 1 diazo-4-diethylamino benzene
- 1 diazo-4-dipropylamino benzene
- 1 diazo-4-morpholino benzene
- 1 diazo-4-morpholino-2,5-dimethoxy benzene
- 1 diazo-4-morpholino-2,5-diethoxy benzene
- 1 diazo-4-pyrrolidino-3-methyl benzene
- 1 diazo-4-pyrrolidino-3-methoxy benzene
- 1 diazo-4-ethyl-hydroxyethylamino benzene
- 1 diazo-4-tolylmercapto-2,5-diethoxy-benzene
- 2 diazo-1-hydroxynaphthalene-5-sulfonic acid; and the like.

The diazo sensitizing compositions of the invention are a modification of the conventional diazo sensitizing compositions described above, in that the azo coupler ingredient is the reaction mixture obtained upon the reaction of a specific class of azo coupler with formaldehyde and a primary or secondary amine or ammonia under Mannich reaction conditions.

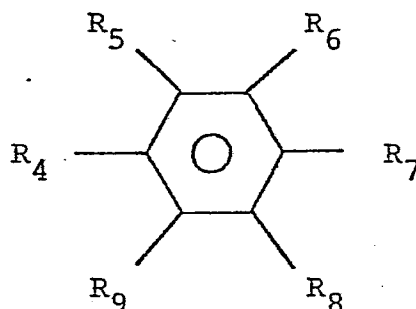
Azo couplers are generally aromatic compounds with phenolic hydroxyl groups with or without other substituent groups. The couplers are generally colorless.

Representative of azo couplers are:

- 5 1. resorcinol and its halogen and alkyl derivatives and ethers and diresorcinol sulfides;
2. resorcylic acids with or without halogen substitution in the ring and their amides and substituted amides;
- 10 3. compounds with active methylene groups such as aceto-acet derivatives and cyano-acet derivatives and the like.

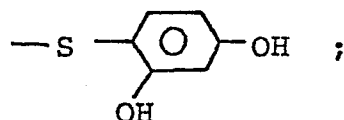
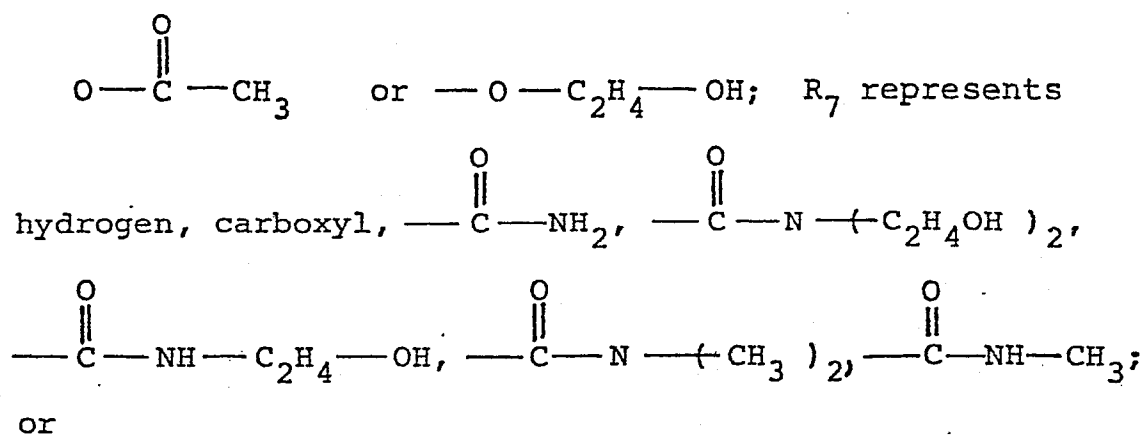
Employed in the present invention are known couplers characterized by possession of an enolic moiety as defined
15 above. Representative of such couplers are those of the formulae:-

(A)



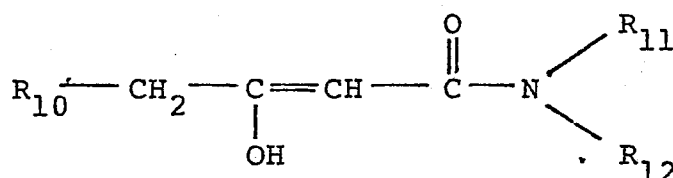
wherein R₄ represents one of hydrogen, hydroxyl or halogen;
R₅ represents one of hydrogen, hydroxyl, methyl or halogen;
20 R₆ represents one of hydrogen, hydroxyl or halogen the group

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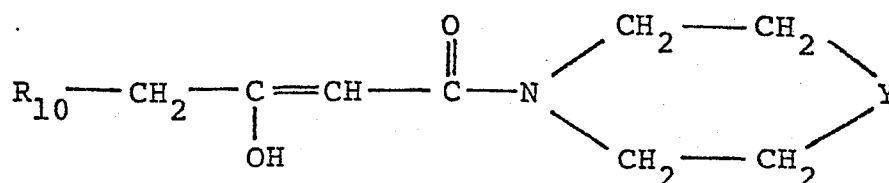
R_8 represents hydrogen; and R_9 is hydrogen or hydroxyl; provided at least two of $\text{R}_4, \text{R}_5, \text{R}_6$ and R_9 is hydroxyl; and at least two of $\text{R}_4, \text{R}_5, \text{R}_6, \text{R}_7$ and R_9 are hydrogen;

(B)



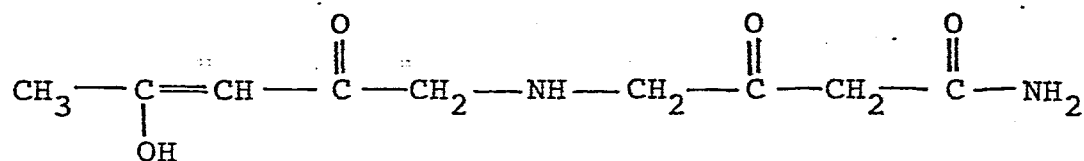
wherein R_{10} represents hydrogen or CN; R_{11} and R_{12} are each independently selected from the group consisting of hydrogen, alkyl, aryl, alkyl substituted aryl, hydroxy substituted aryl, alkoxy substituted aryl and sulfur substituted aryl;

(C)

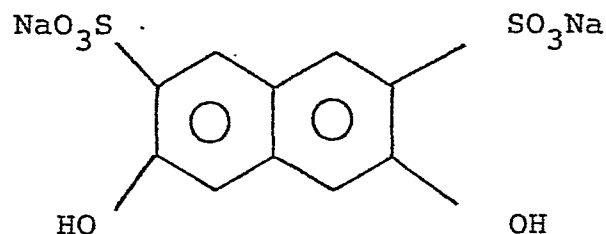


wherein R_{10} is as defined above and y is oxygen, nitrogen or sulfur;

(D)



(E)



It will be appreciated by those skilled in the art that the above-described couplers are tautomers and are generally found in equilibrium mixtures of both the enol and the carbonyl forms of the tautomers. Enolic forms have been depicted in the above structured formulae.

The term "alkyl" as used herein means the monovalent moiety obtained upon removal of a hydrogen atom from a hydrocarbon. Representative of "alkyl" are methyl, ethyl, propyl, butyl, pentyl, heptyl, octyl, nonyl, decyl, dodecyl and isomeric forms thereof.

The term "halogen" is used herein in its conventional sense as embrative of chlorine, bromine, fluorine and iodine and the term "halo" means chloro, bromo, fluoro and iodo respectively.

5 The term "alkoxy" is used herein to mean the monovalent moiety of the formula:-



wherein alkyl is as described above. Illustrative of alkoxy are methoxy, ethoxy, butoxy, pentyloxy, heptyloxy, decyloxy, 10 dodecyloxy and the like.

The term "aryl" includes phenyl and naphthyl.

Representative of preferred azo dye couplers employed in the present invention are:

catechol

15 catechol acetate

catechol-mono hydroxyethyl ether .

resorcinol

resorcinol acetate

resorcinol-monohydroxyethyl ether

20 4-chlororesorcinol

2-methyl resorcinol

2,4-dichlororesorcinol

2,4-dihydroxy benzoic acid amide

2,4-dihydroxy benzoic acid ethanolamide

25 3,5-dihydroxy benzoic acid

3,5-dihydroxy benzoic acid ethanolamide
3,5-dihydroxy toluene
2,6-dihydroxy toluene
4-bromo-3,5-dihydroxy benzoic acid
5 4-bromo-3,5-dihydroxy benzoic acid amide
2,4-3' trihydroxydiphenyl
2-hydroxy naphthalene-3,6-disulfonic acid
2,3-dihydroxy naphthalene
2,3-dihydroxy naphthalene-6-sulfonic acid
10 2,7-dihydroxy naphthalene 3,6-disulfonic acid
cyanoacetamide
cyanoacet morpholide
cyanoacet benzylamide
di-cyanoacet-triethylene tetramine
15 acetoacet anilide
acetoacet benzylamide
acetoaceo-o-methylanilide
ethylene-bis-acetoacetamide
1-phenyl-3-methyl-pyrazolone (5)
20 acetoacet amino aceto acet amide
diresorcinol sulfide

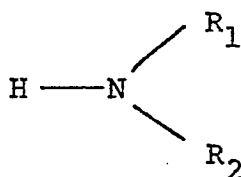
and the like.

The azo dye couplers described above are reacted under Mannich reaction conditions according to the invention with

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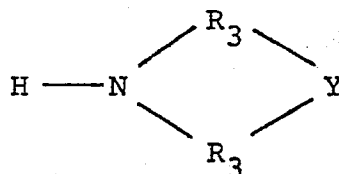
preferably equimolar proportions of formaldehyde and at least one of ammonia, a primary organic amine or a secondary amine.

Primary and secondary organic amines used in the present invention may be represented by the structural formulae:-



(I)

wherein R_1 and R_2 each independently may represent hydrogen, lower alkyl, hydroxyalkyl or aralkyl; or



(II)

wherein R_3 represents ethylene and Y represents one of nitrogen, sulfur or oxygen.

The term "lower alkyl" as used herein means alkyl of 1 to 5 carbon atoms, inclusive, such as methyl, ethyl, propyl, butyl, pentyl and isomeric forms thereof.

The term "hydroxyalkyl" as used herein means alkyl as defined above wherein a hydrogen atom has been replaced with a hydroxyl group, i.e.; for example methoxy, ethoxy, propoxy, butoxy, pentoxy and isomeric forms thereof.

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The term "aralkyl" is used herein to mean aralkyl of 7 to 12 carbon atoms, inclusive, such as benzyl, phenethyl, phenpropyl, phenbutyl, phenpentyl, phenhexyl and the like.

The term "ethylene" is used herein to mean the divalent moiety obtained upon removal of two hydrogen atoms from the parent hydrocarbon, ethane.

Representative of primary and secondary amines which may be used are:

methylamine

ethylamine

propylamine

propanolamine

butylamine

benzylamine

dimethylamine

diethylamine

dipropylamine

dibutylamine

dipropanolamine

dibenzylamine

morpholine

piperazine

and the like.

The above described reaction to obtain the reaction product of the azo dye coupler with the formaldehyde and the

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amine or ammonia may be carried out over a broad range of temperatures and pressures, neither being critical parameter of the reaction. Advantageously the reaction is carried out at a temperature within the range of from about $-10^{\circ}\text{C}.$ to about $50^{\circ}\text{C}.$, preferably at room temperature (circa $26^{\circ}\text{C}.$) and under atmospheric pressures. Advantageously, the reaction is carried out in the presence of the anions of one or more of the acids selected from the group consisting of hydrochloric acid, sulfamic acid, citric acid, tartaric acid, toluenesulfonic acid, sulfosalicylic acid, methanesulfonic acid, diglycolic acid, maleic acid, sulfuric acid, acetic acid and the like; at a pH of below 7.0.

The reaction is generally complete within minutes and is indicated by a drop in temperature of the reaction mixture. While the mechanisms of the effect from the use of the reaction product described above in diazotype compositions is not fully understood, it appears that the mobility of the couplers in the diazo coating layer is affected without forming a permanent link. One would expect that such a link would change the water solubility of the azo dye after coupling but this is not the case.

Those skilled in the art will appreciate that since the coupling agent employed in the present invention need not be isolated from the reaction product mixture, there is a saving of materials and an elimination of the disposal of residual by-products, etc.

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It is of course also possible to introduce more than one methylolamine or substituted methylolamine group into couplers containing more than one enolic moiety as each enolic moiety may undergo the Mannich reaction and such multiple substitutions are also part of the invention.

The diazo compositions of the invention may be prepared by bringing the ingredients together in a suitable vessel. Preferably the diazo compositions of the invention are prepared in an aqueous media for use as an aqueous coating mixture to prepare diazotype reproduction materials of the invention.

The coupling agents of the invention can be considered as Mannich bases of polyhydroxy-benzenes of polyhydroxy-naphthalene-disulfonates and of acetoacet- and cyanoacet-amides.

While they are much more difficult to isolate as crystalline compounds and thus have hardly ever been explored, we have found that there is no need to isolate them and that they can be used with full efficiency in the form of concentrate solutions and that they may even be formed in situ in the diazo sensitizing solutions.

The proportions of the various components of the compositions of the invention described above may be those proportions conventionally used in their use prior to this invention, in the preparation of prior art diazo light-

sensitive compositions (where they were so used). These proportions are well known to those skilled in the art; see for example the disclosures of Kosar, supra., and of U. S. Patents 3,923,518 and 3,996,056. In general, the aqueous diazo coating compositions contain from about 0.1 to about 10 percent by weight of the light-sensitive diazonium compound and sufficient coupler to react with and couple the diazonium compound upon development.

Representative of suitable base supports are thermoplastic polymeric resin films, foils including metal foils, cloth, opaque paper, translucent papers and like supports. Preferred are the commercially available diazotype papers.

For the preparation of diazo materials such as polymeric films and polymeric resin coated papers bearing diazo compositions, the diazonium and other ingredients are dissolved in polaric organic solvents such as alcohols, ketones or glycol ethers. The diazo composition is then applied from the solvent media to the base support material.

The following examples describe the manner and the process of making and using the invention and set forth the best mode contemplated by the inventors for carrying out the invention but are not to be construed as limiting. In reporting the testing of compositions of the invention, an accelerated aging test is referred to. The accelerated aging test is carried out as follows:

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A diazo sensitized reproduction sheet of 11" x 17" dimensions is cut into 2 sheets of 8-1/2" x 11" size. One sheet is exposed in a closed container, with exclusion of light, to an atmosphere of 75% room humidity (R.H.) at 50°C. for a period of 24 hours.

The other sheet is kept in a black polyethylene envelope.

After 24 hours, both sheets are printed in a commercial diazotype copying machine such as the OZAMATIC SUPER OM manufactured by the Ozalid Corporation, Binghamton, New York. The sheets are exposed behind a standard step wedge at a printing speed sufficient to destroy the diazo compound completely behind the light area of the step wedge, to partially destroy the diazo behind the grey intermediate steps of the wedge and insufficient to destroy any diazo compound behind the black maximum density step of the wedge. After exposure the sheets are processed through the development section of the Ozamatic for ammonia development. The loss of maximum print color density of the aged sheet when compared with the non-aged sheet can be caused by partial destruction of the diazo compound or by migration of coupling components or both.

A noticeable print color shift of full tones and half tones in the aged print when compared with the non-aged print indicates migration of coupling components from the

coating layer. A strong coloration of the print background on the aged sheet when compared with the non-aged sheet is the result of precoupling and indicates the diazotype has very limited shelf life.

5 A print color shift of blackline diazotypes, when aged as described above, indicates that at least one coupling component has migrated from the coating layer. Partial destruction of the diazo and precoupling can be remedied through an increase of the stabilizing agents in the diazo coating layer, without changing components.

0 Print color loss and print color shifting could not be remedied (up to now) except for eliminating migrating couplers. Unfortunately, it has been difficult and costly to find replacement couplers for equal shades and rates of development.

5 The present invention overcomes such problems and provides the means to reduce the mobility of couplers that tend to migrate, thus making them useful for the diazotype process.

0 Example 1

This is not an example of the invention but is made for comparative purposes. On a 3 airknife station diazotype coating machine for precoating, sensitizing, and backcoating, equipped with high velocity hot air drying

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passes after each coating, a diazo base paper of 72 g/m² basis weight is consecutively treated on the felt side with:

(1) a precoat composition of:

non-colloidal silicas (1 micron particle size)	50	g
vinyl acetate copolymer	100	ml.
antifoaming agent	1	ml.
water, enough to make	1000	ml.

(2) a sensitizing solution of the following composition:

citric acid	150	g
naphthalene 1-3-6,1-3-7- trisulfonic acid, sodium salt	150	g
thiourea	350	g
2,7-dihydroxynaphthalene- 3,6-disulfonic acid, disodium salt (blue coupler)	160	g
2,4-3' trihydroxydiphenyl (brown coupler)	40	g
isopropyl alcohol	100	ml.
glycerine	300	ml.
1 diazo-4-dimethylamine- benzene, chloride, 1/2 zinc chloride	200	g
zinc chloride	300	g
blue dye, alizarine irisol	0.5	g
water, to complete to	10	liter

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(3) a backcoating solution for curl control:

zinc chloride	40	g	
citric acid	5	g	
water, to complete to	1000	ml.	:

5 The coated and dried diazotype paper is then wound up and cut into sheets. Print tests are made with the paper as it is and after accelerated aging tests as described above.

Example 2

10 The procedure of Example 1, supra., is repeated except for the sensitizing solution (2) composition to which there was added a mixture of:

170 ml. diethanolamine
130 ml. formaldehyde (37%)
65 ml. acetic acid (glacial) and
15 40 ml. water

One sheet produced in each of the Examples 1 and 2 was aged as described above. The aged sheets and the non-aged sheets from both examples were then test printed and developed in an Ozamatic.

20 Both non-aged prints from Examples 1 and 2 showed deep black full tones and neutral grey half tones on a white background. The aged sheet from Example 1 developed to brown shades in full and half tones. The print from the aged sheet from Example 2 developed to slightly
25 blueish-black shades in full tones and to grey in half tones.

The brown color shade of the print from the aged sheet from Example 1 indicates that the blue coupler had migrated from the coating layer during the accelerated aging process and that it was not available for coupling when the print was developed.

Examples 3 and 4

The procedure of Example 1, supra., was repeated except the composition of coating No. 2 which was varied as follows:

	<u>Example 3</u>	<u>Example 4</u>
citric acid	150 g	150 g
thiourea	400 g	400 g
1 diazo-4-dimethylamino benzene chloride, 1/2 zinc chloride	100 g	100 g
zinc chloride	400 g	400 g
resorcinol	25 g	---
A reaction mixture of:		
resorcinol	---	25 g
in isopropanol	---	60 ml.
diethanolamine	---	25 ml.
formaldehyde (37%)	---	20 ml.
hydrochloric acid (d.l.19)	---	25 ml.
water, complete to	10 liter	10 liter

Some sheets from Example 3 and 4 underwent the accelerated aging process described above.

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After printing and developing non-aged and aged sheets, the prints from non-aged sheets from Examples 3 and 4 developed to strong brown print colors. The print from the aged sheet from Example 4 developed to nearly the same print line density as the non-aged sheets. The aged print of Example 3 lost more than half of its original print line density.

Examples 5, 6 and 7

The procedure of Example 1, supra., was repeated except the composition coating No. 2 was varied as follows:

	<u>Example 5</u>		<u>Example 6</u>		<u>Example 7</u>	
citric acid	150	g	150	g	150	g
thiourea	400	g	400	g	400	g
1-diazo-4-dimethyl- amino benzene chloride, 1/2 zinc chloride	100	g	100	g	100	g
4-chlororesorcinol	35	g	.35	g	35	g
a reaction mixture of:						
isopropyl-alcohol	---		60	ml.	---	
diethylamine	---		19	ml.	---	
N-methyl-ethanolamine	---		---		19	ml.
formaldehyde (37%)	---		20	ml.		
hydrochloric acid (d. 1.19)	---		25	ml.	25	ml.
zinc chloride	400	g	400	g	400	g
water, complete to	10	liter	10	liter	10	liter

Some sheets from Examples 5, 6 and 7 underwent the accelerated aging process described in Example 2.

After printing and developing non-aged and aged sheets, the prints from the non-aged sheets from Examples 5, 6 and 7 developed to strong brown colors. The prints from the aged sheets from Examples 6 and 7 produced brown print colors of similar strength as the non-aged prints. The aged print of Example 5 lost more than half of its original print line density.

Examples 8, 9 and 10

The procedure of Example 1, supra., was repeated except for the composition of coating No. 2 which was varied as follows:

	<u>Example 8</u>	<u>Example 9</u>	<u>Example 10</u>
citric acid	125 g	125 g	125 g
thiourea	400 g	400 g	400 g
caffeine	140 g	150 g	150 g
beta hydroxy naphthoic acid diethanolamide (blue coupler)	110 g	110 g	110 g
cyanoacetmorpholide (yellow coupler)	100 g	100 g	100 g
1-diazo-2,5-diethoxy-4-morpholino benzene chloride, 1/2 zinc chloride	150 g	150 g	150 g
dipropylene glycol	150 ml.	150 ml.	150 ml.
isopropyl alcohol	100 ml.	100 ml.	100 ml.

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<u>Examples 8, 9 & 10 Cont.</u>	<u>Example 8</u>	<u>Example 9</u>	<u>Example 10</u>
zinc chloride	400 g	400 g	400 g
saponin	2.5 g	2.5 g	2.5 g
and			
5 A solution of morpholino methyl hydrochloride salt obtained from a mixture of:			
water	---	5 ml.	10 ml.
morpholine	---	7.5 g	15 g
formaldehyde	---	7 g	14 g
10 hydrochloric acid (d: 1/19)	---	7 ml.	14 ml.
water, complete to	10 liter	10 liter	10 liter

15 Sheets from all three Examples 8, 9 and 10 printed and developed in an Ozamatic diazo copier to a black print color in full tones and neutral grey intermediate tones on a white background.

20 When sheets from Examples 8, 9 and 10 underwent accelerated aging as described above, and printing and development was carried out in the same Ozamatic diazo copier, only the print from Example 10 developed to the same black and neutral grey shades as the non-aged sheets. The print from Example 8 developed to print colors with a pronounced blueish cast in full tones and intermediate tones and the print from Example 9 produced somewhat blueish hues

25 that were approximately half-way between the print colors of Examples 8 and 10.

The accelerated aging migration of the yellow coupler cyanoacet morpholide in Example 8 and, to a lesser degree in Example 9, has been completely inhibited in Example 10.

Examples 11, 12 and 13

The procedure of Example 1, supra., was repeated except the 72 g/m² diazo base paper was replaced by a resin transparentized 100% rag base paper of 60 g/m² basis weight and the composition of coating No. 2 was varied as follows:

		<u>Example 11</u>		<u>Example 12</u>		<u>Example 13</u>	
10	citric acid	200	g	200	g	200	g
	thiourea	300	g	300	g	300	g
15	1-diazo-4-diethyl- amino benzene, chloride, 1/2 zinc chloride	300	g	300	g	300	g
	resorcinol	60	g	60	g	60	g
	isopropyl alcohol	100	ml.	100	ml.	100	ml.
	ammonium chloride	---		30	g	---	
20	methane sulfonic acid	---		10	g	55	g
	monoethanolamine	---		---		33	g
	formaldehyde (37%)	---		45	ml.	45	ml.
	diethylene glycol	200	ml.	200	ml.	200	ml.
	zinc chloride	200	g	200	g	200	g
25	saponin	3	g	3	g	3	g
	water, complete to	10	liter	10	liter	10	liter

One sheet from each of the Example 11, 12 and 13 was aged as described above. The aged sheets and non-aged sheets from all 3 examples were then printed and developed in an Ozamatic copier. All non-aged sheets developed to high density brown print dyes of high actinic opacity. The prints were used as second originals and all 3 reproduced diazo copies of excellent quality. The aged print from Example 11 developed to a medium density mauve-brown print dye of low opacity. When used as a second original to make diazo copies, poor quality reprints with weak lines were obtained.

The aged prints from Examples 12 and 13 developed to brown print dyes of almost the same density as the non-aged sheets from the same examples. When used as second originals to make diazo copies, high quality diazo copies with strong print lines were obtained.

Examples 14 and 15

A polyester film, 75 micron thick, which has been surface treated for promotion adhesion was precoated with a cellulose acetate butyrate lacquer and subsequently sensitized with the following compositions.

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		<u>Example 14</u>	<u>Example 15</u>
	isopropylalcohol	5 l.	4.25 l.
	methyl ethyl ketone	3 l.	3 l.
	ethylene glycol monomethyl ether	2 l.	2 l.
5	sulfosalicylic acid	100 g.	100. g.
	thiourea	200 g.	200 g.
	1-diazo-2.5-dibutoxy 4-morpholino benzene borofluoride	250 g.	250 g.
10	resorcinol	150 g.	---
	A reaction mixture of		
	resorcinol	---	150 g.
	in isopropanol	---	360 ml
	ammonia	---	115 ml
15	formaldehyde (37%)	---	100 ml
	acetic acid (glacial)	---	150 m.

Some sheets of Examples 14 and 15 underwent the accelerated aging process described in Example 2, supra. After printing and developing of the aged and non aged sheets, the print of Example 15 showed a higher density of brown dye and a higher actinic opacity than the prints of Example 14 after aging, whereas no difference was apparent on the non-aged sheets. When a second original used to make diazo copies, the aged prints of Example 14 gave good quality reprints and those of Example 15 gave poor quality reprints.

WHAT IS CLAIMED:

1. A diazotype sensitizing composition, which comprises;

(a) a diazonium compound; and

(b) a coupling agent which comprises the reaction mixture obtained upon reaction of

(i) a compound capable of coupling the diazonium compound (a) and having an enolic moiety selected from the group consisting of an aromatic compound of six carbon atoms, substituted with at least 2 hydroxy groups and having at least 3 hydrogen atoms in the ring thereof, an N-mono-substituted acetacetamide, an N-di-substituted acetoacetamide, an N-mono-substituted cyanoacetamide and an N-di-substituted cyanoacetamide; a dihydroxynaphthalene disulfonic acid; and

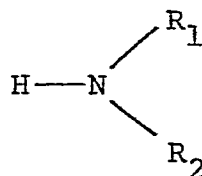
(ii) formaldehyde; with

(iii) a compound selected from the group consisting of a primary organic amine, a secondary organic amine, and ammonia; under Mannich reaction conditions.

2. The composition of claim 1 wherein the reaction leading to the formation of coupling agent (b) is carried out in the presence of anions of one or more of the acids selected from the group consisting of:

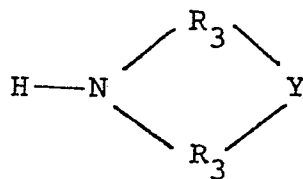
- (a) hydrochloric acid;
- (b) sulfamic acid;
- (c) citric acid;
- (d) tartaric acid;
- (e) toluenesulfonic acid;
- (f) sulfosalicylic acid;
- (g) methanesulfonic acid;
- (h) diglycolic acid;
- (i) maleic acid;
- (j) sulfuric acid and
- (k) acetic acid.

3. The composition of claim 1 wherein the compound (iii) has the structural formula:



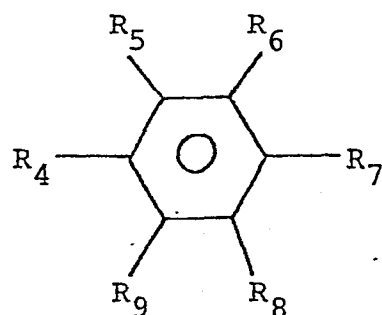
wherein R_1 and R_2 are each independently selected from hydrogen, lower alkyl hydroxyalkyl, aralkyl;

or

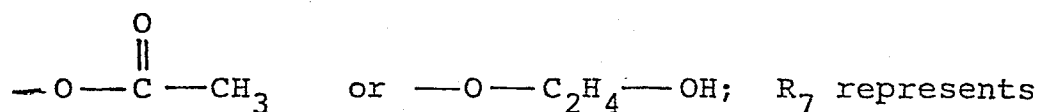


wherein R_3 is ethylene and Y is nitrogen, oxygen or sulfur;
and the coupler (b) is a compound selected from those of the
structural formula:-

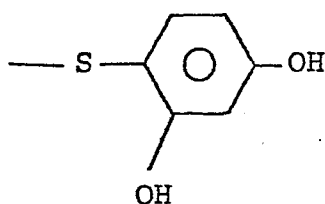
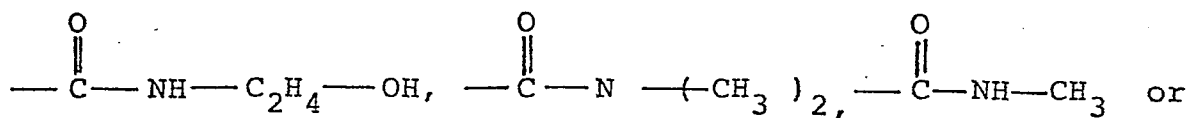
(A)



wherein R_4 represents one of hydrogen, hydroxyl or halogen;
 R_5 represents one of hydrogen, hydroxyl, methyl or halogen;
 R_6 represents one of hydrogen, hydroxyl or halogen; the
group

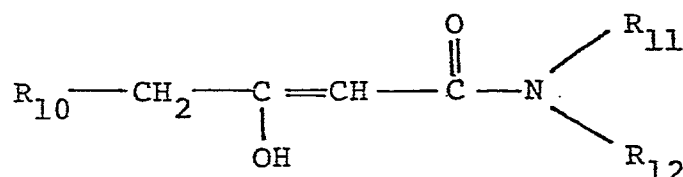


hydrogen, carboxyl, —C(=O)—NH_2 , $\text{—C(=O)—N—(C}_2\text{H}_4\text{OH)}_2$,



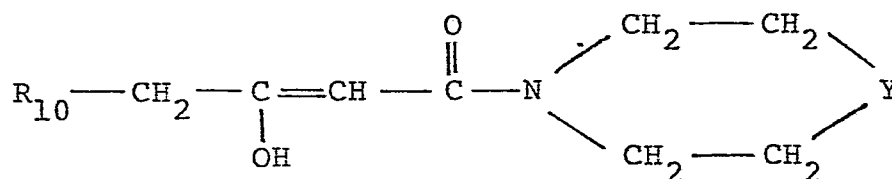
R_8 represents hydrogen; and R_9 is hydrogen or hydroxyl;
 provided at least two of R_4 , R_5 , R_6 and R_9 is hydroxyl; and
 at least two of R_4 , R_5 , R_6 , R_7 and R_9 are hydrogen;

(B)



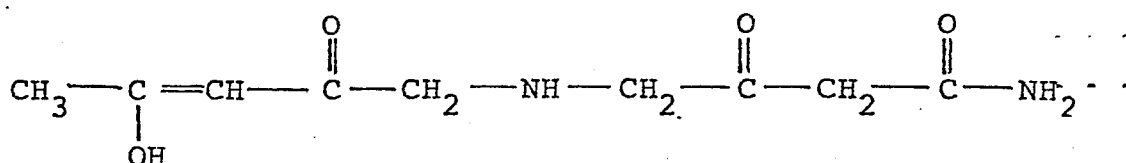
wherein R_{10} represents hydrogen or $-CN$; R_{11} and R_{12} are
 each independently selected from the group consisting of
 hydrogen, alkyl, aryl, alkyl substituted aryl, hydroxy
 substituted aryl, alkoxy substituted aryl and sulfur
 substituted aryl;

(C)

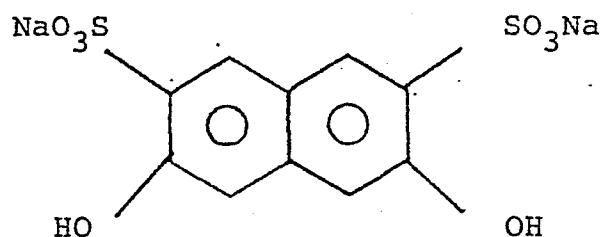


wherein R_{10} is as defined above and y is oxygen, nitrogen or
 sulfur;

(D)



(E)



4. A diazotype reproduction material comprising a base support and one or more coating layers containing at least one light sensitive diazonium compound, at least one acidic stabilizer and at least one coupling compound which is the product of the reaction of
- 5.

- (a) a member selected from N-methylolmorpholine, N-methyloldiethanolamine, or a mixture of formaldehyde and ammonia; with

- 10 (b) a compound selected from the group consisting of 4-chlororesorcinol, 4,6-dichlororesorcinol, 2-methylresorcinol, resorcinol and diresorcinol sulfide; at pH values below 7.

5 5. A diazotype reproduction material comprising a base support and one or more coating layers containing at least one light sensitive diazonium compound, at least one acidic stabilizer and at least one coupling compound which is the product of the reaction of

(a) formaldehyde;

(b) ammonia; and

10 (c) a compound selected from the group consisting of 4-chlororesorcinol, 4,6-dichlororesorcinol, 2-methylresorcinol, resorcinol and diresorcinol sulfide; under Mannich reaction conditions.

5 6. A diazotype reproduction material comprising a base support and one or more coating layers containing at least one light sensitive diazonium compound, at least one acidic stabilizer and at least one coupling compound which is the Mannich reaction product of formaldehyde, resorcinol and an organic amine, said coupling compound being selected from the group consisting of:

1-morpholinomethyl-2,6-dihydroxy-benzene;
1-morpholinomethyl-2,4-dihydroxy-benzene;
10 N,N-dihydroxyethyl-2,4-dihydroxy-benzylamine;
N,N-dihydroxyethyl-2,6-dihydroxy-benzene;
2,4-dihydroxy-benzylamine;
2,6-dihydroxybenzyl-amine.

7. A diazotype sensitizing solution, prepared with:

- (a) a diazonium compound;
(b) a coupler for said diazonium compound,
possessive of an enolic moiety;
5 (c) formaldehyde;
(d) a stabilizing acid;
(e) a compound selected from the group
consisting of a primary organic amine,
a secondary organic amine and ammonia;
10 and
(f) a diluent selected from the group consisting
of water and a polaric organic solvent; said
solution having a pH value below 5.0.