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HEAT-SENSITIVE DIAZOTYPE MATERIALS

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ABSTRACT OF THE DISCLOSURE

Diazotype materials comprising a base sheet (e.g., paper) coated with a diazo compound (e.g., a 4-morpholinobenzenediazonium salt), a coupling component (e.g., resorcinol) and a heat-sensitive aromatic sulfonylurea or sulfonylthiourea developing agent (e.g., N-p-toluenesulfonyl-N'-butylurea).

This invention relates to methods and compositions for developing diazotype materials with aromatic sulfonylureas and sulfonylthioureas. More particularly, this invention pertains to diazotype materials containing compounds of the general formula

$$Ar—SO_2—NH—CX—NH—R$$

wherein Ar is an aromatic radical, R is a nonaromatic hydrocarbon radical and X is oxygen or sulfur.

Heat-sensitive diazotype materials comprise a base member coated with a formulation containing a diazo compound and a coupling component with which the diazo compound reacts under proper conditions to form an azo dye which produces a visible image. In making a print, the diazotype material is exposed to light under a translucent master. In those areas of the diazotype material which are exposed to light, the light-sensitive diazo compound is at least partially destroyed but is unaffected in the shaded areas. The print is then developed by heating the diazotype material and causing the alkaline donor developing agent to emit ammonia or an organic amine which produces the proper pH conditions for interaction of the diazo compound and the coupling component. These react to produce a dye image in the shaded area which corresponds to the graphic material on the master.

In conventional heat-sensitive diazotype materials the alkaline donor developer is commonly a urea or thiourea compound which on decomposition at elevated temperatures yields ammonia which induces the coupling reaction to form the azo dye. Urea and thiourea compounds produce diazotype materials having a relatively poor shelf life due to precoupling of the diazo compound and the coupling component at ambient temperatures. Other heat-sensitive diazotype materials which have longer shelf lives usually require higher temperatures to induce coupling. Generally, these temperatures are too high for office equipment and often they are so high that the diazo compound decomposes more rapidly than it reacts with the coupling component to form the azo dye. To cope with the problem of precoupling, increased amounts of acid have been used to stabilize the formulations, thus requiring increased amounts of alkaline donor to be incorporated into the formula to provide a sufficient source of ammonia to give a suitably dense image. For example, British Patent No. 909,491 proposes the use of certain types of acids which lose their acidity on heating and thereby reduce the required quantity of alkaline donor since at developing temperatures the acid is dissipated.

It is an object of this invention to provide heat-sensitive diazotype materials wherein the alkaline donor is stable at ambient temperature, decomposes to produce alkaline substances at relatively low temperature and does not contribute to precoupling. It is another object of this invention to provide heat-sensitive diazotype materials which form good prints and which have extended shelf life. It is a further object to provide alkaline donor materials for heat-sensitive diazotype materials which decompose at relatively low temperatures to provide alkaline materials which induce dye formation. These and other objects are apparent from and are achieved in accordance with the following disclosure.

In accordance with the present invention, it has been discovered that aromatic sulfonylureas and sulfonylthioureas of the foregoing general formula are particularly useful as alkaline donor developing agents in thermally developed diazotype materials. In these compounds, Ar represents aromatic radicals such as phenyl, tolyl, indenyl, hydrindenyl, xylyl and related aromatic hydrocarbon radicals. Ar also represents aromatic hydrocarbon radicals bearing substituents such as halogen, alkoxyl, alkyl and alkoxyalkoxyl. For instance, Ar can be chlorophenyl, bromophenyl, methoxyphenyl, ethoxyphenyl, ethylphenyl, butylphenyl, methoxyethoxyphenyl, ethoxyethoxyphenyl and the like.

R represents alkyl radicals such as methyl, ethyl, propyl, isopropyl, butyl, t-butyl, amyl, hexyl, octyl, nonyl, lauryl and cetyl; alkenyl radicals such as allyl crotyl, methallyl, and butenyl; alicyclic radicals such as cyclobutyl, cyclopentyl, cyclohexyl, cyclohexylmethyl, cycloheptyl and cyclooctyl; and aralkyl radicals such as benzyl, phenethyl, phenylpropyl and phenylbutyl.

It is important that the alkaline donor incorporated into the heat-sensitive diazotype formulation be stable at room temperatures, and provide sufficient basicity at lower temperatures to neutralize the acid stabilizers so that the diazo compound can couple and produce azo-dye images. It is desirable that the alkaline donors respond at temperatures in the range of 50–150° C. and release the amine when the diazotype material is heated to such temperature.

The aromatic sulfonylureas and sulfonylthioureas described herein decompose when heated to temperatures in the range from 100° to 150° C. and release an amine of the formula RNH_2. This amine raises the pH of the diazotype coating to a range where the diazo compound reacts with the coupling component and forms a colored azo dye. The latter forms a visible image in the areas corresponding to the graphic material on the master.

The light-sensitive diazo compounds which are useful in two-component diazotype systems can also be used to advantage in thermally responsive diazotype materials.

Examples of such compounds 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-β-hydroxyethylaniline
p-amino-N-methyl-N-β-hydroxyethylaniline
p-amino-N,N-di(β-hydroxyethyl)aniline
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-β-hydroxyethyl-m-toluidine
N-p-aminophenylmorpholine
1-amino-2,5-diethoxy-4-morpholinobenzene

The preferred diazo compound is the zinc chloride double salt of 4-morpholinobenzenediazonium chloride

Generally, a number of coupling components may be employed. The preferred coupling component that may be employed to produce the dye image is 2,4-dihydroxynaphthalene-6-sulfonic acid. Other known couplers may be employed such as resorcinol, acetoacetanilide, 4-chlororesorcinol and diacetoacetylethylenediamine. The coupling component is preferably selected to provide a combination in which precoupling at low pH is avoided.

The diazo salts and the couplers may, in and of themselves, tend to give a color reaction prematurely. To prevent precoupling and premature dye formation, there is added an acid component to keep the pH below the level required for coupling. Sulfonic acid derivatives, such as m-benzenedisulfonic acid, are employed as the preferred acid components. Other acids may be used to produce the desired pH such as:

maleic acid
malonic acid
ethanesulfonic acid
benzenesulfonic acid
oxalic acid
citric acid
tartaric acid
lactic acid

In addition to the acid components, there may be added to the diazo formulation certain heavy metal salts such as the sulfates of zinc and cadmium. The inclusion of the heavy metal salts tends to prevent precoupling of the components at near room temperature.

By appropriate combinations of aromatic sulfonylureas and sulfonylthioureas and acids, such as those listed above, it is possible to develop pH ranges between 5 and 12 which will induce reaction between any combination of diazo compound and coupling component.

When the aromatic sulfonylureas and sulfonylthioureas are applied to sheet materials in the production of diazotype materials, they are dissolved or dispersed in fine particulate form in an organic solvent such as toluene and the resulting suspension applied to the sheet material by conventional coating procedures. The aromatic sulfonylureas or sulfonylthioureas are usually present in the solutions or dispersions at concentrations of 5% to 20% by weight, the range from 9% to 11% being preferred. After the solvent evaporates, the aromatic sulfonylureas and sulfonylthioureas form a thin coating of fine crystalline or solid particles which can release an organic amine when activated by heat.

In the photosensitive coating formulations for sheet materials, the amount of diazo compound is usually conventional. It generally constitutes 2% to 6% of the formulation with 4% being preferred. Equivalent quantities of coupling reagent are employed, following conventional practice. The coating formulations are usually applied in amounts which will provide about 15 grams of diazo compound for 3,000 square feet of surface.

The invention is disclosed in more detail by the following examples which are provided for purposes of illustration only. It will be understood by those skilled in the art that various combinations of diazo compounds, coupling components and alkaline donor developers can be used. It will also be understood that the amounts of ingredients in formulations and the operating conditions may be varied within this disclosure without departing from the invention.

EXAMPLE 1

A solution of 2.5 grams of N-p-toluenesulfonyl-N'-butylurea in 100 grams of toluene was applied to standard diazo paper (300 square feet) by a roller applicator and the excess doctored by the conventional air knife method. Then a sensitizing solution of the following formula was applied:

	Grams
Water	100
Citric acid	2
Zinc sulfate	3
Thiourea	3
2,3-dihydroxy-6-naphthalenesulfonic acid	5
4-morpholinobenzenediazonium chlorozincate	1.5
Silica (finely divided)	5
Rice starch	3
Polyvinyl acetate emulsion (5.9%)	8

The treated diazo paper was used to make thermally developed copies by exposing it to actinic light under a transparent original and subsequently developing the exposed sheet by subjecting it to a temperature of 125° C. for five seconds on a heated rotating aluminum drum, a clear and legible blue image being formed.

EXAMPLE 2

Polyester film base, to which a subcoating of cellulose acetate, cellulose acetate butyrate, cellulose propionate or other subcoating capable of accepting the sensitizing solution, was coated with the following sensitizing solution:

Methanol	cc.	60
Acetone	cc.	40
Tartaric acid	g.	2
Thiourea	g.	3
Resorcinol	g.	3
p-Morpholinobenzenediazonium fluoborate	g.	1.5
N-p-toluenesulfonyl-N'-cyclohexylthiourea	g.	5

A reddish brown azo dye was formed when the film was heated to 120° C. for approximately 4 minutes.

I claim:

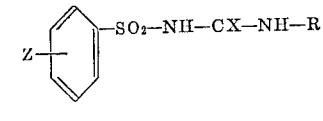
1. A heat-sensitive diazotype material comprising a base sheet coated with a diazo compound, a coupling component and an alkaline donor developer of the general formula

$$Ar—SO_2—NH—CX—NH—R$$

wherein Ar is an aromatic radical, R is a nonaromatic hydrocarbon radical and X is oxygen or sulfur.

2. A heat-sensitive diazotype material as defined in claim 1 wherein Ar is an aryl radical, R is an alkyl radical and X is oxygen.

3. A heat-sensitive diazotype material comprising a base sheet coated with a light-sensitive diazo compound, a coupling component and an alkaline donor substance of the formula



wherein Z is hydrogen, alkyl, halogen, alkoxyl or alkoxyalkoxyl, R is alkyl, cycloalkyl, alkenyl or aralkyl and X is oxygen or sulfur.

4. A heat-sensitive diazotype material as defined by claim 3 wherein Z is alkyl and R is alkyl.

5. A heat-sensitive diazotype material as defined by claim 4 wherein Z is methyl and R is n-butyl.

6. A heat-sensitive diazotype material as defined by claim 4 wherein Z is methyl and R is cyclohexyl.

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