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3,493,374

HEAT-DEVELOPABLE DIAZOTYPE MATERIAL
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10 Claims

ABSTRACT OF THE DISCLOSURE

Heat-developable diazotype material that can be produced inexpensively with very high keeping quality is obtained by providing in intimate association on a support a light-sensitive diazonium compound, an azo-coupling component, an acid-reacting compound and as a developing agent finely divided particles of a solid substance formed by interaction (reaction, complexing or addition) of an amino-1,3,5-triazine compound and an alkane dicarboxylic acid having at least 3 carbon atoms in a straight chain between the carboxylic acid groups. The particles of developing agent have an average size between 0.1 and 10 microns and water solubility of less than 2 g. per liter. Particularly effective materials make use of a finely divided product of the interaction of equimolar proportions of a melamine and an alkane dicarboxylic acid having 9–12 C atoms, applied in an aqueous dispersion with a hydrophilic organic binder comprising polyvinylpyrrolidone.

The invention relates to heat-developable diazotype material which contains a diazonium compound, an azo-coupling component, an acid-reacting compound, and a developing agent.

If the coupling reaction of a diazonium compound and an azo-coupling component is to proceed rapidly, the presence of a substance capable of neutralizing acid in the medium in which coupling occurs is in most cases required. In the development of one-component diazotype materials use is made of one or more buffer salts in the developing liquid. In the development of two-component diazotype materials ammonia vapour acts as the acid-neutralizing substance. In heat-developable diazotype materials the acid-neutralizing substance is usually applied in the material itself, in such a way that it only becomes active upon heating.

It is known that heat-developable diazotype material of particularly high keeping quality can be obtained when the acid-neutralizing substance and, if desirable, the azo-coupling component are applied in a layer other than the light-sensitive one, in such a way that during the formation of the layers and upon storage of the diazotype material under normal conditions no reaction occurs between the acid-neutralizing substance and other substances which are present in the layers. It is only upon heating that the various components come together and that the diazonium compound and azo-coupling component are able to couple. A good separation of the reactants is obtained, for instance, when the diazonium compound and the acid are applied in a hydrophilic layer, the azo-coupling component and the acid-neutralizing substance are applied in a

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hydrophobic film-layer, and if the solvent used for the formation of the second layer is a non-solvent for any of the substances present in the first layer. Premature reaction can also be prevented if the diazonium compound, the azo-coupling component, and the acid are separated from the acid-neutralizing substance by means of a hydrophobic barrier layer.

Such multi-layer materials are relatively expensive.

Less expensive materials are those in which the acid-neutralizing substance (also called the developing agent) is applied in more or less conventional aqueous sensitizing or pre-treatment liquids, which do not yield separate film-layers. Such materials are also known. Generally, in these known materials the developing agent is a water-soluble compound which upon heating decomposes, while splitting off ammonia or an amine, e.g. urea, thiourea, guanidine and their alkyl derivatives, or a salt of an amine with a volatile and/or decomposing acid. See e.g.: Photographic Science & Eng. 5, No. 4, pages 239–243 (1961). Such compounds are often called: alkali generators.

British patent specification No. 907,724 describes heat-developable diazotype material in which the developing agent used is urea, guanidine or an alkyl derivative of these compounds, or a salt of an amino-paraffin with an acid which upon heating volatilizes or decomposes. Preferably, the amino-paraffin is a hydroxyalkylamine, such as tri(hydroxymethyl)aminomethane, 2-amino-2-methyl-1,3-propanediol, ethanolamine, diethanolamine and N-ethyl-N,N-diethanolamine. As volatile or decomposing acids are mentioned malonic acid, gluconic acid, gluconic-δ-lactone, cyanoacetic acid, malic acid and maleic acid. The acid employed for stabilizing the light-sensitive layer is a similar acid volatilizing or decomposing upon heating. Since the developing agents are readily water-soluble and hydrolyse easily in the presence of water, the dry diazotype material has, with a view to its keeping quality, to be free from hygroscopic substances, since such substances tend to absorb and retain moisture and thus furnish a common solvent for the diazonium compound, the azo-coupling component, and the alkali generator.

U.S. patent specification No. 2,653,091 describes heat-developable diazotype material in which a salt of trichloroacetic acid is present as the developing agent, and free trichloroacetic acid as the acid-reacting compound. The cation of the developing agent may be derived from an alkaline earth metal or from an aliphatic amine, such as triethanolamine or diethanolamine. To ensure improved keeping quality, a quantity of tartaric acid may be used in addition to the free trichloroacetic acid. Upon heating, this material develops, because the trichloroacetic acid decomposes and thus leaves behind in the layer a quantity of alkali sufficient to promote the coupling reaction.

French patent specification No. 1,333,723 described heat-developable diazotype material in which as the developing agent a salt of trichloroacetic acid with a heterocyclic base, such as piperidine, morpholine and 2-picoline, is present.

French patent specification No. 1,301,867 describes heat-developable diazotype material comprising a substance which upon heating yields an azo-coupling component through enolization, e.g., 4,6-dioxo-2-alkyl-dihydropyran-1,4.

As a developing agent, morpholine adipate may be added, but this is not necessary. According to this patent specification the keeping quality of the diazotype ma-

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terial is unfavourably affected by the addition of such a substance.

Dutch patent application No. 6,402,881 describes heat-developable diazotype material the light-sensitive layer of which comprises an amino compound decomposing upon heating or activatable by heat. The amino compound may be an amide, such as formamide, acetamide, stearylamine, acrylamide, polyacrylamide, malonamide, benzamide or nicotinamide, or an aliphatic or heterocyclic amine, such as alanine, diallylmelamine, 2,4-diamino-s-phenyltriazine, imidazole, benzimidazole and piperazine. The amines may be used in the form of a salt, e.g. as chloride, sulfate, acetate, bicarbonate or carbonate. Examples of amines and salts of amines which are readily water-soluble, slightly water-soluble or water-insoluble are given. The readily soluble amines are applied in the heat-developable diazotype material or on separate sheets, so-called developing sheets. The slightly soluble or insoluble amines are dissolved in organic solvents, and with these solutions the diazotype materials are precoated or developing sheets are impregnated.

The use of water-soluble developing agents involves the drawback that these agents are inactive only when the diazotype material is completely dry and is stored in a moisture-free environment (e.g. in a moisture-tight wrapping). However, diazotype paper always has some moisture content and has a hygroscopic nature, so that it absorbs moisture whenever possible. In practice the water-soluble developing agents consequently have an unfavourable influence on the keeping quality of the heat-developable diazotype material, so that in this respect this material is very inferior to normal two-component diazotype material. Pre-coating diazotype material with solutions of amines in organic solvents is not attractive, first because organic solvents are usually expensive and often inflammable or poisonous, so that their use requires special precautions which make the additional treatment expensive, and secondly because the amines penetrate deeply into the support material, e.g. paper, on account of which they are only partly available for reaction during development.

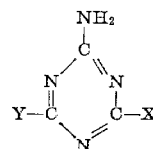
A patent application copending herewith, which issued as United States Patent No. 3,416,924 on Dec. 17, 1968, describes heat-developable diazotype material in which the developing agent used is a water-insoluble salt of a polybasic acid having a dissociation constant between 7×10^{-2} and 1×10^{-4} and an aliphatic primary, secondary, or tertiary amine having at least 16 C-atoms and at least one hydrocarbon chain with at least 8 C-atoms. Suitable acids are oxalic acid, phosphoric acid, metaphosphoric acid, phosphorous acid, diglycolic acid, maleic acid, dimethylmalonic acid, or tartaric acid. Suitable amines are hexadecylamine, octadecylamine, eicosylamine, docosylamine, dioctylamine, dioctadecylamine, N-methyl-N-octadecylamine, N,N-dimethyl-N-octadecylamine, 9-octadecenylamine and 3-(octadecyl)oxypropylamine. The salt must contain at least two cations derived from such amines. It is applied in the form of dispersed particles.

This diazotype material has high keeping quality, it develops rapidly upon heating to approximately 150°C ., and it is inexpensive. The copies show strong azo-dye-stuff images. However, the azo-dye-stuff images on these copies show considerable bleaching upon exposure to daylight.

According to the present invention there is provided a heat-developable diazotype material comprising a diazonium compound, an azo-coupling component, an acid-reacting compound and a developing agent having a solubility in water or less than 2 g. per litre, in which the developing agent is a solid substance present in the material as finely divided particles having an average particle size between 0.1 and 10 microns, said substances having been formed by the interaction of an alkane dicarboxylic acid having at least 3 carbon atoms in a straight

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chain between the carboxylic acid groups and a triazine compound of the general formula



in which X represents hydrogen, alkyl, branched alkyl, aralkyl, or a group of the formula



Y represents hydrogen or a group of the formula



R_1 and R_2 represent identical or different atoms or groups of atoms selected from hydrogen atoms, alkyl, branched alkyl, unsaturated alkyl, cycloalkyl and aralkyl groups or represent the atoms required for the completion of a heterocyclic ring, R_3 and R_4 represent identical or different atoms or groups of atoms selected from hydrogen atoms, alkyl, branched alkyl, unsaturated alkyl, cycloalkyl and aralkyl groups or represent the atoms required for the completion of a heterocyclic ring or R_3 represents a hydrogen atom and R_4 represents an aryl group.

Developing agents according to the above definition permit the manufacture, in an easy and inexpensive way, of a heat-developable diazotype material which has very high keeping quality and develops readily at temperatures which may vary from 100°C . to 150°C .

Compared with heat-developable diazotype material according to Dutch patent application No. 6,402,452, diazotype material according to the present invention yields copies of the azo-dye-stuff image of which shows a better fastness to light.

It is a characteristic of the present invention that the developing agent is incorporated in the diazotype material in the form of finely divided particles which do not dissolve or only slightly dissolve, in the liquid with which they are applied. Developing agents which dissolve more than 2 grams per litre affect the keeping quality of the heat-developable diazotype material adversely. The particle size of the developing agent should not exceed 10 microns, since coarse particles give the copies an unpleasant rough touch. A particle size between 0.5 and 5 microns is preferred. A size smaller than 0.5 micron is less attractive on account of difficulties in making such fine dispersions.

The developing agent is a substance formed by action of an alkane dicarboxylic acid on an amino-1,3,5-triazine compound. The alkane dicarboxylic acids having an alkylene bridge of 3 or more carbon atoms between the carboxylic acid groups are weak acids. The aminotriazine compounds are weak to very weak bases. It is, at least in some cases, uncertain whether the combination of the dicarboxylic acid and the triazine yields a real salt. Nevertheless some chemical and/or physical action (reaction, complexing or addition) has to be assumed because the developing agents which are used according to the present invention differ from simple mixtures of the components.

Acids which can be used for the formation of the developing agent are glutaric acid, adipic acid, β -methyladipic acid, pimelic acid, suberic acid, 2-ethyl-suberic acid, azelaic acid, sebacic acid, nonane dicarboxylic acid, decane dicarboxylic acid, eicosan dicarboxylic acid and tetratriacontane dicarboxylic acid.

Many amino-1,3,5-triazines meeting the above general formula have been described in literature (c.f. Smolin and Rapoport, The Chemistry of Heterocyclic Compounds, s-Triazines and Derivatives (1959), Interscience

Publishers Inc., New York). It has been found that compounds of dicarboxylic acids as defined above with very different amino-1,3,5-triazines are effective developing agents for heat-developable diazotype materials provided that the compound has a melting point below 200° C. and a water-solubility of less than 2 g./litre. Among the melamines which are suitable, are especially mentioned: 2-amino - 1,3,5 - triazine, 2,4 - diamino - 1,3,5 - triazine, 2,4 - diamino - 6 - methyl - 1,3,5 - triazine, 2,4 - diamino-6-isopropyl - 1,3,5 - triazine, 2,4 - diamino - 6 - nonyl-1,3,5-triazine, 2,4-diamino-6-benzyl-1,3,5 - triazine, 2-amino-4-piperidyl(1)-1,3,5-triazine, 1,4 - bis(2,4 - diamino-1,3,5-triazinyl(6)) butane, 2-amino-4-hydroxymethylamino-1,3,5-triazine, 2-amino-4-methylamino - 1,3,5 - triazine, 2-amino-4-ethylamino-1,3,5-triazine, 2 - amino - 4 - cyclopentylamino-1,3,5-triazine, 2-amino-4-benzylamino - 1,3,5-triazine, melamine, 2,4-diamino-6-methylamino-1,3,5-triazine, 2,4-diamino-6-n-propylamino - 1,3,5-triazine, 2,4-diamino-6-benzylamino-1,3,5 - triazine, 2,4 - diamino-6-phenylamino-1,3,5-triazine, 2,4-diamino - 6 - morpholino-1,3,5-triazine, 2,4-diamino-6-diallylamino - 1,3,5 - triazine, 2,4-diamino-6-dimethylamino - 1,3,5 - triazine, 2 - amino 4-n-propylamino-6-dimethylamino - 1,3,5-triazine, 2-amino-4,6-bis(2'-hydroxyethylamino)-1,3,5-triazine, 2-amino-4,6-bis(dimethylamino)-1,3,5-triazine, 2 - amino - 4,6-bis(hydroxymethylamino)-1,3,5-triazine, 2,4 - diamino - 6 - hydroxymethylamino-1,3,5-triazine and 1,2-bis(4,6 - diamino-1,3,5-triazinyl-2-amino)-ethane.

The developing agents contain the triazine derivative and the dicarboxylic acid preferably in an equimolecular proportion. Slight excess of the acid (e.g. a molar excess of 10-20%) does not harm, but the presence of free amino-triazine in the developing agent is to be avoided since it results in a diazotype material of inferior keeping qualities. The developing agents can be prepared by melting together equimolar quantities of the acid and the triazine, homogenizing the melt, cooling and grinding; or by dissolving equimolar quantities of the triazine and the acid in appropriate solvents (e.g. the triazine in hot water and the dicarboxylic acid in ethanol) combining the two solutions while stirring, isolating the product thus formed by cooling and sucking off, or by evaporation of the solvent, or by another equivalent procedure, and obtaining the developing agent as a dry powder. As a rule the developing agent has a lower melting point and smaller water-solubility accordingly as it is derived from a higher alkane dicarboxylic acid.

The developing agents to be used according to the invention can be applied individually, mixed together, or in admixture with developing agents of other types, such as urea, thiourea, guanidine, or the alkyl derivatives thereof, or with the salts described in Dutch patent application No. 6,402,452. In general, however, the diazotype material will present the specific advantages of the invention to a higher degree according as it has a higher content of the developing agent to be used according to the invention.

The developing agents can be dispersed very effectively in water by grinding in a ball mill.

They can be applied in the diazotype material in various ways. Preferably, this is done by means of an aqueous dispersion. They can be dispersed, for instance, in an aqueous sensitizing liquid and then, together with the diazonium compound, the azo-coupling component, and the acid-reacting compound, be applied onto the support material. They may also be dispersed in a liquid other than the sensitizing liquid and be applied either before or after the sensitization. Preferably between 3 and 8 g. of developing agent is applied per m.² of the support surface. With smaller and larger quantities good results can also be obtained.

It is highly desirable to stabilize the dispersions of the developing agent by adding a binder. The binder also enhances the coherence of the particles of the developing agent in the diazotype material according to the inven-

tion. Hydrophilic synthetic binders, such as polyvinyl alcohol, polyvinyl pyrrolidone, polyvinylcaprolactam, copolymers of (1) vinylpyrrolidone or vinylcaprolactam with (2) vinyl esters, vinyl ethers, vinyl chloride, acrylic esters or amides, and also binders such as methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, polyacrylamide, high molecular weight ethylene oxide polymers and mixtures of them are particularly suitable for these purposes. Aqueous dispersions of synthetic resins, such as dispersions of polyvinyl acetate and poly-n-butylmethacrylate, also give reasonable results.

Among the developing agents which are used according to the invention those derived from aliphatic dicarboxylic acids with 6-12 C-atoms are preferred since these acids are readily accessible and form products which are easily wettable with water and consequently well dispersible in aqueous liquids.

The developing agents formed from equimolar quantities of melamine and an alkane dicarboxylic acid with 9-12 carbon atoms, viz. azelaic, sebacic and decane-1,10-dicarboxylic acid, are particularly suitable. They can be very readily dispersed and to a sufficient amount in aqueous liquids yielding dispersions of high stability, and they permit the production of diazotype materials which have excellent keeping quality and show, upon heating to 150° C., copies with strong azo-dyestuff images.

Among the binders which can be used in the diazotype material according to the invention polyvinyl alcohol, methylcellulose and polyvinylpyrrolidone are preferred. Polyvinylpyrrolidone is outstanding. It is a very good stabilizer for the developing agent dispersions and in addition it has a favourable influence on the completeness of the development of the copies. If the diazotype material contains a sufficient quantity of polyvinylpyrrolidone the copies made on it develop under the same conditions more completely than copies on a comparable diazotype material which contains a hydrophilic binder such as methylcellulose or polyvinylalcohol.

It is especially attractive to use polyvinylpyrrolidone in admixture with polyvinylalcohol, since the latter compound improves the adherence of the developer particles to the paper.

In the light-sensitive layer of the diazotype material according to the invention the conventional stabilizing acid-reacting compounds may be used, such as tartaric acid, citric acid, boric acid, maleic acid, gluconic acid, oxalic acid, phosphoric acid, benzene sulfonic acid, potassium hydrogen sulfate, malic acid and aluminium sulfate.

In the diazotype material according to the invention benzene diazonium compounds having a secondary or tertiary amino group in the para-position can be effectively used.

Very suitable results can be obtained, for instance, with 4-diazo-N,N-dimethylaniline, 4-diazo-N,N-diethylaniline, 4 - diazo - N - ethyl - N - 2' - hydroxyethyl-aniline, 4 - diazo - 3 - ethoxy - N,N - diethylaniline, 4-diazo - 2 - chloro - N,N - diethylaniline, 4 - diazo - N-methyl - N - cyclohexylaniline, 4 - diazo - N - ethyl - N-benzylaniline, 4 - diazo - 5 - chloro - 2 - (4' - chlorophenoxy) - N,N - dimethylaniline, 4 - diazo - 5 - chloro-2 - ethoxy - N - methyl - N - benzylaniline, N - (4 - diazophenyl) - morpholine, 4 - diazo - 2,5 - diethoxy - N - ethyl-N - benzylaniline, N - (4 - diazo - 2,5 - diethoxyphenyl) morpholine, N - (4 - diazo - 2,5 - di-n-butoxyphenyl)-morpholine, N - (4 - diazo - 2,5 - dimethoxyphenyl)-piperidine, N - (4 - diazo - 2,5 - dipropoxyphenyl) - N'-methylpiperazine, N - (4 - diazo - 2,5 - diethoxyphenyl) - N'-acetyl-piperazine, 4-diazo-diphenylamine and 4-diazo-2-methoxy-N-methylaniline.

Suitable azo-coupling components are e.g. 2,3-dihydroxynaphthalene, 2,3 - dihydroxynaphthalene - 6 - sulfonic acid, 2,7 - dihydroxynaphthalene - 3,6 - disulfonic acid, 2 - hydroxynaphthalene - 3,6 - disulfonic acid, 1-benzoylamino - 8 - hydroxynaphthalene - 4 - sulfonic acid,

resorcinol, phloroglucinol, 7' - hydroxy - 1',2',4,5 - naphthimidazole, 3,5 - dihydroxybenzoic acid ethanol amide and acetoacetanilide. To obtain a black-developing diazo-type material, in addition to blue-coupling azo-components, such as 2,3 - dihydroxynaphthalene - 6 - sulfonic acid, yellow-coupling components can be used in the diazo-type material according to the invention.

Examples of such azo-coupling components are resorcinol, acetoacetanilide, 3 - hydroxy - acetoacetanilide, 4 - hydroxy-acetoacetanilide, 3 - carboxy-acetoacetanilide, 4 - carboxy-acetoacetanilide, 3 - methoxyphenol, dire-sorcyl sulfoxide, 2 - acetoacetaminonaphthalene - 6 - sulfonic acid, 2 - acetoacetaminonaphthalene - 7 - sulfonic acid and 1 - acetoacetaminonaphthalene - 4 - sulfonic acid.

Use may be made of substances which promote the development of the material, so that the material may be developed in a shorter time and/or at lower temperatures. Such substances are, for example, substances which have a relatively low melting point (e.g. between 40 and 100° C.) and which, when molten, furnish a favourable medium for the azo-dyestuff formation. Examples of development-promoting substances are stearyl alcohol, stearyl amide, and stearic acid, o-chloro-benzoic acid, acetanilide, benzoin, palmitylamide, benenic amide and amides as mentioned in the Dutch patent application No. 6,402,881.

The following examples will serve to illustrate the invention. For convenience, in these examples the developing agents are named as if they are salts, though the question of whether or not all the products are salts remains uncertain. The indication 1/1 refers to an equimolar proportion of the components of the developing agent.

EXAMPLE I

A stock solution containing

400 g. of polyvinyl alcohol of the type Rhodoviol 4/20 P (from Rhône-Poulenc S.A., Paris, France)
100 g. of citric acid

in 10,000 ml. of water is prepared.

From this stock solution five portions of 1000 ml. each are taken.

In these portions are dispersed respectively:

(A) 160 g. of melamine glutarate 1/1
(B) 165 g. of melamine adipate 1/1
(C) 190 g. of melamine azelate 1/1
(D) 200 g. of melamine sebacate 1/1
(E) 210 g. of melamine decane-1,10-dicarboxylate 1/1

by grinding the mixture of the salt and the liquid in a ball mill for 24 hours.

In a solution containing

40 g. of polyvinyl alcohol of the type Rhodoviol 4/20 P
10 g. of oxalic acid

1000 ml. of water is dispersed:

(F) 200 g. of di-(octadecylammonium) oxalate by grinding the mixture of the salt and the liquid in a ball mill for 24 hours.

With each of the dispersions thus obtained a sheet of white base paper of weight 80 g./m.² suitable for the diazotype process is treated in such a way that, after drying, about 5 g./m.² of the developing agent is present on it.

The sheets A, B, C, D and E thus treated are sensitized with a liquid containing

10 g. of 4-morpholino-2,5-diethoxybenzene diazonium sulfate
5 g. of citric acid
25 g. of 2,3-dihydroxynaphthalene-6-sulfonic acid
1 ml. of the wetting agent on polyoxyethylene basis Scurol O (from Rhône-Poulenc S.A.)
20 g. of polyvinyl alcohol (Rhodoviol 4/20 P)

30 g. of hydrolysed potato starch of the type Farinex T.S.D. (from Nationale Zetmeel-industrie N.V., Veen-dam, Holland)

in 1000 ml. of water and dried.

Sheet F is sensitized with a solution containing

10 g. of 4-morpholino-2,5-diethoxybenzene diazonium sulfate
5 g. of oxalic acid
25 g. of 2,3-dihydroxynaphthalene-6-sulfonic acid
1 ml. of the wetting agent Scurol O
50 g. of rice starch
20 g. of polyvinyl alcohol (Rhodoviol 4/20 P)
30 g. of hydrolysed potato starch of the type Farinex T.S.D.

in 1000 ml. of water and dried.

The sensitization is effected in such a way that in each of the materials about 0.45 millimole of diazonium compound is present per m.² of the sensitized surface.

A strip of each of the six light-sensitive papers thus obtained is imaged exposed underneath a transparent ink drawing and then developed by guiding it over a heated roller having a surface temperature of about 150° C., in such a way that the back of the sheet is in contact with the roller surface for about 7 seconds. The copies on the strips A, B, C, D and E show a blue image on a clear white background. The copy on sheet F shows a violet-blue azo-dyestuff image. The copies are exposed for some days to daylight. The azo-dyestuff image of the copy on sheet F has become almost illegible as a result of bleaching. The image on the copies A, B, C, D and E remains properly legible.

EXAMPLE II

White base paper for the diazotype process, which has been pre-coated with a dispersion of non-colloidal silica and then dried, is provided with a layer of developing agent of about 6 g./m.² dry weight by treating it with a dispersion of

180 g. of 2,4-diamino-6-n-propylamino-1,3,5-triazine sebacate 1/1
5 g. of maleic anhydride
0.2 ml. of an anti-foaming agent on a silicone basis
30 g. of methylcellulose of the type Methocel 10 cps. (from The Dow Chemical Co., Michigan, U.S.A.)

in 1000 ml. of water and drying.

The paper thus obtained is then sensitized with a solution of

10 g. of 4-morpholino-2,5-diethoxybenzene diazonium hydrogen sulfate
5 g. of citric acid
25 g. of sodium 2,7-dihydroxynaphthalene-3,6-disulfonate
5 g. of polyvinyl alcohol

in 1000 ml. of water and dried.

A sheet of the diazotype paper thus obtained is image-wise exposed underneath a transparent ink drawing until all the diazonium compound underneath the transparent portions of the drawing has bleached out and is then developed as described in Example I.

The copy shows a blue image on a white background.

EXAMPLE III

(A) A sheet of white base paper of weight 80 g./m.² suitable for the diazotype process is rubbed with powdered 2,4-diamino-6-diallylamino-1,3,5-triazine sebacate 1/1 in such a way that about 5.5 g. of developing agent per m.² is present on the paper.

(B) Another sheet of the same paper is impregnated with a solution containing 200 g. of 2,4-diamino-6-diallylamino-1,3,5-triazine in 1000 ml. of dioxane and dried.

The coated side of both sheets is sensitized with a solution of

10 g. of 4-N,N-di(2'-acetoxyethyl)amino-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt
5 g. of tartaric acid
25 g. of sodium-2,3-dihydroxynaphthalene-6-sulfonate
1 ml. of the wetting agent Scurol O

in 1000 ml. of water and dried.

A strip of each of the diazotype papers thus obtained is imagewise exposed underneath a transparent pencil drawing until the diazonium compound underneath the transparent portions of the drawing has for the major part been bleached out, and is then developed as described in Example I.

The copies show a blue image on a foggy blue background.

Another strip of the two sheets is stored for some time in a room with a temperature of 35° C. and a relative humidity of 75%.

After this, strip B shows an intensive blue colour throughout its surface, in consequence of premature azo-dyestuff formation, whereas on strip A hardly any azo-dyestuff has been formed.

EXAMPLE IV

White base paper of weight 80 g./m.² suitable for the diazotype process is treated with a dispersion containing

200 g. of melamine sebacate 1/1
40 g. of polyvinyl alcohol

in 1000 ml. of water and dried.

The layer thus applied has a dry weight of about 5 g./m.². The coated side of the paper is sensitized with a solution containing

7 g. of 4-diethylaminobenzene diazonium chloride, zinc chloride double salt
7 g. of 2,3-dihydroxynaphthalene
15 g. of caffeine
7.5 g. of m-hydroxyacetoacetanilide
4 g. of resorcinol
5 g. of 2-hydroxymethylbenzimidazole
30 g. of zinc chloride
5 g. of citric acid
1 ml. of the wetting agent Scurol O

in 1000 ml. of water and dried.

The diazotype paper thus obtained contains about 0.5 millimole of diazonium compound per m.² of sensitized surface. A sheet of it is imagewise exposed and developed as described in Example I.

The copy shows a black image on a white background.

EXAMPLE V

350 ml. of water is mixed with
150 g. of melamine adipate 1/1 and
7.5 g. of 8-hydroxy-[1,2-d] naphthimidazole.

The mixture is ground in a ball mill for 10 hours. Then

500 ml. of a 5%-solution of gum arabic in water and
20 g. of oxalic acid

are added to the mixture.

The liquid thus obtained is ground in a ball mill for 5 hours. Then

7 g. of 4-ethylthio-5-methoxy-2-N-ethoxycarbonyl - N-methylaminobenzene diazonium chloride, zinc chloride double salt

is dissolved in the solution and with the aid of the sensitizing liquid thus obtained photographic baryta paper is sensitized in such a way that it contains about 0.5 millimole of diazo compound per m.².

A sheet of the paper thus obtained is imagewise exposed and developed as described in Example I.

The copy shows a red image on a white background.

EXAMPLE VI

A mixture of

250 g. of 2,4 - diamino - 6 - morpholino - 1,3,5 - triazine sebacate 1/1

20 g. of methylcellulose of the type Tylose SL 5 (from Kalle A.G., Wiesbaden-Biebrich, Germany)
50 g. of stearylamine, and
1000 ml. of water

is ground in a ball mill for 15 hours.

With the dispersion thus obtained white base paper of weight 80 g./m.² suitable for the diazotype process is coated with a layer which, after drying, weighs about 4 g./m.².

The side of the paper thus coated is sensitized with a solution containing

14 g. of 4 - N - ethyl - N - hydroxyethylaminobenzene diazonium chloride, zinc chloride double salt

40 g. of sodium - 2,3 - dihydroxynaphthalene - 6 - sulfonate
10 g. of tartaric acid

3 g. of technical lauryl alcohol sulfate Duponol ME (from E. I. du Pont de Nemours and Co., Inc., Wilmington, Del. U.S.A.)

in 1000 ml. of water and dried.

The diazotype paper thus obtained is imagewise exposed and developed as described in Example I.

The copy shows a blue image on a white background.

EXAMPLE VII

A solution is prepared by dissolving

100 g. of sodium - 2,3 - dihydroxynaphthalene - 6 - sulfonate

10 g. of potassium hydrogen sulfate
60 g. of thiourea
60 g. of polyvinylpyrrolidone (K-value 15) and
60 g. of polyvinylalcohol

in 2000 ml. of water.

(A) To a first 1000-ml.-portion of this solution 145 g. of 2 - amino - 1,3,5 - triazine sebacate 1/1 is added.

(B) To the second 1000-ml.-portion of this solution 200 g. of 2,4 - diamino - 1,3,5 - triazine sebacate 1/1 is added.

The liquids A and B are ground in ball mills for 17 hours. To each of the dispersion thus prepared 6 g. of 4 - dimethylaminobenzene diazonium chloride, zinc chloride double salt is added.

With each dispersion a sheet of white base paper of weight 70 g./m.² suitable for the diazotype process is coated. After coating, the sheets are dried.

The light-sensitive heat-developable diazotype materials thus obtained are imagewise exposed and developed as described in Example I. The copies show a blue image on a white background.

EXAMPLE VIII

A mixture containing

175 g. of 2,4 - diamino - 6 - benzylamino - 1,3,5 - triazine sebacate 1/1

20 g. of resorcinol
5 g. of tartaric acid
30 g. of non-colloidal silica
25 g. of hydroxyethyl cellulose
0.04 ml. of an antifoaming agent and
1000 ml. of water

is ground in a ball mill for 17 hours. Then

5 ml. of the wetting agent Scurol O and
8 g. of 4 - morpholinobenzene diazonium chloride, zinc chloride double salt

are added to the dispersion.

With the sensitizing liquid thus prepared transparent

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tracing paper of weight 80 g./m.² is coated. After coating, the sheet is dried.

A sheet of a diazotype paper thus obtained is image-wise exposed and developed as in Example III. The copy shows a yellow-brown image on a foggy yellow-brown background and is suitable as an intermediate copy for further printing on diazotype material.

EXAMPLE IX

Transparent reproduction cloth suitable for sensitization is coated with a light-sensitive dispersion prepared by grinding in a ball mill a mixture containing

200 g. of 2,4-diamino-6-phenylamino-1,3,5-triazine sebacate 1/1
2.5 g. of tartaric acid
40 g. of sodium-2-hydroxynaphthalene-3,6-disulfonate
20 g. of polyvinylalcohol and
600 ml. of water

and by subsequently adding to the dispersion

40 g. of gum arabic
7 g. of 4-morpholino-2,5-diethoxybenzene diazonium hydrogen sulfate
20 ml. of wetting agent Scuriol O and
300 ml. of water.

After coating, the cloth is dried.

The sheet of the diazotype cloth thus obtained is image-wise exposed and developed as in Example I. The copy shows a blue image on a transparent background.

EXAMPLE X

A dispersion is prepared by grinding in a ball mill a mixture of

175 g. of a product formed from equimolar quantities of 2-amino-4,6-bis(hydroxymethylamino)-1,3,5-triazine (Lyofix DM from Ciba A.G., Basel, Switzerland) and decane-1,10-dicarboxylic acid
30 g. of sodium-2,3-dihydroxynaphthalene-6-sulfonate
20 g. of resorcinol
20 g. of polyvinylalcohol
40 g. of polyvinylpyrrolidone (K-value 30)

in 1000 ml. of water.

After grinding, 2.5 g. of oxalic acid and 7 g. of 4-dimethylaminobenzene diazonium chloride, zinc chloride double salt, are added to the dispersion.

White base paper of weight 80 g./m.² suitable for the diazotype process is sensitized with the light-sensitive dispersion thus prepared. After coating, the paper is dried.

A sheet of the diazotype paper thus obtained is image-wise exposed and developed as in Example I. The copy shows a black image on a white background.

EXAMPLE XI

White base paper of weight 80 g./m.² suitable for the diazotype process is coated with a light-sensitive dispersion prepared by grinding in a ball mill a mixture containing

150 g. of 2,4-diamino-6-methyl-1,3,5-triazine decane-1,10-dicarboxylate 1/1
5 g. of citric acid
33 g. of sodium-2,3-dihydroxynaphthalene-6-sulfonate
30 g. of thiourea
30 g. of non-colloidal silica
20 g. of polyvinylalcohol
50 g. of polyvinylpyrrolidone (K-value 30) and
1000 ml. of water

and by subsequently adding

8 g. of 4-morpholino-2,5-diethoxybenzene diazonium hydrogen sulfate
1 ml. of the wetting agent Scuriol O.

After coating, the paper is dried.

A sheet of the diazotype paper thus obtained is image-

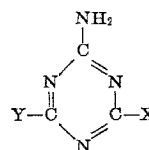
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wise exposed and developed as in Example I. The copy shows a blue image on a white background.

The following words used above are trademarks: Rhodoviol, Scuriol, Fairinex, Methocel, Tylose, Duponol, and Lyofix.

We claim:

1. Heat-developable diazotype material comprising a support having coated thereon and accessible one to another during heating a light-sensitive diazonium compound, an azo-coupling component, an acid-reacting compound and a developing agent, the developing agent being present in a layer containing said diazonium compound or in a layer adjacent thereto, wherein said developing agent is a solid substance present as finely divided particles which have an average particle size between 0.1 and 10 microns and have a solubility in water of less than 2 g. per liter and upon being heated sufficiently will promote coupling of said diazonium compound and said azo-coupling component, said substance being a product of the interaction of an aliphatic dicarboxylic acid having at least 3 carbon atoms in a straight chain between the carboxylic acid groups and a triazine compound of the general formula



in which X represents hydrogen, alkyl, branched alkyl, aralkyl or a group of the formula



Y represents hydrogen or a group of the formula



R₁ and R₂ represent identical or different atoms or groups of atoms selected from hydrogen atoms, alkyl, branched alkyl, unsaturated alkyl, cycloalkyl and aralkyl groups or represent the atoms required for the completion of a heterocyclic ring, R₃ and R₄ represent identical or different atoms or groups of atoms selected from hydrogen atoms, alkyl, branched alkyl, unsaturated alkyl, cycloalkyl and aralkyl groups or represent the atoms required for the completion of a heterocyclic ring, or R₃ represents a hydrogen atom and R₄ represents an aryl group.

2. Heat-developable diazotype material according to claim 1, wherein said developing agent is a product of the interaction of equimolar quantities of said triazine compound and said dicarboxylic acid.

3. Heat-developable diazotype material according to claim 1, wherein said solid substance is a product of the interaction of equimolar quantities of said triazine compound and a said dicarboxylic acid having 6-12 C-atoms.

4. Heat-developable diazotype material according to claim 1, wherein said solid substance is a product of the interaction of equimolar quantities of melamine and a said dicarboxylic acid having 9-12 C-atoms.

5. Heat-developable diazotype material according to claim 1, wherein the layer which contains said developing agent also contains a hydrophilic synthetic binder.

6. Heat-developable diazotype material according to claim 5, wherein said binder is polyvinylpyrrolidone.

7. Heat-developable diazotype material according to

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claim 5, wherein said binder is a mixture of polyvinylpyrrolidone with polyvinylalcohol.

8. A heat-developable diazotype material according to claim 1, wherein a light-sensitive layer on said support comprises a dried aqueous dispersion of an intimate admixture of said diazonium compound, said azo-coupling component, said acid-reacting compound and said developing agent with an organic hydrophilic binder.

9. Heat-developable diazotype material according to claim 1, wherein said substance is a product of the interaction of equimolar proportions of a melamine and a said dicarboxylic acid having 9-12 carbon atoms and said particles are present in a layer which also contains a hydrophilic organic binder comprising polyvinylpyrrolidone.

10. Heat-developable diazotype material according to claim 9, said diazonium compound being a benzene diazonium compound having a secondary or tertiary amino group in the position para to the diazonium group, said azo-coupling component comprising compounds which respectively form blue and yellow dyestuffs by coupling with said diazonium compound.

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