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HEAT-DEVELOPABLE DIAZOTYPE MATERIAL

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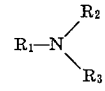
ABSTRACT OF THE DISCLOSURE

Heat-developable diazotype material having improved keeping quality and developable at temperatures below 150° C. contains, with a diazo compound, an azo-coupling component and an acid-reacting stabilizer, a developing agent comprising dispersed particles of a substantially water-insoluble salt of a polybasic acid having a dissociation content between 7×10^{-2} and 1×10^{-4} and an aliphatic amine of the formula



R_1 being an aliphatic hydrocarbon radical having at least 8 C atoms, R_2 and R_3 each being hydrogen or an aliphatic hydrocarbon radical, and R_1, R_2 and R_3 together comprising at least 16 C atoms. Especially suitable is di(octadecylammonium)oxalate present with oxalic acid in a light-sensitive layer containing a hydrophilic binder such as polyvinyl alcohol modified by polyvinyl pyrrolidone.

The invention relates to heat-developable diazotype material which contains a diazo compound, an azo-coupling component, an acid-reacting compound, and a developing agent which, upon heating, is able to neutralize an acid.

Heat-developable diazotype materials are known. As a rule, they differ essentially from the known two-component diazotype materials only in that, besides the diazo compound, the azo-coupling component, and an acid-reacting compound, they also contain the alkali required for the development. This alkali, however, has been incorporated in the material in such a way that it only becomes active after the material has been heated to 100–200° C. The alkali may be present in the light-sensitive layer, e.g. in a neutral, chemically combined state, e.g. in a compound such as urea (which upon heating above 150° C., for instance, shows accelerated decomposition with splitting-off of ammonia), or may be incorporated in a separate layer, which is either in contact with the light-sensitive layer, or separated from the light-sensitive layer by means of a so-called intermediate layer. In the latter case the developing agent may be an aliphatic amine. (See: Kosar J., Photographic Science & Eng. 5, 239–243 (1961).)

The manufacture of a heat-developable multi-layer diazotype material is cumbersome and expensive, especially when use is made of non-aqueous liquids, so that such a material is considerably more expensive than comparable two-component diazotype materials.

Heat-developable diazotype materials in which urea, or a similar compound which upon heating splits off ammonia or an amine, is employed as developing agent and in which all the components required for the formation of the azo-dyestuff have been incorporated in one layer, can be manufactured in a reasonably inexpensive way, but such materials have to be developed at temperatures of about 180° C. if they are to yield sufficiently strong azo-dyestuff images. Such high development temperatures are not desirable. Moreover, these materials cannot be stabilized to the proper degree. When there is incorporated in such a material a sufficient quantity of an acid-reacting compound to obtain a material of good keeping quality, the material shows hardly any development. When the quantity of acid is decreased until the material yields a sufficiently strong azo-dyestuff image upon development, the keeping quality of the material becomes insufficient.

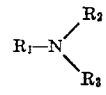
Attempts have been made to overcome this difficulty by stabilizing such materials with acids which decompose and/or volatilize upon heating.

British patent specification No. 907,724 describes heat-developable diazotype material which, besides the diazo compound and the azo-coupling component, contains an acid which volatilizes or decomposes at elevated temperatures, as well as a developing agent which, upon heating, liberates a basic-reacting component. As suitable acids volatilizing or decomposing upon heating are mentioned: malonic acid, gluconic acid, cyanoacetic acid, malic acid and maleic acid. The developing agent is preferably a substance which, upon heating, splits off ammonia or an amine, such as urea, guanidine, and their alkyl derivatives; however, it may also consist of a salt of an alkylamine, and especially of a hydroxyalkylamine, with an acid which volatilizes or decomposes upon heating. The developing agents mentioned in the said British patent specification are readily soluble in water. The diazotype material should be free from hygroscopic substances, such as ethylene gylcol, since these substances keep the moisture content of the light-sensitive layer at such a value, or bring it to such a value, that in the said layer a small amount of solvent for the diazo compound, the azo-coupling component, and the developing agent is always present, which results in premature formation of azo-dyestuff. (See page 1, lines 61–79 of the said British patent specification.)

The diazotype material described in British patent specification No. 907,724 can indeed be kept for some time if it has only a very low moisture content and is kept in a moisture-proof package in a cool place, although even under these favourable conditions it is not very stable in consequence of the high content of water-soluble developing agent and the relatively low acid content. However, when it is exposed to the air, particularly when it is used for making copies, e.g. in an office, it absorbs moisture from the air (particularly when the support is paper) and, notwithstanding the absence of hygroscopic substances, inconvenient premature azo-dyestuff formation soon takes place. For this reason the diazotype material described in the said British patent specification is unsuitable in practice.

The present invention relates to heat-developable diazotype material containing a diazo compound, an azo-coupling component, an acid-reacting compound, and a developing agent which is a water-insoluble salt of a polybasic acid having a first dissociation constant between

7×10^{-2} and 1×10^{-4} and a primary, secondary, or tertiary aliphatic amine of the general formula



in which R_1 is an aliphatic hydrocarbon radical with at least 8 carbon atoms, and R_2 and R_3 stand for a hydrogen atom or an aliphatic hydrocarbon radical, while R_1, R_2, and R_3 together carry at least 16 carbon atoms, the salt containing at least two cations formed from an amine according to the above formula. The various components are distributed over at most two layers.

Generally, the diazotype material according to the invention has much better keeping quality than comparable diazotype material which contains one of the known developing agents. Moreover it can be developed at temperatures below 150° C. to yield copies showing a strong azo-dyestuff image.

It is surprising that the salts defined above can be used as developing agents in heat-developable diazotype materials. Their solubility in water and in the conventional acid aqueous sensitizing liquids is very low and is generally of the order of a few milligrams, or less, per 100 ml. of liquid. Moreover, the amines present in the salts are also practically water-insoluble and they have a hydrophobic rather than a hydrophilic character.

The developing agent may be a salt of an amine such as hexadecylamine, octadecylamine, eikosylamine, dokosylamine, dioctylamine, dioctadecylamine, N - methyl - N-octadecylamine, N,N-dimethyl-N-octadecylamine, 9-octadecenylamine, 3 - (octadecyl) - oxypropylamine. At least two cations derived from such amines must be present in a molecule of the salt in order that the salt shall be useful in the present invention. The cations may be identical or different.

It has been found that as a rule the keeping quality of diazotype material according to the invention is better according as the cations of the developing agent are derived from higher amines. However, in proportion as the molecular weight of the cations increases, the quantity of the developing agent which is required to obtain good development increases, and in consequence the quantity of developing agent which has to be applied to the diazotype material per square metre also increases.

Acids with which salts suitable as developing agents can be formed are, for instance, oxalic acid, phosphoric acid, metaphosphoric acid, phosphorous acid, diglycolic acid, maleic acid, dimethylmalonic acid and tartaric acid.

The salts suitable as developing agents can be used in the diazotype material according to the invention individually or mixed together.

The oxalates are very suitable developing agents on account of the excellent keeping quality of the diazotype material made with them. A particularly suitable developing agent is di(octadecylammonium)oxalate. It is readily accessible, and diazotype material having excellent keeping quality and yielding a strong colour upon development can be made with it.

The acid-reacting compound present in the light-sensitive layer may be one of the acids commonly used in diazotype material, such as tartaric acid and citric acid. However, in the diazotype material according to the invention a moderately strong acid which is not volatile at temperatures below 100° C. is preferably used. Good results can be obtained with non-volatile acids having a dissociation constant greater than 10^{-3}. Such acids are e.g. oxalic acid, phosphoric acid, maleic acid, sulfuric acid, and potassium hydrogen sulfate.

Among these acids oxalic acid is outstanding. It stabilizes very well and the number of gram molecules of this acid which can be used in the diazotype material according to the invention can be greater than that of acids such as phosphoric acid and maleic acid. When a comparatively large quantity of the last-mentioned acids is used and the colour of the azo-dyestuff formed upon development changes upon lowering of the pH, the shade of this azo-dyestuff may be adversely affected. This happens, for instance, with dyestuffs formed from 4-tert. aminobenzene diazo compounds and the important azo-coupling component 2,3-dihydroxynaphthalene-6-sulfonic acid, which are violet-red instead of violet-blue at a pH below 3. Oxalic acid does not cause such a colour shift.

The diazotype material according to the invention can be made by treating the surface of a support material in a conventional manner with an aqueous or non-aqueous sensitizing liquid in which the developing agent has been dispersed.

In order to be able to disperse the developing agent properly and to obtain a reasonably stable dispersion, it is necessary to use a dispersing agent in the sensitizing liquid.

If the sensitizing liquid is an aqueous liquid, the dispersing agent to be used may be a suitable surface-active substance, such as lauryl alcohol sulfate and polyoxyethylene sorbitan monolaurate. Better results are obtained with hydrophilic film-forming organic binders which are soluble in acid aqueous liquids, such as methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, polyvinyl alcohol and gum arabic.

In aqueous liquids, a quantity of an aqueous dispersion of a synthetic resin, e.g. of polyvinyl acetate or poly-n-butylmethacrylate, may often also be used as a dispersing agent with good results.

If the sensitizing liquid is a non-aqueous liquid, a hydrophobic binder which is soluble in the liquid, such as ethyl cellulose, polyvinyl acetate and cellulose nitrate, can be used as a dispersing agent.

The diazotype material according to the invention may also, and often with advantage, be made in two steps, e.g. by first coating a support material with a dispersion of the developing agent and drying, and next sensitizing the dry layer thus formed with a solution of a diazo compound and drying the material again. (The azo-coupling component and the acid-reacting compound may be incorporated in the dispersion or in the sensitizing liquid, as desired.)

Whatever may be the method of manufacture, the diazotype material according to the invention is preferably made as a one-layer material. However, it may also have a two-layer composition.

Diazotype materials according to the invention, made with a binder-containing dispersion, have better keeping quality and develop more rapidly than corresponding materials which have been made with a binder-free dispersion.

During the dispersion of the developing agent in water, a very stable foam is often formed in the dispersion. This form can be very inconvenient, e.g. when a layer is formed on a support material by means of the dispersion. Curiously enough, during the preparation of such aqueous dispersions of the developing agent only little foam, if any, is formed if cations derived from higher secondary amines, such as di(octadecyl)amine, are present in the developing agent. Favourable results are attained with developing agents in which about 30–60% of the cations are di(octadecyl) ammonium ions.

Diazo compounds which are eminently suitable for use in the diazotype material according to the invention are benzene diazo compounds with a secondary or tertiary amino group in para-position. Very suitable results can be obtained with e.g.:

4-diazo-N,N-dimethylaniline,
4-diazo-N,N-diethylaniline,
4-diazo-N-ethyl-N-2'-hydroxyethylaniline,
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,
4-diazophenylmorpholine,
4-diazo-2,5-diethoxy-N-ethyl-N-benzylaniline,
4-diazo-2,5-diethoxyphenylmorpholine,
4-diazo-2,5-di-n-butoxyphenylmorpholine,
4-diazo-2,5-dimethoxyphenylpiperidine,
N-4-diazo-2,5-dipropoxyphenyl-N'-methylpiperazine,
N-4-diazo-2,5-diethoxyphenyl-N'-acetylpiperazine,
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, and 3,5-dihydroxybenzene carbonamide. Besides blue-coupling azo components, such as e.g. 2,3-dihydroxynaphthalene - 6 - sulfonic acid, so-called yellow-coupling shading components may also be used in the diazotype material according to the invention in order to obtain a black-developing material. Examples of such azo-coupling components are aceoacetanilide, 3-hydroxyacetoacetanilide, 4 - hydroxyacetoacetanilide, 3 - carboxyacetoacetanilide, 4-carboxyacetoacetanilide, 3-methoxyphenol, diresorcyl sulfoxide, 2-acetoacetaminonaphthalene-6-sulfonic acid, 2-acetoacetaminonaphthalene-7-sulfonic acid, 2-acetoacetaminonaphthalene-8-sulfonic acid, 2-acetoacetaminonaphthalene-1-sulfonic acid, 1-acetoacetaminonaphthalene-4-sulfonic acid, 1-acetoacetaminonaphthalene-5-sulfonic acid.

The support of the diazotype material according to the invention may be paper, tracing paper, linen, tracing linen, polyester film, cellulose acetate film, synthetic paper, or the like.

The following examples will serve to illustrate the invention. In these examples reference is made to certain compounds by their trade names. Of these the following are registered trademarks: Tylose, Rhodoviol, Tween, Vinnapas, Plextol, Duponol.

Example I

810 g. of octadecylamine is dissolved in 23,000 ml. of ethanol (96%). The solution is heated to 60° C. and, while stirring, such a quantity of a solution of 202 g. of oxalic acid, 2 aq. in 3000 ml. of ethanol (96%) is added gradually until the reaction mixture has a neutral reaction to litmus.

The reaction mixture is cooled to 35° C., the precipitate thus formed is sucked off, and the residue is washed with ethanol. After drying, the residue weighs 832 g. The di(octadecylammonium)oxalate thus prepared melts at 204–205° C.

A. A dispersion containing:

Di(octadecylammonium)oxalate	g--	100
Ethanol (96%)	ml--	100
Water	ml--	1000

is prepared, and this dispersion is ground for 20 hours in a ball-mill.

B. A solution of:

	G.
4-morpholinobenzene diazonium chloride, zinc chloride double salt	20
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid	40
Oxalic acid	27

in 1000 ml. of water is prepared.

Then

Dispersion A	g--	550
Solution B	ml--	200
Water	ml--	250

are added together and the mixture is stirred until it is homogeneous.

White base-paper of weight 80 g./m.² and suitable for the diazotaype process is sensitized with the mixture in such a way that, after drying, a uniform layer of about 7 g./m.² is present on it. From the diazotype paper thus formed a sheet is cut, which is marked with the letter C.

A sheet of the same white base-paper is sensitized with the solution described in Example 7 of British patent specification No. 907,724, in such a way that, after drying, the diazotype paper thus obtainer, which is marked with the letter D, has equal light-sensitivity to the diazotype paper C.

A strip of the two sheets is kept for 24 hours in a room with a temperature of 35° C. and a relative humidity of 75%.

After these 24 hours the strip D shows an intensive blue color throughout its surface, whilst the strip C is practically as yellow as before. The two strips are exposed until all the diazo compound present on them has bleached out. Now, strip C shows a slight, somewhat violet fogginess. Strip D, on the contrary, shows an intensive blue color. The difference in keeping quality appears from the difference in the extent of premature azo-dyestuff formation, and in this respect the diazotype material according to the invention is greatly superior.

The remaining parts of the diazotype papers C and D are imagewise exposed in fresh condition underneath a letter typed on thin paper until underneath the white portions of the letter all the diazo compound has bleached out, and are then guided over a rotating metal cylinder with a surface temperature of about 150° C., their light-sensitive sides being in contact with the cylinder surface for 10 seconds.

The copy on sheet D shows a violet-blue image on a white background, the copy on sheet C a violet image on a white background.

Example II

A. A dispersion containing:

Di(octadecylammonium)oxalate	g--	80
Methyl cellulose of the type Tylose MH 200 K	g--	20
Water	ml--	1000

is prepared, and this dispersion is ground for 20 hours in a ball-mill.

By solution of:

	Grams
4-morpholino-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt	33
Tartaric acid	16.5
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid	100

in 1000 ml. of water is prepared.

Then:

Dispersion A	g--	500
Solution B	ml--	75
Sulfuric acid (0.1 N)	ml--	100
Anti-foaming agent on silicone basis S.A.G. 470	g--	0.2
Water	ml--	20

are added together, and the liquid is stirred until it is homogeneous.

A sheet of white base-paper of weight 80 g./m.² and suitable for the diazotype process is sensitized with this liquid and then dried.

The sensitized sheet is imagewise exposed as described in Example I and developed by guiding it over a rotating metal cylinder with a surface temperature of about 150° C., so that the light-sensitive side is in contact with the cylinder surface for 8 seconds.

The copy shows a strong blue image on a bright white background.

Example III

(1) 100 g. of di(octadecylammonium)oxalate is dispersed in a solution of 15 g. of gum arabic in 500 ml. of water and this dispersion is ground for 20 hours in a ball-mill.

(2) A solution containing:

Polyvinyl alcohol Rhodobiol 30/20 M ---------g--	20
Polyvinyl alcohol Rhodobiol 4/200 P ----------g--	30
Polyvinyl pyrolidone K30 ----------g--	5
Sodium salt of 2-acetoacetaminonaphthalene-6-sulfonic acid ----------g--	1.2
Sodium salt of 1-benzoylamino-8-hydroxy-naphthalene-4-sulfonic acid ----------g--	2.4
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid ----------g--	16.4
Water ----------ml--	400

is prepared.

(3) The dispersion prepared as decribed under (1) is mixed with the solution prepared as described under (2); to the liquid thus obtained is added 18 g. of oxalic acid, and the total volume of the liquid is made up to 1 litre.

With the liquid prepared as described above, white basepaper of weight 80 g./m.^{2} and suitable for the diazotype process is treated, so that a liquid layer of about 50 g./m.^{2} is applied on one side of it, then it is dried.

The side of the paper thus treated is sensitized with a solution of 14 g. of 4-morpholino-2,5-diethoxybenzene diazonium sulfate, 1 g. of polyoxyethylene sorbitan monolaurate (Tween 20) in 1000 ml. of water and dried.

A sheet of the diazotype material thus made is imagewise exposed underneath a letter typed on translucent paper of about 50 g./m.^{2}, until underneath the white portions of the letter nearly all the diazo compound has bleached out.

The imagewise exposed sheet of diazotype material is subsequently developed by guiding it over a heated rotating roller with a surface temperature of about 150° C., so that the back of the sheet is in contact with the roller surface for 8 seconds.

The copy shows a strong black image.

Example IV

A dispersion containing:

Di(octadecylammonium)oxalate ----------g--	400
Polyoxyethylene sorbitan monolaurate (Tween 20) --g--	40
Water ----------ml--	1000

is prepared, and this dispersion is ground for 20 hours in a ball-mill. The dispersion is filtered, the dispersed particles remaining behind as a residue on the filter. This residue is dried.

(a) To a sensitizing liquid containing:

4-diethylaminobenzene diazonium chloride, zinc chloride double salt ----------g--	6
Sodium salt of 2-acetoacetaminonaphthalene-6-sulfonic acid ----------g--	10
Oxalic acid ----------g--	22
Aqueous polyvinyl acetate dispersion Vinnapas H.60 ----------ml--	100
Water ----------ml--	800

is added 60 g. of the above residue, after which the liquid is homogenized by stirring.

A sheet of transparentized paper of weight 50 g./m.^{2} and suitable for the diazotype process is sensitized with this liquid. After drying, the light-sensitive sheet thus obtained is imagewise exposed underneath a transparent ink drawing until underneath the image-free portions of the drawing all the diazo compound has bleached out. The exposed sheet is developed as described in Example II. The copy shows a yellow image on a translucent colour-free background. It is very suitable as an intermediate original for the making of further copies on diazotype material.

(b) To a sensitizing liquid containing:

4-morpholino-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt ----------g--	10
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid ----------g--	25
Tartaric acid ----------g--	40
Aqueous poly-n-butylmethacrylate dispersion Plextol P2n ----------ml--	400
Water ----------ml--	500

is added 100 g. of the above residue, after which the liquid is homogenized by stirring.

A sheet of transparentized paper of weight 50 g./m.^{2} and suitable for the diazotype process is sensitized with this liquid. After drying, the light-sensitive sheet thus obtained is imagewise exposed and developed as described under (a).

The copy shows a violet-blue image on a translucent colour-free background.

Example V

63 g. of oxalic acid is dissolved in 10,000 ml. of ethanol (96%). This solution is heated to 60° C. and 135 g. of octadecylamine is added gradually.

The liquid is then heated to its boiling point, after which the following solution, which has been heated to about 60° C., is added gradually: 256 g. of dioctadecylamine in 5000 ml. of ethanol (96%). After this solution has been completely added to the first-mentioned solution, the liquid thus obtained is heated for ½ hour to 75° C. After the liquid has been cooled to room temperature, the precipitate is sucked off and washed with ethanol (96%). The product thus obtained melts at 153–156° C.

In a solution of 50 g. of ethyl cellulose (low viscosity) in 1000 ml. of ethanol (96%) 120 g. of the product prepared as described above is dispersed. The dispersion thus obtained is ground for 20 hours in a ball-mill.

After the grinding operation, a layer of about 10 g./m.^{2}, dry weight, is formed, on sized natural tracing paper of weight 80 g./m.^{2}, with the ground dispersion.

On this layer a light-sensitive layer is applied by spreading on it a liquid containing:

4-morpholino-2,5-diethoxybenzene diazonium sulfate ----------g--	10
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid ----------g--	20
Polyvinyl alcohol Rhodoviol 4/200 P ---------g--	40
Maleic acid ----------g--	15
Water ----------ml--	1000

and drying.

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

The copy shows a blue image on a transparent background.

Example VI

To 2000 ml. of ethanol (96%) is added 50 ml. of phosphoric acid (85% by weight). This liquid is heated to 50° C., after which 100 g. of octadecylamine is added gradually.

The liquid is then heated to its boiling point. Upon cooling octadecylammonium hydrogen phosphate crystallizes out. The precipitate is filtered and recrystallized from ethanol (96%). A white crystalline powder is obtained.

60.6 g. of this powder is dissolved in 1000 ml. of ethanol (96%). This solution is heated to its boiling point, after which a hot solution of 172 g. of dioctadecylamine in 10,000 ml. of ethanol (96%) is added gradually. The liquid is cooled and the precipitate thus formed is sucked off.

The precipitate is washed with ethanol (96%). The product thus obtained is crystalline and melts at 98–106° C.

A dispersion containing

Phosphate prepared as described above	g.	200
Gum arabic	g.	30
Water	ml.	1000

is prepared, and the dispersion is ground for 20 hours in a ball-mill.

To 500 ml. of this dispersion are added:

Polyvinyli alcohol Rhodoviol 30/20 M	g.	10
Polyvinyl alcohol Rhodoviol 4/200 P	g.	30
Phosphoric acid (85% by weight)	ml.	20
Water	ml.	450

and with the liquid thus obtained white base-paper of 80 g./m.² for the diazotype process is treated on one side. After drying, the side thus treated is sensitized with a liquid containing:

4-p-tolylthio-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt	g.	10
Polyoxyethylene sorbitan monolaurate (Tween 20)	ml.	2
Sodium salt of 2-hydroxynapthalene-3,6-disulfonic acid	g.	20
Water	ml.	1000

and dried again.

A sheet of the diazotype paper thus obtained is imagewise exposed and developed as described in Example II. The copy shows a purple image on a white background.

Example VII

100 g. of octadecylamine is dissolved in 4000 ml. of ethanol (96%). This dispersion is heated to 50° C. and, while stirring, such a quantity of a solution of 28 g. of tartaric acid in 280 ml. of ethanol is added gradually until the reaction mixture has a neutral reaction to litmus.

The reaction mixture is cooled to 0° C. and the precipitate thus formed is sucked off. The residue is washed with ethanol (96%) and dried. The dry residue weighs 115.5 g.

The melting point of the tartrate thus prepared is 108° C.

Di(octadecylammonium)diglycolate is prepared in an analogous way. During the preparation of this product, in the above formula the 28 g. of tartaric acid is replaced by 26 g. of diglycolic acid. In this case the residue weighs 110 g. The di(octadecylammonium)diglycolate thus obtained melts at 87–91° C.

Di(octadecylammonium)maleate is also prepared in an analogous way. For that purpose in the given formula the 28 g. of tartaric acid is replaced by 26 g. of maleic acid. The residue weighs 103.5 g. The di(octadecylammonium)maleate melts at 99–102° C.

To 1000 ml. portions of a solution of 200 g. of methyl cellulose Tylose MH 20 K in 10,000 ml. of water are added successively: (a) 100 g. of di(octadecylammonium)tratrate and 15 g. of oxalic acid; (b) 100 g. of di(octadecylammonium)diglycolate and 15 g. of diglycolic acid; (c) 100 g. of di(octadecylammonium)maleate and 10 g. of maleic acid.

The three dispersions are ground for 29 hours in a ball-mill.

Sheets of white base-paper of weight 80 g./m.² and suitable for the diazotype process are then coated with each of the dispersions on one side with a layer having a weight of 6 to 7 g./m.² after drying.

The sides of the three sheets thus treated are sensitized with a solution of

	G.
4-morpholino-2,5-diethoxybenzene diazonium sulfate	20
The sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid	40
Oxalic acid	0.4
Technical lauryl alcohol sulfate Duponol ME	3

in 1000 ml. of water and dried.

The sheets of diazotype paper are imagewise exposed and developed as described in Example II.

The copies show a violet blue image on a white background.

Example VIII

141.5 g. of N-octadecyl-N-methylamine is dissolved in 1500 ml. of ethanol (96%), and the solution is heated to 50° C. While stirring, such a quantity of a solution of 25 g. of oxalic acid in 500 ml. of ethanol (96%) is added gradually to the solution until the reaction mixture has a neutral reaction to litmus.

The reaction mixture is cooled to 0° C. and the precipitate thus formed is sucked off. The residue is washed with ethanol and dried. The dry residue weighs 105 g. The di(N-methyl-N-octadecylammonium)oxalate thus prepared melts at 145° C. 240 g. of N,N-dimethyl-N-octadecylamine is dissolved in 1500 ml. of ethanol (96%).

While stirring, a solution of 50.4 g. of oxalic acid in 500 ml. of ethanol (96%) is added gradually to this solution. The reaction mixture is diluted with ether to 8000 ml. A white precipitate is thus formed. The precipitate is sucked off, and the residue is washed with ether and dried. The dried residue weighs 102 g.

The di(N,N-dimethyl-N-octadecylammonium)oxalate thus prepared melts at 203–204° C. with decomposition.

The following dispersions are prepared:

(a)

Di(N-octadecyl-N-methylammonium)oxalate	g.	100
Methyl cellulose Tylose MH 20 K	g.	20
Oxalic acid	g.	15
Water	ml.	1000

(b)

Oxalate prepared according to the formula in Example V	g.	100
Methyl cellulose Tylose MH 20 K	g.	20
Oxalic acid	g.	15
Water	ml.	1000

(c)

Di(N,N - dimethyl - N-octadecylammonium)oxalate	g.	100
Methyl cellulose Tylose MH 20 K	g.	20
Oxalic acid	g.	15
Water	ml.	1000

The three dispersions are ground for 20 hours in a ball-mill.

Sheets of opaque linen for the diazotype process are then coated with each of the dispersions in such a way that the dry layer has a weight of about 6 g./m.².

The layer of each sheet is sensitized with a solution of

	G.
4 - N - methyl - N-benzylamino-2-chloro-5-methoxybenzene diazonium chloride, zinc chloride double salt	10
Sodium salt of 2,7-dihydroxynaphthalene-3,6-disulfonic acid	20
Oxalic acid	0.4

in 1000 ml. of water and dried.

The three sheets of diazotype linen are imagewise exposed and developed as described in Example II.

The copies show a violet image on a white background.

Example IX

To the dispersion (b) of Example VIII is added 20 g. of the sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid. The dispersion is then ground, and a layer having a dry weight of about 8–9 g./m.² is formed with

it on white base paper of weight 80 g./m.² and suitable for the diazotype process.

This layer is sensitized with a solution which contains 10 g. of 4-phenylaminobenzene diazonium sulfate in 1000 ml. of water, and has been brought to pH 3 with oxalic acid. After sensitization the layer is dried.

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

The copy shows a blue image on a white background.

Example X

30 g. of tartaric acid is dissolved in 1500 ml. of ethanol (96%). To this solution is added 54 g. of octadecylamine, after which the liquid is heated to its boiling point.

A hot solution of 102 g. of dioctadecylamine in 1500 ml. of ethanol (96%) is added gradually to this liquid.

The mixture is subsequently kept for some time at 75° C., after which it is cooled to 10° C.

The precipitate thus formed is sucked off and dried. The product obtained is a white crystalline powder melting at 92–99° C.

A dispersion containing

Tartrate prepared as described above	g.	100
Methyl cellulose Tylose MH 20 K	g.	25
Phosphoric acid (89% by weight)	ml.	7
Water	ml.	1000

is prepared, and this dispersion is ground for 20 hours in a ball-mill.

With the ground dispersion a layer having a dry weight of 10–11 g./m.² is formed on white base paper of weight 80 g./m.² suitable for the diazotype process.

This layer is sensitized with a solution of:

	G.
4-morpholino-2,5-diethoxybenzene diazonium sulfate	20
Sodium salt of 2,3-dihydroxynaphthalene-6-sulfonic acid	40
Oxalic acid	0.5
Technical lauryl alcohol sulfate Duponol ME	3

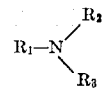
in 1000 ml. of water and dried.

A sheet of the diazotype paper is imagewise exposed and developed as described in Example II.

The copy shows a blue image on a white background.

What is claimed is:

1. Heat-developable diazotype material which comprises a diazo compound, an azo-coupling component, an acid-reacting compound, and a developing agent which, upon heating, is able to neutralize an acid, the various components being distributed over at most two layers of the material and the developing agent being a water-insoluble salt of a polybasic acid having a first dissociation constant between 7×10^{-2} and 1×10^{-4} and an aliphatic amine of the general formula



in which R_1 is an aliphatic hydrocarbon radical of at least 8 carbon atoms, and R_1 and R_3 stand for a hydrogen atom or an aliphatic hydrocarbon radical, while R_1, R_2, and R_3 together carry at least 16 carbon atoms, the said salt containing at least two cations formed from an amine of the said formula.

2. Heat-developable diazotype material according to claim **1** wherein the deveolping agent is a salt of oxalic acid.

3. Heat-developable diazotype material according to claim **2**, wherein the developing agent is di(octadecylammonium) oxalate.

4. Heat-developable diazotype material according to claim **1**, wherein the acid-reacting compound is oxalic acid.

5. Heat-developable diazotype material according to claim **1**, which contains, in addition, a water-soluble hydrophilic binder for some or all of the said components.

6. Heat-developable diazotype material according to claim **1**, wherein 30–60% of the cations present in the developing agent are di(octadecyl)ammonium ions.

7. Heat-developable diazotype material according to claim **1**, which comprises a water-soluble hydrophilic organic binder for some or all of the said constitutuents, and wherein the acid-reacting compound comprises oxalic acid and the developing agent comprises di(octadecylammonium)oxalate.

8. Heat-developable diazotype material according to claim **1**, comprising a flexible sheet having formed thereon a light-sensitive layer containing the said constituents and also containing polyvinyl alcohol and polyvinyl pyrrolidone as binders.

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