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PROCESS AND DEVELOPER FOR DEVELOPING EXPOSED ONE-COMPONENT DIAZOTYPE MATERIALS

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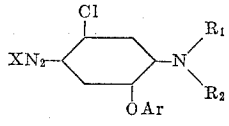
6 Claims. (Cl. 96—49)

The invention relates to a process for developing diazotype copies according to the so-called semi-dry method, and to novel developer compositions for use in said process. The invention is more particularly concerned with a process, in which a thin layer of an acid-reacting, aqueous, buffered developing liquid, which contains phloroglucinol as the sole or as the principal coupling component, is spread over the surface of imagewise exposed one-component diazotype paper, which has been sensitized with a diazo compound of the formula:



in which X is an anion, R_1 and R_2 are methyl or ethyl groups, and in which, when R_1 is a methyl group, R_2 may also be a cyclohexyl group, and Ar is a phenyl radical, or a phenyl radical carrying at most two substitutents.

After imagewise exposure, one-component diazotype material is normally developed according to the so-called thin-layer method. According to this method a thin layer of an aqueous buffered developing liquid is uniformly spread over the light-sensitive side, and, in order to promote the flatness of the developed copies, often also over the non-light-sensitive side of the imagewise exposed diazotype material. The quantity of developing liquid applied on one side of the diazotype material is normally expressed in the number of grams of liquid per m.² of material. If the quantity is small, such as 6–9 g./m.², the developing method is called "semi-wet" or "semi-dry." Developing liquids which are suitable for this method have to be very reactive, which means that they have to neutralize rapidly the acid that is present in the diazotype material and the acid that is liberated in the azo-dyestuff formation, and they have to contain actively coupling azo components. Such an azo component is phloroglucinol. In practice use is made of weakly acid and weakly alkaline developing liquids which contain phloroglucinol.

The weakly acid developing liquids can be buffered with ammonium, alkali metal, or alkaline earth metal salts of weak acids such as formic acid, acetic acid, succinic acid, malic acid, citric acid, tartaric acid, benzoic acid, phenylamido acetic acid, molybdic acid, tungstic acid, stannic acid, phosphoric acid, phthalic acid, glutaric acid, adipic acid, β-methyladipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, isosebacic acid, antidimethylsuccinic acid, aspartic acid, glutamic acid, itaconic acid, 2-ethyl-suberic acid, 2,5-dimethyladipic acid, and propane tricarboxylic acid. See British patent specification 425,235 and British patent application 31,362/60.

In practice, however, sodium formate and sodium benzoate, often together with sodium citrate, are almost exclusively used as buffer salts.

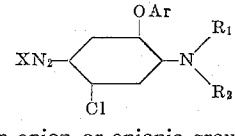
The weakly acid developing liquids applied in practice have a pH between 5 and 7 and generally have very good keeping qualities. They are used for developing diazotype materials which have been sensitized with a very actively coupling diazo compound, such as p-diazo-2,5-diethoxybenzoylamidobenzene, p - diazo - 2,5 - diethoxy-(4'-methyl)-phenylmercaptobenzene, and p-diazo-2,5-diethoxy - (4' - methoxy) - phenylbenzene. They are not suitable for the development of diazotype materials which have been sensitized with less actively coupling diazo compounds, because in that case the coupling of the phloroglucinol with the diazo compound takes place so slowly that complete development is not obtained.

The keeping qualities of the weakly alkaline developing liquids containing pholorglucinol are not nearly so good. Their pH lies between 7 and 10. As buffer salts for these developing liquids the alkali metal salts of acetic acid, propionic acid, adipic acid, citric acid, maleic acid, phthalic acid, carbonic acid, phosphoric acid, and boric acid have been proposed. In practice carbonate, phosphate, and borate buffers are mainly used in the weakly alkaline developing liquids.

The weakly alkaline developing liquids are used to develop diazotype materials which contain rather slowly coupling diazo compounds, such as p-diazo-N-ethyl-N-benzylaniline and p-diazo-o-chloro-diethylaniline.

If diazotype materials sensitized with a very actively coupling diazo compound are developed with these weakly alkaline liquids, "over-developed" copies are obtained, the azo-dyestuff of which is, for instance, red-brown instead of black. It is believed that this may be ascribed to the formation of predominant amounts of monoazo-dyestuff instead of the desired tris-azo-dyestuff from phloroglucinol. Phloroglucinol is able to couple in one, two, or three positions.

British patent application 37,797/59 and British patent application 7,359/61 describe diazotype papers which have been sensitized with diazo compounds according to the formula



in which X is an anion or anionic group, R_1 and R_2 are methyl or ethyl groups, and in which, when R_1 is a methyl group, R_2 may be a cyclohexyl radical, and Ar is a phenyl radical or a phenyl radical carrying at most 2 substituents.

These diazotype papers are very interesting because of their great light-sensitivity and the possibility of developing them with a weakly acid phloroglucinol developer according to the thin layer method, in which they yield, both in the non-exposed and in the partly exposed portions, azo-dyestuffs with the same colour without any inconvenient additional shade. With the known weakly acid developing liquids containing phloroglucinol, which have been buffered with formate, benzoate, citrate, they develop into black azo-dyestuffs, but the development often proceeds slowly and/or incompletely. In many cases the diazotype paper has to be heated after the application of the thin layer of developing liquid in order to ensure a fast and, at the same time, complete development.

It is true that with the papers according to British patent application 7,359/61, which besides a diazo compound according to the above general formula contain a relatively small quantity of a very actively coupling diazo compound, the azo-dyestuff formation starts immediately after the application of the developing liquid, which considerably improves the control of the development, but a complete conversion of the diazo molecules into azodyestuff often fails to be achieved even with these papers, especially when the developing liquid has a relatively low temperature, such as room temperature or somewhat lower, and when the paper is developed therewith according to the semi-wet method and is not heated after the application of the developing liquid.

Increasing use is made in offices of simple photo-printing machines in which the copies are developed according to the semi-dry method and are not heated after the application of the developing liquid. In such machines it is preferred to use weakly acid developing liquids which are of such stability that the developing section of the machines has to be cleaned only occasionally, for instance, once a week. Under cold weather conditions the developing liquid often has a relatively low temperature in the morning, while later in the day or under different conditions it has a higher temperature. Fluctuations in the temperature of the developing liquid in such photo-printing machines between 15° and 30° C. will frequently occur.

It goes without saying that, whatever may be the conditions it is desirable that the copies should always be developed rapidly and completely. However, adjustment of the pH of the conventional weakly acid developing liquids to the highest possible value, i.e. just below 7 is of little avail.

The development of the diazotype papers according to the said patent applications with a weakly alkaline developing liquid containing phloroglucinol does proceed rapidly and completely, but in that case the azo-dyestuffs formed are not black, but a rather unattractive red-brown.

It has now been found that these diazotype papers can be developed extremely well accordingly to the semi-dry method if the developing liquid contains, as the principal buffer salt, potassium and/or lithium maleate and has a pH between 6.5 and 7.

This developing liquid effects a distinctly faster and more complete development of these diazotype papers than the conventional weakly acid developing liquids, particularly also when its temperature is on the low side and the copies are not heated after the application of the developing liquid.

The process according to the invention is very suitable for application in offices using simple photo-printing machines. These machines are preferably equipped with a light-source that can be switched on and off at any time.

Suitable light-sources of this kind are actinically fluorescent low-pressure mercury vapour lamps, which, however, do not have a particularly great luminous intensity. In machines equipped with such lamps, very light-sensitive materials are therefore preferably used. The diazotype papers which are used in the process according to the invention are very light-sensitive and have reasonable keeping qualities. The developing liquid too has good keeping qualities. Moreover it has a lesser tendency to dry up in the developing machines, as compared with the conventional weakly acid developing liquids, which often form inconvenient crystal crusts. All this prevents fouling of the machines and is very important if the developing liquid is used in a developing device with liquid-applying rollers provided with capillary grooves according to British patent specification 544,882.

Indeed, if hard and poorly soluble crystals are deposited in the grooves, which happens when the conventional weakly acid developing liquids are used, these rollers lose their capillary activity and proceed to operate as smooth rollers, in consequence of which, dependent on the construction of the developing machine, too much or too little developing liquid is applied, Development then no longer proceeds according to the semi-dry method.

Developing liquids according to the present invention may be prepared by dissolving in water, besides the usual substances such as the azo component, reducing agents such as thiourea, stabilizers such as hydroquinone monosulphonic acid, wetting agents, substances which counteract the discoloration of the developing liquid, such as a very small quantity (5% of the total quantity of buffer salt for instance,) of sec. alkali phosphate, the desired quantity of maleic acid or maleic anhydride and then adjusting the pH of the liquid to the correct value with potassium hydroxide solution or lithium hydroxide solution.

It is also possible to add a quantity of dipotassium or dilithium maleate to a phloroglucinol solution containing the other usual substances, and then to adjust this solution to the desired pH with maleic acid or with another acid or acid-reacting salt, preferably one with buffering capacity.

Besides the maleate, the developer may contain a relatively small quantity of one or more other buffer salts. These can be added as such, but the acids forming such buffer salts can also be used.

The developer may be formulated as a ready-for-use liquid, or in the form of powder mixtures or tablets, which have to be dissolved in the requisite quantity of water before use.

For the preparation of the diazotype paper and of the diazo compounds necessary for its manufacture reference is made to British patent application 37,797/59 and British patent application 7,359/61.

The following examples will serve to illustrate the invention:

Example I

White base-paper of weight 80 g./m.² and suitable for the diazotype process is sensitized with a solution of:

17.5 g. of 4-diethylamino 3-(4'-chlorophenyl)oxy-6-chlorobenzene diazonium chloride, zinc chloride double salt
4 g. of tartaric acid
1 g. of boric acid
20 cm.³ of polyvinyl acetate dispersion (Vinnapas H.60 from Wacker-Chemie G.m.b.H., Munich, Germany)
In 1000 cm.³ of water

and dried.

The light-sensitive side of a sheet of the diazotype paper is covered with a sheet of tracing-paper, on which a pencil drawing has been made, and exposed in a printer equipped with actinically fluorescent low-pressure mercury vapour lamps.

The exposure is continued until in the portions of the diazotype paper which are in contact with the blank portions of the drawing, only a small quantity of diazo compound is left. The moment at which the exposure has to be terminated is soon reached.

The latent diazotype copy obtained is developed according to the semi-dry method by applying on the image side a layer of 9 g./m.² of a deveolping liquid of the following composition:

70 g. of maleic acid
30 g. of lithium hydroxide
10 g. of thiourea
6.5 g. of phloroglucinol
2 cm.³ of Tergitol O8 (from Union Carbide Chemicals Co., New York, U.S.A.)
1000 cm.³ of water,

which liquid has been adjusted to a pH of 6.7 by addition of a small quantity of 0.10 N hydrochloric acid, and the copy is thereafter dried in the atmosphere. Even if the temperature of the developing liquid is relatively low, such as 15° C., the copy is developed rapidly and com-

pletely. It shows a black image on a uniformly foggy background having a greyshade. The azo-dyestuff in the foggy background has the same colour as that in the black image portions.

The developer has excellent keeping qualities. With a conventional acid developer with an equivalent quantity of sodium formate, which has the same pH, the paper is developed markedly less rapidly and completely, especially when the temperature of the developing liquid is on the low side.

Example II

White base-paper of weight 80 g./m.^{2} and suitable for the diazotype process is sensitized with a solution of:

16.8 g. of 4-dimethylamino 3-(4'-chlorophenyl)oxy-6-chlorobenzene diazonium chloride, zinc chloride double salt
4.3 g. of 4-(4'-methylphenyl)mercapto-2,5-diethoxybenzene diazonium chloride, zinc chloride double salt
5 g. of tartaric acid
30 cm.^{3} of polyvinyl acetate dispersion (Vinnapas H.60)
In 1000 cm.^{3} of water

and dried.

A sheet of the diazotype paper is imagewise exposed as described in Example I. The endpoint of the exposure is soon reached.

The latent diazotype copy thus obtained is developed according to the semi-wet method by applying on the image side a layer of approximately 8 g./m.^{2} of a developing liquid of the following composition:

93 g. of dipotassium maleate
3 g. of maleic anhydride
3 g. of sec. sodium phosphate (2 aq.)
4 g. of phloroglucinol
10 g. of thiourea
3 g. of sulphonated di-isobutyl succinate (commercially available under the trade name of Aerosil I.B. from American Cyanamid Co., New York, U.S.A.)
950 cm.^{3} of water

and then drying it in the atmosphere. The developing liquid has a pH of 6.8 and a temperature of 18° C. This is also the temperature of the room.

The copy is developed rapidly and completely, the image becoming visible immediately after the application of the developer.

The azo-dyestuff has a fine black colour and does not show any off-shades. The developer dries very slowly on the parts of the developing device which are moistened with it. With a conventional acid developer of the same temperature (18° C.), such as that described in Example II of British patent application 7,359/61, the image also soon becomes visible. During the time which the copy needs for drying, however, by no means all the diazo molecules are converted into azo-dyestuff, not even when, by addition of a small quantity of alkali, the pH of that developer has also been adjusted to 6.8. The copies consequently are rather faint. This developer dries much faster in the developing device, while inconvenient crystals are formed.

Good results are also obtained if, during the manufacture of the diazotype paper, instead of 16.8 g. of 4-dimethylamino - 3-(4'-chlorophenyl)oxy-6-chlorobenzene diazonium chloride, zinc chloride double salt, use is made of 15.5 g. of 4-N-methyl N-cyclo-hexylamino 3-phenoxy-6-chlorobenzene diazonium chloride.

Example III

White base-paper of weight 80 g./m.^{2} and suitable for the diazotype process is sensitized with a solution of:

21 g. of 4-diethylamino-3-(4'-chlorophenyl)oxy-6-chlorobenzene diazonium chloride, zinc chloride double salt
4 g. of citric acid
25 cm.^{3} of polyvinyl acetate dispersion (Vinnapas H.60)
In 1000 cm.^{3} of water

and dried.

The paper is very light-sensitive. Exposure is carried out as in Example I.

The copy is developed according to the semi-wet method by applying on the image side a layer of approximately 7.5 g./m.^{2} of a developing liquid of the following composition:

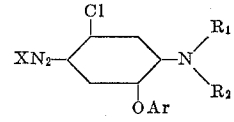
52 g. of maleic anhydride
97.5 cm.^{3} of potassium hydroxide solution (13.5 N)
3 g. of potassium benzoate
4 g. of phloroglucinol
1 g. of resorcinol
3 cm.^{3} of Tergitol O8 (from Union Carbide Chemicals Co., New York, U.S.A.)
900 cm.^{3} of water

and then drying it in the atmosphere. The developing liquid has a pH of 6.6 and has the temperature of the room (17° C.).

The copy is developed rapidly and completely, the image becoming visible immediately after the application of the developer. The azo-dyestuff is black and does not show any off-shades. The developer has very good keeping qualities and does not give any difficulties with respect to crystallization.

We claim:

1. Process for the production of diazotype copies according to the one-component diazotype method wherein a thin layer of an aqueous developing liquid is applied to the sensitized side of one-component diazotype paper, which comprises applying to imagewise exposed one-component diazotype paper, which has been sensitized with a diazo compound of the formula:



in which X is an anion, R_1 and R_2 are selected from the class consisting of methyl groups, ethyl groups, a methyl group and an ethyl group, and a methyl group and a cyclohexyl group, and Ar is a phenyl radical carrying at most two substituents, a thin layer of an acid-reacting, aqueous, buffered developing liquid, which contains phloroglucinol as at least the principal coupling component, and which contains alkali metal maleate selected from the class consisting of potassium maleate, lithium maleate and mixtures thereof as the principal buffer salt and has a pH between 6.5 and 7.

2. A developer composition for one-component diazotype material, which comprises phloroglucinol as at least the principal coupling component, which contains as the principal buffer salt alkali metal maleate selected from the class consisting of potassium maleate, lithium maleate and mixtures thereof and which has in aqueous solution a pH of 6.5 to 7.

3. A developer composition according to claim 2 wherein the ingredients are dissolved in water and the pH of the solution is 6.5 to 7.

4. A developer composition for one-component diazotype material, which comprises phloroglucinol as at least the principal coupling component, which contains dipotassium maleate as the principal buffer salt and which has in aqueous solution a pH of 6.5 to 7.

5. A developer composition for one-component diazotype material, which comprises phloroglucinol as at least the principal coupling component, which contains dilithium maleate as the principal buffer salt and which has in aqueous solution a pH of 6.5 to 7.

6. A developer composition for one-component diazotype material, which comprises phloroglucinol as at least the principal coupling component, which contains as the

principal buffer salt a mixture of dipotassium and dilithium maleates and which has in aqueous solution a pH of 6.5 to 7.

References Cited by the Examiner

UNITED STATES PATENTS

2,037,542	4/1936	Schmidt et al.	96—91
2,113,944	4/1938	Leuch	96—49
2,405,523	8/1946	Sease et al.	96—91 X
2,597,306	5/1952	Eaton et al.	96—48 X
2,657,137	10/1953	Kessels	96—49

FOREIGN PATENTS

1,122,651	5/1956	France.
425,235	3/1935	Great Britain.

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