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DEVELOPER FOR DIAZO PRINTS

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This invention relates to the development of photo-prints of the diazo type, and particularly to developers which eliminate or reduce the discoloration which commonly occurs when exposed and developed diazo prints are exposed to the action of actinic light.

One of the principal disadvantages of diazo type photographic papers has been the lack of stability in the white areas of the finished print.

In one commonly used method for preparing and using diazo-type papers, the paper (or other support as film, cloth, etc.) is coated with a layer comprising a light-sensitive diazo compound, which is capable, under proper conditions, of coupling with a azo-dyestuff-forming component to form an azo dye. When such a paper is exposed to light under a tracing or other transparent positive to be duplicated the diazo compound in those areas which are transparent in the original positive is decomposed. In those areas which are opaque in the original positive, the diazo compound is not affected.

Such an exposed paper is developed by applying to the exposed surface an azo-dyestuff-component such as phloroglucinol or other phenolic compounds, in a solution made alkaline by the addition of an alkaline salt of an alkali metal or a mixture of such salts. In this alkaline medium the azo-dyestuff component couples with the unaltered diazo compound in the areas not affected by light, forming an azo dye. No coupling, of course, occurs in the areas which have been exposed to light. In the process, commonly referred to as the "semi-dry process," the developing solution is applied to the paper surface in a thin film and the paper is dried without washing or other means of removing unreacted chemicals.

Positive diazo prints prepared in this manner show desirable properties when first made, including satisfactory dark lines and satisfactory white areas. However, there remains in the white areas a residue which includes the decomposition products of the diazo compounds, the azo-dyestuff-forming component of the developer, and residual alkali from the developer. Under conditions of exposure to light during use, and particularly when the prints are exposed to sunlight or other actinic light, these substances react to form yellow or brown colored products, which discolor the white areas and reduce the contrast between the white and dark areas. Various means have been suggested and tried for overcoming this discoloration, including for example the use of reducing agents in the developer, but no method has been found which eliminates the trouble, and diazo prints as made by this process are subject to the discoloration described above.

In other forms of diazo printing papers, the diazo compound and the azo-dyestuff-forming component or coupling agents are both present in the light-sensitive layer, but they are prevented from coupling to form an azo dye by one of several means; usually by the presence of acid in the light sensitive layer, since coupling is inhibited by acid. Such papers are exposed in the same manner as above described, and are then developed by alkali alone. This can be applied in the form of an aqueous solution, for example, a solution of an alkaline salt of an alkali metal; in which case the residue remaining after development is the same as in the previous case, and discoloration proceeds in the same manner.

A third type of diazo paper is sensitized with a diazo compound and an azo-dyestuff-component in acid medium, and after exposure is developed by passing through an atmosphere saturated with ammonia and water vapor. Under these conditions, development occurs. However, development is generally slow by this method, and in addition the fumes of ammonia are objectionable. Special apparatus must be provided to prevent escape of the ammonia fumes, and in many cases the contrast between white and dark areas is not as great as desirable.

According to this invention, by the use of other alkaline substances in place of the alkali metal salts commonly used, it is possible to reduce or eliminate this discoloration. We have found that the use of volatile amines in the developing solution makes it possible to obtain satisfactory development of the exposed papers, and at the same time reduce the extent of the discoloration of the white areas upon subsequent exposure of the developed prints to light. While the invention is not limited to the specific amines disclosed, but includes any volatile amine as defined above, amines which can be used in this manner under this invention include diethylamine, triethylamine, morpholine, ethylenediamine, monoamyl amine, and the various methylamines.

The volatile amine can be applied in aqueous solution, together with the azo-dyestuff-forming component, to develop a diazo paper which contains only the diazo compound in the light sensitive layer; or the volatile amine can be applied alone to a paper which contains the diazo compound and the azo-dyestuff-forming component in the light-sensitive layer.

A probable explanation for the reduction in discoloration caused by the use of volatile amines as alkaline agents lies in the nature of the resi-

dues remaining on the white areas in the developed diazo print. The substances commonly used as azo-dyestuff-forming components or coupling compounds are phenolic in nature, e. g. phloroglucinol, resorcinol, and various substituted phenolic substances. In addition, it is believed that the decomposition products of the diazo compounds formed under the action of light during exposure are also phenolic compounds. It is a well known fact that phenolic compounds are darkened by oxidation, and that oxidation of these bodies is accelerated in alkaline medium. It is believed that the discoloration of the white areas is caused by oxidation of such phenolic compounds, which is accelerated by any residual alkali remaining from the developer.

While our invention is not limited by this hypothesis, this theory offers a possible explanation for the beneficial effect of the volatile amines used in developers according to this invention. A volatile amine added to the developer renders it alkaline so that coupling between the diazo compound and the azo-dyestuff-forming component can take place. Upon subsequent drying of the moistened sheet, the amine being volatile evaporates, leaving no alkaline residue to accelerate discoloration. For this reason, discoloration is reduced.

While it has been found that volatile amines in general produce a beneficial effect in stabilizing the white areas of the developed diazo paper, as described above, there are definite differences among the various volatile amines in the degree to which they prevent discoloration. We prefer the use of diethyl amine or morpholine, but the scope of this invention is not limited to these specific substances.

We have also found that it is advantageous to incorporate a non-volatile acid substance in the developer with the volatile amine, in a quantity less than an amount chemically equivalent to the quantity of amine used, so that the developer is alkaline in reaction (pH greater than 7). This has two effects: First it reduces the alkalinity of the developing solution, thus aiding in preventing deterioration of the developer before use, since oxidation and hence deterioration of the developer is greater in a more alkaline solution. Second, it stabilizes the residue remaining on the paper after development, ensuring that it will remain slightly acidic after evaporation of the excess amine. It is found that when a solution containing a non-volatile acid, and a volatile amine in excess, which has a pH greater than 7, is evaporated, and the residue dissolved in water, the pH of the resulting solution is less than 7. Typical examples of such mixtures, with the pH of the original solution and the pH of the final solution, are given in the following Table I.

TABLE I

Solution	Initial solution		Solution of residue in water	
	Volume	pH	Volume	pH
Diethyl amine (in excess) and oxalic acid	25 ml.	10.73	25 ml.	5.90
Morpholine (in excess) and oxalic acid	25 ml.	8.32	25 ml.	6.90

The data in Table I indicates that when a solution containing a non-volatile acid and a volatile amine is evaporated, the residue remaining is acid in reaction.

The following examples serve to illustrate this invention, but are not intended to limit it thereto:

Example I.—0.6 g. of phloroglucinol and 10.0 g. of morpholine are dissolved in 100 ml. of water. Paper previously coated with a light sensitive diazo compound and exposed under a pattern or tracing is developed by lightly coating it with the above solution and allowing it to dry. The lines or dark areas are a deep red brown and the white areas are a clean white.

Other methods of applying the developer, such as by dipping or immersing the exposed print, or by spraying, can also be used, and are within the scope of this invention. Data on the pH of this solution, discoloration of paper developed as described above, and pH of a solution of residual material left on the paper after developing and drying are appended below in Table II.

Example II.—0.6 g. of phloroglucinol and 8.3 g. of diethylamine are dissolved in 100 ml. of water. A diazo paper made and exposed as described above is developed with this solution and dried. Data on pH of this solution, original color and color after exposure to sunlight, and pH of residue remaining after development and drying are given in the table below, together with similar data for the other examples given.

Example III.—Phloroglucinol, 0.6 g., diethylamine 8.3 g., and oxalic acid, 6.8 g., are dissolved in 100 ml. of water. This solution is used as a developer in the manner described above or in any other manner.

Example IV.—Resorcinol, 0.5 g., diethylamine, 10.0 g. and oxalic acid, 6.8 g. are dissolved in 100 ml. of water.

Example V.—Phloroglucinol, 0.3 g., diethylamine 9.2 g., oxalic acid 6.8 g., and resorcinol, 0.3 g., are dissolved in water, 100 ml.

Example VI.—To the developer from Example III is added sodium thiosulphate, 10 g., and the solution is used as a developer as before. Improved stability of the white area results.

The following table gives data relative to the foregoing developers including pH as prepared, relative whiteness of exposed areas on a commercial diazo-sensitized paper, immediately after development and drying, relative whiteness after exposure to sunlight, and pH of washings from the paper after development and drying. These data clearly show the increased acidity of the residue remaining on the paper when amines are used in the developer. For comparison, similar data with a commercial developer (designated as "Developer A"), and with a developer prepared with a non-volatile alkaline salt and an amount of oxalic acid less than equivalent to the amount of alkali (designated as "Developer B") are also given. The composition of Developer B is as follows:

Developer B

Potassium carbonate	g.	11.2
Phloroglucinol	g.	0.6
Oxalic acid	g.	6.8
Water to make	ml.	100

"Developer A" has the following composition:

Carbonate, as potassium carbonate	g.	3.4
Thiosulphate, as sodium thiosulphate	g.	4.7
Chloride, as sodium chloride	g.	3.0
Phloroglucinol and resorcinol	g.	0.7
Water to make	ml.	100

TABLE II

Characteristics of typical developers

	pH	pH of washings developed paper [1]	Relative whiteness before sunlight exposure [2]	Relative whiteness after exposure to sunlight for 25 hrs. [2]	Color of dark areas
Example I	9.34	5.75	7	6	Dark purple.
Example II	11.15	5.62	6	3	Do.
Example III	8.13	5.62	3	4	Do.
Example IV	9.80	5.91	1	1	Orange brown.
Example V	9.80	5.70	2	2	Brownish black.
Example VI	8.18	5.60	5	5	Dark purple.
Developer A	7.97	6.28	4	7	Brownish black.
Developer B	8.28	6.86	8	8	Dark purple.

[1] Washings from an area 1" x 4" with 25 ml. of distilled water.
[2] 1, whitest; 9, least white.

The increased stability of the white areas resulting from the use of volatile amines in the developer is clearly shown in the above table, which shows that papers treated with Developers A and B after exposure to light had poorer whites than any of the other papers, even though Developer A showed quite good whites initially; while the darkening of papers developed in solutions containing amines was less serious.

We claim:

1. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the step of developing such prints which comprises contacting the sensitized paper or similar supporting material with a developing liquid containing an azo-dyestuff-forming compound and a volatile amine, said developing liquid having a pH greater than 7.

2. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the step of developing such prints which comprises contacting the sensitized paper or similar supporting material with a developing liquid containing an azo-dyestuff-forming compound and diethylamine, the developing liquid having a pH greater than 7.

3. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the step of developing such prints which comprises contacting the sensitized paper or similar supporting material with a developing liquid containing an azo-dyestuff-forming compound, a volatile amine, and a non-volatile acid, the developing liquid having a pH greater than 7.

4. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the step of developing such prints which comprises contacting the sensitized paper or similar supporting material with a developing liquid containing an azo-dyestuff-forming compound, a volatile amine having a degree of volatility of the general order of that of diethylamine, and a non-volatile acid, the developing liquid having a pH greater than 7.

5. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the step of developing such prints which comprises contacting the sensitized paper or similar supporting material with a developing liquid containing an azo-dyestuff-forming compound in the form of a phenolic substance and a volatile amine, said developing liquid having a pH greater than 7.

6. In a method of preparing diazo photo prints whereby discoloration of "white areas" is inhibited, the steps of effecting development of said prints which include, contacting the sensitized paper or similar supporting material with a liquid volatile amine.

7. A developing liquid for diazo photo prints having the property of inhibiting discoloration of the "white areas" of sensitized paper or similar supporting material after contact with said developing liquid, said developing liquid having a pH greater than 7 and containing an azo-dyestuff-forming compound and a volatile amine.

8. A developing liquid for diazo photo prints having the property of inhibiting discoloration of the "white areas" of sensitized paper or similar supporting material after contact with said developing liquid, said developing liquid having a pH greater than 7 and containing an azo-dyestuff-forming compound and diethylamine.

9. A developing liquid for diazo photo prints having the property of inhibiting discoloration of the "white areas" of sensitized paper or similar supporting material after contact with said developing liquid, said developing liquid having a pH greater than 7 and containing an azo-dyestuff-forming compound, a non-volatile acid, and a volatile amine.

10. A developing liquid for diazo photo prints having the property of inhibiting discoloration of the "white areas" of sensitized paper or similar supporting material after contact with said developing liquid, said developing liquid having a pH greater than 7 and containing an azo-dyestuff-forming compound, a non-volatile acid, and diethylamine.

11. A developing liquid for diazo photo prints having the property of inhibiting discoloration of the "white areas" of sensitized paper or similar supporting material after contact with said developing liquid, said developing liquid having a pH greater than 7 and containing an azo-dyestuff-forming compound, a non-volatile acid, a volatile amine having a degree of volatility of the general order of that of diethylamine.

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