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MONOBASIC SALTS OF PHOSPHATE ACIDS AS STABILIZERS FOR DIAZOTYPE PRINTS

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7 Claims. (Cl. 95—88)

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This invention relates to an improvement in the production of photographic prints by the diazotype process.

In the preparation of diazotype prints as ordinarily carried out, a carrier surface or base bearing a light-sensitive diazo compound is exposed to light of locally varied intensity (e. g. under a photographic transparency or an opaque design or line drawing on a transparent sheet) so as to destroy the diazo compound partly or completely in the illuminated areas. In developing the print, the residual diazo compound corresponding to the image to be reproduced is coupled with an azo coupling component, which may be originally incorporated with the diazo compound on the carrier, or subsequently applied thereto in a developer composition. When the azo coupling component is originally present together with the light-sensitive diazo compound on the photoprinting material, development can be advantageously effected by the dry process (i. e. by exposure to an alkaline vapor such as ammonia). Such prints can also be developed by a semi-wet process wherein the exposed print in moistened with small amounts of a solution adapted to effect coupling (e. g. a solution of alkaline reacting substance), such solution being allowed to dry on the resulting print. When no coupling component is included in the photoprinting material, it may be applied together with the alkaline reagent which promotes coupling in the solution employed in the semi-wet developing process.

In the aforesaid dry and semi-wet developing processes, the excess coupling component and also decomposition products of the light-sensitive diazo compound, remain on the surface of the finished print, particularly in the background areas. These materials cause serious discoloration of the background on exposure of the print to light and/or air, whereby the appearance and clarity of the copy is seriously impaired. Numerous attempts have been made to improve the aging qualities of such prints, for example by incorporating stabilizers in the sensitizing or developing composition, but such proposals are generally only partly effective.

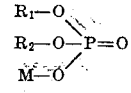
It has also been proposed to remove the injurious byproducts and excess coupling component by washing the developed print with water. Considerable improvement is effected thereby insofar as the stability of the background to discoloration is concerned, but such treatment often causes undesirable color changes in the developed image. For example, black dyed prints when washed with water have a marked tendency to

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shift their coloration toward purple. This is especially true in the case of black images on gelatin-coated paper. Such color shifts are especially undesirable in making copies of photographs wherein a range of shadows of varying depth but of the same color (particularly black) is to be produced.

I have discovered that diazotype prints produced by the dry or semi-wet development processes and therefore carrying substantial amounts of coupler and diazo compound decomposition products on the surface of the print, can be effectively stabilized against discoloration on exposure to light and/or air without causing undesirable changes in the color of the image, by washing the prints with an aqueous solution of a water-soluble mono-basic salt of a phosphate acid, particularly a mono-alkali metal or ammonium salt of phosphoric acid or of lower alkyl mono- or di-esters of phosphoric acid, the solution having a pH of at least 5 and less than 7.

Phosphoric acid derivatives employed in accordance with my invention may be represented by the following general formula:



wherein R_1 and R_2 are selected from the group consisting of hydrogen and lower alkyl groups (i. e. alkyl groups of 1 to 3 carbon atoms) and M is selected from the group consisting of alkali metals and the ammonium radical.

The aforesaid salts, represented by the above formula, are advantageously employed in an aqueous solution in a concentration of at least 1% and preferably of about 5%. When the color compound of the image is relatively soluble in water, any tendency of the color to run during the washing treatment can be overcome by including a neutral salt (e. g. NaCl or Na_2SO_4) in the washing solution, for example in a concentration of about 5%.

After the washing treatment is complete, the print is allowed to dry. The resulting copies are substantially immune to discoloration upon exposure to light and/or air, and the color of the print as originally developed is preserved without change, even when the sensitized base material is a layer of gelatin.

My invention is illustrated by the following examples:

Example 1

Gelatin-coated baryta filled paper was sensi-

tized in the usual manner by impregnation with sensitizing compositions containing the following combinations of diazo compound and coupler:

A. 2-diazo-1-naphthol-4-sulfonic acid and phloroglucinol
B. p-Diazo-diphenylamine sulfate and 2-naphthol-3,6-disodium sulfonate
C. Zinc chloride double salt of p-diazo dimethylaniline and 2,3-dihydroxynaphthalene

After drying, the sensitized sheets prepared as stated above were exposed to light under a positive photographic transparency, line drawing or similar master to be copied, and thereupon subjected to dry development by exposure to ammonia vapor, or to semi-wet development by moistening with small amounts of an alkaline-reacting solution (e. g. aqueous sodium carbonate), followed by drying.

The images on the resulting prints were colored red, dark purple, and dark blue to black shades respectively. Such prints, on exposure to light and air, become very much discolored, particularly in the background areas.

The developed prints were washed in accordance with my invention with a 5% aqueous solution of sodium dihydrogen phosphate and thereupon dried. The resulting washed copies showed no yellowing or discoloration on exposure to light and air for prolonged periods, and the color of the print as originally developed remained unchanged.

Example 2

A series of prints prepared and developed in the same manner as in Example 1 and having strongly-contrasting image and background areas, were washed with an aqueous solution containing 5% sodium dihydrogen phosphate and 5% sodium chloride and thereupon dried. The copies thus obtained possessed stability against discoloration similar to that obtained in the foregoing example, and the edges of the image portion were perfectly defined, showing no tendency of the color to run.

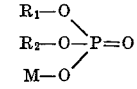
Example 3

A third set of prints prepared and developed as in Example 1 were washed with a 5% aqueous solution of sodium or potassium monoethyl hydrogen phosphate, and thereupon dried. The copies thus obtained likewise possessed excellent stability to discoloration as was the case with the prints of the preceding examples.

Instead of the sodium or potassium salts employed in the foregoing examples, the corresponding ammonium salts can be used. Similarly, other mono-alkali metal salts of lower alkyl (i. e. methyl, ethyl, propyl or isopropyl) mono- or di-esters of phosphoric acid can be used instead of the sodium or potassium ethyl hydrogen phosphate in Example 3. The pH of the washing solution in each of the foregoing examples is between 5 and 7. If necessary, small amounts of buffers, acids or alkalies can be added to adjust the pH of the solution to the aforesaid range. For example, small amounts of acid may be advantageously used in connection with mono-alkali metal dialkyl phosphates. The washing treatment of my invention can be applied with a similarly advantageous effect to diazotype prints having other kinds of bases or carriers (e. g. ordinary paper, cellulosic films or the like).

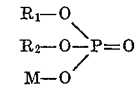
I claim:

1. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution of a compound having the general formula:



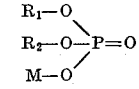
wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, and M is selected from the group consisting of alkali metals and the ammonium radical, said solution having a pH of at least 5 and less than 7.

2. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution of a neutral water-soluble inorganic salt and a compound having the general formula:



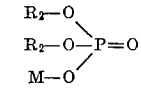
wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, and M is selected from the group consisting of alkali metals and the ammonium radical, said solution having a pH of at least 5 and less than 7.

3. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution containing at least 1% of a compound having the general formula:



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, and M is selected from the group consisting of alkali metals and the ammonium radical, said solution having a pH of at least 5 and less than 7.

4. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution containing 5% by weight of a compound having the general formula:



wherein R_1 and R_2 are selected from the group consisting of hydrogen and alkyl groups of 1 to 3 carbon atoms, and M is selected from the group consisting of alkali metals and the ammonium radical, said solution having a pH of at least 5 and less than 7.

5. The process for improving the stability to discoloration of a diazotype print, bearing resid-

ual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution of sodium dihydrogen phosphate.

6. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution containing sodium dihydrogen phosphate and sodium chloride.

7. The process for improving the stability to discoloration of a diazotype print, bearing residual unreacted coupling component and diazo compound decomposition products on the background areas thereof, which comprises the step of washing said print after its development with an aqueous solution containing an alkali metal monoethyl hydrogen phosphate.

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