

UNITED STATES PATENT OFFICE

2,113,944

PRODUCTION OF PHOTOGRAPHIC DIAZO-
TYPE PRINTS

Werner Paul Leuch, Denmark Hill, London, Eng-
land, assignor to Eugene Dietzgen Company,
New York, N. Y.

No Drawing. Application August 7, 1934, Serial
No. 738,814. In Great Britain September 11,
1933

9 Claims. (Cl. 95—6)

This invention relates to the production of photographic diazotype prints and has for its object to provide improvements therein.

In the production of diazotype prints, three compounds are generally used, namely:

(1) A diazo-salt which bleaches out when exposed to light under a drawing.

(2) A coupling component capable of forming an azo-dyestuff with the undecomposed diazo-body.

(3) Alkali, or an alkaline reacting salt which permits the coupling to take place.

There are two methods by which the diazotype process has been carried out so far on a commercial scale, namely:

(a) The paper is prepared with a solution containing both the diazo-body and the coupling component. In this case, to bring about the development of the picture, after the paper had been exposed to the light under a drawing, only the third component, namely, alkali, has to be added. This is generally done by exposing the print to the action of ammonia fumes.

(b) The paper is prepared with a solution containing the diazo-body only (generally in presence of an acid or acid salts). For the development of this paper, a liquid developer containing, in addition to the alkali, also the coupling component, has to be applied in a thin layer.

Method (a) is generally described as the dry development process, and Method (b) as the semi-dry development process. Both processes are used on a large scale. The present invention is concerned only with Method (b), namely, the semi-dry development of diazotype prints by means of phenolic coupling components.

In the case of Method (b) the use of alkali involves several serious drawbacks. In the case where polyhydroxy compounds of benzene or naphthalene are used as coupling components (such as is generally the case in order to produce dark shades of dyes) the developer deteriorates rapidly on account of the oxidation which sets in in the presence of alkali. In a very short period such developers are so strongly oxidized that they stain the print at once and do not produce a clean white background. Various methods have been devised for counteracting this oxidation, such as, for instance, the use of weak alkaline salts of the type of borax, secondary sodium phosphate and alkaline bicarbonates in place of the alkaline carbonates or hydroxides generally used. By these various methods the keeping qualities of the developers have certainly been improved, but the presence of alkali, no matter how weak, is defi-

nately detrimental in one or more directions. For instance, the alkali in excess attacks the sizing in the paper so that ink-lines written on the print become blurred and colours applied change their shades, and the developer itself is always unstable and subject to air-oxidation, which produces coloured substances.

In a chapter on diazotype processes, Prof. Dr. J. M. Eder and Dr. Adam Trumm, in their book *Ausführl. Handbuch der Photographie* 4th volume, part IV (pages 236 and 237) have pointed out that there is a possibility of developing diazotype prints without any alkali, if a diazo compound of sufficiently energetic coupling activity is used that is capable of combining with phenols to form azo-dyestuffs. They further mention that it can readily be seen that such a method of development would have great advantages in itself.

Generally speaking, diazo-compounds combine readily with phenols only in presence of alkali, but as has been mentioned by Prof. Dr. J. M. Eder and elsewhere, there are diazo compounds which have such a high coupling activity that no alkali need be present for the formation of an azo-dyestuff with a phenol. Such diazo compounds generally have substitutions in the ring which impart to the compound a strongly acidic nature, such as OH, COOH, Cl, Br, NO₂, HSO₃ or alkyl or aralkyl ether, or aryl ether groups such as OCH₃, OCH₂C₆H₅ or OC₆H₅ or any other substituents of a negative character which increase the coupling activity of the diazo compounds. Such substitutions are preferably in the ortho and/or para position. The aralkyl and aryl substituent groups may also be themselves substituted, preferably by halogen in order still further to increase their coupling capacity.

The object of the present invention is to provide a paper which may be developed with phenolic developers without the use of materials having an alkaline reaction, and according to the present invention excellent diazotype prints may be prepared by developing in acid conditions.

Another object of the present invention is to provide a means of development for paper having the above-mentioned advantages which will give a substantially dry print.

It is not necessary for the purpose of the present invention to enumerate in detail all the diazo compounds that can be used for this process, and I will describe them generally as diazo compounds which are capable of coupling with a phenolic component in an acid condition (i. e. at a pH value of less than 7). While I have found that it is possible to produce diazo prints from such diazo

compounds without the use of any alkali whatsoever, I have not been able to bring about, without further modifications, a sufficiently rapid coupling of the two components to make the process commercially useful. It is evident that the coupling must take place instantaneously, as otherwise the dye formed on the lines of the drawing would smear and an unsharp line and also a stained background would be the result. This disadvantage has been overcome by the present invention, according to which instantaneous coupling is effected by adding to the developer containing the phenolic coupling component, or to the light-sensitive layer (i. e., that containing the diazo compound) a substance which appears to react with the diazo compound in such a way as to produce a diazo derivative capable of coupling much more rapidly than the diazonium chloride or diazonium sulphate or similar diazonium compound originally present in the light-sensitive layer. The substances used to fulfill this function of coupling accelerators are of the nature of salts of strong bases with weak acids and they appear to react with the diazonium compounds by double decomposition according to the scheme



where R of course represents the organic radical of the diazonium compound and M represents an equivalent of a strong base such as sodium or potassium or a strongly basic organic radical, and X represents the equivalent of an acid radical generally of a weaker nature than M. In the case shown, RN_2Cl is of course a diazonium chloride but similar results are obtained with diazonium sulphates or diazonium nitrates. Without necessarily basing the invention on this hypothesis, we find that the coupling is rendered almost instantaneous by the addition of the substances hereafter mentioned.

It is of course obvious that when using a salt of a weak acid with a strong base and adding it to the developer, care must be taken that the base is not so strong in comparison with the acid that the salt has an alkaline reaction, as otherwise the disadvantages previously set out concerning alkaline developers would return.

If it is desired to use a salt which in itself has a strong alkaline reaction, as, for example, borax, it is necessary to add sufficient of a weak acid to give the resulting solution an acid reaction before use.

According to the present invention, therefore, diazo-type prints are produced from papers coated with light-sensitive diazo compounds capable of coupling under acid or neutral conditions by using in the development a coupling accelerator, namely, a substance which reacts with or influences the diazonium compound in such a way as to cause the coupling to be practically instantaneous.

Suitable substances for promoting the rapidity of coupling according to the present invention are the acetates, formates, succinates, adipates, malonates, malates, citrates, tartrates, benzoates, phenylamidoacetates, as well as molybdates, tungstates or stannates of sodium, potassium or ammonium, and also the calcium, strontium, or barium salts of these acids in those cases where they are soluble in water. Salts of these acids with strong organic bases, such as ethylamine, diethylamine, triethylamine or ethanolamine, may also be used. It is also possible to use slightly acid mixtures of primary and secondary phosphates, phthalates and their polybasic salts.

These materials are generally employed in concentrations varying from 5 to 10% or, if necessary, even higher.

In order to ensure the absolute sharpness of the lines of the prints, small quantities of sodium chloride, or of any other salt which prevents the diazo compound on the paper from dissolving partly on the surface before the dyestuff is completely formed, can be added to the developer.

Such developers have the great advantage that they are far more stable against oxidation and that even a large excess applied to the print has no detrimental effect on the colour of the background or the size in the paper. They can be exposed to light and air without undue discoloration and can be satisfactorily used many days after they have been made.

The addition of small quantities of acid or acid salts to these developers increases their stability still further without affecting the coupling speed in a detrimental way.

The following examples illustrate various methods of carrying out the invention in practice, but these examples are by way of illustration only and are not limitative.

Example 1.—A paper is coated with a solution of the following composition:

Zinc chloride double salt of the diazonium compound obtained from 5-amino-2-benzoylamino 1,4-diethoxybenzene 30 grams, sodium dihydrogen phosphate 10 grams, made up to 1000 cc. with water. After exposure to light in the usual way, this paper is developed with a solution of phloroglucine 4 grams, sodium chloride 50 grams, crystallized sodium acetate 120 grams, tartaric acid 1 gram, dissolved in 1000 cc. with water.

Example 2.—A paper is coated with a solution made by tetrazotizing 20 grams of 3,3'-dichlorodianisidine (5.5') in dilute hydrochloric acid, the excess of nitrite being removed by the addition of urea, if necessary. 20 grams of potassium alum are then added and the solution made up to 1000 cc. with water.

A paper coated in this way after exposure to light may be developed by the same developer as that in Example 1. Another developer suitable for this paper and other papers has the following composition:

	Grams
Phloroglucine	2
Resorcline	3
Sodium formate	100
Barium chloride	20
Ammonium dihydrogen phosphate	2

made up to 1000 cc. with water.

Example 3.—A developer is used containing phloroglucine 4 grams potassium citrate 115 grams, sodium chloride 50 grams, citric acid 1 gram, made up to 1000 cc. with water.

Example 4.—A developer is made up containing a solution of 80 grams potassium metaborate and is treated with sufficient tartaric acid to give a neutral solution, 4 grams of phloroglucine is then added and the solution made up to 1000 cc. with water.

Example 5.—A developer is made up containing:

	Grams
Phloroglucine	5
Sodium benzoate	150
Sodium chloride	20

made up to 1000 cc. with water.

If it is desired to use a developer which does

not wet the paper, this may be done according to the present invention by laying the paper after exposure to light face downwards on to a gelatinous composition containing the coupling component. For example, a solution is prepared containing:

	Grams
Phloroglucine	3
Sodium acetate	60
Glycerine	20-30
Gelatine	60

in 500 cc. of warm water.

This solution can be poured into a flat tray, plate or similar vessel and allowed to cool, whereupon it sets to a jelly. The exposed print is pressed face downward on to the jelly. The moisture of the jelly is sufficient to bring about development in a few seconds, leaving a dry print. In order to render it more easy to detect contamination of the surface of the jelly with dirt or foreign matter, the jelly may be rendered opaque by incorporating 50 grams of barium sulphate in the formula given above, or a corresponding proportion of any other opaque and inert pigment may be used for this purpose. From time to time the jelly may be re-melted by gentle heat and re-cast in the flat tray or vessel for further use.

While the invention has been illustrated herein as applied to diazotype prints employing paper as a supporting base, it will be obvious that the present invention is not so limited, but may be employed in conjunction with any conventional supporting materials.

What I claim and desire to secure by Letters Patent is:—

1. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with a weak acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

2. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with an organic acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

3. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with an aliphatic organic acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

4. A method of producing diazotype photographic prints from a support coated with a light

sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with an aliphatic monocarboxylic organic acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

5. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with a dibasic organic acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

6. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with an acetic acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

7. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with a tartaric acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

8. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a mixture containing primary and secondary phosphates which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

9. A method of producing diazotype photographic prints from a support coated with a light sensitive diazotype compound capable of coupling under acid conditions which consists in exposing said support to light under a design and applying to said support a developer which contains a phenolic coupling component and a salt of a strong base with a weak acid which acts as a coupling accelerator whereby coupling is rendered almost instantaneous, said developer containing also an inert salt whereby to inhibit "bleeding" of the print, the ingredients of said developer being in such proportions as to give a pH value of less than 7.

WERNER PAUL LEUCH.