Patented July 23, 1940 2,209,087

UNITED STATES PATENT OFFICE

2,209,087

PRODUCTION OF PHOTOGRAPHIC DIAZOTYPE PRINTS

Werner Paul Leuch, London, England, assignor to Eugene Dietzgen Company, New York, N. Y.

No Drawing. Application October 25, 1934, Serial No. 749,925. In Great Britain October 27, 1933

9 Claims. (Cl. 95—6)

This invention relates to the production of photographic diazotype prints and has for 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 a substance having an alkaline reaction 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 has 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.

In papers prepared according to method (*a*) the diazo bodies chosen must either be such that only couple under alkaline conditions or else some process such as acute dehydration must be employed to prevent the coupling process taking place before development: and even if some such process is employed the diazo bodies chosen must be bodies which react only slowly in neutral or acid conditions. I, however, have found that if the coupling component is introduced into the film containing the diazo body, by dusting the coupling component in powder form over the film when dry, I can use any diazo body which is not either a diazo-anhydride or which has not basic substitutions which are not neutralized by suitable negative substitutions (for instance, amino-acylamino compounds can be used and derivatives of the diphenyl series are particularly suitable, as well as those of the di- and triphenylmethane), and yet I do not find that even in prolonged storage of the prepared paper coupling has taken place prior to the actual development.

The object of the present invention is to provide a paper which can be developed in a simpler and more advantageous manner, namely, one which shows the following features:

1. The use of either the gaseous method of development or the semi-dry method for the same paper.

2. The avoidance of the use of alkali or alkaline reacting substances for development.

3. The carrying out of the gaseous method of development by means simply of water vapour, thus avoiding the use of ammonia fumes.

According to the present invention I prepare a diazotype paper coated with a light-sensitive layer containing a diazo compound that is capable of coupling in neutral or acid conditions, and which would not permit the inclusion of the phenolic coupling component in the light-sensitive layer owing to premature coupling taking place. After sensitizing and drying, the paper is then treated with a coupling component by subsequently dusting it over with a fine powder containing either the coupling component alone or in admixture with other substances, the use of which is more fully described later. The paper, when ready for use, contains therefore the light-sensitive diazo substance in the coating, and also carries the coupling component capable of forming a dyestuff with the undecomposed diazo body.

After exposure to light in the usual way, the print may be developed simply by the action of water. It is particularly advantageous to use water for development in such a way as not appreciably to wet the paper so that development may be carried out by the dry process as previously defined. This may advantageously be done by exposing the paper to steam or other form of water vapour. In order to develop the print in reasonable time, it is of course advantageous to use water vapour in a concentrated form, namely, in the form of steam or water vapour arising from heated water.

In addition to water vapour other methods can be used for developing the print, and in particular other methods which do not appreciably wet the paper. For example, instead of water vapour the paper may be treated with a quick drying liquid, such as moist methylated spirit, or moist acetone.

Another method of dry development by means of water is to use a gelatine composition. A flat tray, plate or other support, of suitable dimen-

sions containing a jelly formed of gelatine and water is used and the print, after exposure, is pressed face downwards on to the jelly. The moisture in the jelly is sufficient to bring about development in a few seconds, leaving a dry print. A jelly of suitable composition is one containing 60 grams of gelatine and 20–30 cc. of glycerine in 500 cc. of water.

Development may also conveniently be carried out by utilizing the loosely combined moisture in a suitable hydrated salt, such as hydrated sodium sulphate. For example, hydrated sodium sulphate may be incorporated in the paper before coating, or it may be incorporated in the light-sensitive layer or it may be incorporated in the powder containing the coupling component. In any of these cases the exposed print is developed simply by gentle heating which causes the hydrated salt to dissociate, so that the water vapour liberated brings about the development of the print, which print is of course dry.

In any of these ways the advantage is achieved of obtaining a print which is practically dry and which, owing to the absence of wetting, preserves a sharp line. If, however, for any reason it is desired to use the semi-dry developing process, this may also be done by using an ordinary developing machine containing water. In this case it may be found advantageous to add a substance such as the salt of a weak acid with a strong base either to the sensitive layer or to the coupling component; a substance of this type has the property of acting as a coupling accelerator and also its saline nature helps to prevent the line from "running." Alternatively, instead of using water alone in the developing machine, a substance which prevents the line from "running," such as potassium sulphate, or sodium chloride or a substance which not only prevents the line from "running" but also acts as a coupling accelerator, such as sodium acetate, may be dissolved in the water used for the developer. If it is desired to carry out the development by this semi-dry process, namely, using an aqueous salt solution on a developing machine, this has the great advantage over the ordinary semi-dry developer with a developing machine in that the developer used is merely the solution of sodium acetate or potassium sulphate or the like which has the property of keeping indefinitely and does not deteriorate like the ordinary developers which contain readily oxidisable or otherwise unstable substances. If, however, it is desired for any reason to use a developer containing an alkali or to develop under alkaline conditions, this may also be done according to the present invention, as the compounds capable of coupling under acid conditions can also couple under alkaline conditions. Even in this case, however, the developers would not deteriorate, as they would not need to contain readily oxidisable or otherwise unstable substances (coupling components).

It has previously been stated that other substances may be mixed with the coupling component. The use of a hydrated salt has already been referred to. Also, for example, it may be desired to dilute the coupling component, such as β-naphthol, with an inert substance such as starch or dextrin. Alternatively, other substances may be mixed with the coupling component in order to increase the speed of coupling, sodium tartrate being a suitable substance for this purpose. Furthermore, the coupling component may be any of the well-known coupling components, such as a phenol or base, examples being β-naphthol or phloroglucinol.

The following examples illustrate how the invention may be carried out in practice, but it is obvious that the invention is capable of a great variety of methods of application and is in no way limited to the details given in these examples:

Example 1.—The paper is coated with a solution of 60 grams of zinc chloride double salt of 5-benzoyl-amino-1:4-diethoxy-2-diazonium chloride, 30 grams of aluminium sulphate made up to 1000 cc. with water and dried. After drying, the paper is dusted over the entire sensitive surface with a powder composed of 60 grams of flour and 10 grams of phloroglucinol. After dusting with the powder, the powder is well rubbed on and into the surface of the paper and excess of powder removed by brushing. The paper may then be stored for a considerable length of time before exposure to light and development. After exposure to light the paper can be developed either by exposure to steam or by the gelatine method already herein described, or by the semi-dry method. A suitable developer for development by the semi-dry method is one containing 100 grams of sodium acetate crystals, and 2 grams of tartaric acid in 1000 cc. of water. It will be seen that this developer is one which will keep indefinitely.

Example 2.—The paper is coated with a light-sensitive layer as described in Example 1 and dried. After drying, the paper is dusted over the entire sensitive surface with a powder composed of 30 grams of flour, 10 grams of phloroglucinol and 30 grams of sodium benzoate. After dusting with the powder, the powder is well rubbed on and into the surface of the paper and excess of powder removed by brushing. The paper may then be stored for a considerable length of time before exposure to light and development. In this case development of the print can be carried out simply by contact with water which can advantageously be applied in an ordinary developing machine.

Many diazo compounds will couple under neutral or acid conditions at a speed which is far too slow to be of any use in diazotype papers of this kind, and I declare that when in my claims I use the words "a diazo compound capable of coupling in neutral or acid conditions" I mean a diazo compound which under neutral or acid conditions will couple with such speed that the diazo compound and coupling component could not be put together in the light sensitive layer without coupling prematurely, either during drying or storage, whether a dehydration has taken place or not.

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

1. As a new article of manufacture, a light-sensitive element comprising a carrier coated with a dry, light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, said element carrying, adhered to its surface in the form of a dry powder or dust, a coating containing the coupling component.

2. As a new article of manufacture, a light-sensitive element comprising a carrier coated with a dry, light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, said element car-

rying, adhered to its surface in the form of a dry powder or dust, a coating containing the coupling component, and also a substance capable of acting as a coupling accelerator.

3. As a new article of manufacture, a light-sensitive element comprising a carrier coated with a dry, light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, said element carrying, adhered to its surface in the form of a dry powder or dust, a coating containing the coupling component, the article also containing a hydrated salt capable of liberating moisture.

4. As a new article of manufacture, a carrier coated with a dry, light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, said light-sensitive layer carrying, adhered to its surface in the form of a dry powder or dust, a coating containing the coupling component.

5. A process for preparing diazotype photographic papers by coating a paper with a light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, drying the paper, and subsequently coating the paper with a substantially dry coupling component so that it adheres to the surface of the sensitive layer, exposing the paper to light behind the pattern it is desired to reproduce, and subsequently developing by treatment with moisture.

6. A process for preparing diazotype photographic prints by coating a paper with a light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, drying the paper, subsequently dusting the paper with a coupling component so that it adheres to the surface of the sensitive layer, exposing the paper to light behind the pattern it is desired to reproduce, and subsequently developing by treatment with moisture.

7. A process for preparing diazotype photographic prints by coating a paper with a light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, drying the paper, subsequently dusting the paper with a coupling component so that it adheres to the surface of the sensitive layer, exposing the paper to light behind the pattern it is desired to reproduce, and subsequently developing by treatment with water vapour at an elevated temperature.

8. A process of developing diazotype photographic prints by coating a paper with a light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, drying the paper, subsequently dusting the paper with a coupling component so that it adheres to the surface of the sensitive layer, exposing the paper to light behind the pattern it is desired to reproduce, and subsequently developing by applying, in a developing machine, an aqueous solution of a neutral salt to prevent the line from "running."

9. A process of developing diazotype photographic prints by coating a paper with a light-sensitive layer containing a diazo compound capable of coupling when treated with a coupling component and moisture in the absence of alkaline substances, drying the paper, subsequently dusting the paper with a coupling component so that it adheres to the surface of the sensitive layer, exposing the paper to light behind the pattern it is desired to reproduce, and subsequently developing by applying in a developing machine an aqueous solution of a coupling accelerator.

WERNER PAUL LEUCH.