July 8, 1930. H. D. MURRAY 1,770,352

MANUFACTURE OF DIAZOTYPE SENSITIVE PAPERS AND THE LIKE

Filed Sept. 28, 1929

Fig. 1.

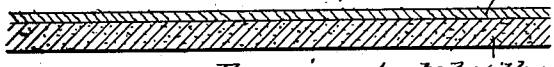


Fig. 2.

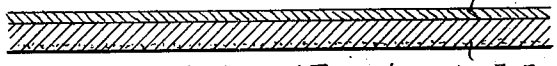


Fig. 3.

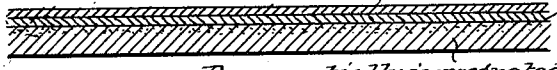
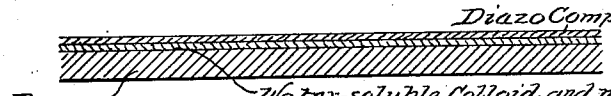


Fig. 4



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UNITED STATES PATENT OFFICE

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MANUFACTURE OF DIAZOTYPE SENSITIVE PAPERS AND THE LIKE

No Drawing. Application filed September 28, 1929, Serial No. 395,989, and in Great Britain June 14, 1928.

The present invention is for improvements in or relating to the production of photographic images by the diazo-type process, and has particular reference to the manufacture of improved sensitive papers, or other hydrophilic bases, for application in this art.

In brief, the diazo-type process consists in exposing a light-sensitive diazo-compound on a suitable supporting medium, such as paper, to light beneath a design, whereby the said compound is decomposed where unprotected by the outlines of the design, and the power of combining with an azo-dyestuff coupling component is destroyed. After the exposure, the surface is treated with a suitable solution of a coupling component, or, when said component has been an original co-ingredient with the diazo-compound on the paper or other support, with an alkali, so that a replica of the original tracing is obtained as a coloured dye image on a more or less white ground.

When coupling solutions are employed, they usually contain a non-volatile alkali, and as dye image prints are seldom washed with water, an excess of this alkali and of coupling component remains on the surface of the dye image print. After some time, according to the circumstances and the nature of the compounds employed, the background of such prints discolours, possibly in consequence of the oxidation of the excess of coupling component in the presence of the non-volatile alkali. Such alkali may be used to promote coupling when the diazo-compound and coupling component therefor are present together on the base, and the same disadvantage tends to arise.

This darkening can be greatly retarded by removing the excess of said alkali in the surface of the paper or like support by the application of a solution of an acid after the development, but with certain combinations of diazo-compounds and coupling components, the application of such acid solution modifies the normal colour of the dye image.

The present invention concerns that form of the diazo-type photographic process wherein development is effected by aid of a solution of non-voltatile alkali, the use of which, as just stated, tends to result in subsequent deterioration of the print. The invention is therefore particularly applicable to a process in which diazo-compounds are employed which couple readily only in definitely alkaline solution.

The invention may be best understood by reference to the accompanying drawing in which Figures 1 to 4, inclusive, are enlarged sectional views of sensitized papers, manufactured in accordance with the principles of the present invention, the four views illustrating four different modifications of the invention.

According to this invention, the manufacture of papers or the like for the diazo-type process is characterized by combining with the paper or the like discretely from the sensitizing substance a neutralizing agent for non-volatile alkali.

Thus, the said neutralizing agent may be incorporated in the paper or like supporting material at the time of preparation of such paper or material as illustrated in Figure 1. In this event, the light sensitive diazo- compound alone or together with an azo-coupling component, may be conveniently coated upon the support in the form of a solution with a water-miscible colloid, such as gelatine, which serves to prevent premature diffusion of the neutralizing agent during such coating. The so-impregnated support may also be coated on its surface with a water-miscible colloid, such as gelatine, and the diazo-compound, alone or together with the azo-coupling component, deposited upon the colloid coating, this modification of the process being illustrated in Figure 3 of the drawing.

In alternative, as illustrated in Figure 2, the said neutralizing agent may be coated on one side of the supporting material, for example, by applying a solution of the agent to one side of a thin, absorbent paper, the other side of which is coated with the diazo-compound, with or without an azo-coupling component as may be desired.

A second alternative is to coat the supporting material with the said neutralizing agent in the form of a solution with a water-soluble colloid, such as gelatine, and then to apply to

the colloid surface the coating of the diazo-compound, alone or in conjunction with an azo-coupling component as shown in Figure 4.

Or again, the surface of the supporting material may be treated with the neutralizing agent, a gelatine or like coating overlaid upon the so treated surface, and the diazo-compound applied over all with or without an azo-coupling component, this modification being also illustrated in Figure 3 of the drawing. In this case, the diazo-compound may be advantageously applied in some solvent in which the neutralizing agent is only sparingly soluble. For example, a supporting base impregnated with ammonium chloride may be coated with the diazo-compound in alcoholic solution.

It is well known practice in the art to prepare diazotype papers and like bases with sensitizing solutions containing an acid, and no claim is made herein to such manufacturing per se. According to the present invention, the supporting base of paper or the like carries distinct from the sensitizing layer and apart from any acid contained therein a neutralizing agent for non-volatile alkali. In the preferred embodiment of this invention, the supporting base carries more acid than is contained in the sensitized surface. This excess of acid (or equivalent neutralizing agent for non-volatile alkali) produces its effect only when the base has been made sufficiently moist during development to permit of diffusion of the acid or the like; whereas acid accompanying the diazo-compound does not function in such manner, because neutralization must take place before the associated diazo-compound can couple. There is likewise no broad claim made herein to the impregnation of paper or the like with acids, but solely to such impregnation for the manufacture of diazotype papers and the like as and for the purpose described.

The application of an alkaline solution to the side of the supporting material which carries the diazo-compound results first in effecting the combination of this compound with the coupling component, either present with the said compound upon the surface of the supporting material, or dissolved in the alkali solution; and then as the said solution penetrates the surface of the supporting material or gelatine layer and reaches the neutralizing agent, the diffusion of such neutralizing agent as is dissolved in the solution results in the destruction of the free alkali, so that when dried, the surface of the supporting material is non-alkaline or acid, a condition which, as aforesaid, inhibits discolouration by oxidation.

The neutralizing agent for the non-volatile alkali may be an acid or an acid salt, but of not too corrosive a nature as adversely to affect the supporting material in a reasonable time; or an ammonium salt may be employed. Solid organic acids represent the type of acid most conveniently utilizable. One preferred acid of this class is oxalic acid, and a 5 per cent solution thereof has been found both convenient and effective for any of the methods of application already described. Ammonium chloride is both a convenient and satisfactory salt of ammonium to employ as neutralizing agent; and potassium bioxalate and sodium hydrogen tartrate are examples of suitable acid salts.

When an aqueous solution containing a fixed alkali, such as sodium hydroxide, or a substance, such as sodium biborate which gives an alkaline reaction when dissolved in water, is applied to a supporting base containing an ammonium salt such as ammonium chloride, reaction takes place between the alkali (hydroxyl ions) in solution and the ammonium salt (ammonium ions) in the paper. Ammonium hydroxide is formed which breaks down into water and ammonia gas, and the latter escapes from the surface of the supporting base, the alkalinity of which is reduced in the same way as if a portion of the alkali in the solution had been neutralized by acids. As the paper dries, all the ammonia gas set free leaves the paper, and the reaction of the latter approaches neutrality or, especially if the alkalinity of the applied solution has been produced by hydrolysis as aforesaid, becomes definitely acid.

Example I

A hard surface paper is coated with an aqueous solution containing 1% of gelatine and 4% of oxalic acid, and dried. There is then applied a mixture of a light-sensitive diazonium compound and oxalic acid (1% of the mixture) and the paper again dried. After exposure to light beneath the desired design, development is effected with a solution containing:—

1.0 part 2-naphthol—6 sulphonic acid.
8.0 parts sodium carbonate.
100.0 parts water.

Example II

A somewhat absorbent paper such as is used as a base for ferricyanid papers is coated on one side with an aqueous 10 p. c. solution of ammonium chloride, dried, then coated on the other side with a solution of a light-sensitive diazonium compound containing 1% of oxalic acid, and again dried. Development after exposure is effected with a solution of:—

0.5 part phloroglucinol.
2.5 parts borax.
15.0 parts potassium citrate.
100.0 parts water.

It will be understood that term "paper" as used in the appended claims is intended to

include any suitable base of a porous material such as may be used in the art to which this invention relates.

Claims:

1. A diazo-type sensitized paper having a light sensitized layer, said paper being impregnated discretely from said layer with a neutralizing agent for non-volatile alkali.

2. A diazo-type sensitized paper having a surface coating of a light sensitive diazo-compound in admixture with a water soluble colloid, said paper being impregnated discretely from said layer with a neutralizing agent for non-volatile alkali.

3. A diazo-type sensitized paper having a surface coating of a light sensitive diazo-compound in admixture with a water soluble colloid, the opposite surface of said paper being impregnated with a neutralizing agent for non-volatile alkali.

4. A diazo-type sensitized paper having a surface coated with a water miscible colloid and having a light sensitive diazo-compound upon the coating, said paper being partially impregnated discretely from said layer with a neutralizing agent for non-volatile alkali.

5. A diazo-type sensitized paper having a light sensitized layer, and bearing separately and discretely therefrom a neutralizing agent for non-volatile alkali.

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