

UNITED STATES PATENT OFFICE

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LIGHT SENSITIVE PAPERS AND OTHER BASES AND LIGHT SENSITIVE LAYERS THEREFORE

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This invention relates to the art of making light sensitive layers and the production of sensitive papers or other suitable bases provided with such layers.

It has been known for a long time that many diazo-compounds are sensitive to light and this property had made it possible to use them in the production of photographic or copy paper. If a layer of diazo-compound be exposed under a transparent positive, the portions of the diazo-compound which are not protected by the dark portions of the picture will be destroyed and there remains a positive picture formed by the portions of the diazo-compound that have not been attacked. The picture may be visible or not, depending on whether the diazo-compound be coloured or not-coloured. The slightly coloured picture which is unstable when exposed to light may be transformed into a coloured and stable picture by treatment with a suitable compound, such as a phenol or an amine, under such conditions that the coupling reaction of the diazo-compound with the other component can take place. This coupling reaction of the diazo-compound may be produced, for example by treating the latent picture with an alkaline solution of a phenol.

Attempts have been made to simplify the process by incorporating the coupling component with the diazo-compound in the sensitive layer applied to the paper or other suitable base. In such case, however, it is necessary to add an acid to the mixture constituting the sensitive layer in order to prevent premature coupling during storage. Proofs thus obtained can thus be developed by subjecting the sensitive layer to the action of an alkali, for example by treating the sensitive layer with an alkaline solution or with an atmosphere of gaseous ammonia.

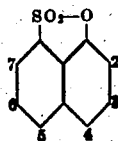
In a particular case, where phloroglucine was used as the coupling component, it was found that premature coupling can be prevented by the addition to the mixture constituting the sensitive layer, before exposure, of hydroxylamine, which converts the phloroglucine into a body (triacetohexamethylene-

trioxime) in which the coupling capacity is suspended, but can be restored by developing with an alkaline developer.

In accordance with my invention, layers sensitive to light, or papers or other suitable bases provided with such layer, and which can be developed by the simple action of an alkaline developer, are produced by mixing with the diazo-compound in the sensitive layer, not a coupling component (phenol or amine for example) itself, but a substance which will produce the necessary coupling component (a phenol or an amine for example) when subjected to the action of an alkaline developer. As the substance in question will not couple with the diazo-compound, few, if any, precautions are necessary to avoid premature coupling. The substance used to produce the coupling component for the diazo-compound should be stable in a neutral or slightly acid medium and be very rapidly transformed into the coupling component for the diazo-compound, by the alkali used in the developer.

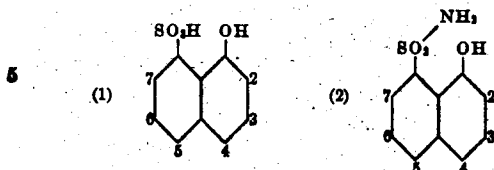
It will be seen that my invention is based upon an entirely different principle, and is fully distinguished from the two earlier processes above referred to.

I have obtained excellent results by using naphthalene sultones as substances susceptible to form coupling components for the diazo-compounds. Sultones do not combine with diazo-compounds and are stable in a non-alkaline medium. On the other hand, in the presence of an alkali, they are converted, by release of the sultone bond, into compounds having coupling capacity. It is well known that these products having the general formula



(with the possibility of substitution at 2, 3, 4, 5, 6 or 7) give naphthol sulfonate (1) in the presence of an alkali, such as sodium hydroxide, carbonate of sodium, etc. and a naph-

thol sulphamide (2) in the presence of ammonia.



10 The use of the above mentioned products enables photographic proofs to be made, which can be kept and stored without any coupling action in the presence of very small quantities of acid or without the addition of

15 any acid whatever even though the diazo-compound used may be possessed of very great coupling power. The addition of metallic salts makes for a better fixing of the proof and enables its colour to be changed.

20 The colour will also vary according as an ammonia alkali or a non ammonia alkali be used.

It is well known that sultones may be obtained by heating the diazo-compound of a 1-8-naphthylamine-sulphonic acid whether substituted or not. Under certain conditions therefore, it may be advantageous to apply a diazo-compound of this character to the paper or other base and to convert it into a sultone by suitably heating said paper or other base before exposure. If the sensitive diazo-compound used be stable at the temperature at which the diazo-compound of the 1-8-naphthylamine-sulphonic acid is converted into sultone, the heating may be carried out after both the diazo-compounds have been applied to the paper or other base.

I shall now give several examples to indicate the mode and manner of putting my invention into execution, but it is to be understood that my invention is not to be considered as limited to the examples given, nor any of them.

Example 1

45 3.1 parts of sulphate of thioaniline are diazotized in the usual manner in the presence of hydrochloric acid with a slight excess of sodium nitrite; after having removed the excess of nitrous acid with a solution of urea, a solution containing 6.2 parts of naphthalene-1-8-sultone-4-sulphonate of sodium (obtained by heating 1-naphthylamine-4-8-disulphonic acid) is added. The volume having been brought to 300 parts, the paper or other suitable base is covered with the liquid and dried. After exposure to light and on developing with an aqueous solution of an alkali, for example sodium carbonate, a red proof will be obtained; development in an ammoniacal atmosphere gives a more bluish tint.

Example 2

55 1.6 parts of 4-amino-diphenylamine-2-sulphonic acid are diazotized in the usual

manner in the presence of hydrochloric acid and are then mixed with a solution of 1.9 parts of naphthalene 1-8-sultone-3-sulphonic acid. The total volume of the solution is brought to 200 cc. Photographic proofs obtained with this solution are treated in the same manner as in the preceding example. Development in an ammoniacal atmosphere gives a violet-blue picture.

If a metallic salt be added the proofs are more resistant to washing with water and their shade changes; sulphate of nickel, for example, produces a marked change in the shade which becomes highly reddish.

Example 3

0.5 parts of diphenylamine-4-diazonium sulphate are dissolved in water and to this is added a solution of the diazo-compound, obtained by diazotizing 0.5 parts of 1-amino-naphthalene-4-8-disulphonic acid in the presence of hydrochloric acid, and also 1.5 parts of citric acid. The total volume is brought to 50 parts.

The photographic paper obtained with this solution is dried in an oven at 80° C. until a test proof obtained in the same manner, but without the addition of the diphenyldiazonium salt and placed in the oven at the same time with the other, shows no signs of coupling with an alkaline solution of Beta-naphthol.

Exposure and development is effected as in the previous examples. The proof developed in ammonia is violet black and that developed with a non-ammoniacal alkali is brownish-red.

Very similar results are obtained by substituting the diazo-compound of 1-naphthylamine-3-6-8-trisulphonic acid for the diazo-compound of naphthylamine disulphonic acid.

Example 4

A weak hydrochloric acid solution of a diazo-compound obtained from 3.2 parts of amino-naphtholdisulphonic RR acid (2 amino-8-naphthol-3-6-disulphonic acid) obtained from an alkaline fusion of 2-naphthylamine 3-6-8-trisulphonic acid is mixed with a solution of 3.2 parts of the sodium salt of naphtho-sultone-sulphonic 1-8-4 acid. The total volume having been brought to 300 parts, the solution is applied to the paper or other base.

Development with gaseous ammonia gives a reddish violet proof.

An analogous paper can be obtained by substituting for the naphthosultone-sulphonic-1-8-4 acid its isomeric acid 1-8-3.

Example 5

A sensitive paper or other base obtained with a weak (100 cc.) hydrochloric acid solution of the diazo-compound of thioaniline

alone (obtained from 1.6 grams of sulphate of thioaniline) is developed with an alkaline solution of Schaeffer salt (sodium salt of 2-naphthol-6-sulphonic acid); the proof obtained is red.

Example 6

The same mode of operation as in Example 4 is followed, but the sultone is replaced by 2.3 parts of naphthol-6-sulphonate of sodium and 9 parts of oxalic acid are added. Upon developing in sodium carbonate or with gaseous ammonia a bright red proof is obtained.

So far as I am aware, I am the first to discover that diazo-compounds obtained by diazotizing thioaniline, aminonaphtholdisulphonic RR acid and 4-aminodiphenylamine-2-sulphonic acid can be used as light sensitive diazo-components in light sensitive layers.

It is to be understood that the foregoing description is to be considered in all respects as illustrative and not restrictive, reference being had to the appended claims rather than to said description to indicate the scope of the invention.

I claim:

1. Process for making light sensitive layers or a paper or other suitable base provided with such layer, which comprises mixing with a suitable light sensitive diazo-compound, a naphthalene sultone adapted to form a coupling component for said diazo-compound when subjected to the action of an alkali.

2. Process for making light sensitive layers or a paper or other suitable base provided with such layer, which comprises removing the excess of nitrous acid from about 3.1 parts of sulphate of thioaniline diazotized in the presence of hydrochloric acid with a slight excess of sodium nitrite, and adding a solution containing about 6.2 parts of naphthalene-1-8-sultone-4-sulphonate of sodium.

3. Process for making light sensitive layers or a paper or other suitable base provided with such layer, which comprises mixing with about 1.6 parts of 4-aminodiphenylamine-2-sulphonic acid, diazotized in the presence of hydrochloric acid, a solution of about 1.9 parts of naphthalene-1-8-sultone-3-sulphonic acid.

4. Process for making light sensitive layers, or a paper or other suitable base provided with such layer, which comprises mixing with a weak hydrochloric acid solution of a diazo-compound obtained from about 3.2 parts of aminonaphtholdisulphonic RR acid, a solution of about 3.2 parts of the sodium salt of naphthosultone-sulphonic 1-8-4 acid.

5. A light sensitive layer, or a paper or other suitable base provided with such layer, which comprises a mixture of a light sen-

sitive diazo-compound and a naphthalene sultone to form a coupling component for said diazo-compound when subjected to the action of an alkali.

6. A light sensitive layer or a paper or other suitable base provided with such layer, which comprises a mixture of about 6.2 parts of naphthalene-1-8-sultone-4-sulphonate of sodium and about 3.1 parts of sulphate of thioaniline which has been diazotized in the presence of hydrochloric acid with a slight excess of sodium nitrite and from which the excess of nitrous acid has been removed.

7. A light sensitive layer or a paper or other suitable base provided with such layer, which comprises a mixture of about 1.9 parts of naphthalene-1-8-sultone-3 sulphonic acid with about 1.6 parts of 4-aminodiphenylamine-2-sulphonic acid diazotized in the presence of hydrochloric acid.

8. A light sensitive layer or a paper or other suitable base provided with such layer, which comprises about 3.2 parts of a sodium salt of naphtho-sultone-1-8-4-sulphonic acid with about 3.2 parts of aminonaphtholdisulphonic RR acid applied in a weak hydrochloric acid solution.

9. Process for making light sensitive layers, or a paper or other suitable base provided with such layer, which comprises mixing with a weak hydrochloric acid solution of a diazo-compound obtained from about 3.2 parts of aminonaphtholdisulphonic RR acid, a solution of about 3.2 parts of the sodium salt of naphthosultone-sulphonic 1-8-3 acid.

10. A light sensitive layer or a paper or other suitable base provided with such layer, which comprises about 3.2 parts of a sodium salt of naphtho-sultone-sulphonic-1-8-3 acid with about 3.2 parts of aminonaphtholdisulphonic RR acid applied in a weak hydrochloric acid solution.

In testimony whereof, I have signed my name to this specification.

ROBERT LANTZ.