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LIGHT-SENSITIVE MATERIAL

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The invention relates to light-sensitive materials.

It is known to produce negative copies with the help of light-sensitive layers which contain diazo sulphonates. Although this process is already very old it has not been put into practice to any notable extent. This is due to the fact that it is difficult to find diazo sulphonates which satisfy the varying requirements occurring in practice.

It has now been found that light-sensitive layers suitable for producing negative diazotype copies can be obtained if there are used as light-sensitive compounds, diazo sulphonates which contain in the nucleus, carrying the diazo sulphonate group, two etherified oxy groups but no amino groups or substituted amino groups. The compounds may also contain more than two etherified oxy groups, for example three oxy groups, although it is chiefly the compounds with only two etherified oxy groups which have practical importance. The etherification is preferably carried out by low molecular aliphatic alcohols with few carbon atoms, such as methyl alcohol or ethyl alcohol, as in the presence of high molecular ether residues the solubility of the diazo sulphonates in water decreases. As, however, in the production of printing papers according to the normal production process aqueous diazo sulphonate solutions of a definite minimum concentration are required, the diazo sulphonates should be easily soluble in water. The etherification can, however, also take place by means of phenols so far as the diazo sulphonates obtained still show the necessary solubility in water.

It has already been suggested to use the sodium salt of 1-benzoylamino-2.5-diethoxy-4-diazo benzene-N-sulphonic acid together with a diazo compound for the production of printing papers. The diazo sulphonates free from amino groups, which are used according to the invention are, however, superior to the said compound both as regards permanence and contrasts in the copies produced.

According to the invention compounds are preferably used which are derived from hydroquinone. It is, however, also possible to use diazo sulphonates which are derived from other aromatic dioxy or polyoxy compounds, particularly those of the benzene series, so long as they are free from amino groups. Thus resorcindiether-diazo sulphonates come into question, for example, ethers of 2.4-dioxybenzene-1-diazo sulphonate. Also pyrocatechin - diether - diazo sulphonates are suitable, for example ethers of the 3.4-dioxybenzene-1-diazo sulphonate. In the dialkoxy compounds the position of the diazo sulphonate group or of the two alkoxy groups with respect to each other is preferably such that two but not more than two of the three said groups are adjacent each other. Of the trialkoxy compounds the 2.4.5-trialkoxy-1-diazo sulphonates are particularly suitable.

The compounds used according to the invention can also be substituted by other substituents of the kind which are also generally used in normal diazo-type copying. As the image dyes produced should preferably be insoluble in water so that the fixing of the pictures can be effected in the usual manner by washing out, substituents which increase the solubility in water to a great extent, such as sulpho groups, are in general unsuitable. It is necessary, as is known, to combine sufficient water-solubility of the diazo-sulphonates with water-insolubility of the dyestuffs produced with the diazo sulphonates. Diazo sulphonates of the kind described which contain halogens, such as chlorine or bromine, as substituents, have shown themselves to be particularly good. Also alkyls, such as methyl and ethyl, act favorably as substituents, particularly with regard to the depth of color of the dyes produced with the diazo sulphonates. Preferably, however, the alkyls should not contain more than four carbon atoms. Also aryls or cyclohexyl are suitable as substituents so long as the substituted compounds are still sufficiently soluble in water. The substituents mentioned, so far as hydroquinonediether diazo sulphonates come into question, are preferably in the para-position to the diazo sulphonate group. Nitro groups have in general not proved to be good as substituents inasmuch as they often make the dyes produced with the diazo sulphonates lighter in color.

The diazo sulphonates used according to the invention are distinguished by the fact that with the use of the normal azo components, they generally lead to dyes with dark tones, so that the production of easily legible copies is facilitated. Moreover, they are very stable. The printing materials produced with the diazo sulphonates are, therefore, very stable. The dyes obtained are, in general, resistant to water while the diazo sulphonates themselves have a good solubility in water, so that the copies produced with the new light-sensitive layers can be quickly and easily fixed in the known manner by soaking.

The coupling intensity of the diazo sulphonates

can be considerably increased in the known manner by the addition of carbonyl compounds to the light-sensitive layers. In addition to the compounds already suggested for this purpose, aliphatic ketonic acids, for example pyroracemic acid, are suitable, in particular, as carbonyl compounds. The latter compound, moreover, acts still more favorably in that it makes possible the production of copies with particularly clear grounds. In the absence of pyroracemic acid a light grey dyeing sometimes occurs if the materials are stored for a long time. An increase in the coupling intensity can, moreover, be produced by the presence of thiourea or its derivatives in the light-sensitive layer.

In order, when using paper as the support, to prevent the diazo sulphonate preparation from sinking into the paper felt, it is recommended to add certain colloids to the sensitizing solution, or to previously coat the paper with solutions of these colloids. In doing this, however, care must be taken not to use colloids which influence the properties of the light-sensitive layer. It has, for example, become evident that when using gelatine an increase in the period of exposure and an unfavorable displacement of the tone of the dye obtained takes place. Colloids suitable for use are, for example, gum arabic and sodium polyacrylate. Also the addition of polyvinyl alcohols has proved to be favorable. The additions to the diazo sulphonate layers mentioned generally have the tendency to make the gradation curve steeper.

The following examples illustrate the invention:

1. 4 grams of the sodium salt of 2.5-dimethoxybenzene diazo sulphonic acid are dissolved in 100 c. c. of water together with 4 grams of benzaldehyde-o-sodium sulphonate and 2 grams of phloroglucine. Plain photographic paper is coated with this solution. After exposure under an original, a brown negative picture is obtained which is soaked for some minutes in order to fix it. The production of the 2.5-dimethoxybenzenediazo-sulphonic acid is effected by the diazotization of the 2.5-dimethoxy-1-amino-benzene, separation of the diazo compound as zinc chloride double salt and double decomposition with sodium sulphite.

2. 5 grams of the sodium salt of the 2.5-diethoxy-4-chlorobenzene-diazo-sulphonic acid are dissolved in 100 c. c. of water with 3 grams of sodium pyroracemate and 2 grams of phloroglucine. Paper is prepared with this solution. On exposure of the material under an original a dark brown picture is obtained. The production of the sodium salt of 2.5-diethoxy-4-chlorobenzene-diazo-sulphonic acid proceeds as follows: The 2.5-diethoxy-1-amino-benzene is transformed by the diazo compound into 2.5-diethoxy-1-chlorobenzene according to Sandmeyer. This compound is nitrated in glacial acetic acid whereafter the 2.5-diethoxy-1-chloro-4-nitrobenzene obtained is reduced in the usual manner, for example with iron and hydrochloric acid to 2.5-diethoxy-1-chloro-4-amino-benzene. This compound is then diazotized in the usual manner in a hydrochloric solution. The diazo compound separated out as zinc chloride double salt is converted into the diazo sulphonate by means of sodium sulphite.

3. 5 grams of the sodium salt of the 2.5-diethoxy-4-methylbenzene-diazo-sulphonic acid, 4 grams of benzaldehyde-o-sodium sulphonate, 2 grams of 2.3-dioxynaphthalene and 10 grams of gum arabic are dissolved in 100 c. c. of water. With layers which are produced with the help of this preparation, there are obtained from well graded photographic negatives dark blue-violet positive copies rich in detail. The production of the sodium salt of 2.5-diethoxy-4-methyl-benzene-diazo-sulphonic acid is effected by the ethylation of 2.5-dioxytoluene with soda lye and diethyl sulphate, nitration of the 2.5-diethoxytoluene obtained, reduction, diazotisation and double decomposition with sodium sulphite. Instead of the said diazo sulphonate the sodium salt of 2.4.5-triethoxy-benzene-diazo-sulphonic acid can also be used. Obviously other sufficiently easily soluble salts of the said diazo sulphonic acid may be used, for example the potassium or ammonium salt. Instead of the triethoxy compound the corresponding trimethoxy compound can also be used. Also the 2.5-diethoxy-4-bromo-benzene-diazo sulphonate is suitable.

4. Paper is coated with a solution of 6 grams of the sodium salt of 2.4-diethoxy-5-chlorobenzene diazo sulphonic acid, 3 grams of phloroglucine and 4 grams of sodium pyroracemate. With this material brown copies are obtained; the gradation is fairly flat. If copies rich in hard contrasts are required a cellulose hydrate sheet is placed between the original and copying layer during copying which sheet has been saturated with a solution of .5 gram of the diazo compound of para-aminodiphenylamine and 1.5 grams of tartaric acid in 100 c. c. of water. By increasing the concentration of the diazo compound in the sheet the gradation of the pictures may be made as steep as desired, while the exposure period is lengthened correspondingly. Good results are also obtained if instead of the said diazo sulphonate the 2-chloro-4.5-dimethoxybenzene-diazo-sulphonate is used.

We claim:

1. Light-sensitive layer comprising a coupling component and a diazo sulphonate which carries in the nucleus containing the diazo sulphonate group at least two etherified oxy groups and no amino group.

2. Light-sensitive layer according to claim 1, characterised in that the said diazo sulphonate belongs to the benzene series.

3. Light-sensitive layer comprising a coupling component and a diazo sulphonate of the benzene series which carries in the benzene nucleus containing the diazo sulphonate group at least two alkoxy groups but no amino group.

4. Light-sensitive layer according to claim 3, characterised in that the said alkoxy groups contain at most two carbon atoms.

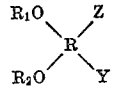
5. Light-sensitive layer comprising a coupling component and a diazo sulphonate of the benzene series which carries in the benzene nucleus containing the diazo sulphonate group at least two ethoxy groups but no amino group.

6. Light-sensitive layer comprising a coupling component and a diazo sulphonate of the benzene series which carries in the benzene nucleus containing the diazo sulphonate group two alkoxy groups but no amino group, the diazo sulphonate group and the two alkoxy groups being positioned with regard to each other in such a way that two but not more than two of the said three groups are adjacent each other.

7. Light-sensitive layer according to claim 6 wherein the said alkoxy groups contain not more than two carbon atoms.

8. Light-sensitive layer comprising a coupling

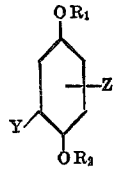
component and a diazo sulphonate of the following general formula:



wherein R stands for a benzene nucleus, R_1 and R_2 for alkyl groups, Y for a diazo sulphonate group and Z is a member of the group consisting of hydrogen, chlorine, bromine and alkyl.

9. Light-sensitive layer according to claim 8 wherein two but not more than two of the three groups, R_1O-, R_2O- and Y are ortho to each other in the nucleus R.

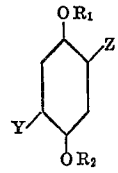
10. Light-sensitive layer comprising a coupling component and a diazo sulphonate of the following general formula:



wherein R_1 and R_2 stand for alkyl groups, Y for a diazo sulphonate group and Z is a member of the group consisting of hydrogen, chlorine, bromine and alkyl.

11. Light-sensitive layer according to claim 10 wherein the said alkyl groups R_1 and R_2 contain not more than two carbon atoms.

12. Light-sensitive layer comprising a coupling component and a diazo sulphonate of the following general formula:



wherein R_1 and R_2 stand for alkyl groups, Y for a diazo sulphonate group and Z is a member of the group consisting of hydrogen, chlorine, bromine and alkyl.

13. Light-sensitive layer according to claim 12 wherein the said alkyl groups R_1 and R_2 contain not more than two carbon atoms.

14. Light-sensitive layer comprising the 2.5-diethoxy-4-chlorobenzene-diazo sulphonate and a coupling component.

15. Light-sensitive layer comprising the 2.5-diethoxy-4-bromobenzene-diazo sulphonate and a coupling component.

16. Light-sensitive layer comprising the 2.5-diethoxy-4-methylbenzene-diazo sulphonate and a coupling component.

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