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2,975,053

# REPRODUCTION MATERIAL

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20 Claims. (Cl. 96—33)

The present invention concerns the production of copies from originals. More particularly, it is concerned with the production of a material comprising a support layer coated with a light sensitive water soluble or water swellable colloid layer.

For several decades, papers and foils which were light sensitized by means of diazo compounds have been in use in the graphic arts. They are widely used for the reproduction of drawings and other transparent originals. Many atempts have been made in the photo-reproduction field to replace the chromates, which in combination with water soluble colloids, are used in a series of technically important processes, e.g. in copper intaglio printing, zinc plate printing, offset printing, photo-lithographic processes, and in the production of pigment papers. Recently, suggestions have been made to replace the chromates used in offset printing, by higher molecular diazo compounds.

However, in those diazotype processes in which water soluble colloids must be used for the production of tanned images, e.g. for making collotypes or for the copper intaglio printing process, chromates are still used, in spite of their being poisonous and having other disadvantages.

It is one object of the present invention to provide a novel reproduction material consisting of a layer support and a light sensitive, water soluble or water swellable colloid layer coated thereon, free from chromates, which can be used for the production of tanned images. The further use of said tanned images depends to a far degree on the layer support. Tanned images on metallic supports or on plastic sheets may be used as printing plates. Tanned images on paper support are suitable as substitutes for imaged pigment papers.

A further object of the invention is the use of certain quinone diazides in a colloid layer coated on a base material to produce tanned images upon exposure to a light image.

The light sensitive substances to be used according to this invention in the colloid layer are sulfonic acids, and the salts of such sulfonic acids, of p-quinone-diazide sulfonic acid derivatives, which are sulfo esters as well as sulfon amides, said derivatives containing two or more p-quinone-diazide sulfonyl groups in their molecules. The colloid being the most important component of the novel reproduction material, these light sensitive substances are mostly used in a minor amount as compared with the amount of colloid in the colloid layer. The major portion of the layer is in general the colloid. Layers containing more than 60 percent of the light sensitive substance are not within the scope of this invention.

The reproduction material prepared according to the present invention, after it is exposed under a transparent original and developed by treatment with water, results in tanned images which are very suitable for numerous purposes in the reproduction field.

Heretofore it was known that neither the ortho- and para-benzoquinone-diazide sulfonic acids and paranaphthquinone-diazide sulfonic acids, nor the sulfonic acids of o-quinone-diazide esters or o-quinone-diazide sulfonic



acid amides (even if they contained several light sensitive o-quinone diazide residues in their molecules) were capable of hardening water soluble colloids to such a degree that suitable tanned images are obtained by light exposure and subsequent development with water. It was, therefore, very surprising to determine that the specific group of bis-compounds of the invention could accomplish the purpose.

The compounds, which must be present as the light sensitive substance in the colloidal layer, can be mixed with various water soluble or water swellable colloids and then be used for the production of light sensitive layers, by coating the solution onto a suitable support, in a manner similar to the way known chromate layers are made.

Colloids suitable for use in accordance with the present invention are either natural colloids, such as gelatine or casein; or synthetic colloids, e.g. high viscous polyvinylpyrrolidones, acrylic acid amides, polyvinyl alcohol, or similar water soluble or water swellable substances. Dyestuffs, sensitizers, pigments or plasticizers, e.g. glycerine, may be added to the colloid layers, as well as other additives customarily used in diazotype processes.

According to one method of the present invention, a water swellable colloid layer, e.g. a gelatine or cellulose hydrate layer, is sensitized by coating it with a solution of the compound to be used as the light sensitive substance.

One method of producing the light sensitive substance in the colloid layer is, for example, by causing p-quinonediazide sulfonic acid chlorides to react with aromatic sulfonic acids or aromatic carboxylic acids containing at least one amino group as well as at least one hydroxy group in their aromatic nucleus.

If the visibility of the tanned images of the invention, obtained after exposure to light, should not be good enough, they can be colored before or after development with water by using dyestuff solutions of, e.g., basic dyestuffs, such as methylene blue or methyl violet. Frequently, a further hardening of the images results from such coloration. However, such hardening effect may also be obtained by an after-treatment with a tanning agent, e.g. formaldehyde.

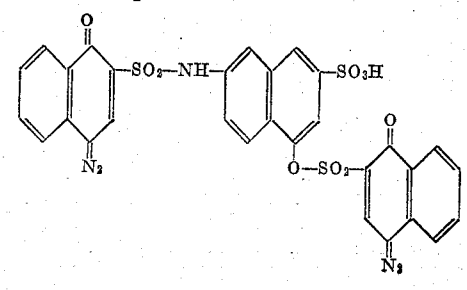
Suitable base materials or supports for the light sensitive colloid layers may be: Paper, films, plastic foils, metal foils, metal plates and metal cylinders, e.g. of aluminum, zinc, copper or brass, or they may be of glass or textile fabrics.

The light sensitive reproduction material according to the present invention may be used for all processes in which chromates were hitherto used for sensitization, especially for intaglio and offset printing. It is also of practical importance in obtaining pigment images, copying originals, or for the production of stencils.

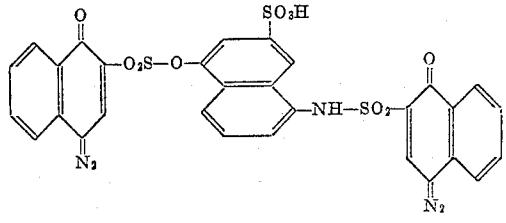
The light sensitive layers according to the present invention have an excellent shelf life. As compared with the diazo and nitro compounds previously proposed for the production of tanned images, the new material has the advantage that it bleaches out more strongly, and thus avoids weakness in contrast of the images obtained.

The following compounds are discussed in further detail in the examples:

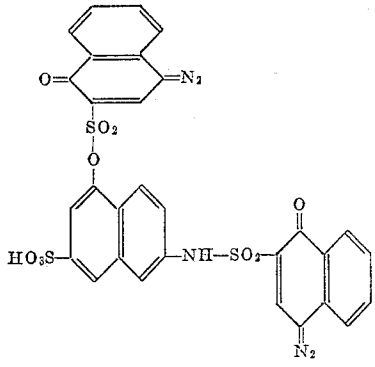
(1)



(2)



(3)



The invention will be further illustrated by reference to the following specific examples:

*Example I*

A solution containing 0.3% of the compound corresponding to Formula 1 (condensation product of 1 mol of 2-amino-5-hydroxy-naphthalene—7-sulfonic acid with 2 moles of naphthoquinone—(1,4)-diazide-(4)-2-sulfochloride), 0.15% of erythrosin, and 3% of gelatine in aqueous alcohol (80%), is coated onto a brushed or superficially oxidized aluminum foil and dried. The layer is then exposed under a transparent original, using, a closed carbon arc lamp of 18 amp. as the light source, and then rinsed with water of 40° C. A vividly violet colored image is obtained, which adheres very firmly to the plate even after an exposure of only 15–20 seconds.

Instead of erythrosin, eosin may be used. If erythrosin is not contained in the coating solution, and the plate is exposed for 1½ minutes to the light of an open carbon arc lamp at a distance of 1 m., the image adheres very firmly to the support, when being rinsed with water.

In order to prepare the compound corresponding to Formula 1, 2.4 g. of 2-amino-5-hydroxy-naphthalene-7-sulfonic acid are dissolved in 25 cc. of water and 2.5 cc. of 10% caustic soda solution, to form the sodium salt of the acid. To this solution there is added first a suspension of 5.4 g. of naphthoquinone-(1,4)-diazide-(4)-2-sulfochloride in 25 cc. of dioxane and, subsequently, at a temperature of about 40° C. and with agitation, as much of a 10% sodium carbonate solution as is necessary to obtain a clear solution. The solution is cooled down, poured into 300 cc. of a saturated sodium chloride solution, and slightly heated again. A dark green product precipitates which is drawn off. It is dissolved in a little water, and the solution is first mixed with animal charcoal and then filtered. Hydrochloric acid is added to the filtrate until an acid reaction is obtained, whereupon the condensation product separates, which is then drawn off. It is dissolved in hot alcohol (90%) and the solution is filtered off from the deposit. The product corresponding to Formula 1 crystallizes from the filtrate in the form of brownish-yellow crystals. Upon dissolving this product in dilute sodium carbonate solution, it forms a yellow solution. It does not couple with other diazo compounds.

*Example II*

0.3 g. of the sodium salt of the N,O-bis [naphthoquinone - (1',4') - diazide - (4') - 2' - sulfonyl - ] -1-amino-5-hydroxy-naphthalene-7-sulfonic acid, corresponding to Formula 2 are dissolved in 100 ml. of a 3% aqueous



solution of gelatin. An aluminum foil, the surface of which has been roughened by means of brushing, is coated with the solution mentioned above by means of whirlcoating and is subsequently dried with warm air. The dried and sensitized foil is then exposed under a transparent negative, e.g. at a closed arc lamp of 18 amp./120 v. and at a distance of about 70 cm. and is then inked with a 1% aqueous solution of Victoria Blue B (see Schultz "Farbstofftabellen," 7th edition, volume 1 (1931), No. 822, page 347). Development of the image thus formed on the foil is effected by rinsing or bathing the exposed foil with water having a temperature of 40° C. Thus, a colored positive image remains on the foil. After drying, the foil can be used for the production of stencils or as a printing plate in a conventional printing apparatus.

The sodium salt of the diazo compound corresponding to Formula 2 is prepared as follows:

2.4 g. of 1-amino-5-hydroxy-naphthalene-7-sulfonic acid are suspended in 25 ml. of water and neutralized by adding a 10% solution of caustic soda. A suspension of 5.4 g. of naphthoquinone-(1,4)-diazide-(4)-2-sulfochloride in 25 ml. of dioxane is added to the obtained solution and, at a temperature of 40° C., 20 ml. of a 10% aqueous solution of sodium carbonate are added, drop by drop, to the mixture, while stirring. At a temperature of 40° C., the reaction mixture is again stirred for 15 minutes, poured into 300 ml. of a saturated sodium chloride solution and separated from the liquid. The filter cake is first washed with 50 ml. of alcohol and then with ether. The raw reaction product is purified by reprecipitation from ethylene glycolmonomethylether. The sodium salt of the diazo compound corresponding to Formula 2 is a greenish-yellow substance.

*Example III*

A solution, prepared using 50% aqueous alcohol as a solvent and containing 1.5% of highly viscous polyvinylpyrrolidone and 0.15% of the sodium salt of the N,O - bis - [naphthoquinone - (1',4') - diazide - (4') - 2'-sulfonyl-]-2-amino-8-hydroxy-naphthalene-6-sulfonic acid corresponding to Formula 3, is coated onto an aluminum foil, the surface of which was previously roughtened by means of brushing. After drying the foil with warm air, it is exposed under a transparent negative and developed as described in Example 2. After development, the foil shows a blue colored positive image and can be used for the production of stencils or as a printing plate in a conventional printing apparatus.

The sodium salt of the diazo compound corresponding to Formula 3 is prepared as follows:

2.4 g. of 2-amino-8-hydroxy-naphthalene-6-sulfonic acid are suspended in 25 ml. of water and neutralized by adding a 10% solution of caustic soda. A suspension of 5.4 g. of naphthoquinone-(1,4)-diazide-(4)-2-sulfochloride in 25 ml. of dioxane is added to the resulting solution and, at a temperature of 40° C., 20 ml. of 10% aqueous solution of sodium carbonate are added, drop by drop, to the mixture, while heating. At a temperature of 40° C., the reaction mixture is again stirred for 15 minutes, poured into 300 ml. of a saturated sodium chloride solution and separated from the liquid. The filter cake is first washed with 50 ml. of alcohol and then with ether. The raw reaction product is purified by reprecipitating it from ethylene glycolmonomethylether. The sodium salt of the diazo compound corresponding to Formula 3 is a greenish-yellow substance.

*Example IV*

A commercial gelatin paper the gelatin layer of which may be colored by a pigment is bathed in a 5% aqueous solution of the sodium salt of the N,O-bis-[naphthoquinone - (1',4') - diazide - (4') - 2' - sulfonyl] - 2-amino-8-hydroxy-naphthalene-6-sulfonic acid corresponding to Formula 3 at a temperature of 5° C. and is thereby sensitized. The paper being still wet is pressed with

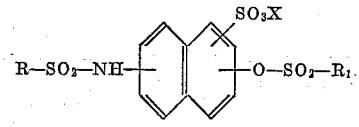
its layer side onto a glass plate which has been cleaned by means of ox gall. By applying a felt onto the back side of the paper and loading with another glass plate, the paper is dried at room temperature until it is lifted off by itself. The paper thus dried is then exposed for 5 minutes under a transparent positive pattern, wetted with water and subsequently transferred onto a copper plate or a copper cylinder. When bathing in water which has a temperature from between 35 to 40° C., the paper support and the gelatin which has not been hardened by light are detached from the surface of the metal and a negative gelatin relief image of the pattern which can be etched according to the intaglio printing process, remains on the copper.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

This application is a continuation-in-part of application Serial No. 725,801, filed April 2, 1958, which in turn is a continuation-in-part of application Serial No. 566,093, filed February 17, 1956, and now abandoned.

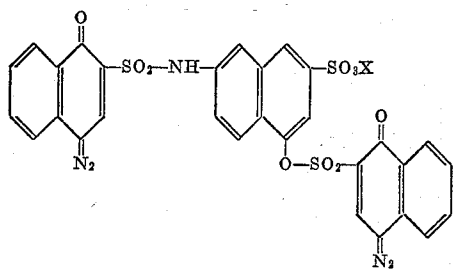
What is claimed is:

1. A compound having the formula



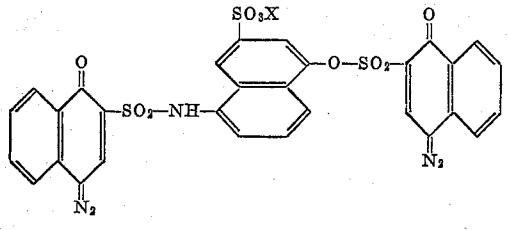
in which R and $R_1$ are quinone-(1,4)-diazide radicals, and X is selected from the group consisting of hydrogen and a metal cation.

2. A compound having the formula



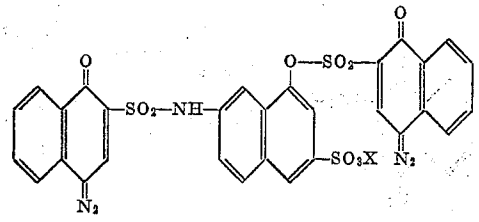
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

3. A compound having the formula



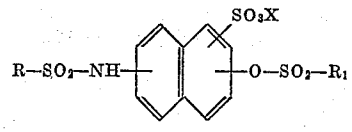
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

4. A compound having the formula



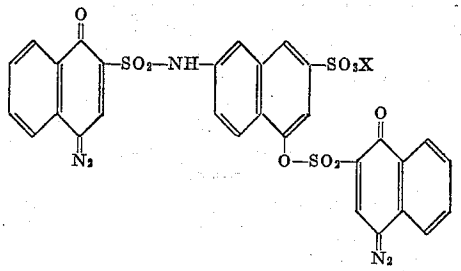
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

5. Light sensitive material comprising a base material coated with a layer comprising a water-soluble organic colloid and a compound having the formula



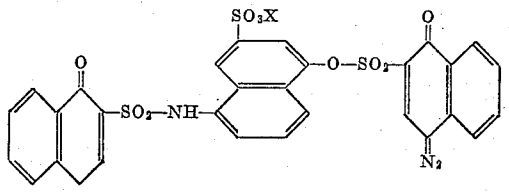
in which R and $R_1$ are quinone-(1,4)-diazide radicals, and X is selected from the group consisting of hydrogen and a metal cation.

6. Light sensitive material comprising a base material coated with a layer comprising a water-soluble organic colloid and a compound having the formula



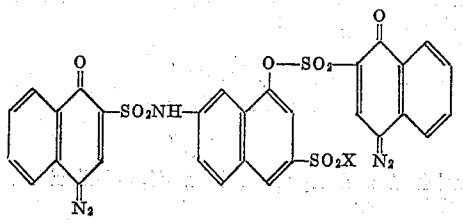
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

7. Light sensitive material comprising a base material coated with a layer comprising a water-soluble organic colloid and a compound having the formula



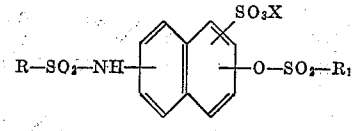
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

8. Light sensitive material comprising a base material coated with a layer comprising a water-soluble organic colloid and a compound having the formula



in which X is selected from the group consisting of hydrogen and an alkali metal cation.

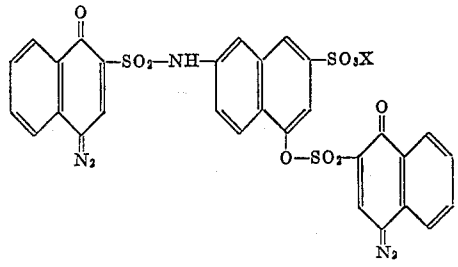
9. A method of making light sensitive material which comprises coating a base material with a layer comprising a water-soluble organic colloid and a compound having the formula



in which R and $R_1$ are quinone-(1,4)-diazide radicals, and X is selected from the group consisting of hydrogen and a metal cation.

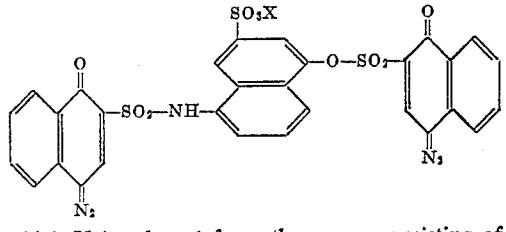
10. A method of making light sensitive material which comprises coating a base material with a layer comprising

a water-soluble organic colloid and a compound having the formula



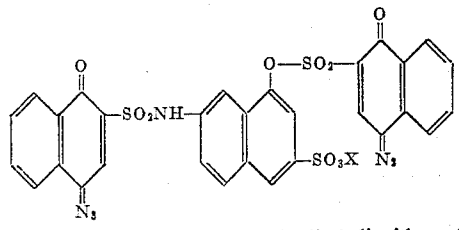
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

11. A method of making light sensitive material which comprises coating a base material with a layer comprising a water-soluble organic colloid and a compounds having the formula



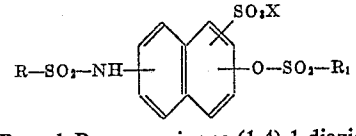
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

12. A method of making light sensitive material which comprises coating a base material with a layer comprising a water-soluble organic colloid and a compound having the formula



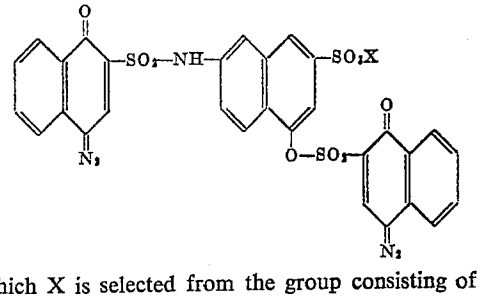
in which R and $R_1$ are quinone-(1,4)-1-diazide radicals, drogen and an alkali metal cation.

13. A presensitized gelatin paper comprising paper stock coated with a layer comprising gelatin and a compound having the formula



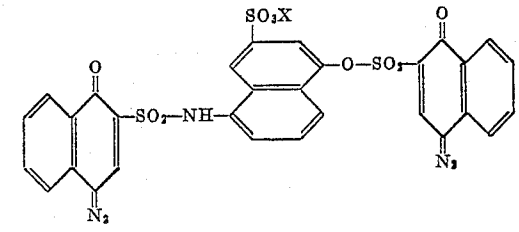
in which R and $R_1$ are quinone-(1,4)-1-diazide radicals, and X is selected from the group consisting of hydrogen and a metal cation.

14. A presensitized gelatin paper comprising paper stock coated with a layer comprising gelatin and a compound having the formula



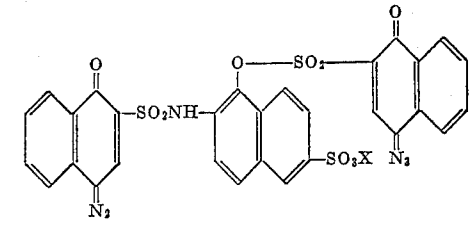
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

15. A presensitized gelatin paper comprising paper stock coated with a layer comprising gelatin and a compound having the formula



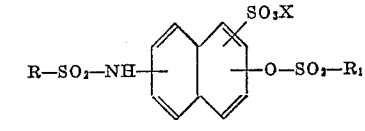
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

16. A presensitized gelatin paper comprising paper stock coated with a layer comprising gelatin and a compound having the formula



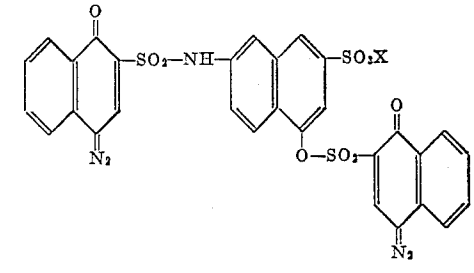
in which X is selected from the group consisting of hydrogen and an alkali metal cation.

17. A method of making a presensitized gelatin paper comprising coating paper stock with a layer comprising gelatin and a compound having the formula



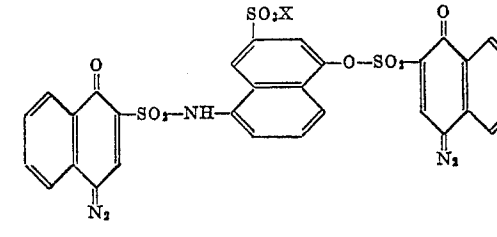
in which R and $R_1$ are quinone-(1,4)-diazide radicals, and X is selected from the group consisting of hydrogen and a metal cation.

18. A method of making a presensitized gelatin paper comprising coating paper stock with a layer comprising gelatin and a compound having the formula



in which X is selected from the group consisting of hydrogen and an alkali metal cation.

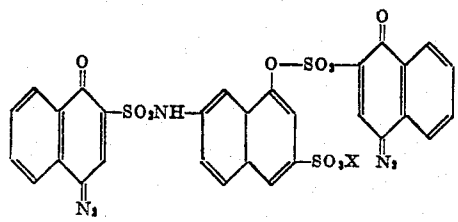
19. A method of making a presensitized gelatin paper comprising coating paper stock with a layer comprising gelatin and a compound having the formula



in which X is selected from the group consisting of hydrogen and an alkali metal cation.

20. A method of making a presensitized gelatin paper

comprising coating paper stock with a layer comprising gelatin and a compound having the formula





in which X is selected from the group consisting of hydrogen and an alkali metal cation.


**References Cited** in the file of this patent

UNITED STATES PATENTS

2,754,209 Schmidt et al. ---------- July 10, 1956

FOREIGN PATENTS

706,028 Great Britain ---------- Mar. 24, 1954