

PATENT SPECIFICATION

(11) 1347 759

1347 759

- (21) Application No. 28574/71 (22) Filed 17 June 1971
 (23) Complete Specification filed 9 June 1972
 (44) Complete Specification published 27 Feb. 1974
 (51) International Classification G03C 1/60
 (52) Index at acceptance
 G2C C4A1 C4C2B2 C4C3A2 C4C3A4 C4C3AX C4C3C
 C4D3D C4G2
 (72) Inventors PETER JOHN SMITH and
 FRANK EDWARD SMITH



(54) IMPROVEMENTS IN OR RELATING TO LIGHT SENSITIVE MATERIALS

(71) We, HOWSON - ALGRAPHY LIMITED, a British company of Vickers House, Millbank Tower, Millbank, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to positive working light-sensitive materials, and is concerned with such materials which are suitable for, for example, the production of printing plates by photo-mechanical methods.

Photo-mechanical methods of preparing printing plates comprise producing a light-sensitive plate by applying a light-sensitive material to a suitable support, e.g. of anodised aluminium, image-wise exposing the light-sensitive plate so that the light-struck areas of the material and the non-light-struck areas of the material have differing solubility in a solvent, and then developing the image-wise exposed plate with the solvent to selectively remove the more soluble of the areas. In the case where the light-sensitive material is a negative working material, the non-light-struck areas are removed whereas the light-struck areas are removed in the case where the light-sensitive material is positive working.

In these procedures it is desirable for a colour change to take place in the light-struck areas so as to render them visible: this is especially the case in step-and-repeat work where it is necessary to align successive images on the plate. In some cases the colour change inherent in the light-sensitive system used (e.g. in azide sensitised layers) may be sufficient in itself. In other cases, although some colour change occurs on image-wise exposure to light, this is rarely sufficient in practice to enable the image to be visibly inspected. This is particularly the case with light-sensitive materials based on quinone diazides and diazonium salts.

Light-sensitive materials comprising positive working quinone diazides, usually in admixture with a novolak resin, are used to a

large extent in printing plate manufacture but, as aforementioned, they suffer from the disadvantage that they do not ordinarily undergo an adequate colour change on exposure to light. On exposure of light-sensitive materials based on such quinone diazides, light converts the quinone diazide to an indene carboxylic acid [via a ketene intermediate: Cf. O. Süss, Annalen, 556, 65—84 (1944)], thus rendering it soluble in and developable by an aqueous developer of pH about 11.5. Although there is a slight colour change from the original yellow colour on exposure, even with the aid of the addition of a contrast-providing dye, for example a violet dye, it is difficult to see the light-struck areas in the yellow safe-light that is usually employed in the working area.

An attempt is made to overcome this problem in British Patent Specification No. 1,039,475: In accordance with that Specification a pH indicator is admixed with an o-naphthoquinone diazide light sensitive material to obtain a colour change on exposure. In accordance with British Patent Specification No. 1,170,458 an attempt is made to obtain a colour change on exposure when using negative working benzoquinone 1,4-diazides by admixing specified substances therewith.

In an attempt to find an alternative solution to the problem, it appeared to us to be attractive, because of the strong colour change involved, to follow the teaching of Example 2 of British Patent Specification No. 1,041,463 where, in a different light-sensitive system, a phosphotungstic acid is liberated on exposure and causes a pH indicator, the yellow dye 4-phenylazodiphenylamine, to turn mauve. However, we found that this indicator was useless in the conventional quinone diazide system because the carboxylic acid formed on exposure of the quinone diazide was too weak to affect the indicator.

We have now devised a light-sensitive material which can be used as a colour change indicator in quinone diazide based materials.

According to one aspect of the present

[Price 25p]

SPECIFICATION AMENDED - SEE ATTACHED SLIP

invention there is provided a positive working light-sensitive material which exhibits a colour change upon exposure to light, which material comprises in admixture a diazonium salt, a novolak resin and a hydroxy substituted aryl azo compound which undergoes a colour change in the presence of the acid produced by the diazonium salt on exposure to light.

The material of the present invention may be used as a colour change material for incorporation in light-sensitive materials based on quinone diazides for the photomechanical production of lithographic printing plates whereby there is provided a light-sensitive material which is essentially based on a quinone diazide but which undergoes a colour change on exposure.

On the other hand, the light sensitive material of the present invention constitutes a material of the type generally described in British Patent Specification No. 944,884 but with the advantage that it produces a colour change on exposure. Thus, the material of the present invention may be used *per se* in the production of light sensitive plates for printing plate manufacture by photomechanical techniques.

In use, the light-sensitive material of the invention, either including quinone diazide or not as the case may be, is applied as a coating to a suitable support e.g. a conventional zinc, aluminium or bi- or tri-metal support to form a light-sensitive plate. Upon image-wise exposure of the light-sensitive plate, the light-struck areas of the coating undergo a clearly visible colour change due to the reaction of the azo compound with the light-decomposition products of the diazonium salt and hence it can be readily ascertained that the light-sensitive plate has been correctly exposed. Protonation of the azo nitrogens by the acid produced by the diazonium salt on exposure to light causes the azo compound to undergo the colour change. Subsequently, the image-wise exposed coating can be processed in conventional manner to obtain a lithographic printing plate. The presence of the azo compound in a quantity adequate to give a marked change of colour does not cause any reduction in the solubility differential between the light-struck and non-light-struck areas.

Generally, the diazonium salt is a salt of an acid having a dissociation constant above about 1×10^{-3} . The acid will usually be, but is not necessarily, an inorganic acid. The term "novolak" is used herein in its conventional sense to mean the alcohol soluble fusible resin produced by condensing together, under acidic conditions, a phenol having two or more reactive aromatic ring hydrogen positions (such as phenol itself), usually in a slight molar excess, and an aldehyde (such as formaldehyde) or an aldehyde liberating compound capable of undergoing phenol-aldehyde condensation. Any novolak resin conventionally

used in the art may be used. Similarly the diazonium salts used are conventional. Examples of suitable diazonium salts are given in the Examples hereinafter described; more can be found in British Patent Specification No. 944,884.

It will be appreciated that the colour formed while the plate is being exposed acts as a light filter and thus increases the time needed to expose the plate. For this reason, when a quinone diazide is included, it is convenient and expedient to use what is known to the diazotype industry as a "slow diazo" so that the colour forms strongly only late in the exposure period of the plate.

The amount of azo compound present in the light-sensitive material is not particularly critical. For example, from 0.1 to 20% by weight (based on the total weight of the material) may be used. Generally, the greater the amount of azo compound present, the more pronounced is the colour change on exposure to light but it has been found sufficient to use from 0.5 to 2% by weight, based on the total weight. The minimum amount of diazonium salt corresponds molecularly to the amount of the azo compound.

As described above, a quinone diazide may be admixed with the light-sensitive material. The presence of the quinone diazide is not essential in order to obtain the required colour change. Nevertheless, it is preferred to include the quinone diazide since it enhances the lithographic properties of the eventual printing plate. Indeed, the light sensitive material may include a relatively large amount of quinone diazide compared to the amount of diazonium salt.

When a direct image printing plate needs to have a long printing life, it is usual to employ a support formed of abrasion-resistant anodised aluminium which will preserve the water-carrying properties of the non-image areas for as long as possible. Unfortunately, as is well known from architectural and other uses of aluminium, it is all too easy to dye indelibly anodised aluminium. Thus if, during processing of the plate, the back-ground areas of the plate were to become stained, these areas would be likely to accept ink while the plate is running on the press. A marked reduction in this tendency to stain has been observed by utilising light sensitive materials comprising alkali-developer-soluble hydroxy aryl azo compounds in accordance with the present invention instead of the indicators described in British Patent Specification No. 1,039,475 and No. 1,041,463.

The azo compound used may be for example a hydroxyphenylazodiphenylamine or a similar phenolic azo-dye made by coupling a novolak with a suitable diazotised base, such as diazotised p-aminodiphenylamine.

The azo compound can be produced by dissolving a phenol, naphthol or a novolak resin

in a solvent containing a suitable base (e.g. ammonia or diethylamine) and then adding diazonium salt. This results in the formation of an azo-dye which can then be added to a conventional light-sensitive system comprising diazonium salt and novolak resin to produce a light sensitive material according to the present invention. However, the azo-dye may be produced *in situ* in the light sensitive diazonium salt/novolak resin system by adding to the system a small amount of a base to cause a proportion of the diazonium salt and the novolak resin to couple together. In this way, it is not necessary to add the azo-dye as such to the system. Accordingly, a second aspect of the present invention provides a process for producing a light sensitive material which exhibits a colour change on exposure to light and which is suitable for the production of a printing plate by a photo-mechanical technique, which process comprises admixing a diazonium salt and a novolak resin and adding to the mixture a base to couple together a part of the diazonium salt and a part of the novolak resin to obtain an azo compound which undergoes a colour change in the presence of the light-decomposition products of the remaining non-coupled diazonium salt. Generally, from 0.1 to 20% by weight of the total amount of diazonium salt present in the light sensitive material is in the form of the azo-dye but it is normally sufficient for from 0.1 to 2.0% by weight of the diazonium salt to be present in the form of the azo-dye. In the case where the azo compound used is an azo-dye produced by coupling together novolak resin and diazonium salt, the major part of the resultant azo molecule consists of novolak resin. Thus, the azo compound is readily soluble in alkali and highly compatible with the other constituents of the light sensitive material.

The light-sensitive materials of the present invention have an important advantage over other proposed systems which change colour on exposure in that the non-light-struck areas remaining after development contain the diazonium salt in admixture with novolak resin and constitute an image forming material as is described in British Patent Specification No. 944,884, whereas by methods such as those of British Patent Specifications No. 1,204,917 and No. 1,187,814, the colour changing material is a material foreign to the image-forming material proper and is therefore likely to weaken the printing image. Further, in some processes the image-forming light sensitive material is used as a resist, e.g. an etch resist in the case of the production of a bimetallic plate or of a printed circuit sheet. In such cases the acid resistance of the resist may also deteriorate in the presence of a "foreign" material.

The following Examples illustrate the invention.

EXAMPLE 1

12 g. of a cresol-based novolak resin known under the trade designation Alnovol 429K, 2 g. of diphenylamine - 4 - diazonium fluoroborate (known under the designation ZABF₄ of Fisons Ltd.), 100 ml. acetone, and 100 ml. ethyl methyl ketone were admixed together and 6 ml. of a 1% solution of 0.880 ammonia in acetone were added. The word "Alnovol" is a Trade Mark. The resultant mixture was whirled on to a grained and anodised aluminium sheet at 100 rpm and dried. The resultant light-sensitive plate was exposed to a 4,000 watt xenon lamp for 2½ minutes at 2 feet. Before exposure, the coating was yellow in colour. After image-wise exposure, the light-struck areas were blue in colour and were easily visible in the yellow light of the dark room. The exposed plate was then developed using 1% sodium hydroxide solution to remove the light struck areas. Development was quite satisfactory and no staining of the anodised aluminium sheet occurred. The plate was mounted on a printing press and good copies were produced.

EXAMPLE 2

An electrograined aluminium plate was coated in a whirler with the following formulation: 2,5 - diethoxy - 4 - (4' - tolyl) - mercaptobenzene diazonium borofluoride 4 g., PF 402 20 g., 0.880 ammonia solution 0.3 ml., acetone 150 ml., ethyl methyl ketone 150 ml. When the plate was exposed under a positive master for 2 minutes at 2 ft. to a 4000 watt xenon lamp the exposed areas turned to an intense blue. The plate could be developed with 5% trisodium phosphate. (PF 402 is a phenol novolak of I.C.I. Ltd.).

EXAMPLE 3

A similar plate to the above was coated with the following formulation: 2,5 - diethoxy - 4 - (4' - tolyl) - mercaptobenzene diazonium chloride 4 g., PF 402 20 g., 0.880 ammonia solution 0.3 ml., acetone 150 ml. When the plate was exposed as in Example 2 the same blue colour was produced in the exposed areas but in this case the colour retained its intensity after standing for several days. The plate could be developed with 5% trisodium phosphate.

EXAMPLE 4

(a) External preparation of azo compound
A solution of diphenylamine - 4 - diazonium hydrogen sulphate (58.6 g., 0.2 mole) in 300 ml of water, and a solution of sodium carbonate (21.2 g., 0.2 mole) in 3000 ml of water were added simultaneously at the same rate to a stirred solution of phenol (18.8 g., 0.2 mole) in 2000 ml of 4% aqueous sodium hydroxide. During this procedure the pH remained at a constant value of around 10 and a brown precipitate was formed. The

precipitate was separated, washed and dried in a vacuum desiccator. The precipitate was shown, by thin layer chromatography, to be a mixture of three isomeric hydroxy phenyl-azodiphenylamines all of which were acid/base indicators. The final yield of dried product was 49.0 g. (85%) melting at 100—105°C.

(b) Use of the azo compound in printing plate manufacture

25 g. of a quinone diazide was added to a solution of 50 g. novolak resin (Alnovol 429K) in a mixture of 250 ml acetone and 250 ml ethyl methyl ketone. 3 g diphenylamine - 4 - diazonium fluoroborate and 1 g. of the above azo compound were added to the solution. When dissolution was complete, the resultant solution was whirler coated onto an electrograined and anodised aluminium sheet and dried. The quione diazide used was 2,3,4-trihydroxy benzophenone mononaphthoquinone - (1,2) - diazide - (2) - 5 - sulphonate made in accordance with British Patent Specification No. 739,654. On exposure of the resultant light sensitive plate to the light of a carbon arc lamp using a positive, the light struck areas became dark blue in colour and were easily visible in the "dark room" lighting. These areas were alkali developable and, after being processed in conventional manner, the plate performed satisfactorily on a printing machine.

Other suitable azo compounds are 4-hydroxyphenylazodiphenylamine; 2 - hydroxynaphthyl azo diphenylamine and the azo dyes prepared from 4 - aminodiphenylamine and salicylic acid or the phenol novolak PF 402 or the cresol novolak Alnovol 429K (R.T.M.).

EXAMPLE 5

1 g. of the novolak azo dye prepared from Alnovol and ZABF₄ was added to 2 g. of 2,4',5' - triethoxy diphenyl diazonium oxalate and 10 g. of PF 402 novolak in 50 cc. acetone and 50 cc. MEK. The coating was whirled on to an electrograined and anodised aluminium plate and subsequently exposed as described in Example 2. The same blue colour change appeared although in this case it was less intense than that in Examples 1 or 3. The developed plate was almost free of stain in the background areas and showed good adhesion during printing.

EXAMPLE 6

This is an example of the preferred use of a "slower" rather than a "fast" diazonium salt.

1 g. of the novolak azo dye used in Example 5 was added to a solution of 12 g. Alnovol 429K as novolak resin, 2 g. of 2,5 - diethoxy-4 - morpholinobenzene diazonium borofluoride as diazonium salt, 4 g. of a quinone diazide (see below), 100 ml. acetone, 100 ml. ethyl methyl ketone. An electrograined aluminium

plate was coated with the above formulation in a whirler and exposed for 2 minutes under a continuous tone step wedge to the light source described in Example (2). The colour change showed that the first six steps had been fully degraded but on development with 10% trisodium phosphate solution only the first step developed clean. When the diazonium salt was replaced with the same weight of 4-diethylaminobenzene diazonium borofluoride the number of steps indicated by the colour change as having degraded was the same as the number of steps which developed out with 10% trisodium phosphate.

The quinone diazide used was the condensation product of naphthoquinone - (1,2)-diazide - (2) - 5 - sulphonyl chloride and resorcinol monobenzoate produced in accordance with British Patent Specification No. 1,053,866.

EXAMPLE 7

40 g. of Alnovol 429K, 5 g. of ZABF₄, 10 g. of the quinone dioxide of Example 6, 250 ml. of 2-ethoxyethanol and 1.5 ml. 0.880 ammonia were mixed together. The mixture was whirled onto a grained and anodised aluminium sheet and exposed as described in Example 2. The light-struck areas of the coating became blue in colour and were readily distinguished from the non-light-struck areas. The image-wise exposed plate was developed using 5% sodium metasilicate solution to remove the light struck areas. This developer is preferred to sodium hydroxide since it is less injurious to the aluminium background surface. Development was satisfactory and no staining of the anodised surface occurred. The developed plate was mounted on a printing press and many good copies were obtained.

EXAMPLE 8

The same coating solution as described in Example 4 was coated on to a bimetal plate comprising a chromium plated copper foil laminated to a polyester film base. Exposure under a negative pattern gave a strong blue positive which was developed with alkali leaving a yellow negative resist image. The chromium which had been laid bare was etched away by application of an hydrochloric acid etch, the resist removed by rubbing with alcohol and the result used as a lithographic plate with a long working life.

WHAT WE CLAIM IS:—

1. A positive working light sensitive material which exhibits a colour change upon exposure to light and which is suitable for the production of a printing plate by a photomechanical technique, which material comprises in admixture a diazonium salt, a novolak resin, and a hydroxy substituted aryl azo compound which undergoes a colour change in the presence of



precipitate was separated, washed and dried in a vacuum desiccator. The precipitate was shown, by thin layer chromatography, to be a mixture of three isomeric hydroxy phenyl-azodiphenylamines all of which were acid/base indicators. The final yield of dried product was 49.0 g. (85%) melting at 100—105°C.

(b) Use of the azo compound in printing plate manufacture

25 g. of a quinone diazide was added to a solution of 50 g. novolak resin (Alnovol 429K) in a mixture of 250 ml acetone and 250 ml ethyl methyl ketone. 3 g diphenylamine - 4 - diazonium fluoroborate and 1 g. of the above azo compound were added to the solution. When dissolution was complete, the resultant solution was whirled coated onto an electrograined and anodised aluminium sheet and dried. The quione diazide used was 2,3,4-trihydroxy benzophenone mononaphthoquinone - (1,2) - diazide - (2) - 5 - sulphonate made in accordance with British Patent Specification No. 739,654. On exposure of the resultant light sensitive plate to the light of a carbon arc lamp using a positive, the light struck areas became dark blue in colour and were easily visible in the "dark room" lighting. These areas were alkali developable and, after being processed in conventional manner, the plate performed satisfactorily on a printing machine.

Other suitable azo compounds are 4-hydroxyphenylazodiphenylamine; 2 - hydroxynaphthyl azo diphenylamine and the azo dyes prepared from 4 - aminodiphenylamine and salicylic acid or the phenol novolak PF 402 or the cresol novolak Alnovol 429K (R.T.M.).

EXAMPLE 5

1 g. of the novolak azo dye prepared from Alnovol and ZABF₄ was added to 2 g. of 2,4',5 - triethoxy diphenyl diazonium oxalate and 10 g. of PF 402 novolak in 50 cc. acetone and 50 cc. MEK. The coating was whirled on to an electrograined and anodised aluminium plate and subsequently exposed as described in Example 2. The same blue colour change appeared although in this case it was less intense than that in Examples 1 or 3. The developed plate was almost free of stain in the background areas and showed good adhesion during printing.

EXAMPLE 6

This is an example of the preferred use of a "slower" rather than a "fast" diazonium salt.

1 g. of the novolak azo dye used in Example 5 was added to a solution of 12 g. Alnovol 429K as novolak resin, 2 g. of 2,5 - diethoxy-4 - morpholinobenzene diazonium borofluoride as diazonium salt, 4 g. of a quinone diazide (see below), 100 ml. acetone, 100 ml. ethyl methyl ketone. An electrograined aluminium

plate was coated with the above formulation in a whirler and exposed for 2 minutes under a continuous tone step wedge to the light source described in Example (2). The colour change showed that the first six steps had been fully degraded but on development with 10% trisodium phosphate solution only the first step developed clean. When the diazonium salt was replaced with the same weight of 4-diethylaminobenzene diazonium borofluoride the number of steps indicated by the colour change as having degraded was the same as the number of steps which developed out with 10% trisodium phosphate.

The quinone diazide used was the condensation product of naphthoquinone - (1,2)-diazide - (2) - 5 - sulphonyl chloride and resorcinol monobenzoate produced in accordance with British Patent Specification No. 1,053,866.

EXAMPLE 7

40 g. of Alnovol 429K, 5 g. of ZABF₄, 10 g. of the quinone dioxide of Example 6, 250 ml. of 2-ethoxyethanol and 1.5 ml. 0.880 ammonia were mixed together. The mixture was whirled onto a grained and anodised aluminium sheet and exposed as described in Example 2. The light-struck areas of the coating became blue in colour and were readily distinguished from the non-light-struck areas. The image-wise exposed plate was developed using 5% sodium metasilicate solution to remove the light struck areas. This developer is preferred to sodium hydroxide since it is less injurious to the aluminium background surface. Development was satisfactory and no staining of the anodised surface occurred. The developed plate was mounted on a printing press and many good copies were obtained.

EXAMPLE 8

The same coating solution as described in Example 4 was coated on to a bimetal plate comprising a chromium plated copper foil laminated to a polyester film base. Exposure under a negative pattern gave a strong blue positive which was developed with alkali leaving a yellow negative resist image. The chromium which had been laid bare was etched away by application of an hydrochloric acid etch, the resist removed by rubbing with alcohol and the result used as a lithographic plate with a long working life.

WHAT WE CLAIM IS:—

1. A positive working light sensitive material which exhibits a colour change upon exposure to light and which is suitable for the production of a printing plate by a photomechanical technique, which material comprises in admixture a diazonium salt, a novolak resin, and a hydroxy substituted aryl azo compound which undergoes a colour change in the presence of

the acid produced by the diazonium salt on exposure to light.

2. A light sensitive material as claimed in Claim 1, which further includes a quinone diazide.

3. A light sensitive material as claimed in Claim 1 or 2, wherein the azo compound is a hydroxy substituted aryl azo diphenylamine.

4. A light sensitive material as claimed in Claim 3, wherein the azo compound is a hydroxyphenyl or hydroxynaphthyl azo diphenyl amine.

5. A light sensitive material as claimed in Claim 4, wherein the azo compound is 4-hydroxy phenyl azo diphenylamine.

6. A light sensitive material as claimed in Claim 1, wherein the azo compound is the product obtained by coupling together a diazonium salt and a novolak resin in alkaline medium.

7. A light sensitive material as claimed in Claim 1, substantially as hereinbefore described in Example 1 or 7.

8. A light sensitive material as claimed in Claim 1, substantially as hereinbefore described in any one of Examples 2 to 6 and 8.

9. A process of producing a light sensitive material as claimed in Claim 1 which com-

prises admixing together the diazonium salt and the novolak resin and adding to the mixture a base to form the azo compound by coupling together a part of the diazonium salt and a part of the novolak resin.

10. A process according to Claim 9, substantially as hereinbefore described in Example 1 or 7.

11. A process according to Claim 9 substantially as hereinbefore described in Example 2 or 3.

12. A light sensitive material whenever produced by the process claimed in any one of Claims 9 to 11.

13. A light sensitive plate comprising a support coated with a light sensitive material as claimed in any one of Claims 1 to 8 or Claim 12.

HASELTINE, LAKE & CO.,
Chartered Patent Agents,
Hazlitt House,
28 Southampton Buildings,
Chancery Lane,
London, WC2A 1AT,
and
9 Park Square,
Leeds LS1 2LH.
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



* C L M S *