

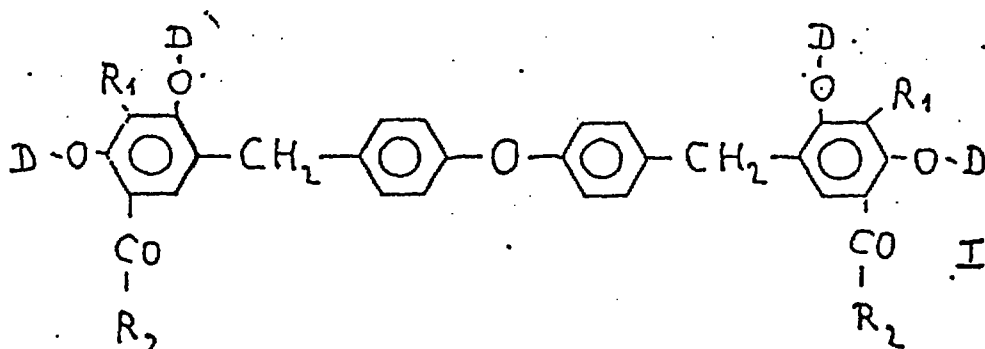
The invention relates to a light-sensitive mixture which essentially contains a 1,2-naphthoquinone-2-diazide-sulfonic acid ester and a resinous binder which is insoluble in water and soluble or at least swellable in aqueous-alkaline solutions. The invention also relates to a reproduction material produced with this mixture.

Light-sensitive compounds based on 1,2-naphthoquinone-diazides are known from DE-C 938,233 corresponding to GB-B 739,654, US-A 3,802,885, DE-A 3,100,077 corresponding to US-A 4,424,270 and EP-A 0,052,788 corresponding to US-A 4,407,926. These compounds are di- or trihydroxy-benzophenones which are partially or completely esterified with 1,2-naphthoquinone-diazide-sulfonic acids. The compounds are mainly used as completely esterified representatives, ie. they no longer contain any free phenolic hydroxyl groups. Compounds of this type have, however, the disadvantage of a light sensitivity which is unduly low for some purposes, or the disadvantage of inadequate solubility in the organic solvents normally used for coating supports such as printing plates. Moreover, in combination with binders such as novolaks, they give layers which, in the unexposed state, are not sufficiently resistant to the commonly used alkaline developer solutions. The layers are attacked to a certain extent during printing in offset printing presses when alcohol-containing fountain solutions are used, and also by petroleum hydrocarbons such as are frequently used during printing for washing off the oleophilic printing ink from the plate.

DE-C 1,118,606 corresponding to GB-C 935,250 has disclosed 1,2-naphthoquinone-diazide-sulfonic acid esters of phenolic compounds such as derivatives of diphenylmethane. For reasons of adhesion, these esters contain at least one free hydroxyl group.

It was the object of the invention to propose a light-sensitive, positive-working mixture which contains a 1,2-naphthoquinone-2-diazide-sulfonic acid ester as the light-sensitive compound and which, in its printing and reproduction technology properties is comparable with the best hitherto known mixtures of this type, but which has a higher chemicals resistance and a better resistance to aqueous-alkaline developer solutions and to the organic solvents used in offset printing.

The achievement of this object starts from a light-sensitive mixture which essentially contains a 1,2-naphthoquinone-2-diazide-4- or -5-sulfonic acid ester as the light-sensitive compound and a resinous binder which is insoluble in water and soluble or at least swellable in aqueous-alkaline solutions, the mixture comprising a naphthoquinone-diazide-sulfonic acid ester of the general formula I



in which

- 25 D is a 1,2-naphthoquinone-2-diazide-4-sulfonyl or 1,2-naphthoquinone-2-diazide-5-sulfonyl radical, R₁ is hydrogen or an -OH group and R₂ is alkyl or substituted or unsubstituted aryl.

Particularly preferably, the mixture contains an ester of the general formula I, in which

R₂ is alkyl having 1 to 10 carbon atoms or substituted or unsubstituted phenyl.

The alkyl radical R₂ can be straight-chain or branched. The aryl radical R₂ is preferably mononuclear and can be substituted by lower alkyl or lower alkoxy groups or halogen atoms. Compounds in which R₂ is an aryl radical, especially a phenyl radical, are preferred. Accordingly, a 1,2-naphthoquinone-2-diazide-sulfonic acid ester is preferably used which is the esterification product obtained from 1 mol of 4,4'-bis-(5-benzoyl-2,3,4-trihydroxybenzyl)-diphenyl ether and 6 mol of 1,2-naphthoquinone-2-diazide-sulfonic acid chloride.

The 1,2-naphthoquinone-diazides contained in the mixture according to the invention are prepared, analogously to known processes, by esterifying the phenolic hydroxyl groups of the parent compounds with 1,2-naphthoquinone-diazide-sulfonic acids or reactive derivatives thereof, for example the sulfonic acid chlorides.

The corresponding parent compounds, for example the 4,4'-bis-(2,3,4-trihydroxy-5-acylbenzyl)-diphenyl ethers, are obtained in good yield by reacting the corresponding 4-acyl-pyrogallols with 4,4'-bis-(methoxymethyl)-diphenyl ether in an inert solvent, for example diglycol dimethyl ether, at 130 - 140°C in the presence of methanesulfonic acid as a condensing agent.

The mixtures according to the invention are distinguished by high light sensitivity and good resistance to overdevelopment.

They also show high resistance to alcohol-containing fountain solutions and to petroleum hydrocarbons.

Due to its relatively large molecule, the compound according to the invention has a low diffusivity. It is therefore also advantageously suitable for copying layers which are employed for certain color test methods in multi-color printing such as, e.g., in color testing by the so-

called surprint method. In this case, a multi-color image is produced by transferring positive color separation images to a common receiving sheet or producing them on the latter, without a separate application of interlayers being necessary.

The concentration of the 1,2-naphthoquinone-diazide-sulfonic acid esters according to the invention in the light-sensitive mixture can vary within relatively wide limits. Preferably, the proportion is 3 to 50 and especially 7 to 25 percent by weight, relative to the content of non-volatile constituents of the light-sensitive mixture.

If desired, the 1,2-naphthoquinone-diazide-sulfonic acid esters can also be used as a mixture with other quinone-diazides or with mixtures of compounds having at least one C-O-C bond, which can be cleaved by acid, together with a compound which forms a strong acid on exposure to light.

The light-sensitive mixtures according to the invention also contain a polymeric, water-insoluble resinous binder which dissolves in the solvents used for the mixture according to the invention and is also soluble or at least swellable in aqueous alkalies.

The novolak condensation resins, proven in many positive reproduction materials based on 1,2-quinone-diazides, have here again proved to be a suitable binder. The novolaks can be additionally modified in a known manner by reaction of a part of their hydroxyl groups with, for example, chloroacetic acid, isocyanates, epoxides or carboxylic acid anhydrides. Polyhydroxyphenyl resins, which are prepared by condensation from phenols and aldehydes or ketones, copolymers of styrene and maleic anhydride, polyvinylphenols or polymers or copolymers of acrylic acid or methacrylic acid are used as further binders which are soluble in alkali or swellable in alkali. Polymers or copolymers of acrylic and/or methacrylic acid, which have been esterified with a phenol, in particular a polyhydric

phenol, are preferred. The nature and quantity of the binder can vary depending on the intended use. Proportions between 90 and 39 and especially between 85 and 55 percent by weight in total solids are preferred.

5 Moreover, numerous other resins can also be used in addition, preferably epoxy resins and vinyl polymers such as polyvinyl acetate, polyacrylates, polyvinyl acetals, polyvinyl ethers, polyvinylpyrrolidones and the copolymers of their underlying monomers as well as hydrogenated or partially hydrogenated colophony derivatives. The most advantageous proportion of these resins depends on the application requirements and on the effect on the development conditions, and it is in general not more than 50 percent by weight, preferably about 2 to 35 percent by weight, of the binder employed. For special requirements, such as flexibility, adhesion, gloss and coloration, the light-sensitive mixture can in addition also contain small quantities of substances such as polyglycols, cellulose derivatives such as ethylcellulose, wetting agents, dyes, adhesion promoters and finely disperse pigments and, if required, UV absorbers.

Moreover, for the color change after exposure, small quantities of radiation-sensitive components, which form or release preferably strong acids on exposure and cause a color change in a secondary reaction with a suitable dye, can also be added to the light-sensitive mixture. Examples of such radiation-sensitive components are 1,2-naphthoquinone-diazide-4-sulfonic acid chloride, halogenomethyl-s-triazines substituted by a chromophore or diazonium compounds in the form of their salts with complex acids such as fluoboric acid or hexafluorophosphoric acid.

The invention also relates to a light-sensitive reproduction material composed of a support and a light-sensitive layer which contains the mixture according to the invention.

- For coating a suitable support, the mixture is in general dissolved in a solvent or solvent mixture. The choice of solvent should be matched to the intended coating process, to the layer thickness and to the drying conditions. Suitable solvents are ketones such as methyl ethyl ketone, chlorinated hydrocarbons such as trichloroethylene and 1,1,1-trichloroethane, alcohols such as n-propanol, ethers such as tetrahydrofuran, alcohol ethers such as ethylene glycol monoalkyl ethers, and esters such as butyl acetate.
- 10 For special purposes, solvent mixtures can in addition also contain further solvents such as acetonitrile, dioxane or dimethylformamide. In principle, all solvents can be used which do not irreversibly react with the layer components. Partial ethers of glycols, in particular ethylene glycol
- 15 monomethyl ether and propylene glycol methyl ether, or the corresponding monoacetates are particularly preferred.

- The supports used for layer thicknesses of less than about 10 μm are in most cases metals. For offset printing plates, it is possible to use: bright-rolled, mechanically or
- 20 electrochemically grained and, if appropriate, anodically oxidized aluminum which can additionally also have been chemically pretreated, for example with polyvinylphosphonic acid, silicates, phosphates, hexafluorozirconates or with hydrolyzed tetraethyl orthosilicate.
- 25 The coating of the support is carried out in the known manner by spin-coating, spraying, dipping, rolling by means of slot dies, doctor blades or by coater application. Exposure is carried out with the light sources conventional in technology.
- 30 For developing, aqueous-alkaline solutions of graded alkalinity are used, which preferably have a pH in the range of 10 - 14 and can also contain small quantities of organic solvents or wetting agents.

- For producing a printing form, the light-sensitive material is imagewise exposed under a positive original and
- 35

then developed by means of an aqueous-alkaline developer. For the imagewise exposure, the usual types of copying apparatus, such as tubular lamps, pulsed xenon lamps, metal halide-doped mercury vapor lamps or carbon arc lamps
5 can be used.

The light-sensitive mixtures are preferably used in the production of reproduction materials such as printing forms, ie. especially forms for offset printing, autotype gravure printing and screen printing, or in photoresists
10 and so-called dry resists.

The printing plates produced with the use of the 1,2-naphthoquinone-diazides according to the invention have a high light sensitivity in practice and an improved resistance to alkaline developers and those organic solvents
15 which are normally used during copying work or during the printing process on the printing presses. The 1,2-naphthoquinone-diazides themselves are distinguished by good solubility in the usual solvents, by a pronounced oleophilic character and by good compatibility with the other constituents of the copying layer.
20

The invention is explained in more detail by reference of the examples which follow, wherein parts by weight (p.b.w.) and parts by volume (p.b.v.) are in the same relationship as the g and cm³. Unless otherwise stated, percentages
25 are percent by weight.

Example 1:

An electrochemically grained and anodically oxidized aluminum plate having an oxide weight of 3 g/m² was coated with a solution of
30 1.60 p.b.w. of the esterification product obtained from 1 mol of 4,4'-bis-(5-benzoyl-2,3,4-trihydroxybenzyl)-diphenyl ether and 6 mol of 1,2-naphthoquinone-2-diazide-5-sulfonic acid chloride,

7.00 p.b.w. of a cresol/formaldehyde novolak having a melting range of 127-145°C,

0.06 p.b.w. of 2,4-bis-(trichloromethyl)-6-p-stilbenyl-s-triazine and

5 0.07 p.b.w. of crystal violet in

40 p.b.v. of ethylene glycol monomethyl ether and

60 p.b.v. of tetrahydrofuran.

Before the application of the light-sensitive layer, the anodized aluminum support had been treated with an aqueous
10 solution of polyvinylphosphonic acid, as is described in DE-C 1,621,478 corresponding to US-A 4,153,461.

The light-sensitive material thus obtained, having a weight of the light-sensitive layer of about 2.3 g/m², was exposed imagewise under a transparent positive original and
15 then developed with a 4% aqueous solution of sodium metasilicate.

The areas of the copying layer struck by light were removed by the development, and the unexposed image areas remained on the support, so that a printing stencil corresponding
20 to the original was obtained. The printing form thus produced gave about 150,000 perfect prints in an offset printing press. The printing stencil was distinguished by outstanding resistance to overdevelopment and adhesion to the substrate.

25 In order to extend the print run and to consolidate the printing stencil, the printing form thus produced can also be subjected to a heat treatment. For this purpose, the printing form, dried after development, was heated in a baking oven for 5 minutes to 230°C.

30 The heating of the printing form resulted in a consolidation of the printing stencil, and the layer became resistant to chemicals and hence insoluble in organic solvents such as acetone, alcohols, dimethylformamide, toluene or xylene. About 400,000 perfect prints were obtained in an
35 offset printing press.

The 1,2-naphthoquinone-diazide used can also be employed with advantage as a photosensitizer in layers such as are used in practice for color test methods for checking color separation films. Typical compositions of appropriate light-sensitive coating solutions are indicated, for example, in EP-A 0,179,274 corresponding to US-A 4,659,642.

In the examples which follow, further coating solutions are indicated, with which results similar to those in this example were obtained. Unless otherwise stated, the support, preparation and processing of the printing plates obtained with these solutions correspond to the data given above.

Example 2

Coating solution:

- 15 1.60 p.b.w. of the esterification product obtained from
1 mol. of 4,4'-bis-(5-octanoyl-2,3,4-trihydroxy-
benzyl)-diphenyl ether and 6 mol of 1,2-naph-
thoquinone-2-diazide-5-sulfonic acid chloride,
- 7.00 p.b.w. of a cresol/formaldehyde novolak having a
20 melting range of 127 - 145°C,
- 0.06 p.b.w. of 2,4-bis-(trichloromethyl)-6-p-stilbenyl-
s-triazine and
- 0.07 p.b.w. of crystal violet in
- 40 p.b.v. of ethylene glycol monomethyl ether and
- 25 60 p.b.v. of tetrahydrofuran.

Example 3

- 1.80 p.b.w. of the esterification product obtained from
1 mol of 4,4'-bis-(5-benzoyl-2,3,4-trihydroxy-
benzyl)-diphenyl ether and 6 mol of 1,2-
30 naphthoquinone-2-diazide-4-sulfonic acid
chloride,
- 7.00 p.b.w. of a cresol/formaldehyde novolak having a
melting range of 127 - 145°C,

0.06 p.b.w. of 2,4-bis-(trichloromethyl)-6-p-stilbenyl-
s-triazine and
0.07 p.b.w. of crystal violet in
40 p.b.v. of ethylene glycol monomethyl ether and
5 60 p.b.v. of tetrahydrofuran.

Example 4

1.80 p.b.w. of the esterification product obtained from
1 mol of 4,4'-bis-(5-acetyl-2,3,4-trihydroxy-
benzyl)-diphenyl ether and 6 mol of 1,2-naph-
10 thoquinone-2-diazide-5-sulfonic acid chloride,
7.20 p.b.w. of a cresol/formaldehyde novolak having a
melting range of 127 - 145°C,
0.06 p.b.w. of 2,4-bis(trichloromethyl)-6-p-stilbenyl-
s-triazine,
15 0.07 p.b.w. of crystal violet in
40 p.b.v. of ethylene glycol monomethyl ether and
60 p.b.v. of tetrahydrofuran.

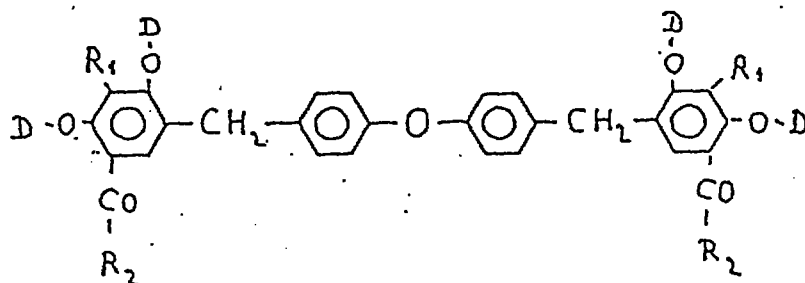
Example 5

1.60 p.b.w. of the esterification product obtained from
20 1 mol of 4,4'-bis-(5-benzoyl-2,4-dihydroxy-
benzyl)-diphenyl ether and 4 mol of 1,2-naph-
thoquinone-2-diazide-5-sulfonic acid chloride,
6.80 p.b.w. of a cresol/formaldehyde novolak having a
melting range of 127 - 145°C,
25 0.06 p.b.w. of 2,4-bis(trichloromethyl)-6-p-stilbenyl-
s-triazine,
0.07 p.b.w. of crystal violet in
40 p.b.v. of ethylene glycol monomethyl ether and
60 p.b.v. of tetrahydrofuran.



Patent Claims

1. A light-sensitive mixture which essentially comprises a 1,2-naphthoquinone-2-diazide-4- or -5-sulfonic acid ester and a resinous binder which is insoluble in water and soluble or at least swellable in aqueous-alkaline solutions, characterized in that it comprises a naphthoquinone-diazide-sulfonic acid ester of the formula I



in which

D is a 1,2-naphthoquinone-2-diazide-4-sulfonyl or 1,2-naphthoquinone-2-diazide-5-sulfonyl radical,
R₁ is hydrogen or an -OD group and
R₂ is alkyl or substituted or unsubstituted aryl.

2. A mixture as claimed in claim 1, wherein, in the formula I,
R₂ is alkyl having 1 to 10 carbon atoms or substituted or unsubstituted phenyl.
3. A mixture as claimed in claim 1, wherein the 1,2-naphthoquinone-2-diazide-sulfonic acid ester is the esterification product obtained from 1 mol of 4,4'-bis-(5-benzoyl-2,3,4-trihydroxybenzyl)-diphenyl ether and 6 mol of 1,2-naphthoquinone-2-diazide-5-sulfonic acid chloride.



4. A mixture as claimed in claim 1, wherein, relative to its content of non-volatile constituents, 3 to 50 percent by weight of compounds of the formula I are contained.
5. A mixture as claimed in claim 1, wherein the binder is a novolak condensation resin.
6. A mixture as claimed in claim 1, wherein the binder is a polymer or copolymer of acrylic and/or methacrylic acid esterified with a polyhydric phenol.
7. A light-sensitive reproduction material, comprised of a support and a light-sensitive layer comprising a mixture as claimed in any of claims 1 to 6.