

### Description

The invention relates to desensitised forms of explosive organic diazo or azido compounds for radiation-sensitive compositions.

Organic diazo and azido compounds - that is to say compounds which contain at least one diazo group consisting of two nitrogen atoms or at least one azido group consisting of three nitrogen atoms in the molecule - in general fulfil at least one of the criteria of the Explosives Law of the Federal Republic of Germany. Although most of these substances are neither intended nor suitable as explosives in the actual sense, as "explosive substances" they are subject to the provisions of this law during preparation, handling and transportation.

This particularly applies to a number of certain diazo or azido compounds, such as are used in large amounts in the preparation of radiation-sensitive compositions. Radiation-sensitive compositions which contain diazo or azido compounds serve to produce positive or negative relief images and are used in the production of printing plates or as photo-resists in the manufacture of semiconductors. In this context, corresponding substrates are coated with the radiation-sensitive materials, exposed image-wise to actinic radiation and subjected to a development operation, the positive or negative relief structures then being obtained on the substrate.

Mixtures which, in addition to an alkali-soluble polymeric binder, which in general consists of a condensation product of the novolak resin type, contain diazo compounds of the o-quinone diazide type as radiation-sensitive components have been used for a long time for printing plates and positive photo-resists. The latter compounds are usually esterification products of 1-oxo-2-diazo-naphthoquinone-4- or -5-sulfonic acid with in most cases low-molecular components carrying phenolic hydroxyl groups, such as are described, for example, in German Patent Specification 938,233 and numerous subsequent publications, as well as German Patent Application 3,220,816. One of the compounds of this type - these were previously frequently designated naphthoquinone diazide sulfonyl derivatives - used most often at present is the esterification product of naphthoquinone diazide 5-sulfochloride with trihydroxybenzophenone.

Radiation-sensitive compositions for negative photo-resists consist very frequently of partially cyclised polyisoprene and contain aromatic azido compounds as crosslinking agents activated by radiation. Such compounds are described, for example, in U.S. Patent Specifications 2,852,379 and 2,940,853 and in German Patent Application 3,234,301. One of the most frequently used crosslinking agents activated by radiation for negative photo-resists based on polyisoprene is the bis-azido compound 2,6-bis-[(4-azidophenyl)methylene]-4-methylcyclohexanone.

Radiation-sensitive compositions for producing both positive and negative relief images are used as solutions in organic solvents, which are prepared by dissolving the pure components in the solvents.

This preparation of the radiation-sensitive compositions has the disadvantage that it is necessary here to handle the pure diazo or azido compounds which cause the sensitivity to radiation. Since these compounds are regarded as explosive substances, their preparation, isolation, storage and transportation and their further processing in the pure form can be effected only with very

expensive safety measures and using relatively small amounts.

In view of the current widespread industrial application of these substances, it is therefore desirable to provide these compounds in a stabilised form, so that they are no longer explosive and can be handled without danger.

From the field of explosives, it is known that the sensitivity of explosive substances can be reduced by adding desensitising agents, such as, for example, water or organic substances, such as, for example, oil, paraffin or wax. Kieselguhr is customary as the sole mineral desensitising agent specifically only for liquid nitro glycerin, this being absorbed into the hollow cavities of the porous crystalline structure of the kieselguhr.

However, these methods are unsuitable for stabilising the above diazo or azido compounds. Since the properties of radiation-sensitive compositions, for example their sensitivity to radiation, dissolving power and adhesion, depend decisively on the purity of their individual components, these compounds must also be in a highly pure form. Quantitative removal of additives, such as are known for desensitising explosives, from these diazo or azido compounds would, however, be impossible to achieve or be possible only with a considerable separation expenditure. Moreover, mixing with the desensitising agents would have to be carried out with these methods, which in turn would constitute handling of the pure explosive compounds.

German Offenlegungsschrift 3,126,015 proposes the stabilisation of explosive intermediates, containing several nitrogen atoms, for pharmaceutical active substances in the form of their solutions in organic solvents. Application of this method to the present problem would be unfavourable - independently of the question of whether desensitising could likewise thereby be achieved in the case of the present problem - inasmuch as the large number of explosive diazo and azido compounds which are at present customary as sensitisers or crosslinking agents activated by radiation for the preparation of radiation-

sensitive compositions and the large number of radiation-sensitive mixtures used for the most diverse application purposes frequently require very different solvents. The most diverse solutions would therefore have to be kept ready for the particular different intended use.

German Offenlegungsschrift 3,100,077 proposes the elimination of the explosiveness of naphthoquinone diazide sulfonyl derivatives by using, for photosensitive compositions, only those derivatives which are obtained by esterification of naphthoquinone diazide sulfochloride with a mixture of a low-molecular compound and a polymeric compound. The naphthoquinone diazide sulfochloride should preferably react with the low-molecular component to give the corresponding esterification product. This is then isolated as a mixture with the polymeric compound.

This method is unfavourable inasmuch as the large number of radiation-sensitive compositions with a positive action at present used for the most diverse application purposes frequently contain the most diverse polymeric compounds, besides the naphthoquinone diazide sulfonyl derivative.

A large number of mixtures with the most diverse polymeric compounds would thus have to be prepared separately for the particular intended use.

A generally applicable method for stabilising diazo and azido compounds such as are at present required for the preparation of positively operating and negatively operating radiation-sensitive compositions was not to be discovered from the prior art.

There was thus the object of discovering desensitised forms of explosive organic diazo or azido compounds which are suitable for the preparation of radiation-sensitive compositions.

This object has been achieved by the present invention.

It has been found, surprisingly, that desensitised forms of explosive organic diazo or azido compounds which contain insoluble pulverulent inorganic absorbents as desensitising agents show no explosiveness at all and

are therefore outstandingly suitable for the preparation of radiation-sensitive compositions.

The invention thus relates to desensitised forms of explosive organic diazo or azido compounds for use in radiation-sensitive compositions which contain insoluble pulverulent inorganic absorbents as desensitising agents.

The invention furthermore relates to a process for the preparation of desensitised forms of organic diazo or azido compounds for use in radiation-sensitive compositions. These are deposited here by precipitation from their solutions in the presence of insoluble pulverulent inorganic absorbents as desensitising agents.

The invention likewise relates to a process for the preparation of radiation-sensitive compositions containing organic diazo or azido compounds, the desensitised forms thereof being mixed in solution with the other components of the radiation-sensitive composition. These diazo or azido compounds desensitised with insoluble pulverulent inorganic absorbents are here dissolved in the solvent and the insoluble inorganic material is separated off before or after mixing with the other components of the radiation-sensitive composition.

The invention moreover relates to the use of diazo or azido compounds desensitised by insoluble pulverulent inorganic absorbents for the preparation of radiation-sensitive compositions.

Suitable desensitising agents according to the invention for explosive organic diazo or azido compounds are all the pulverulent inorganic absorbents which are insoluble in organic solvents. These can be, for example, clays, bleaching earths, aluminium oxide, kieselguhr, silica gel and similar materials. Kieselguhr, silica gel and aluminium oxide are preferred. The particle size is as a rule between 0.015 and 0.5 mm, but is not critical.

The desensitised form contains these inorganic absorbents in an amount of 5 - 50% by weight, preferably 10 - 30% by weight, based on the organic diazo or azido compound.

According to the invention, all the organic diazo or azido compounds customary for the preparation of radiation-sensitive compositions can be converted into a desensitised form, that is to say a form which is no longer explosive, with the materials mentioned.

Diazo compounds are to be understood as meaning, for example, those naphthalene diazide sulfonyl derivatives which are obtained by esterification of 1-oxo-2-diazo-naphthalene-4- or -5-sulfonic acid or -sulfonyl halide with low-molecular phenol components carrying phenolic hydroxyl groups. These compounds are used as radiation-sensitive components in positively operating photosensitive compositions based on alkali-soluble condensation products of the novolak resin type. Derivatives which are preferred for conversion, according to the invention, into desensitised forms are the esterification products of 1-oxo-2-diazo-naphthalene-5-sulfonic acid with derivatives of benzene, benzoic acid, benzoic acid esters, benzoic acid amides, aryl alkyl ketones and benzophenone which carry up to 3 hydroxyl groups, and the isomer forms of cresol. Esterification products with phloroglucinol, 2,4-dihydroxybenzophenone, 2,3,4-trihydroxybenzophenone, gallic acid esters, trihydroxyphenyl alkyl ketones and p-cresol are particularly preferred.

Azido compounds are those which contain one or more azido groups bonded to an aromatic ring in the molecule. They are used as crosslinking agents activated by radiation in negatively operating radiation-sensitive compositions, such as are used for producing relief structures, for example as negative photo-resists based on cyclised isoprene. The compound 2,6-bis-[(4-azidophenyl)-methylene]-4-methylcyclohexanone is particularly preferred for conversion, according to the invention, into a desensitised form.

The process according to the invention for the preparation of desensitised forms of those diazo and azido compounds which are explosive in the pure form is carried out by a procedure in which these are deposited from their solutions by precipitation in the presence of the insoluble

pulverulent inorganic absorbents mentioned, which have been added to the solutions or the precipitating agent before the precipitation. The diazo or azido compound is here first prepared in a manner which is known per se, as described in the publications quoted by way of example above, but without being isolated in the pure, dry and thus explosive form. Rather, the still water-moist or solvent-moist products are dissolved in one of the usual solvents, one of the inorganic adsorbents according to the invention which act as desensitising agents is now added and the diazo or azido compound is deposited, in the form desensitised by the adsorbent, by precipitation with one of the precipitating agents described as suitable. The deposition of the products in the desensitised form can also be effected by adding the solutions of the diazo or azido compounds to a mixture of desensitising agent and precipitating agent. The particular product can then be separated off by filtration and dried without problems.

This process is very easy to carry out and is not critical, within a wide range, in respect of the amount of desensitising agent added. Effective desensitisation is achieved if the inorganic adsorbents are added in an amount of 5 - 50% by weight, based on the amount of diazo or azido compound. The most advantageous results are achieved with an amount of 10 - 30% by weight.

In contrast to the corresponding pure compounds, the diazo and azido compounds converted into a desensitised form by the process according to the invention no longer show any explosiveness at all. This is demonstrated by certain tests in accordance with the provisions of the Explosives Law (see Ullmann, Enzyklopadie der technischen Chemie [Encyclopaedia of Industrial Chemistry], Volume 21, pages 649 - 650 and page 652).

According to these provisions, substances are classified as explosive if

- a) an explosion takes place in the falling hammer test at an impact energy of 40 joules (10 kg fall weight, 40 cm fall height) or less, or
- b) an explosion occurs in the steel shell test at a nozzle

diameter of 2 mm or more, or

c) an explosion, ignition or decrepitation occurs in the friction test under a stud load of 360 N or less.

5 The forms, desensitised according to the invention, of organic diazo or azido compounds fulfil none of the above criteria of explosiveness. They can thus be handled without problems and in any desired amount, as conventional chemicals.

10 The forms, desensitised according to the present invention, of organic diazo or azido compounds are outstandingly suitable for the preparation of radiation-sensitive compositions such as are used for obtaining positive or negative relief images in the production of printing plates or as photo-resists in the manufacture  
15 of semiconductors. In view of the high demand for and consumption of radiation-sensitive compositions, their problem-free handling, because of the absence of any danger of explosion, makes them particularly useful for industrial application.

20 The process according to the invention for the preparation of radiation-sensitive compositions containing organic diazo or azido compounds is carried out by a procedure in which the components are mixed in an organic solvent in the customary manner, according to the formulations which are known per se, the diazo or azido compounds desensitised with insoluble, pulverulent inorganic  
25 adsorbents first being dissolved in the solvent and the insoluble inorganic material then being separated off, before or after mixing with the other components of the radiation-sensitive composition. This separation can be  
30 effected by filtration. The process for the preparation of radiation-sensitive compositions is particularly advantageous, since the filtration of the finished solutions, which is in any case necessary, is facilitated by the presence of the insoluble inorganic adsorbents and the  
35 customary addition of filtration auxiliaries can therefore be dispensed with.

Solutions which are identical in all respects to those prepared using the pure explosive diazo or azido

compounds and with which radiation-sensitive coatings of corresponding quality can be produced are obtained in this manner.

Example 1:

- 5 Preparation of the esterification product of 1-oxo-2-diazo-naphthalene-5-sulfonyl chloride and 2,3,4-trihydroxybenzophenone, desensitised with kieselguhr

The esterification product is prepared in accordance with the statements in German Patent Specification  
10 938,233, but without the resulting water-moist crude product being isolated in the pure, dry form.

10 g of this crude product are dissolved in 40 ml of acetone at room temperature. This solution is slowly added to an intensively stirred suspension of 1 g of kieselguhr in 165 ml of 1% hydrochloric acid. The esterification product is thereby precipitated and is isolated in the form desensitised with kieselguhr by filtration. The product contains 10.2% by weight of kieselguhr, based on the esterification product used.

- 20 The following have been prepared analogously:

the esterification product of 1-oxo-2-diazo-naphthalene-5-sulfonyl chloride and 2,4-dihydroxybenzophenone, desensitised with kieselguhr

the esterification product of 1-oxo-2-diazo-naphthalene-5-sulfonyl chloride and phloroglucinol, desensitised with kieselguhr

25 the esterification product of 1-oxo-2-diazo-naphthalene-5-sulfonyl chloride and p-cresol, desensitised with kieselguhr and

30 the esterification product of 1-oxo-2-diazo-naphthalene-5-sulfonyl chloride and ethyl gallate, desensitised with kieselguhr.

Example 2:

Esterification products stabilised with aluminium oxide

- 35 The procedure followed is as in Example 1, with the difference that aluminium oxide (0.2 g/g of dissolved substance) is used instead of kieselguhr.

Example 3:

Esterification products stabilised with silica gel

The procedure followed is as in Example 1, with the difference that silica gel (0.1 g/g of dissolved substance) is used instead of kieselguhr.

Example 4:

- 5 Preparation of a bis-azido compound stabilised with kieselguhr

10 10 g of crude solvent-moist or water-moist 2,6-bis[(4-azidophenyl)methylene]-4-methylcyclohexanone, which has been prepared according to U.S. Patent 2,940,853, are dissolved in 100 ml of dimethylformamide at 50°C, with stirring. The resulting solution is allowed to run slowly into an intensively stirred suspension of 2 g of kieselguhr in a mixture of 700 ml of water and 12 ml of concentrated hydrochloric acid. The bis-azido compound thereby  
15 precipitates in a form desensitised with kieselguhr and is isolated by filtration. Content of kieselguhr: 16%.

To test the explosiveness, the substances were investigated by the falling hammer test, the steel shell test and the friction test in accordance with the provisions of the Explosives Law. None of the desensitised  
20 forms responded to these tests, whilst the pure substances alone already showed a clearly positive reaction in the falling hammer test.

Example 5:

- 25 Preparation of a photosensitive solution for the production of positive relief images

38.8 g of desensitised product according to Example 1 are introduced into 340 ml of ethoxyethyl acetate at room temperature and the mixture is stirred at room  
30 temperature for 30 minutes. The undissolved constituents are then filtered off.

125 g of a cresol/formaldehyde resin (average molecular weight 5500) are dissolved in the filtrate at room temperature, with further stirring. After renewed  
35 filtration via a pressure filter, the photosensitive solution is ready for use.

The photosensitive solution is applied by centrifugal coating to silicon platelets which have been thermally oxidised on the surface, the solvent is removed in

vacuo and the resulting photosensitive coating is exposed image-wise and developed with an alkaline developer solution. The properties of the photosensitive coating thus obtained and of the positive relief images produced by  
5 exposure and development completely correspond (in respect of photosensitivity, dissolving power and adhesion) to those which are obtained when 35 g of pure, dried esterification product are used for the preparation of the photosensitive solution instead of the stabilised derivative.

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Patent claims

1. Desensitised forms of explosive organic diazo or azido compounds for use in radiation-sensitive compositions, characterised in that these contain insoluble, pulverulent inorganic absorbents (sic) as desensitising agents.
2. Desensitised forms according to Claim 1, characterised in that these contain 5 - 50% by weight, preferably 10 - 30% by weight, of desensitising agents, based on the organic diazo or azido compounds.
3. Process for the preparation of desensitised forms of organic diazo or azido compounds for use in radiation-sensitive compositions, characterised in that these are deposited from their solutions in the presence of insoluble, pulverulent inorganic adsorbents as desensitising agents.
4. Process according to Claim 3, characterised in that 5 - 50% by weight, preferably 10 - 30% by weight, based on the organic diazo or azido compound, of insoluble, pulverulent inorganic adsorbents is added.
5. Use of insoluble, pulverulent inorganic adsorbents for desensitising explosive organic diazo or azido compounds in the preparation of radiation-sensitive compositions.
6. Process for the preparation of radiation-sensitive compositions which contain organic diazo or azido compounds, the components being mixed in an organic solvent, characterised in that diazo or azido compounds desensitised with insoluble, pulverulent inorganic adsorbents are



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dissolved in the solvent and the insoluble inorganic material is removed before or after mixing with the other components of the radiation-sensitive composition.

7. - Use of diazo or azido compounds desensitised by insoluble, pulverulent inorganic adsorbents for the preparation of radiation-sensitive compositions.

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As printed

### Revendications

1. Formes phlegmatisées de composés organiques explosibles du type diazoïque ou azide conçues pour l'utilisation dans des compositions sensibles aux rayonnements, caractérisées en ce qu'elles contiennent en tant qu'agents phlegmatissants des adsorbants minéraux pulvérulents insolubles.

2. Formes phlegmatisées selon la revendication 1, caractérisées en ce qu'elles contiennent de 5 à 50, de préférence de 10 à 30% en poids, d'agent phlegmatissant par rapport aux composés organiques du type diazoïque ou azide.

3. Procédé de préparation de formes phlegmatisées de composés organiques du type diazoïque ou azide, conçues pour l'utilisation dans des compositions sensibles aux rayonnements, caractérisé en ce que l'on sépare ces composés de leurs solutions en présence d'agents adsorbants minéraux pulvérulents insolubles qui servent d'agents phlegmatissants.

4. Procédé selon la revendication 3, caractérisé en ce que l'on ajoute de 5 à 50, de préférence de 10 à 30% en poids d'adsorbants minéraux pulvérulents insolubles par rapport au composé organique du type diazoïque ou azide.

5. Utilisation d'adsorbants minéraux pulvérulents insolubles pour la phlegmatisation de composés organiques explosibles du type diazoïque ou azide, à la préparation de compositions sensibles aux rayonnements.

6. Procédé de préparation de compositions sensibles aux rayonnements contenant des composés organiques du type diazoïque ou azide, dans lequel on mélange les composants dans un

solvant organique, caractérisé en ce que l'on dissout dans le solvant les diazoïques ou azides phlegmatisés par des adsorbants minéraux pulvérulents insolubles et on sépare la matière minérale insoluble avant ou après le mélange avec les autres composants de la composition sensible aux rayonnements.

7. Utilisation de composés du type diazoïque ou azide, phlegmatisés par des adsorbants minéraux pulvérulents insolubles, pour la préparation de compositions sensibles aux rayonnements.

### Claims

1. Desensitised forms of explosive organic diazo or azido compounds, characterised in that these contain insoluble, pulverulent inorganic adsorbents as desensitising agents.

2. Desensitised forms according to Claim 1, characterised in that these contain 5-50% by weight, preferably 10-30% by weight, of desensitising agents, based on the organic diazo or azido compounds.

3. Process for the preparation of desensitised forms of organic diazo or azido compounds, characterised in that these are deposited from their solutions in the presence of insoluble, pulverulent inorganic adsorbents as desensitising agents.

4. Process according to Claim 3, characterised in that 5-50% by weight, preferably 10-30% by weight, based on the organic diazo or azido compound, of insoluble, pulverulent inorganic adsorbents is added.

5. Use of insoluble, pulverulent inorganic adsorbents for desensitising explosive organic diazo or azido compounds.

6. Process for the preparation of radiation-sensitive compositions which contain organic diazo or azido compounds, the components being mixed in an organic solvent, characterised in that diazo or azido compounds desensitised with insoluble, pulverulent inorganic adsorbents are dissolved in the solvent and the insoluble inorganic material is removed before or after mixing with the other components of the radiation-sensitive composition.

7. Use of diazo or azido compounds desensitised by insoluble, pulverulent inorganic adsorbents for the preparation of radiation-sensitive compositions.