CONVENTION APPLICATION FOR A PATENT

61,740

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We hereby apply for the grant of a Patent for an invention entitled:

PRODUCTION OF PURE 1-NITROANTHRAQUINONE

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered

P 22,53,276.9

for a patent or similar protection made in Germany on

31st October, 1972,

Our address for service is Messrs. F. R. Waters & Sons, Patent Attorneys,

50 Russell Street, Melbourne, Victoria, Australia.

Dated this 23rd day of October, 1973

BASF AKTIENGESELLSCHAFT.

by

John [Signature]
COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

61740

In support of the Convention Application made by **BASE Aktiengesellschaft** Badische Anilin & Soda-Fabrik Aktiengesellschaft, a Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany; (hereinafter referred to as the applicant) for a Patent for an invention entitled,

**PRODUCTION OF PURE 1-NITROANTHRATHRINONE**

We, Dr. DIETMAR WITTENBERG and Dr. HARTMUT WURZLER, citizens of the Federal Republic of Germany; residing, respectively, at 25 Rheindammstrasse, 6800 Mannheim; and 76 Hohezollernstrasse, 6700 Ludwigshafen; Federal Republic of Germany;
do solemnly and sincerely declare as follows:

1. That authorized by the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in the Federal Republic of Germany under No. 2253276.9 on the 31st day of October 1972 by **Badische Anilin- & Soda-Fabrik Aktiengesellschaft**.

3. **KARL-HEINZ BANTEL, and HEINZ EILINGSFELD**, citizens of the Federal Republic of Germany, residing, respectively, at 17 Loderer Ring, 6700 Ludwigshafen; and 9a Pferdstrasse, 6710 Frankenthal; Federal Republic of Germany;

are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of **KARL-HEINZ BANTEL, and HEINZ EILINGSFELD**

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at 6700 Ludwigshafen, Federal Republic of Germany this 16th day of October 1973.
Application Number: 61740/73
Lodged: 24-10-73

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Related Art:

Name of Applicant: BASF AKTIENGESELLSCHAFT,

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Complete Specification for the invention entitled:

PRODUCTION OF PURE 1-NITROANTIPRAQUINONE.

The following statement is a full description of this invention, including the best method of performing it known to us.
The present invention relates to a process for the production of pure 1-nitroanthraquinone from nitroanthraquinone mixtures.

In the nitration of anthraquinone a mixture of various nitro compounds is always obtained. Mononitration cannot be carried out uniformly and 1-nitroanthraquinone can only be obtained contaminated with 2-nitroanthraquinone and various dinitro compounds. When nitration is carried out in concentrated sulfuric acid products are obtained as a rule which contain from about 60 to 75% of 1-nitroanthraquinone.

Since the tinctorial properties of dyes prepared from derivatives of 1-nitroanthraquinone are often adversely affected by impurities present in the starting material, it is desirable to start from 1-nitroanthraquinone which is as pure as possible.
It is an object of the present invention to obtain pure 1-nitroanthraquinone from nitration products of anthraquinone obtained by prior art nitration methods.

We have now found that 1-nitroanthraquinone is obtained from nitroanthraquinone mixtures in a good yield and excellent purity by treating the nitroanthraquinone mixture containing 1-nitroanthraquinone in an aprotic polar organic solvent (which may contain up to 10% by weight of water) in the presence of a catalytic amount of an initiator with a compound which has at least one -CH₂- group which is activated by one or more carbonyl groups.

Undesirable byproducts from the nitration are converted by this treatment into readily soluble compounds and may therefore be separated from the unreacted 1-nitroanthraquinone. It is surprising that the reaction is limited practically exclusively to the dinitroanthraquinones. Mononitroanthraquinones are attacked to only a very slight extent if at all. When a suitable solvent is used, any small amounts of 2-nitroanthraquinone present in the nitroanthraquinone mixture remain in the mother liquor, so that a very pure 1-nitroanthraquinone can be isolated in a high yield according to this process.

Nitroanthraquinone mixtures which can be subjected to the purification process according to this invention may be mixtures obtainable according to conventional nitration methods and which as a rule contain only up to 75% by weight of 1-nitroanthraquinone. Naturally, mixtures having a higher content of 1-nitroanthraquinone may be purified more easily.
Suitable initiators to be used according to the invention include compounds yielding nitrite, thiocyanate, iodide, bromide, chloride, fluoride, phenolate or alcoholate ions under the reaction conditions.

Examples of compounds which yield the abovementioned ions as initiators under the reaction conditions are alkali metal nitrites or alkaline earth metal nitrites such as sodium, potassium, magnesium or calcium nitrite, alkali metal thiocyanates such as sodium or potassium thiocyanate, alkali metal halides and alkaline earth metal halides such as sodium, potassium, lithium, magnesium or calcium iodide, sodium, potassium, lithium, magnesium, strontium or calcium bromide, sodium, potassium, lithium, magnesium or calcium chloride, sodium, potassium, lithium, or magnesium fluoride, alkali metal phenolates, alkaline earth metal phenolates, alkali metal alcoholates or alkaline earth metal alcoholates such as sodium, potassium, lithium, magnesium or calcium phenolate, sodium, potassium, magnesium or calcium methylate, ethylate, propylate or butylate or phenol.

The compounds which yield the initiators are added to the reaction mixture in a catalytic amount.

A catalytic amount in the context of the present invention means from 0.1 to 10% by weight based on the nitroanthraquinone mixture.

The nitrite ion \( \text{NO}_2^- \) is particularly preferred as the initiator.

Suitable compounds containing \(-\text{CH}_2-\) groups (which are hereinafter referred to as methylene-active compounds and
whose -CH₂- group is activated by one or more -CO- groups) are aliphatic, cycloaliphatic, araliphatic and also heterocyclic unsubstituted or substituted ketones, \( \beta \)-ketocarboxylic esters, or amides, \( \beta \)-carbonyl compounds and cyclic carbonamides. Specific examples of methylene-active compounds are methyl ethyl ketone, diethyl ketone, methyl propyl ketone, ethyl propyl ketone, dipropyl ketone, methyl butyl ketone, ethyl butyl ketone, propyl butyl ketone, dibutyl ketone, isopropyl ethyl ketone, isopropyl propyl ketone, cyclopentanone, cyclohexanone, cyclooctanone, acetylacetone, benzoylacetone, ethyl acetoacetate, acetoacetanides such as the anilide, malonic esters, cyanoacetates, acetophenone, propiophenone and 3-methyl-1-phenylpyrazolone-5.

Liquid methylene-active compounds which are manufactured industrially are preferred for economic and technical reasons. Methyl ethyl ketone, diethyl ketone, cyclopentanone, cyclohexanone, ethyl acetoacetate, propiophenone, malonates and mixtures of the same are particularly preferred because of their particularly high activity in the treatment of nitroanthraquinone mixtures. A very pure 1-nitroanthraquinone in which dinitroanthraquinone can no longer be detected by thin layer chromatography is obtained by means of the said compounds. 1-aminoanthraquinone obtained from such 1-nitroanthraquinone fulfills all the requirements placed on precursors which are to serve for the production of dyes whose tinctorial properties are very sensitive to the presence of impurities.

The amount of methylene-active compound which is necessary for the process according to the invention depends on the type
and above all on the amount of the impurities. The optimum amount of methylene-active compound may be determined in a few simple experiments, the treated product being investigated by thin layer chromatography. The amount of methylene-active compound (or mixture of the same) used is generally from 0.3 to 3 moles and preferably from 0.5 to 2 moles per mole of dinitro compounds in the nitroanthraquinone mixture.

In carrying out the process the solvent is as a rule so selected that the desired 1-nitroanthraquinone has the lowest possible solubility therein and the products formed by the treatment have the highest possible solubility therein.

It has been found that polar aprotic solvents such as the N-alkylamides or N,N-dialkylamides of carboxylic acids and particularly of propionic acid, acetic acid and very particularly of formic acid and N-methylpyrrolidone as well as dimethylsulfoxide, hexamethylphosphoric triamide or tetramethylurea are particularly suitable for this purpose. These solvents may contain up to 10% by weight of water without the purity of the 1-nitroanthraquinone being impaired.

Preferred solvents are N,N-dimethylpropionamide, N,N-dimethylformamide, N-methylformamide, N-methylpyrrolidone, dimethylsulfoxide, hexamethylphosphoric triamide and tetramethylurea.

The amount of solvent used depends particularly on the solubility of the reaction products formed in the treatment with the methylene-active compound. The amount of solvent used is as a rule from about half to about ten times the amount of nitroanthraquinone mixture. When carrying out the process on a
commercial scale the amount of solvent used in the process should be kept as small as possible for economic reasons so that a high space-time yield of pure 1-nitroanthraquinone is achieved and the amount of 1-nitroanthraquinone dissolved in the solvent is as small as possible.

The reaction is generally carried out at a temperature of from 40° to 250°C; the preferred temperature range is from 70° to 150°C. When temperatures below 70°C are used the reaction periods are as a rule prolonged and at temperatures above 150°C there is a risk that undesired byproducts may be formed. The process according to the invention is conveniently carried out by heating to the desired reaction temperature a mixture of the nitroanthraquinone mixture, the methylene-active compound and the initiator and the solvent while stirring, and allowing the whole to cool to room temperature after the reaction is over. The pure 1-nitroanthraquinone is separated from the reaction mixture by a conventional method, freed from mother liquor by washing and if desired dried.

The nitroanthraquinone may be used in dry finely ground form or in the form of water-moist material. If it is desired to carry out the treatment in a nonaqueous medium, the adherent water may be removed by washing with a low-boiling water-miscible solvent and, if desired, distilling off the low-boiling solvent from the reaction medium which has a higher boiling point. The moist nitroanthraquinone mixture may also be dried by distilling off the water with the solvent used and then carrying out the treatment in the same solvent.

1-nitroanthraquinone obtained according to the process
may be reduced to l-aminoanthraquinone by conventional methods. Because of its outstanding purity the l-amino-anthraquinone thus obtained is outstandingly suitable for the production of dyes and dye precursors.

The mother liquor may be worked up by a conventional method so that the conversion products of the dinitroanthraquinones are obtained as a residue. In contrast to the dinitroanthraquinones themselves, the conversion products obtained as a residue can be burnt in conventional incinerators. This constitutes another advantage of the process according to the invention.

The invention is further illustrated by the following Examples in which parts and percentages are by weight.

**EXAMPLE 1**

50 parts of nitroanthraquinone mixture (which contains about 75% of 1-nitroanthraquinone, about 3 to 5% of 1,5-dinitroanthraquinone, 3 to 5% of 1,8-dinitroanthraquinone, about 10% of 1,6-, 1,7- and 2,7-dinitroanthraquinone and some 2-nitroanthraquinone), 50 parts of N,N-dimethylformamide, 7 parts of cyclopentanone and 1 part of sodium nitrite are stirred for two hours at 130°c. After cooling the whole is suction filtered and the residue is washed with 10 parts of cold N,N-dimethylformamide, then with 20 parts of methanol and finally with water and dried. 28.9 parts of pure 1-nitroanthraquinone is obtained.

To determine purity the isolated 1-nitroanthraquinone is reduced to l-aminoanthraquinone and the latter is analyzed by thin layer chromatography; (silica gel; developer toluene/
ethyl acetate/pyridine 20:2:1 by volume). No other components can be seen in the chromatogram.

EXAMPLE 2

The procedure of Example 1 is followed but 7 parts of cyclooctanone is used instead of 7 parts of cyclopentanone. 31.6 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 3

The procedure of Example 1 is followed but 7 parts of diethyl ketone is used instead of 7 parts of cyclopentanone. 33 parts of 1-nitroanthraquinone is obtained which contains traces of 1,5-dinitroanthraquinone.

EXAMPLE 4

The procedure of Example 1 is followed but 7 parts of cyclohexanone is used instead of 7 parts of cyclopentanone. 32.5 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 5

The procedure of Example 1 is followed, but 7 parts of propiophenone is used instead of 7 parts of cyclopentanone. 33.7 parts of 1-nitroanthraquinone is obtained which contains a trace of 1,5-dinitroanthraquinone.

EXAMPLE 6

The procedure of Example 1 is followed but 6 parts of ethyl acetoacetate is used instead of 7 parts of cyclopentanone. 36.2 parts of 1-nitroanthraquinone is obtained which contains a trace of 1,5-dinitroanthraquinone.

EXAMPLE 7

The procedure of Example 1 is followed but 8 parts of diethyl malonate is used instead of 7 parts of cyclopentanone. 32 parts of 1-nitroanthraquinone is obtained which is
contaminated with a trace of 1,5-dinitroanthraquinone.

EXAMPLE 8

The procedure of Example 1 is followed but 7 parts of methyl ethyl ketone is used instead of 7 parts of cyclopentanone. 31 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 9

The procedure of Example 1 is followed but 8 parts of acetophenone is used instead of 7 parts of cyclopentanone. 30.5 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 10

The procedure of Example 1 is followed but 9 parts of 3-methyl-1-phenylpyrazolone-5 is used. 29.8 parts of 1-nitroanthraquinone is obtained which is contaminated with a trace of 1,5-dinitroanthraquinone and 1,8-dinitroanthraquinone.

EXAMPLE 11

The procedure of Example 1 is followed but 9 parts of benzoylacetonc is used instead of 7 parts of cyclopentanone. 30.5 parts of 1-nitroanthraquinone is obtained which contains a trace of 1,5-dinitroanthraquinone.

EXAMPLE 12

The procedure of Example 4 is followed but 1.5 parts of sodium thiocyanate is used instead of 1 part of sodium nitrite. 30.5 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 13

The procedure of Example 10 is followed but 8 parts of acetylacetone is used instead of methylphenylpyrazolone-5. The yield is 29.5 parts of 1-nitroanthraquinone which contains a trace of 1,5-dinitroanthraquinone and 1,8-dinitroanthraquinone.
EXAMPLE 14

50 parts of nitroanthraquinone mixture (composition as in Example 1), 50 parts of dimethylsulfoxide, 7 parts of cyclohexanone and 1 part of sodium nitrite are stirred for three hours at 120°C. The product is worked up as in Example 1. The yield is 29.3 parts of pure 1-nitroanthraquinone.

EXAMPLE 15

50 parts of nitroanthraquinone mixture (75% of 1-nitroanthraquinone), 50 parts of hexamethylphosphoric triamide, 7 parts of cyclohexanone and 1 part of sodium nitrite are stirred for three hours at 120°C and then worked up. 27.1 parts of pure 1-nitroanthraquinone is obtained.

EXAMPLE 16

50 parts of nitroanthraquinone mixture (75% of 1-nitroanthraquinone), 50 parts of tetramethylurea, 7 parts of cyclohexanone and 1 part of sodium nitrite are stirred for three hours at 130°C and worked up as in Example 1. The yield is 31.0 parts of pure 1-nitroanthraquinone.

EXAMPLE 17

50 parts of nitroanthraquinone mixture (75% of 1-nitroanthraquinone), 50 parts of N-methylformamide, 7 parts of cyclohexanone and 1 part of sodium nitrite are stirred for three hours at 120°C and worked up as in Example 1. The yield is 31.2 parts of pure 1-nitroanthraquinone.

EXAMPLE 18

55 parts of a nitroanthraquinone mixture of the composition specified in Example 1 and containing 10% of water, 60 parts of dimethylformamide, 7 parts of cyclohexanone
and 1 part of sodium nitrite are stirred for two hours at 130°C and then worked up. 32.5 parts of pure 1-nitroanthraquinone is obtained.
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

What we claim is:

1. A process for the production of pure or virtually pure 1-nitroanthraquinone from a nitroanthraquinone mixture which comprises treating the mixture containing 1-nitroanthraquinone in an aprotic polar organic solvent which may contain up to 10% by weight of water in the presence of a catalytic amount of an initiator with a compound which has at least one \(-\text{CH}_2-\) group which is activated by one or more carbonyl groups.

2. A process as claimed in claim 1, wherein a compound which yields nitrite, chloride, bromide, iodide, fluoride, thiocyanate, alcoholate or phenolate ions is used as the initiator.

3. A process as claimed in claim 1 or 2, wherein N,N-dimethylformamide, N-methylpyrrolidone, N-methylformamide, N,N-dimethylpropionamide, dimethylsulfoxide, hexamethylphosphoronic triamide or tetramethylurea is used as the polar aprotic solvent.

4. A process as claimed in claim 1, 2 or 3, wherein diethyl ketone, cyclohexanone, acetoacetic ester, propiophenone, a malonic ester or a mixture of two or more of these is used as the compound containing at least one \(-\text{CH}_2-\) group which is activated by one or more carbonyl groups.

5. A process as claimed in any of claims 1 to 4, wherein the initiator is used in an amount of from 0.1 to 10% by weight based on the nitroanthraquinone mixture.

6. A process as claimed in any of claims 1 to 5, wherein the methylene-active compound is used at the rate of from 0.3 to 3 moles per mole of dinitroanthraquinones in the nitroanthraquinone mixture.
7. A process as claimed in any of claims 1 to 6, wherein the methylene-active compound is used at the rate of from 0.5 to 2 moles per mole of dinitroanthraquinones in the nitroanthraquinone mixture.

8. A process as claimed in any of claims 1 to 7 carried out at a temperature of from 400°C to 250°C.

9. A process as claimed in any of claims 1 to 8 carried out at a temperature of from 700°C to 150°C.

10. A process as claimed in any of claims 1 to 9, wherein the weight of solvent used is from half to ten times the weight of the nitroanthraquinone mixture.

11. A process as claimed in any of claims 1 to 10, wherein the initiator used is a nitrite.

12. A process as claimed in claim 1 carried out substantially as described in any of the foregoing Examples.

13. Pure or virtually pure 1-nitroanthraquinone when obtained by the process claimed in any of claims 1 to 12.