

UNITED STATES PATENT OFFICE

2,280,072

SUBSTITUTED PHTHALOCYANINES

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No Drawing. Application May 17, 1940, Serial
No. 335,871. In Great Britain May 25, 1939

5 Claims. (Cl. 260-314)

The present invention relates to particular processes for making tetra-aminophthalocyanines.

It is known that from tetra-(4)-acylamino-phthalocyanines of the benzene series the acyl radicals are removed on treatment with, for example, sulphuric acid of about 95%; the resulting amino-phthalocyanines yield with acids blue salts the colour of which becomes dull green when they are treated with alkali. It is also known that these amino-phthalocyanines can be diazotised by suspending them in acid medium and treating them in the usual way with sodium nitrite.

This invention relates to the manufacture of metal-free and metallic tetra-(4)- and tetra-(3)-aminophthalocyanines. It is an object of the present invention to provide tetra-amino phthalocyanines, as defined below, by reduction of the corresponding tetranitro phthalocyanines.

According to the invention I make the said tetra-aminophthalocyanines by reducing the corresponding tetra-nitrophthalocyanines by the reducing agents specified below. There may be employed, for instance, copper tetra-4-nitro- or tetra-3-nitro-phthalocyanine. Mixtures of phthalocyanines may also be utilised, for example, a mixture of copper tetra-(4)-nitro and tetra-(3)-nitrophthalocyanines. Other metallic tetra-nitrophthalocyanines, for instance, those of cobalt, nickel, aluminium, lead or magnesium, may also be used. Metallic tetra-nitrophthalocyanines are conveniently made, for example, from a compound of the desired metal or the metal itself, together with the appropriate nitro-phthalodinitrile or nitro-phthalic anhydride, in conjunction with urea. Metal-free tetra-nitrophthalocyanines which may be made by heating the requisite nitro-phthalodinitrile with calcium oxide, are likewise useful as starting materials.

Many substances have been applied as agents for the purpose of reducing organic compounds. A considerable number of these reducing agents may be said to be largely equivalent inasmuch as one is often capable of taking the place of another with similar or nearly the same effect. I have now found unexpectedly that whereas the majority of the known reducing agents are useless for the purpose of the present invention, owing to failure to reduce at all or to do more than effect a partial reduction, or are otherwise unsatisfactory, some reducing agents are able, not only readily to reduce tetra-nitrophthalocyanines affording tetra-aminophthalocyanines,

but to do so in such a way that the reduction of the four nitro groups proceeds smoothly and without side-reactions. The reducing agents which are used in this invention are those of the alkali sulphide class, in which expression are included sodium sulphide, sodium hydrogen sulphide and sodium disulphide. Stannous chloride and sodium hydrosulphite (sodium hyposulphite) are also used as reducing agents according to the invention. By this means there are obtained in good yield tetra-aminophthalocyanines. These compounds are green in colour and insoluble in water. They are turned blue by the action of acids, for example, hydrochloric acid, seemingly owing to salt-formation.

Tetra-aminophthalocyanines are readily diazotised and are useful as intermediates, namely, diazocomponents, in the preparation of colouring matters.

The diazotisation of tetra-aminophthalocyanines which have been made from tetra-nitrophthalocyanines by the above reduction process, constitutes part of the present invention. The invention includes also the precipitation of the tetra-diazo compounds in a form suitable for technical handling, and so in solid state, by adding to the solutions thereof, zinc chloride, cadmium chloride or other salt suitable for the production of double salts, or of naphthalene or other sulphonic acids which will give sulphonic acid salts of the tetra-diazo compounds sparingly enough soluble in water to be precipitated.

It has been proposed to make tetra-aminophthalocyanines from aminophthalic acid derivatives. Thus what appears to be copper tetra-aminophthalocyanine can be made by heating aminophthalimide with urea and cuprous chloride. Such products however cannot be diazotised. Tetra-aminophthalocyanines obtained by de-acylating tetra-acylamino-phthalocyanines may be diazotised, as already mentioned, but owing to gross decomposition of the phthalocyanine molecule having occurred during deacylation the yield of diazo-phthalocyanine is relatively low. By working according to the present invention, tetra-aminophthalocyanines may be obtained and diazotised in excellent yield.

The invention is illustrated but not limited by the following examples, in which the parts are by weight.

Example 1

50 parts of copper tetra-(4)-nitrophthalocyanine (made from 4-nitrophthalimide) in the form of an aqueous paste is mixed with 1400

parts of water, 200 parts of 33% aqueous sodium hydroxide and 150 parts of sodium hydrosulphite. The mixture is stirred and heated at 50–55° C. for 1 hour. The blue suspension becomes bright green. The mixture is filtered. The filter cake is stirred with 1000 parts of boiling 20% sodium chloride solution, filtered, washed with cold 10% sodium chloride solution and dried. There is thus obtained a dark green pulverulent solid which dissolves in concentrated sulphuric acid to give a bright yellowish green solution. It is almost insoluble in high boiling organic solvents. When stirred into dilute aqueous mineral acids the colour changes to blue seemingly by salt formation although the substance does not dissolve. When this blue substance is treated with aqueous sodium hydroxide, the colour changes back to green.

When the same quantity of copper tetra-3-nitro-phthalocyanine (made from 3-nitro-phthalic anhydride) is used instead of copper tetra-4-aminophthalocyanine, copper tetra-3-aminophthalocyanine is obtained. It is similar in appearance and chemical properties to the product obtained in the first part of this example.

Example 2

10 parts of copper tetra-(4)-nitrophthalocyanine in the form of a finely milled 10% aqueous paste is stirred in an ice-bath. 34 parts of 30% aqueous sodium hydrogen sulphide solution are added at such a rate that the temperature of the mixture does not exceed 25° C. After 20 hours, the dark green suspension is diluted with 70 parts of 10% sodium sulphite solution. The product is filtered off, washed with 5% aqueous sodium sulphite and then with water. It may now be dried to a green powder or conveniently the wet filter-cake may be used for a subsequent chemical operation, e. g. diazotisation.

The purity of the copper tetra-4-aminophthalocyanine so-obtained is about 96% when assessed in the following manner. 3.25 parts of copper tetra-4-aminophthalocyanine as a 10% aqueous paste are mixed with 3 parts by volume of 10% aqueous sodium nitrite solution and introduced into the closed limb of a Lunge nitrometer. 30 parts by volume of concentrated hydrochloric acid are added and the mixture shaken. A solution of cuprous chloride in hydrochloric acid is introduced. Ferrous sulphate solution is added to absorb the excess of nitrous gases. The tetra-aminophthalocyanine that was present is calculated from the residual volume of nitrogen.

Example 3

10 parts of copper tetra-(4)-nitrophthalocyanine in the form of a finely milled 15% aqueous paste are stirred with 200 parts of 33% aqueous hydrochloric acid till a smooth paste is formed. The suspension is cooled to 5° C. and 50 parts of crystalline stannous chloride added gradually so that the temperature of the mixture does not exceed 10° C. The reduction is complete when a test portion added to water gives a violet coloured precipitate which rapidly changes to bright blue when exposed to air. After dilution with an equal volume of water the product is then filtered off and sucked as dry as possible on the filter. The filter cake is made into a paste with 200 parts of a 16% sodium hydroxide solution and the mixture boiled for 5 minutes after which it is filtered hot. This process is repeated until the product is free from tin and finally, the copper tetra-4-aminophthalocyanine, so obtained, is

washed with water until free from inorganic matter and dried. The purity of this material is found to be 98% by the method of Example 2. It is green in colour and becomes blue on treatment with sulphuric acid.

Copper tetra-(4)-aminophthalocyanine is diazotized as follows. 30 parts thereof as a finely milled aqueous paste are stirred with 20 parts of sodium nitrite and in all 500 parts of cold water. To this mixture (at below 10° C.) is quickly added with stirring 500 parts of 33% aqueous hydrochloric acid. After a few minutes stirring a clear deep green solution of the tetradiazo compound is obtained.

The same result is obtained when the suspension of tetra-amino compound in aqueous sodium nitrite is added to the aqueous hydrochloric acid.

Example 4

10 parts of copper tetra-(4)-nitrophthalocyanine in the form of a finely milled 10% aqueous paste are stirred in a vessel immersed in a bath of cold water, and 24 parts of crystalline sodium sulphide, dissolved in the minimum quantity of water, added slowly so that the temperature does not exceed 20° C. After stirring for 20 hours 100 parts of 10% sodium sulphite solution are added. The dark green product is filtered off, washed well with water and dried.

Instead of 24 parts of crystalline sodium sulphide, 21 parts of 27% sodium disulphide solution may be used.

The zinc chloride double salt of copper tetra-(4)-diazonium-phthalocyanine chloride is made as follows. 12.3 parts of finely divided copper tetra-(4)-aminophthalocyanine in the form of an aqueous paste are mixed with 120 parts of water and 6 parts of sodium nitrite. This mixture, cooled to 5° C., is then added to 90 parts of concentrated aqueous hydrochloric acid (sp. gr. 1.16) previously cooled to 0° C. To the clear dark green solution of diazo compound thus obtained there is added a solution of 25 parts of zinc chloride in 50 parts of 0.5% aqueous hydrochloric acid. There is formed a dark green finely divided precipitate. This is filtered off, washed with acetone and dried. This is a zinc double salt. It is readily soluble in cold water to give a greenish blue solution.

Example 5

64 parts of cobalt tetra-(4)-nitrophthalocyanine in the form of a finely milled 10% aqueous paste are stirred in an ice-bath and 224 parts of 30% sodium hydrogen sulphide solution added at such a rate that the temperature of the mixture does not exceed 25° C. After stirring for 20 hours, 300 parts of 10% sodium sulphite solution are added. The dark green suspension is filtered and the filter cake washed with 5% sodium sulphite solution and then with water. After drying it is a dark green solid which when added to 2N-hydrochloric acid changes in colour from green to bluish violet. The purity of this material is about 92%.

When nickel tetra-4-nitrophthalocyanine is reduced as described above, nickel tetra-4-aminophthalocyanine is obtained. It is a dark green substance which becomes blue when treated with 2N-hydrochloric acid.

Example 6

30 parts of metal-free tetra-(4)-nitrophthalocyanine (made by heating 4-nitrophthalonitrile with quick lime) in the form of a finely milled 10% aqueous paste are stirred in an ice-bath

and 145 parts of 30% sodium hydrogen sulphide solution added at such a rate that the temperature of the mixtures does not exceed 20° C. After stirring for 20 hours 220 parts of 10% sodium sulphite solution are added. The suspension is filtered, the filter cake washed with 5% sodium sulphite solution and then with water and dried. The so-obtained product is a dark green powder which gives a blue suspension when stirred with 2N-hydrochloric acid.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to specific embodiments except as defined in the appended claims.

I claim:

1. A process for the manufacture of tetraamino derivatives of phthalocyanine compounds selected from the group consisting of metal-free and metallic phthalocyanines, which comprises subjecting the corresponding tetranitro phthalocyanine compounds to reduction by means of a reducing agent selected from the group consisting

of stannous chloride, sodium hydrosulfite, and the alkali sulfide class.

2. A process for the manufacture of tetramino-copper-phthalocyanine, which comprises reducing tetranitro-copper-phthalocyanine in aqueous medium by the aid of a reducing agent of the alkali sulfide class.

3. A process for the manufacture of tetramino-copper-phthalocyanine, which comprises reducing tetra-nitro-copper-phthalocyanine in alkaline aqueous medium by the aid of an alkaline hydrosulfite.

4. A process for the manufacture of tetramino-copper-phthalocyanine, which comprises reducing tetranitro-copper-phthalocyanine in acid aqueous medium by the aid of stannous chloride.

5. A process for the manufacture of tetra-amino derivatives of phthalocyanine compounds selected from the group consisting of metal-free and metallic phthalocyanines, which comprises subjecting the corresponding tetranitro phthalocyanine compounds to reduction in aqueous medium by the aid of sodium hydrogen sulfide.

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