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**PROCESS FOR THE MANUFACTURE OF MIXTURES OF ALKALI METAL AND METAL-FREE PHTHALOCYANINES**

Walter Wettstein, Riehen, Switzerland, assignor to Ciba Limited, Basel, Switzerland, a Swiss firm

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It is known that mixtures of alkali metal phthalocyanines and metal-free phthalocyanines can be made by reacting phthalonitrile with an alkali metal alcoholate, for example, sodium amylate or sodium cyclohexanolate or the like, in the solution of the alcohol used for the alcoholate. The yields obtainable in this manner hardly exceed 50 per cent. of the theoretical yield.

The present invention is based on the observation that mixtures of alkali metal phthalocyanines and metal-free phthalocyanines can be made in good yield by reacting phthalonitrile in the presence of an alcohol, which may be diluted with an organic solvent inert with respect to the reaction components, with an alkali metal. The phthalonitrile dissolves in the alcohol used while the alkali metal is unexpectedly consumed substantially without the evolution of hydrogen. An alkali metal phthalocyanine is first formed in proportion to the quantity of the metal added and with a strong evolution of heat, the alkali metal phthalocyanine being partially converted directly into the metal-free phthalocyanine. In this manner there is obtained a mixture of alkali metal phthalocyanine and metal-free phthalocyanine. The alkali metal phthalocyanine, may, if desired, be converted in known manner into metal-free phthalocyanine. The mixture obtainable by the process of the invention may be worked up in the usual manner to a pigment.

As stated above, the reaction proceeds with a strong evolution of heat, so that it is necessary to maintain the temperature within the range of about 100–190° C., advantageously 130–140° C., by cooling until the addition of the metal is complete, the rate of addition of the metal being suited to the effectiveness of the cooling conditions. After the addition of the necessary quantity of metal the reaction mixture is heated at about 160–200° C., advantageously about 180° C., in order to complete the reaction.

With regard to the choice of the alcohol to be used attention should be paid to the following: Since the alkali metal is preferably introduced at a temperature of 130–140° C., it is of advantage to choose an alcohol having a boiling point above 140° C. As such alcohols there may be used those of the aliphatic series, for example, those which contain at least 7 carbon atoms, for example, secondary isoctyl, lauryl, cetyl or stearyl alcohol, further alcohols of the araliphatic or hydroaromatic series, such as benzyl alcohol, phenylethyl alcohol, cyclohexanol or homologues of these alcohols. Lower boiling alcohols may be used, such as propyl, butyl or amylalcohol, but then somewhat lower yields are obtained. The quantity of the alcohol used may vary within wide limits, but it must amount to at least 1 mol or advantageously at least 1.5 mols per mol of the phthalonitrile present. Otherwise yield and purity of the dyestuff obtained are reduced.

The reaction may take place in the presence of an organic solvent inert with regard to the reaction components. This method leads in general to an increased yield of dyestuff. As inert organic solvents there are used those which react neither with the alkali metal nor with the alcohol used or with phthalonitrile, and the solvent advantageously has a boiling point above 140° C. As such solvents there are suitable liquid hydrocarbons boiling above 140° C. or solid hydrocarbons which are liquid at the reaction temperature, such as those of the aliphatic series having more than 8 carbon atoms, for

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example, n-nonane or mixtures of such hydrocarbons as are present in a petroleum fraction boiling at a temperature between 160° C. and 240° C., and also those of the aromatic or hydroaromatic series, for example, naphthalene, tetrahydronaphthalene, decahydronaphthalene, the higher boiling homologues of benzene, as for example xylols, cymols, or the like. However, there are also suitable derivatives of these hydrocarbons, for example, dichlorobenzenes, trichlorobenzenes,  $\alpha$ -chloronaphthalene or the like, further ethers boiling about 140° C., such as ethyleneglycoldibutylether, dibenzylether, anisol, phenetol, diphenyloxide or the like, and also tertiary amines of the aromatic or heterocyclic series, such as dimethylaniline, quinoline or the like. There may, of course, also be used mixtures of the aforesaid solvents. It should be noted that chlorinated hydrocarbons may react to a small extent with the alkali metal in accordance with the Fittig-Wurtz reaction, so that in such cases a somewhat larger amount of alkali metal is necessary than in the case of solvents which are completely inert towards alkali metals. The use of primary or secondary amines as diluents would lead to poor yields. Nitro compounds are partially reduced and therefore also lead to poor yields. The quantity of solvent may vary within wide limits; however, in order to obtain a substantially higher yield, it should not be less than 1 part by weight and not more than 10 parts by weight for every 2 parts of the alcohol. There is advantageously used 1 part of solvent for each part of the alcohol.

All metals belonging to the group of alkali metals, especially lithium and sodium, may be used, but for reasons of economy the use of sodium is preferred. In accordance with theory two atomic proportions of alkali metal are required to react with 4 molecular proportions of phthalonitrile. As, however, the alkali metal phthalocyanine is partially converted into metal-free phthalocyanine, 1.2 atomic proportions of alkali metal for every 4 molecular proportions of phthalonitrile lead to optimum yields.

It has also been found that the yield can generally be still further increased by adding to the reaction mixture a small amount of sulfur before the addition of the alkali metal. The quantity of sulfur may vary within wide limits. The addition of 1 part of sulfur for every 10 parts of alkali metal suffices to produce a positive effect, preferably there is used 1 part of sulfur for every 3 parts of alkali metal, and in any case not more than 1 part of sulfur for every 1 part of alkali metal. The sulfur may be replaced by an equivalent amount of anhydrous sodium sulfide or by introducing an equivalent amount of hydrogen sulfide.

The following examples illustrate the invention, the parts being by weight:

*Example 1*

41 parts of phthalonitrile are dissolved in 125 parts of decahydronaphthalene and 125 parts of benzyl alcohol while stirring and raising the temperature. When the temperature of the reaction mixture reaches 130° C., the application of heat is discontinued, and 2 parts of sodium are added in the course of 40–60 minutes in portions each amounting to about 0.1 part, the temperature being brought down to 130° C. by cooling after each addition. When all the sodium has been introduced, the reaction mass is heated, while stirring, for about 40 minutes at 180° C. The dyestuff may be separated from the solvent mixture in the usual manner and worked up into a pigment. The yield amounts to about 26.5 parts calculated as metal-free phthalocyanine.

The decahydronaphthalene used as inert solvent may be replaced by a corresponding quantity of tetrahydronaphthalene, dimethylaniline or quinoline which produce the same result.

*Example 2*

41 parts of phthalonitrile are dissolved in 125 parts of trichlorobenzene and 125 parts of benzyl alcohol while stirring and raising the temperature. When the temperature of the reaction mixture reaches 130° C., the application of heat is discontinued, and 3 parts of sodium are added in the course of 40–60 minutes in portions each

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amounting to about 0.1 part, the temperature being brought down to 130° C. by cooling after each addition. When all the sodium has been introduced, the reaction mass is heated, while stirring, for about 40 minutes at 180° C. The dyestuff may be separated from the solvent mixture in the usual manner. It consists of a mixture of metal-free phthalocyanine and sodium phthalocyanine the latter of which may be converted into the metal-free phthalocyanine in known manner. The yield amounts to about 28 parts, calculated as metal-free phthalocyanine.

Instead of trichlorobenzene there may with equal results be used  $\alpha$ -chloronaphthalene.

#### Example 3

The procedure is the same as that described in Example 1, except that at the outset there is added 0.6 part of sulfur. In this case the yield amounts to about 30 parts, calculated as metal-free phthalocyanine.

Instead of benzyl alcohol there may just as successfully be used phenylethyl alcohol, cetyl alcohol or stearyl alcohol. When the sodium is replaced by the equivalent quantity of potassium, the reaction proceeds in the same manner, but the yield is only about 21 parts, calculated as metal-free phthalocyanine.

#### Example 4

0.7 part of sulfur is added to a mixture of 125 parts of decahydronaphthalene, 125 parts of dodecyl alcohol and 41 parts of phthalonitrile, and in other respects the procedure is the same as in Example 1. There are obtained about 28 parts of dyestuff, calculated as metal-free phthalocyanine.

Instead of dodecyl alcohol there may also be used an equivalent quantity of isooctyl alcohol.

#### Example 5

To 125 parts of decalin, 125 parts of benzyl alcohol and 43 parts of phthalonitrile there is gradually added while stirring 0.5 part of lithium at 165–175° C. and heating is carried on for a further 45 minutes at 180° C. The dyestuff is filtered off and washed with benzene. It consists of a mixture of metal-free phthalocyanine and lithium phthalocyanine. The latter may be converted in known manner into metal-free phthalocyanine and the whole may be worked up in the usual manner to a pigment. The yield amounts to approximately 34 parts, calculated as metal-free phthalocyanine.

An addition of sulfur does not improve the yield.

What I claim is:

1. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in an alcohol, which is diluted with an organic solvent inert with respect to the reaction components, the addition of the alkali metal being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

2. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in an alcohol having a boiling point above 140° C., which is diluted with an organic solvent inert with respect to the reaction components, the addition of the alkali metal being effected in small portions and at a

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temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

3. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in benzyl alcohol, which is diluted with an organic solvent inert with respect to the reaction components, the addition of the alkali metal being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

4. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in cyclohexanol, which is diluted with an organic solvent inert with respect to the reaction components, the addition of the alkali metal being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

5. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in benzyl alcohol, which is diluted with decahydronaphthalene, the addition of the alkali metal being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

6. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding an alkali metal to a solution of phthalonitrile in benzyl alcohol, which is diluted with decahydronaphthalene and which contains sulfur in the proportion of 1 to 10 parts of sulfur for 10 parts of the alkali metal, the addition of the alkali metal being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

7. A process for the manufacture of mixtures of alkali metal phthalocyanines and metal-free phthalocyanines comprising adding sodium to a solution of phthalonitrile in benzyl alcohol, which is diluted with decahydronaphthalene and contains sulfur in the proportion of 1 to 3 parts of sulfur for 10 parts of sodium, the addition of sodium being effected in small portions and at a temperature within the range of 100 to 190° C., and thereupon heating the reaction mixture at a temperature within the range of 160 to 200° C. until the reaction is complete.

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