

PATENT SPECIFICATION

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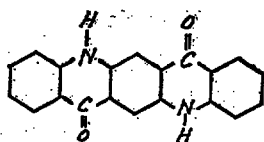
- (72) Inventors HANS BOHLER and FRITZ KEHRER

(54) PROCESS FOR THE PRODUCTION OF THE
 β -CRYSTAL MODIFICATION OF LINEAR
 TRANS-QUINACRIDONE



(71) We, SANDOZ LTD., of Lichtstrasse 35, Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of the β -modification of the linear trans-quinacridone of the formula



The violet β -quinacridone is a valuable pigment and consequently there have been many attempts to produce this crystal modification in a simple and economical manner. One suggestion that has been made is to dissolve quinacridone in a solvent and to precipitate it in the β -form with water or specific organic liquids; another suggestion is to heat quinacridone in an organic liquid in which it does not dissolve. Further, grinding of the quinacridone in the presence of a grinding assistant such as sodium chloride and an organic liquid such as toluene, tetrachloroethylene or dimethyl sulphoxide has been proposed.

These known methods have been found to be technically inconvenient, costly and not without hazard. They yield pigments which frequently contain a substantial amount of red α -quinacridone and/or γ -quinacridone and which often prove to have unsatisfactory application and service properties, for instance the desired shade of blue and brightness of shade, dispersibility in plastics and paint media, heat stability and light fastness.

A pigment much sought after is pure β -quinacridone, which has a pronounced bluish shade (German published patent application 1,278,394). One of its applications is in combination with high-grade red or orange pigments for the production of red shades which have excellent light fastness and weathering resistance.

It has been found that β -quinacridone can be produced in a highly valuable form for technical application, that is to say, in a degree of blueness never before attained, and moreover at economic cost, by grinding quinacridone in the absence of a liquid at a temperature above 90°C but preferably not higher than 250°C, and more especially in a range of from 120°C to 200°C inclusively. That such a high quality pigment should result is surprising since it is known that when quinacridone is ground in the absence of a liquid at temperatures up to about 60°C it passes into the α -crystal form (German published patent applications 1,137,156 and 1,278,394). The above temperatures and those given subsequently are temperature at the exterior of the milling machine used for process. The temperature in the interior of the machine is normally somewhat higher.

The quinacridone used as the starting material may be in any desired crystal form, or it may be a mixture of different crystal forms. Although it is only optional to carry out the grinding in the presence of a grinding assistant, it is, in fact, preferable to add sodium chloride or another salt which is soluble in water or in dilute acid or alkali solution, for example potassium chloride, ammonium chloride, anhydrous calcium chloride, sodium sulphate, aluminium sulphate or calcium carbonate. A weight ratio of quinacridone to grinding assistant between 1:4 and 1:10 is given special preference; the ratio may however be greater or smaller if desired. Besides the grinding assistant, other additives commonly used in grinding can be included

in the mixture, such a colophony (common rosin) or one of its metal salts and fillers, in particular non-ionic or cationic surface-active compounds. These additives are generally employed in an amount of from 1% to 10% inclusively, and preferably 1% to 5%, on the weight of the pigment.

Any of the milling machines of standard design can be used in which the particles are comminuted by abrasion and shearing; notable types are ball mills, roller mills and edge mills. The grinding time depends primarily on the construction and dimensions of the machine. Generally, grinding is terminated when the average particle size of the resulting β -quinacridone is approximately 0.05 to 0.2 micron, or more specifically 0.05 to 0.1 micron. The grinding assistant and the impurities are then eliminated by extraction with dilute acid, after which the final pigment is worked up to the commercial form by conventional methods.

In the following Examples the parts and percentages are by weight. The temperatures are given in degrees centigrade. Unless otherwise stated, the term "quinacridone" refers to a mixture of different linear trans-quinacridone crystal modifications.

Example 1

A roller mill is employed which is equipped with 3750 parts of cylindrical metal rods measuring 4 cm in diameter and 12 cm in length. The mill is heated to 150° by an air bath and 80 parts of dry sodium chloride and 20 parts of dry quinacridone are introduced. The latter consists of approximately 75% of α -quinacridone and about 25% of β -quinacridone, and is prepared by purifying crude quinacridone in dilute sulphuric acid by a conventional method.

The dry mixture is ground for 48 hours at 90 revolutions per minute. The assistant and the impurities are then extracted with hot 5% sulphuric acid solution and the product is filtered, washed and dried. The β -quinacridone is obtained in almost 100% yield.

After grinding for only 24 hours, transformation to the β -crystal modification is complete. However, by extending the grinding time to 48 hours as above, the "hiding power" of the pigment is reduced, i.e. its transparency is greater, and because of its shade and brilliance it is a more valuable product for application in linseed oil medium for full shades. An extension of the grinding time to 72 hours does not produce any further alteration in the application properties. Thus, after transformation to the β -modification is complete, the application properties of the product can be changed as desired by continuing grinding for a shorter or longer period of time.

Example 2

A mixture of 20 parts of quinacridone and 600 parts of dry sodium chloride is ground in a ball mill of a type fitted with 7000 parts of steel balls of 2.5 cm diameter and 4 steel chains 20 cm in length. The mill is heated from the outside to 200°.

The mixture is ground for 72 hours at 90 revolutions per minute, and the product isolated as described in Example 1. The yield of β -quinacridone is again almost quantitative.

Example 3

A mixture of 100 parts of α -quinacridone and 400 parts of dry sodium chloride is ground in a ball mill of the type used in Example 2, externally heated to 150° by an air bath. The grinding is carried out for 96 hours and 90 revolutions per minute. The resulting product is mixed with a warm aqueous solution of 17.8 parts of the sodium salt of colophony. It is then precipitated in admixture with the colophony, by the addition of mineral acid, filtered, washed and dried. A colophony-modified β -quinacridone of soft grain texture is obtained which is highly suitable for the pigmentation of plastics and paint media. In place of the 100 parts of α -quinacridone, 100 parts of γ -quinacridone can be treated in this manner with equal success.

Example 4

A mixture of 100 parts of quinacridone and 400 parts of dry sodium chloride is ground in the ball mill described in Example 2 for 102 hours at an air bath temperature of 150°. The product is purified and isolated as described in Example 1. The very bluish red β -crystal modification of the quinacridone is obtained in excellent yield. The grinding time may be extended to 144 hours to give a pigment with somewhat lower hiding power.

If grinding is carried out at 120° under otherwise identical conditions, the β -quinacridone is obtained with a slightly more reddish shade.

WHAT WE CLAIM IS:—

1. A process for the production of the β -crystal modification of linear trans-quinacridone by grinding quinacridone in the absence of a liquid at a temperature above 90°C.

2. A process according to claim 1 wherein grinding is carried out at a temperature above 90°C but not more than 250°C.

3. A process according to claim 2, wherein grinding is carried out at a temperature within a range of from 120°C to 200°C inclusively.

4. A process according to any one of the

in the mixture, such a colophony (common rosin) or one of its metal salts and fillers, in particular non-ionic or cationic surface-active compounds. These additives are generally employed in an amount of from 1% to 10% inclusively, and preferably 1% to 5%, on the weight of the pigment.

Any of the milling machines of standard design can be used in which the particles are comminuted by abrasion and shearing; notable types are ball mills, roller mills and edge mills. The grinding time depends primarily on the construction and dimensions of the machine. Generally, grinding is terminated when the average particle size of the resulting β -quinacridone is approximately 0.05 to 0.2 micron, or more specifically 0.05 to 0.1 micron. The grinding assistant and the impurities are then eliminated by extraction with dilute acid, after which the final pigment is worked up to the commercial form by conventional methods.

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A roller mill is employed which is equipped with 3750 parts of cylindrical metal rods measuring 4 cm in diameter and 12 cm in length. The mill is heated to 150° by an air bath and 80 parts of dry sodium chloride and 20 parts of dry quinacridone are introduced. The latter consists of approximately 75% of α -quinacridone and about 25% of β -quinacridone, and is prepared by purifying crude quinacridone in dilute sulphuric acid by a conventional method.

The dry mixture is ground for 48 hours at 90 revolutions per minute. The assistant and the impurities are then extracted with hot 5% sulphuric acid solution and the product is filtered, washed and dried. The β -quinacridone is obtained in almost 100% yield.

After grinding for only 24 hours, transformation to the β -crystal modification is complete. However, by extending the grinding time to 48 hours as above, the "hiding power" of the pigment is reduced, i.e. its transparency is greater, and because of its shade and brilliance it is a more valuable product for application in linseed oil medium for full shades. An extension of the grinding time to 72 hours does not produce any further alteration in the application properties. Thus, after transformation to the β -modification is complete, the application properties of the product can be changed as desired by continuing grinding for a shorter or longer period of time.

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2. A process according to claim 1 wherein grinding is carried out at a temperature above 90°C but not more than 250°C.

3. A process according to claim 2, wherein grinding is carried out at a temperature within a range of from 120°C to 200°C inclusively.

4. A process according to any one of the

preceding claims substantially as herein described and exemplified.

- 5 5. The β -crystal modification of linear trans-quinacridone whenever prepared by a process according to any one of the preceding claims.

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