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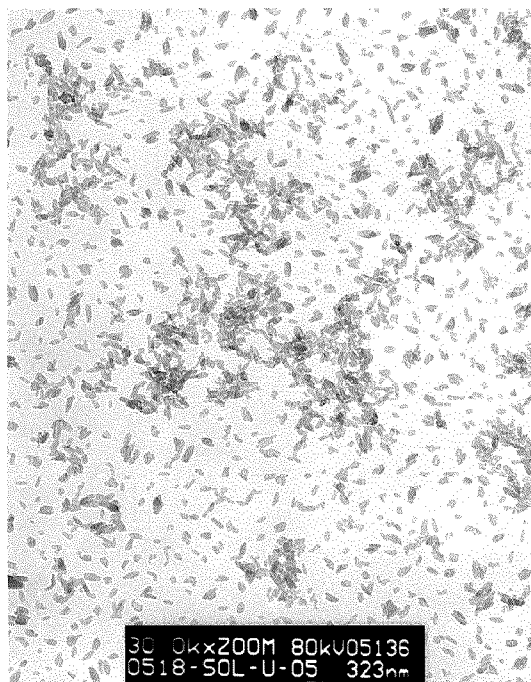
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(54) Title: PROCESS OF PREPARING PRODUCT BASED ON COPPER PHTHALOCYANINE (CuPc) PARTICLES

Fig. 1



(57) Abstract: A process for preparing a product based on copper phthalocyanine (CuPc) particles, said process comprising adding, to the CuPc particles, during or after their preparation, at least one non-polar solvent in an amount of less than 10 % by weight of the CuPc particles.



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Process of Preparing Product Based on Copper Phthalocyanine (CuPc)
Particles

This application claims priority to European patent application No. EP 10196463.3 filed on 22 Dec 2010, the whole content of this application being incorporated herein by reference for all purposes.

Technical Field

5 The present invention generally relates to copper phthalocyanine (CuPc) and processes of preparing the same. More particularly, the present invention relates to a new efficient and economical process for preparing CuPc pigments with better dispersibility, said CuPc pigments being especially suitable for the preparation of color filters used for displaying colour images, to the CuPc
10 pigments prepared thereby, as well as to liquid crystal display devices in which the foregoing pigments are incorporated.

Background Art

Copper phthalocyanine blue (C.I. Pigment Blue 15) is without exception the most significant of any synthetic organic pigment produced today due to its
15 excellent color strength and durability. It has a high molar absorption coefficient (ca. 105), and its light fastness and weather fastness are superior to all other organic pigments. Additionally, its synthesis is readily performed from lower cost materials (phthalic anhydride, urea and copper salts), thereby making production of this complex molecule both facile and economic. Thus, it is
20 typically employed as a blue colorant for paints or plastics. Among pigments, copper phthalocyanine is very stable and more desirable since it possesses a variety of fastness.

Copper phthalocyanine has many crystal forms. Among such crystal forms, those known to have actual applications include alpha, beta and epsilon
25 crystal forms of copper phthalocyanine. It is a common practice to use the beta crystal form to impart a greenish blue colour, while using the alpha crystal form to impart a reddish blue colour. Further, the epsilon crystal form is employed when a blue colour, which is more reddish than that produced using the alpha crystal form, is required.

30 Copper phthalocyanine is commercially available in three crystal forms, namely, alpha, beta and epsilon. The alpha crystal, which uses the Colour Index

nomenclature, is described as Pigment Blue 15, 15:1 and 15:2, and is a clean, bright red shade blue. The beta crystal, which is described as Pigment Blue 15:3 and 15:4, is a clean green shade blue, and the important epsilon form is the most reddish shade of blue. Its halogenated derivatives are also used as important green pigments.

Typically, the commercially available "crude" copper phthalocyanine particles include various crystal forms, most of which exhibit beta-crystallographic form. There are many techniques available for the conversion of crude copper phthalocyanine into pigmentary form, e.g., by acid pasting to give 100 % alpha form, or salt-milling involving progressive conversion to the alpha form. It is preferred that they are prepared from copper phthalocyanine particles exhibiting a β crystallographic form by using an acid paste method. The beta crystal form copper phthalocyanine is commercially available from various companies such as Toyo Ink (Japan), Dainippon Ink & Chemicals Co. (Japan), etc. The beta crystal form copper phthalocyanine is subjected to crystal phase conversion into alpha crystal form by acid pasting, which is described, for instance, in Ullmann's Encyclopedia of Industrial Chemistry, Fifth Completely Revised Edition, 1992, Volume A20, pp. 225-226, incorporated herein by reference.

Copper phthalocyanine (CuPc) particles exhibiting an ϵ crystallographic form are typically prepared from CuPc particles with at least 50 wt % of the particles exhibiting an α crystallographic form as a starting material.

Various methods have been proposed for producing a phthalocyanine pigment with each crystal form. A typical process of producing epsilon crystal form copper phthalocyanine is the solvent salt milling process, wherein copper phthalocyanine particles exhibiting alpha crystal form and copper phthalocyanine particles exhibiting epsilon crystal form are milled in an organic solvent.

For example, WO 2009/037233 discloses a process wherein CuPc particles exhibiting alpha-crystallographic form are subjected to heating in a solvent, optionally with milling beads, for crystallographic conversion to epsilon type. The heating is then followed by a kneading process for micronizing the epsilon type CuPc particles. In WO 2009/062995, after obtaining alpha-type CuPc particles from the acid-pasting step, the alpha-type CuPc particles are kneaded under different temperature conditions. During the kneading step, two CuPc derivatives are sequentially added.

As to a process of preparing alpha form copper phthalocyanine from the beta form, pigmentation processes using sulfuric acid, which is one of the mineral acids, have been known in the art. That is, an acid pasting process (treating crude copper phthalocyanine when dissolved in a large amount of concentrated sulfuric acid) and an acid slurry process (treating crude copper phthalocyanine with a large amount of sulfuric acid having a concentration insufficient for dissolving the pigment to form a sulfate) are used.

However, the products obtained by the above processes are produced in the form of agglomerates, which do not display the desired performance properties.

In order to subsequently achieve optimum application properties, the so-called finish is carried out in, for example, solvents while adding surface-active agents as disclosed in GB1096192A and GB2039290. EP1580239A1 also discloses a process for the production of an epsilon-crystal form copper phthalocyanine comprising heating a copper phthalocyanine in an organic solvent, such as t-amylbenzene, sulfolane, etc., in the presence of a Lewis acid.

WO 08/083799A discloses a pigment composition of copper phthalocyanine exhibiting epsilon crystallographic form, which is produced with application of a wet grinding process, more particularly a salt kneading operation.

US 4239685A discloses a process for preparation of phthalocyanine pigments from a phthalocyanine press paste obtained by hydrolysis of a sulphuric solution of phthalocyanine, in which a small quantity of a water-insoluble crystallizing solvent, in the presence or absence of a non-crystallizing solvent, is incorporated with stirring in said press paste, and then the solvent or solvents is or are eliminated and the paste is dried, and the pigments thus obtained are collected.

US 3801591A discloses a production of metal phthalocyanine pigment composed almost exclusively of the α I polymorph in which crude metal phthalocyanine is subjected to controlled precipitation in two stages followed by conditioning of the resultant slurry under intense agitation to generate an air/liquid interface and thereby facilitate flocculation, hence filtration.

GB 1411880A discloses a process for the production of copper phthalocyanine in the form of the pure or practically pure ϵ -modification copper phthalocyanine which process comprises converting α -modification, γ -modification and/or δ -modification copper phthalocyanine to an α -/ ϵ -modification mixture by grinding in a ball mill, treating the mixture with a

liquid at a temperature at which no or substantially no conversion into the β -modification takes place (liquid-specific limiting temperature) to effect conversion of α -modification to ε -modification and to form a mixture of the liquid with pure or substantially pure ε -modification and optionally isolating the
5 pure or substantially pure ε -modification of copper phthalocyanine.

However, the above-described methods of preparing copper phthalocyanine particles have problems in that the resulting CuPc particles still lack dispersibility, which results in still to improve color filter pigments, for instance regarding the contrast ratio of the color filters prepared from the copper
10 phthalocyanine particles. Thus, there has been a strong desire in the art to develop a method of effectively improving dispersibility of the resultant copper phthalocyanine particles to increase the performance of a final pigment for color filter, without the above-described drawbacks.

Disclosure of Invention

15 The purpose of the present invention is to resolve the problems of the conventional preparation process, e.g. relatively low dispersibility resulting in poor contrast ratios from the resultant color filter pigment.

The present invention therefore relates to a process for preparing a product based on copper phthalocyanine (CuPc) particles, said process comprising
20 adding, to the CuPc particles, during or after their preparation, at least one non-polar solvent in an amount of less than 10 % by weight of the CuPc particles.

The inventors of the present invention have indeed discovered that the performance of the final color filter pigment for producing blue pigments may be improved when some non-polar solvents were added in an amount of less
25 than 10 % by weight of the copper phthalocyanine particles during or after the preparation of copper phthalocyanine particles exhibiting epsilon form.

Hereinafter, the present invention is described in detail.

The present invention is directed to developing a new and more efficient process of preparing copper phthalocyanine-based products, which satisfies the
30 above-mentioned features.

Copper phthalocyanine (CuPc) is typically developed for effective use as a blue pigment of color filters for LCDs. Such color filters must be highly transparent, homogeneous and be prepared in a layer with uniform thickness. These features are decided by several factors including chemical purity,
35 crystallographic purity, primary particle size and particle size distribution of

copper phthalocyanine particles. In this regard, the disclosure teaches a new and more efficient process of preparing copper phthalocyanine.

Even though any type of non-polar solvent known in the art may be used in the process of the present invention, it is preferable to use at least one non-polar solvent selected from alicyclic and aromatic compounds. Suitable examples of non-polar solvents are those selected from the group consisting of n-hexane, pentane, cyclopentane, petroleum ether, cyclohexane, benzene, naphthalene, toluene, or cumene, preferably cyclohexane, benzene or naphthalene.

The amount of the non-polar solvent is not limited but the non-polar solvent is generally added in an amount of at least 0.1 % by weight of the CuPc particles, particularly at least 0.5 % by weight, more particularly at least 1 % by weight. The non-polar solvent is commonly added in an amount of less than 10 % by weight of the CuPc particles, particularly at most 5 % by weight, more particularly at most 3 % by weight. The amount of non-polar solvent may typically be from 0.1 to less than 10 % by weight of the CuPc particles, preferably from 0.5 to 5 %, more preferably from 1 to 3 % by weight.

In a specific embodiment of the invention, the at least one non polar solvent may be combined with at least one polar solvent. The at least one polar solvent may be present preferably in an amount of from 3.3 to 20 % by weight of the CuPc particles, more preferably from 5 to 10 % by weight, in particular from 5 to less than 10 % by weight.

In another embodiment of the present invention, a surfactant acting as a dispersant may be added in the process of the invention, especially in the same process step as the non-polar solvent. Suitable surfactants include organic carboxylic or sulfonic acids, amines or ammonium compounds, or rosin and its derivatives, for instance lauric acid, capric acid, citric acid, oleic acid, stearic acid, dodecylbenzene sulfonic acid (DBSA), p-toluenesulfonic acid (pTSA), lauryl amine, benzylamine, hexadecylamine, dodecylamine, aniline, 6-aminohexanoic acid, 4-(aminomethyl)benzoic acid, cetyltrimethyl ammonium chloride, and combinations thereof, preferably cetyltrimethyl ammonium chloride, rosin and its derivatives, and combinations thereof.

Such surfactants are believed to form an electrical double layer through interaction with the surface of CuPc particles, which leads to better dispersion stability of the resultant dispersions by prevention of particle agglomeration. The interaction may be ionic or pi-pi-type interaction between the surfactant molecule and the surface of copper phthalocyanine particles.

The term "rosin" is defined herein as a solid form of resin obtained from pines and some other plants, mostly conifers, which chiefly consists of different resin acids, especially abietic acid. Mixtures of this kind that are readily available and occur in nature include, but are not limited to, tall oil rosin, gum rosin or wood rosin. These natural mixtures may comprise rosin acids of the abietic type and/or the pimaric type such as abietic acid, palustric acid, neoabietic acid, levopimaric acid, pimaric acid, isopimaric acid or dehydroabietic acid, among others, in varying amounts. In addition to rosin acids with one carboxylic acid functionality, rosin acids with two or more carboxylic acid functionalities are also considered as rosin acids in the meaning of the present invention. The expression "rosin derivatives" is defined as any derivative of the rosin, for example, hydrogenated rosin, dimerized rosin, poly-pale rosin, rosin substituted by ester groups, etc.

When a surfactant is added, its amount is not limited but is in general from 0.1 to 25 % by weight of the CuPc particles, preferably from 0.5 to 20 % by weight, more preferably from 1 to 15 % by weight.

In a further embodiment, at least one of an alkaline or alkaline earth metallic salt may be added during and/or after the kneading step. The alkaline metal of the alkaline metallic salt is typically selected from sodium, potassium and lithium, in particular sodium. The alkaline earth metal of the alkaline earth metallic salt is often selected from calcium and magnesium, most often calcium. The metallic salt is advantageously an alkaline earth metallic salt. Suitable examples of alkaline and alkaline earth metallic salts are alkaline and alkaline earth metal chlorides such as NaCl, KCl, LiCl, CaCl₂, MgCl₂; carboxylic acid salts such as CH₃COONa, (CH₃COO)₂Ca; acidic or basic salts such as NaHCO₃, NaHSO₄, Na₂HPO₄, Ca(OH)Cl, Ba(OH)Cl, etc.; especially CaCl₂ and MgCl₂.

When an alkaline or alkaline earth metallic salt is added, its amount is not limited, but it is generally added in an amount from 0.1 to 25 % by weight of the CuPc particles, preferably from 0.5 to 20 % by weight, more preferably from 1 to 15 % by weight.

In the present invention, it has surprisingly been found that by adding non-polar solvent in an amount of less than 10 % by weight, a better dispersibility of the pigment particles can be obtained. It has also been found that the resulting particles exhibit a rounder particle shape. This leads to an improved contrast ratio of the resultant color filter prepared from the pigment particles, as well as to an improved brightness of said color filters.

The present invention therefore also relates to copper phthalocyanine (CuPc) particles having a round shape, in particular to CuPc particles showing an average aspect ratio from 1:1 to 2:1, preferably 1:1 to 1.5:1, more preferably 1.1 to 1.3:1, most preferably around 1:1. The aspect ratio is defined herein as the length of a pigment particle with respect to the width thereof. The aspect ratio is usually determined by an image analysis of pictures taken by transmission electron microscopy (TEM) or scanning electron microscopy (SEM). The mean length (L) can be determined by several methods including measurement of the maximal Feret diameter, the length of the rectangle in which the particle can be inserted or the length L. Likewise, the mean width of the particles can be determined according to the diameter of a circle of equivalent projection area, the minimal Feret diameter, the width of the rectangle in which the particle can be inserted or the width l. Thus, the aspect ratio (L/l) corresponds to the ratio between a length (L) and the related width (l), especially the maximal Feret diameter on the minimal Feret diameter, the maximal Feret diameter on the diameter of a circle of equivalent projection area, the length of the rectangle in which the particle can be inserted on the width of the rectangle in which the particle can be inserted or the length measured directly on the width measured directly. The aspect ratio of a population of particles is defined as the mean of the aspect ratio of each particle. In a preferred embodiment, the aspect ratio is the averaged ratio of the length of particles measured directly on the width of particles measured directly, said lengths and widths being measured on images obtained by TEM.

The process of the present invention is especially suitable for preparing CuPc particles exhibiting an ϵ crystallographic form.

In one aspect of the present invention, the product (CuPc) particles exhibit an ϵ crystallographic form and the CuPc particles to which the at least one non-polar solvent is added comprise CuPc particles exhibiting an α crystallographic form. Preferably, the CuPc particles to which the at least one non-polar solvent is added comprise CuPc particles with at least 50 wt % of the particles exhibiting an α crystallographic form.

In a particular embodiment of this aspect, copper phthalocyanine particles exhibiting an ϵ crystallographic form are added, as seed particles, to the CuPc particles to which the at least one non-polar solvent is added, in an amount of from 10 wt % to 90 wt %, preferably 15 wt % to 50 wt % relative to the total amount of CuPc particles.

In a first specific embodiment, copper phthalocyanine particles exhibiting an ϵ crystallographic form may be prepared by heating a starting material comprising at least 50 wt % of CuPc particles exhibiting an α crystallographic form at a temperature higher than or equal to 50°C in the presence of at least one organic liquid and optional milling in the presence of beads. The organic liquid may for instance be selected from the group consisting of N-methyl-2-pyrrolidone, sulfolane, N,N-dimethylformamide, glycols such as propylene glycol monomethyl ether acetate, diethylene glycol, alcohols such as diacetone alcohol, acetonitrile, monochlorobenzene, ethylene glycol butyl ether, ketones and quinolines. Milling, as defined herein, means a process by which the solids are subjected to attrition, grinding, etc. to achieve particle size reduction.

In a second specific embodiment, ϵ CuPc particles may be prepared by kneading a starting material comprising at least 50 wt % of CuPc particles exhibiting an α crystallographic form in the presence of at least one liquid and of at least one inorganic salt. The liquid is generally selected from the group consisting of N-methyl-2-pyrrolidone, sulfolane, N,N-dimethylformamide, diethylene glycol, diacetone alcohol, glycerin, ethylene glycol, propylene glycol, polypropylene glycol, 2-butoxy ethanol, methylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, ketones and quinolines. Preferably, kneading is conducted under temperature conditions such that the temperature profile as a function of time exhibits at least two derivatives of temperature with respect to time (dT/dt) being equal to 0. The two temperatures are associated with the derivatives equal to 0 differing by at least 10°C. In another embodiment, kneading is conducted under a constantly or stepwise changing temperature profile. Preferably, kneading is conducted at the first temperature and then at the second temperature, wherein the first temperature is 80-150°C (preferably 100-120°C) and the second temperature is 30-70°C (preferably 50-60°C). This embodiment provides modification of the temperature during the kneading step by which CuPc particles exhibiting α -crystallographic form is converted to ϵ crystallographic form and their particle size is significantly reduced.

The specific conditions of the kneading or heating step (e.g., duration, beads, inorganic salts, etc.) are described in International Patent Applications WO 2009/037233 and WO 2009/062995, all of which are incorporated herein by reference in their entirety.

After preparation of copper phthalocyanine according to those methods, to remove byproducts and additives added in the previous step(s), the resultant mixture may be stirred for a period of time, and filtered. The filter cake may be washed by reslurrying several times in distilled water, optionally in the presence of an organic solvent.

The process of the present invention is also especially suitable for preparing CuPc pigment compositions comprising CuPc particles exhibiting an ϵ crystallographic form.

In another specific embodiment of the invention, the non-polar solvent may be added during preparation of a CuPc pigment composition comprising CuPc particles exhibiting an ϵ crystallographic form. Specifically, the non-polar solvent may be added in a kneading step, or in a re-slurry step where the filter cake obtained after the kneading step is reslurried in a solvent such as water, a water-miscible solvent or a mixture thereof. In this embodiment, by adding the at least one non-polar solvent to CuPc particles exhibiting an ϵ crystallographic form, preferably during a re-slurry or kneading step (size reduction), a rounder shape of the CuPc particles can be obtained. In some further specific embodiments, a non-polar solvent may be added during the kneading step, and subsequently another non-polar solvent may be added during the re-slurry step. The present invention thus also relates to copper phthalocyanine (CuPc) pigment compositions comprising CuPc particles exhibiting an ϵ crystallographic form obtainable according to the process of the invention. Also, it is related to a color filter comprising copper phthalocyanine particles exhibiting the epsilon crystallographic form obtainable by the process of the present invention.

The present invention also relates to copper phthalocyanine (CuPc) particles exhibiting an ϵ crystallographic form, obtainable by the process of the invention.

In view of the above, another aspect of the present invention is related to the use, in preparing a product based on CuPc particles, of at least one non-polar solvent in an amount of less than 10 % by weight of the copper phthalocyanine (CuPc) particles.

The present invention is further illustrated below without limiting the scope thereto.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the

present application to the extent that it might render a term unclear, the present description shall take precedence.

Examples

Example 1 (Conversion of beta-CuPc to alpha-CuPc)

5 50 g of crude copper phthalocyanine were added to 500 g of 95 wt %
sulfuric acid in a 2L glass beaker. Further, the resultant mixture was stirred by a
stirring impeller (Teflon centrifugator, rotation speed of 300 rpm) at 30°C for
2 hours to prepare a suspension or solution of sulfate in the sulfuric acid. The
suspension or the solution was poured twice into 5L of water to obtain an alpha
10 crystal form copper phthalocyanine, which was then dried under hot air. After
pulverizing the resulting solid, the alpha crystal form copper phthalocyanine was
obtained almost quantitatively in terms of crystallographic yield, which was
confirmed by a XRD study.

Example 2 (Conversion of alpha-CuPc to epsilon-CuPc in the presence of 15 cyclohexane)

To a lab-scale kneader, 50 g of the copper phthalocyanine particles
exhibiting an alpha crystallographic form, which were obtained in Example 1
and 12 g of epsilon-type copper phthalocyanine were added with 3.0 g of
cyclohexane, 80 g of diethylene glycol and 400 g of sodium chloride. The
20 mixture was kneaded for 6 hours at 130°C with a rotation speed of 50 rpm
(1st stage), and then for 8 hours at 80°C with an identical rotation speed
(2nd stage). After kneading, the resultant particles were filtered and washed
several times with distilled water.

The wet cake was reslurried in deionized water and then 10g of rosin were
25 added while maintaining stirring, and a copper phthalocyanine composition was
obtained. After the re-slurry step was completed, the slurry was purified by
filtration, and dried at a temperature of 80°C and pressure of 104 Pa. The dried
product was then pulverized and analyzed by a Transmission electron
microscope (TEM). Fig. 1 illustrates a TEM image for the copper
30 phthalocyanine particles.

Example 3 (Conversion of alpha-CuPc to epsilon-CuPc in the presence of benzene)

Copper phthalocyanine particles exhibiting epsilon crystallographic form
were obtained in an identical manner to that of Example 2, except that 3.0 g of
35 benzene were added during the kneading step.

Example 4 (Comparative – no addition of non-polar solvent and surfactant)

Copper phthalocyanine particles exhibiting epsilon crystallographic form were obtained in an identical manner to that of Examples 1 and 2, except that no non-polar solvent, no surfactant and no metallic salts were added. Upon
5 analyzing some dried samples of the resultant copper phthalocyanine particles exhibiting epsilon crystallographic form with the transmission electron microscope (TEM), they were shown to exhibit more agglomeration in the image (Figure 2).

As shown in the TEM images of Figures 1 and 2, the epsilon-CuPc
10 particles obtained according to the process of the present invention, in the presence of a non-polar solvent (Example 2), exhibit a higher dispersion level compared to the epsilon-CuPc particles produced according to Example 4, without addition of a non polar solvent. Further, the CuPc particles of the invention have an aspect ratio close to 1:1, which is advantageous for higher
15 contrast ratio.

Examples 5 to 7 (Comparative – no addition of a non polar solvent)

Copper phthalocyanine particles exhibiting epsilon crystallographic form were obtained in an identical manner to that of Example 2, except that 0.5 g of rosin and 0.5 g of calcium chloride, or 1.5 g of rosin and 1.5 g of calcium
20 chloride, or 10.0 g of rosin were respectively added during the re-slurry step.

Example 8 (Conversion of alpha-CuPc to epsilon-CuPc in the presence of cyclohexane and no addition of surfactant)

Copper phthalocyanine particles exhibiting epsilon crystallographic form were obtained in an identical manner to that of Examples 1 and 2, except that no
25 surfactant and no metallic salts were added. The dried product was then pulverized and the particle shape was better, compared to those of Example 4.

Test of the particles in color filters

Color filters fabricated using the pigment from the ϵ form copper phthalocyanine pigment particles prepared according to Examples 2 and 3
30 yielded improvements in contrast ratio by approximately 8 % and 10 %, respectively, compared to those of Example 4, as shown in Table 1.

In Table 1, the CuPc pigment in which the non-polar solvent and optionally surfactant were added exhibited improved contrast ratio of the color filter pigment millbase. Such improvement would be derived from better
35 dispersibility and optimized shape of the resultant CuPc particles.

Thus, such increased dispersibility and good particle shape has led to the improved contrast ratio of the downstream color filter.

Table 1

Examples	Non-polar solvent / surfactant	Contrast Ratio
Ex.2	3.0g cyclohexane + 10.0g rosin + 0.5g CaCl ₂	8 % improvement
Ex.3	3.0g benzene + 10.0g rosin + 0.5g CaCl ₂	10 % improvement
Ex.4	-	1 (a.u.)
Ex.5	0.5g rosin + 0.5g CaCl ₂	3 % improvement
Ex.6	1.5g rosin + 1.5g CaCl ₂	1 % improvement
Ex.7	10.0g rosin	1 % improvement

Brief Description of Figures in the Drawings

5 Fig. 1 is an image from a Transmission Electron Microscope (TEM) for the copper phthalocyanine particles exhibiting epsilon crystallographic phase prepared by the method according to Example 2.

10 Fig. 2 is an image from a TEM for the copper phthalocyanine particles exhibiting epsilon crystallographic phase prepared by the method according to Example 4.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

15 Industrial Application

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. Thus, it is intended that the present invention covers the modifications and variations of this invention provided they come within the
20 scope of the appended claims and their equivalents.

CLAIMS

1. A process for preparing a product based on copper phthalocyanine (CuPc) particles, said process comprising adding, to the CuPc particles, during or after their preparation, at least one non-polar solvent in an amount of less than 10 % by weight of the CuPc particles.
2. The process according to Claim 1, wherein the at least one non-polar solvent is added in an amount from 0.1 to less than 10 % by weight of the CuPc particles, preferably from 0.5 to 5 %, more preferably from 1 to 3 %.
3. The process according to Claim 1 or 2, wherein the product (CuPc) particles exhibit an ϵ crystallographic form and the CuPc particles to which the at least one non-polar solvent is added comprise CuPc particles exhibiting an α crystallographic form.
4. The process according to any one of Claims 1 to 3 which further comprises adding to the CuPc particles to which the at least one non-polar solvent is added, CuPc particles exhibiting an ϵ crystallographic form, in an amount of from 10 wt % to 90 wt %, preferably 15 wt % to 50 wt % relative to the total amount of CuPc particles.
5. The process according to Claim 3 or 4, wherein the at least one non-polar solvent is selected from a group consisting of n-hexane, pentane, cyclopentane, petroleum ether, cyclohexane, benzene, naphthalene, toluene, cumene and mixtures thereof, preferably cyclohexane, benzene, naphthalene and mixtures thereof.
6. The process according to any one of Claims 1 to 5, wherein the at least one non polar solvent is combined with at least one polar solvent, said at least one polar solvent being present in an amount of from 3.3 to 20 % by weight of the CuPc particles, preferably from 5 to 10 % by weight, more preferably from 5 to less than 10 % by weight.
7. The process according to any one of Claims 1 to 6, wherein at least one surfactant is further added.

8. The process according to Claim 7, wherein the surfactant is at least one selected from the group consisting of rosin and its derivatives, lauric acid, capric acid, citric acid, lauryl amine, benzylamine, hexadecylamine, dodecylamine, aniline, 6-aminohexanoic acid, 4-(aminomethyl)benzoic acid, cetyltrimethyl ammonium chloride, and combinations thereof, preferably from rosin and its derivatives, cetyltrimethyl ammonium chloride, and combinations thereof.

9. The process according to any one of Claims 1 to 8, wherein at least one of an alkaline or alkaline earth metallic salt is added.

10. The process according to any one of Claims 1 to 9, further comprising adding at least one organic liquid selected from the group consisting of N-methyl-2-pyrrolidone, sulfolane, N,N-dimethylformamide, glycols such as propylene glycol monomethyl ether acetate, diethylene glycol, alcohols such as diacetone alcohol, acetonitrile, monochlorobenzene, ethylene glycol butyl ether, ketones and quinolines, or at least one liquid selected from the group consisting of N-methyl-2-pyrrolidone, sulfolane, N,N-dimethylformamide, diethylene glycol, diacetone alcohol, glycerin, ethylene glycol, propylene glycol, polypropylene glycol, 2-butoxy ethanol, methylene glycol, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, dipropylene glycol monomethyl ether, 1-methoxy-2-propanol, 1-ethoxy-2-propanol, ketones and quinolines, to the starting material.

11. The process according to any one of Claims 1 to 10 for preparing CuPc particles exhibiting an ϵ crystallographic form, said process comprising kneading CuPc particles containing at least 50 wt % of particles exhibiting an α crystallographic form as a starting material in the presence of the at least one non-polar solvent.

12. The process according to any one of Claims 1 to 10 for preparing a CuPc pigment composition comprising CuPc particles exhibiting an ϵ crystallographic form, wherein the at least one non-polar solvent is added to CuPc particles exhibiting an ϵ crystallographic form, preferably during a re-slurry or kneading step.

13. Copper phthalocyanine (CuPc) pigment composition comprising CuPc particles exhibiting an ϵ crystallographic form, said CuPc particles being prepared according to the process of Claim 11, or said composition being prepared according to the process of Claim 12.

5 14. Copper phthalocyanine (CuPc) particles exhibiting an ϵ crystallographic form prepared according to the process of Claim 11.

10 15. Copper phthalocyanine (CuPc) particles exhibiting an ϵ crystallographic form, the average aspect ratio of said particles being from 1:1 to 2:1, preferably 1:1 to 1.5:1, more preferably 1:1 to 1.3:1, most preferably around 1:1.

Fig. 1

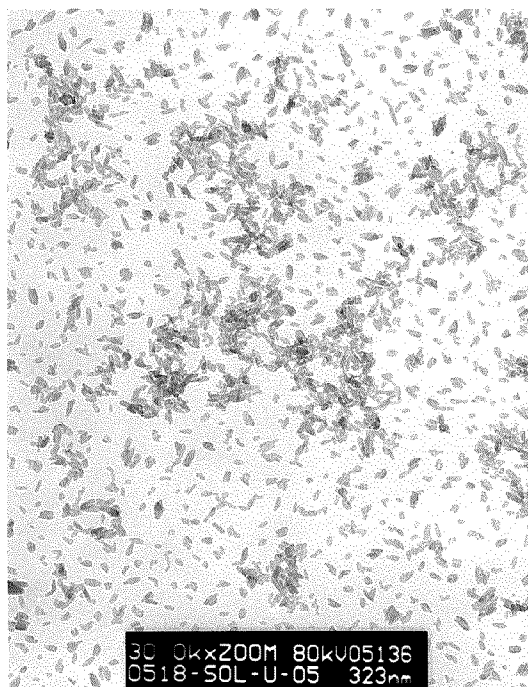
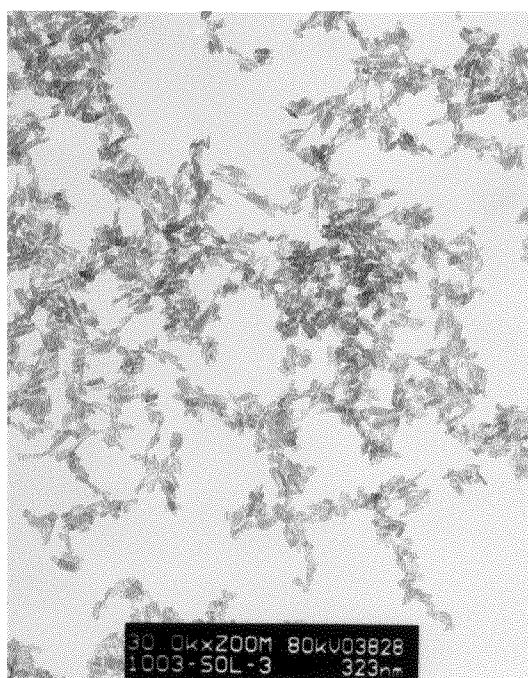


Fig. 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/073238

A. CLASSIFICATION OF SUBJECT MATTER INV. C09B67/00 G02B5/22 G03F7/00 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C09B G02B G03F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 239 685 A (PIGASSE DANIEL [FR]) 16 December 1980 (1980-12-16) column 2, lines 14-31 column 2, line 66 - column 4, line 5 examples 1-9 claims 1-17	1-12
X	----- US 3 801 591 A (JACKSON J) 2 April 1974 (1974-04-02) column 2, lines 41-69 examples 1-5 claims 1-3 ----- -/-	1,2,5-8
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
8 March 2012	14/03/2012	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Constantinescu, R	

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/073238

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 580 239 A1 (TOYO INK MFG CO [JP]) 28 September 2005 (2005-09-28) cited in the application paragraphs [0009], [0014], [0018], [0020] examples 4,6 claims 1-10 -----	13-15
X	EP 2 039 727 A1 (SOLVAY [BE]) 25 March 2009 (2009-03-25) cited in the application paragraphs [0020], [0021], [0041], [0042], [0076] claims 1-16 -----	3,4,9-15
X	EP 2 060 608 A1 (SOLVAY [BE]) 20 May 2009 (2009-05-20) cited in the application paragraphs [0041], [0050] claims 1-17 -----	3,4,9-15
X	GB 1 411 880 A (BASF AG) 29 October 1975 (1975-10-29) page 1, lines 65-80 page 2, lines 18-24, 52-85, 124-130 page 3, lines 7-31, 47-51 example 6 claims 1-9 -----	1-15
X	US 2006/112856 A1 (BRYCHCY KLAUS [DE] ET AL) 1 June 2006 (2006-06-01) column 2, line 1 - column 3, line 41 column 4, lines 20-67 column 5, lines 10-23 column 5, line 46 - column 6, lines 36, 49-55 claims 1-8,10, 11, 20 -----	1-8
X	US 2010/086868 A1 (METZ THOMAS [DE] ET AL) 8 April 2010 (2010-04-08) cited in the application paragraphs [0016] - [0027], [0035] claims 1-5,12-14 -----	13-15
A	US 4 459 233 A (FABIAN WOLFGANG [DE] ET AL) 10 July 1984 (1984-07-10) examples 1-9, 15 claims 1-15 -----	1-15
A	US 3 730 750 A (FABIAN W) 1 May 1973 (1973-05-01) column 2, lines 22-37 examples 1-3, 7 claims 1-10 -----	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/073238

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4239685	A	16-12-1980	BE 874177 A1	16-08-1979
			BR 7901072 A	02-10-1979
			DE 2906749 A1	23-08-1979
			DK 70979 A	22-08-1979
			ES 477915 A1	01-07-1979
			FR 2417531 A1	14-09-1979
			GB 2016503 A	26-09-1979
			IT 1119914 B	19-03-1986
			JP 54126231 A	01-10-1979
			NL 7901344 A	23-08-1979
			US 4239685 A	16-12-1980
US 3801591	A	02-04-1974	BE 800697 A1	10-12-1973
			US 3801591 A	02-04-1974
EP 1580239	A1	28-09-2005	EP 1580239 A1	28-09-2005
			US 2005215780 A1	29-09-2005
EP 2039727	A1	25-03-2009	EP 2039727 A1	25-03-2009
			JP 2010539309 A	16-12-2010
			KR 20100091157 A	18-08-2010
			TW 200927842 A	01-07-2009
			WO 2009037233 A2	26-03-2009
EP 2060608	A1	20-05-2009	CN 101918496 A	15-12-2010
			EP 2060608 A1	20-05-2009
			JP 2011503313 A	27-01-2011
			KR 20100113486 A	21-10-2010
			TW 200930766 A	16-07-2009
			WO 2009062995 A2	22-05-2009
GB 1411880	A	29-10-1975	AU 476846 B2	07-10-1976
			AU 5257273 A	29-08-1974
			BE 795946 A1	27-08-1973
			CA 992940 A1	13-07-1976
			CH 568366 A5	31-10-1975
			DE 2210072 A1	06-09-1973
			DK 132765 B	02-02-1976
			FR 2174089 A1	12-10-1973
			GB 1411880 A	29-10-1975
			IT 977502 B	20-09-1974
			JP 1230388 C	19-09-1984
			JP 48101419 A	20-12-1973
			JP 57035210 B	28-07-1982
			NL 7302732 A	04-09-1973
US 2006112856	A1	01-06-2006	CN 1705718 A	07-12-2005
			CN 1705719 A	07-12-2005
			DE 10257498 A1	01-07-2004
			EP 1572809 A1	14-09-2005
			EP 1572810 A1	14-09-2005
			ES 2266888 T3	01-03-2007
			ES 2308009 T3	01-12-2008
			JP 4738813 B2	03-08-2011
			JP 2006509081 A	16-03-2006
			JP 2006509083 A	16-03-2006
			KR 20050084218 A	26-08-2005
			KR 20050085476 A	29-08-2005

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/073238

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
		US 2006112856 A1	01-06-2006	
		US 2006137573 A1	29-06-2006	
		WO 2004052996 A1	24-06-2004	
		WO 2004052997 A1	24-06-2004	

US 2010086868	A1	08-04-2010	CN 101563426 A	21-10-2009
			DE 102007001851 A1	17-07-2008
			EP 2121851 A1	25-11-2009
			JP 2010515789 A	13-05-2010
			KR 20090122183 A	26-11-2009
			US 2010086868 A1	08-04-2010
			WO 2008083799 A1	17-07-2008

US 4459233	A	10-07-1984	AU 8256282 A	21-10-1982
			DE 3114928 A1	28-10-1982
			EP 0063321 A2	27-10-1982
			JP 57180666 A	06-11-1982
			US 4459233 A	10-07-1984

US 3730750	A	01-05-1973	CA 965556 A1	08-04-1975
			CH 557862 A	15-01-1975
			DE 2013818 A1	21-10-1971
			FR 2085008 A5	17-12-1971
			GB 1344389 A	23-01-1974
			JP 56005789 B	06-02-1981
			NL 7103831 A	27-09-1971
			US 3730750 A	01-05-1973
