Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Aug 2012.

To cite this article: Yousuke Miyashita , Koichi Baba , Hitoshi Kasai , Hachiro Nakanishi & Tokuji Miyashita (2008): A New Production Process of Organic Pigment Nanocrystals, Molecular Crystals and Liquid Crystals, 492:1, 268/[632]-274/[638]

To link to this article: http://dx.doi.org/10.1080/15421400802330606

Mol. Cryst. Liq. Cryst., Vol. 492, pp. 268/[632]–274/[638], 2008

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400802330606

A New Production Process of Organic Pigment Nanocrystals

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By using the reprecipitation method known as an organic nanocrystal preparation method, the preparation of organic pigment nanocrystals with a particle size of about 25 nm was easily achievable. When they were used for the color filter of liquid crystal displays, clear improvement in the contrast ratio was confirmed.

Keywords: color filter; light scattering; organic pigment nanocrystals; reprecipitation method

1. INTRODUCTION

Organic pigments have been widely used in printing and coating industries as the coloring agents for plastics and synthetic fibers. In recent years, some organic pigments have an attention as organic photoconductors such as electrophotographic photoreceptors and

Present work was partially supported by NEDO (New Energy and Industrial Technology Development Organization) of Japan. The authors wish to thank Mr. Shinichi Horino and Miss Keiko Kawase for their assistance in performing various experiments, and to express our sincere gratitude to Professor Hidetoshi Oikawa, Assistant Professor Akito Masuhara, Assistant Professor Takayuki Ishizaka, Mr. Kenji Sugai, and many students of Oikawa laboratory for preparation of organic pigment nanocrystals by the reprecipitation method.

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organic EL materials [1]. In addition, organic pigments are used for ink-jet inks to produce photographic-quality pictures and color filters that are essential materials for the full-colorization of digital cameras and liquid crystal displays (LCDs).

To increase the performance of the color filter, it is absolutely essential to cancel out the light scattering by reducing the particle size of organic pigment. As the way to reduce the particle size, the breakdown method using beads and/or inorganic salts has been commonly used. However, the low energy-efficiency, the inclusion of contaminants such as bead materials (e.g., zirconia) and/or inorganic salts, and the difficulty to reduce the particle size less than 50 nm are caused as industrial problems. Therefore, the solution of these problems has been strongly desired.

To overcome these problems, in this research, mass production procedure of organic pigment nanocrystals by the newly developed reprecipitation method and the possibility of their application to color filter for LCDs were investigated.

2. EXPERIMENTAL

2.1. Materials

Quinacridone pigment, diketopyrrolopyrrole-based pigment, and solvents were purchased from Wako Pure Chemical Industries, and used without further purification.

2.2. Preparation of Organic Pigment Nanocrystals and Pigment-Dispersion Film

Organic pigment nanocrystals were prepared by the reprecipitation method described to the literature [2–4]. Namely, the pigment dissolved good solvent was injected into a vigorously stirred poor solvent. Then, organic pigment nanocrystals dispersed in the poor solvent were prepared. Organic pigments nanocrystals were separated from the poor solvent by the centrifuge method and/or the filtration method. For the preparation of pigment-dispersion film, first, the collected organic pigments nanocrystals were redispersed in a solvent with a binder polymer. Then, the obtained organic pigments dispersion liquid was spin-coated by spin coater (1H-D7, MIKASA) to fabricate the pigment-dispersion film. The film thickness was controlled in a range of 0.1 to 2.0 μm by adjusting the rotation speed of the spin coater.

2.3. Characterization of Organic Pigment Nanocrystals and the Color Filter

The size and size distribution of the prepared organic pigment nanocrystals were measured by the statistical treatment of their scanning electron microscopy (SEM) images (S-5200, HITACHI). A thin film with a thickness about 300 nm was formed on a silicon wafer by spin-coating of the pigment dispersion liquid and was observed by SEM without pretreatment. From the obtained SEM images a circle-equivalent diameter was calculated. The light scattering intensity was measured by goniometer (GP-1-3D, OPTICS). The light scattering intensity was quantified by integrating the region whose scattering angle was larger than 5 degrees.

3. RESULTS AND DISCUSSION

3.1. Mass-Production of Organic Pigment Nanocrystals Prepared by the Newly Developed Reprecipitation Method

There have been many reports on the preparation of organic nanocrystals using the reprecipitation method and the size effect of organic nanocrystals [3,4]. However, in the viewpoint of the production amount, the maximum amount of organic nanocrystals obtained in one batch was only about 1 mg. To evaluate the prepared organic pigment nanocrystals as a functional material, it is necessary to significantly increase their preparation amount. For the realization, a highly concentrated pigment solution and an improvement in the injection rate of the solution were necessary. Based on the literature [5], the system using a pulsation-free pump was built as shown in Figure 1. In this newly developed reprecipitation method, it became possible to increase the preparation amount of nanocrystals by 10^4–10^6 times.

3.2. Characterization of Organic Pigment Nanocrystals

Figure 2 shows the SEM images of organic pigment nanocrystals prepared by the newly developed reprecipitation method (Fig. 2a), pigments prepared by the conventional milling method (Fig. 2c), and improved milling methods (Fig. 2b), respectively. This figure is clearly indicating that the organic pigment nanocrystals prepared by the reprecipitation method (Fig. 2a) are finer in mono-dispersed property, compared with the conventional products (Figs. 2b,c). The sizes of 300 pigment particles in SEM images were measured to calculate their

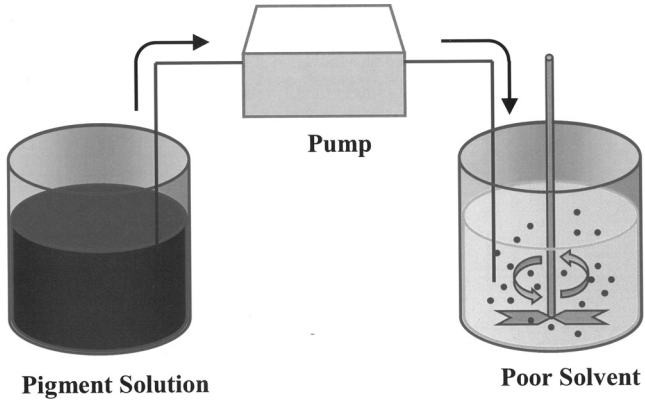

FIGURE 1 Schematic diagram of the mass-production system of organic pigment nanocrystals by the reprecipitation method.

average particle size using circle-equivalent diameter. As the result, it was found that the average size of pigment nanocrystals prepared by the reprecipitation method was 25 nm (Fig. 2a) and that of the pigments prepared by the breakdown improved milling method was 39 nm (Fig. 2b), and the former was in finer size dispersion (i.e., mono-dispersion). The relationship between the particle formation mechanism and particle size in the reprecipitation method is also under study [6].

To clarify the reduction of the light scattering that is affected by the reduced size of pigment particles, the light scattering intensity was measured using a goniometer as shown in Figure 3. The pigment-dispersion films prepared by spin coating method were used for the

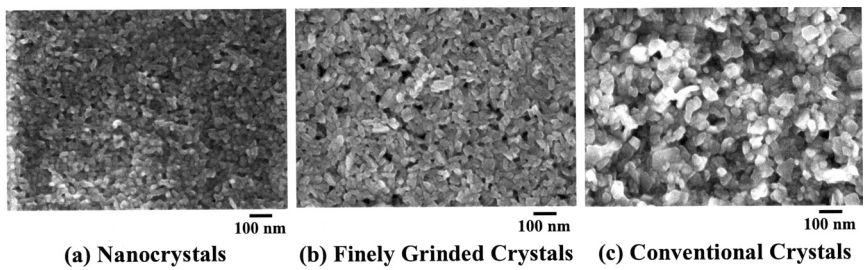

FIGURE 2 SEM images of (a) organic pigment nanocrystals prepared by the reprecipitation method, (b) finely grinded crystals, and (c) conventional crystals.

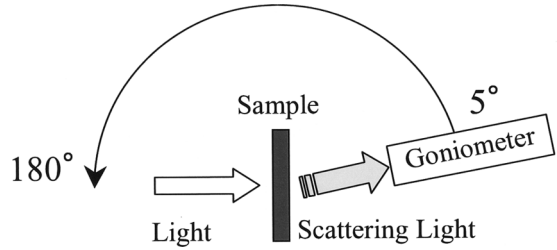

FIGURE 3 Optical arrangement of the light scattering measurement system.

specimen. It was found that the light scattering intensity of organic pigment nanocrystals prepared by the reprecipitation method was much lower than that of the conventional pigments as shown in Figure 4.

3.3. Application of Organic Pigments Nanocrystal to the Color Filers for LCDs

In LCDs, if the light scattering occurs by pigment particles, the reduction of the display contrast or the luminance ratios become a serious problem when the display is ON/OFF because of the LCD's

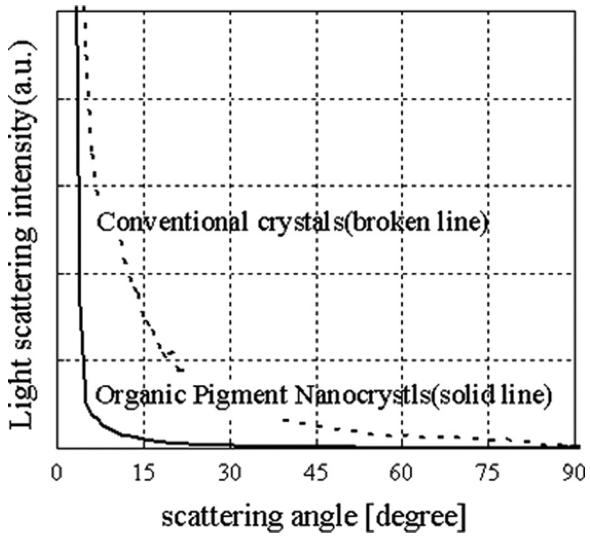

FIGURE 4 Comparison of light scattering caused by organic pigment nanocrystals and conventional crystals.

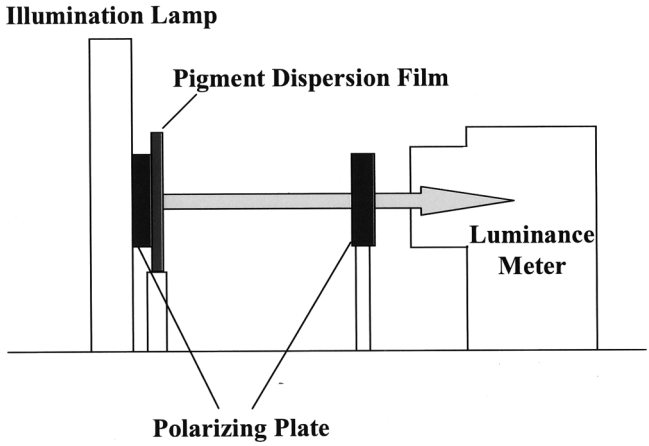

FIGURE 5 Schematic diagram of the contrast ratio measuring system.

displaying principle. To evaluate the contrast ratio of pigment-dispersion films, equation (1) was defined, and the contrast ratios were measured using a measuring instrument as shown in Figure 5.

$$\text{Contrast Ratio} = \frac{\text{Luminance at parallel nicols}}{\text{Luminance at crossed nicols}} \quad (1)$$

In Figure 6, it is apparent that the use of pigment nanocrystals prepared by the reprecipitation method can significantly increase the contrast ratio of LCDs, which is one of the most important performances. As seen in Figure 4, the high contrast achieved was due to the

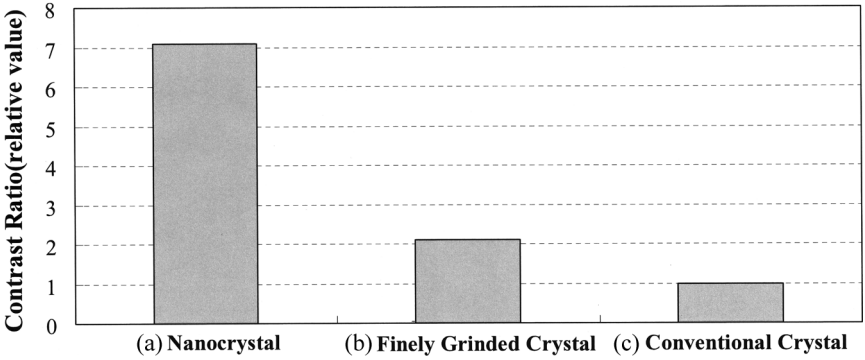

FIGURE 6 Contrast ratio of color filters composed of organic pigment nanocrystals, finely grinded crystals and conventional crystals.

reduction of the light scattering in fine size and well dispersed organic pigment nanocrystals prepared by the reprecipitation method.

4. CONCLUSION

It was found that organic pigment nanocrystals with the particle size about 25 nm were successfully achieved by the reprecipitation method. Because the fine size-controlled organic pigment nanocrystals lead to very little light scattering, they are considered to be useful for improving the performance of color filters that are an essential component of liquid crystal displays.

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