Technical Report

Development of Black Resist Ink for High-resolution Displays

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Abstract

Black resist (BK) ink is mainly used in color filters, which are the color display components of liquid crystal displays. To improve the image quality of displays, BK ink is required to have three main high properties: high light shielding, high resolution, and high insulation. However, each property has a trade-off relationship, and it is difficult to satisfy all three properties at the same time. Therefore, we focused on the thermal shrinkage rate of the main raw material, cardo resin, and developed a new cardo resin that suppresses this while promoting light and heat curing, thereby achieving high insulation while maintaining high light shielding properties. Furthermore, by applying the new cardo resin to the dispersion resin of carbon dispersion and improving the shape by using a high molecular weight acrylic material, they were able to develop a BK ink that meets the target properties.

1. Introduction

The black resist (BK) ink developed by Nippon Steel Chemical & Material Co., Ltd. is a material that forms black fine lines (black matrix) in the μ m range on glass substrates and is mainly used in color filters (CFs), which are color display components of liquid crystal displays (LCDs). LCDs are used for a variety of purposes, primarily in TVs and mobile devices. With the spread of smartphones, tablets, and head-mounted displays in particular, there is an increasing demand for improved functionality to improve image quality. Among these, the main properties required of the BK ink are a high light shielding property, high resolution, and a high insulation property.

As shown in Fig. 1, the CF is formed by coating a glass substrate, drying the solvent, exposing it to light, developing it with an alkali, and thermally curing it to form a black matrix. Then, the red, green, and blue (RGB) pixels are formed by repeating the same process. The role of the black matrix is to prevent RGB color mixing and to block the light from the backlight. A light transmittance of 0.01% or less is required to make the RGB colors stand out and appear vivid.

LCD image quality is generally expressed in ppi (pixels per inch). As shown in Fig. 2, three RGB pixels make up one pixel, which expresses the number of pixels per inch of screen size. The higher the ppi, the clearer the image that can be displayed. As shown in Fig. 3, the larger the ratio of the area occupied by RGB (aperture ratio), the brighter the screen will be, making it possible to realize an LCD with low power consumption and high image quality. Thus,

there is a demand for high-resolution black matrices.

Currently, smartphones have a black matrix with a line width of

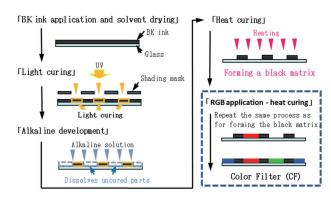


Fig. 1 CF manufacturing process

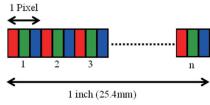


Fig. 2 Pixel configuration

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 $5 \mu m$, an aperture ratio of 75% or more, and 400 ppi or more. However, for head-mounted displays, the market demands 1500 ppi or more, and the line width of the black matrix must be $2 \mu m$ or less.

The high insulation of the black matrix is required in the inplane switching (IPS) method, a representative wide viewing angle technology. Liquid crystals have the property of moving in response to an electric field, and the smaller the inclination of the liquid crystal with respect to the glass substrate, the smaller the change in brightness and color due to the viewing angle. The IPS method, in which the liquid crystal molecules move horizontally, has less liquid crystal inclination and provides a wide viewing angle. Almost all smartphones use the IPS method. With the IPS method, however, if the insulation of the black matrix is low, the electric field is disturbed, causing problems with uneven display. High insulation (volume resistivity of $10^{13}~\Omega$ cm or more) is thus required (Fig. 4).

2. Main Body

In response to the above-mentioned technological trends, this report describes in detail how we have developed a black ink that simultaneously achieves high light shielding, high resolution, and high insulation properties through the development of carbon dispersion and binder resin, which are the main raw materials of the

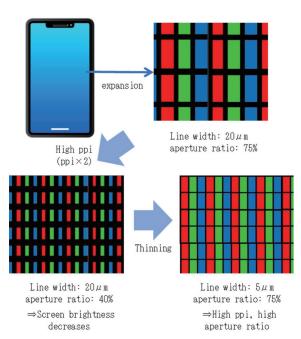


Fig. 3 Thinning of black matrix for higher image quality

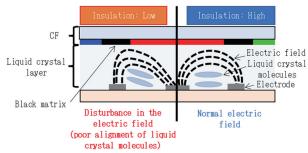


Fig. 4 Relationship between insulation and electric field in IPS

BK ink.

2.1 Components and issues of BK ink

Nippon Steel Chemical & Material's BK ink is composed of carbon dispersion, cardo resin, acrylic material, photoinitiator, additives, and solvent. These components have the functions shown in **Table 1**.

High light shielding can be achieved by increasing the carbon content, but the proximity of conductive carbon reduces insulation. In addition, the relative reduction in the amount of cardo resin and acrylic material added in the black ink composition makes it difficult to achieve high resolution. High light shielding is in a trade-off relationship with high resolution and high insulation. Therefore, we developed the following technology to achieve high resolution and high insulation while maintaining high light shielding.

2.2 Improvement in insulation by the development of new cardo resin

As shown in **Fig. 5**, cardo resin has a bisphenol fluorene skeleton with excellent heat resistance. As acryloyl groups that contribute to curing and carboxyl groups that are alkaline soluble are arranged within the molecules, the cardo resin is a material that exhibits multiple functions and is an ideal resin for the BK ink. ^{1, 2)}

To improve insulation, we must suppress the shrinkage of the cardo resin before and after thermal curing by not placing it in close proximity to conductive carbon. Therefore, with the aim of increasing the repeating structural unit shown in Fig. 5, we investigated the addition equivalent of acid dianhydride and acid mono anhydride in order to increase the number of acryloyl groups with curing properties within one molecule of the cardo resin and promote the reaction during light and heat curing. Consequently, in a new cardo resin designed to achieve both alkaline solubility and thermal shrinkage re-

Table 1 Components and functions of BK ink

Raw materials		Function	
Cardo resin		Hardening	
		Heat resistance	
		Alkaline solubility	
Carbon dispersion	Carbon	Light blocking	
	Dispersants		
	Solvent		
Acrylic material		Hardening	
		Shape control	
Photoinitiator		Photocuring reaction begins	
Additives		Coating properties	
Solvent		Coating properties	

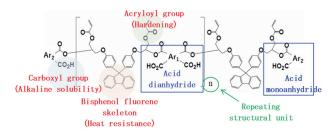


Fig. 5 Structure and function of cardo resin

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Table 2 Performance comparison of different cardo resins

	Black ink evaluation	
Resin	Heat shrinkage rate	Insulation
	(%)	$(\Omega \cdot cm)$
Conventional cardo resin	14	1.0×10 ¹¹
New cardo resin	8	3.0×10^{13}

duction, we improved the thermal shrinkage rate from 14% to 8%, achieving a significant improvement in insulation by more than two orders of magnitude (**Table 2**).

2.3 Improvement in fine line formation capability for higher resolution

2.3.1 Improvement in fine wire formation through carbon dispersion development

The carbon dispersion consists of carbon, dispersant, and solvent, as shown in Table 1. The dispersant suppresses the aggregation of carbon particles. On the other hand, since it is a component that does not contribute to photocuring, the photocuring property is reduced, making it difficult to form fine lines.

Nippon Steel Chemical & Material owns the technology to use cardo resin as a dispersing resin and impart photocuring while maintaining the dispersibility of carbon, making it possible to reduce the amount of the dispersant used (**Fig. 6**). Therefore, we investigated the optimization of dispersant reduction when using the newly developed cardo resin as a dispersing resin.

Consequently, we succeeded in reducing the amount of the dispersant by 60% by applying a new cardo resin with a large molecular weight. We found that it was possible to narrow the line width from $10 \, \mu \mathrm{m}$ with the existing technology to $6 \, \mu \mathrm{m}$ (Table 3).

2.3.2 Black matrix shape control using acrylic materials

It has been confirmed that the cross-sectional shape of the black matrix changes to a semicircular shape during the thermal curing process (**Fig. 7**).³⁾ As a result, the line width tends to increase by 1 μ m or more, which is a major problem for a material for fine lines. Therefore, with the aim of forming even finer lines, we focused on acrylic materials and conducted shape control studies.

Conventionally, a monomer acrylic material with a molecular weight of about 800 was used. This time, we focused on a resinous polymer acrylic material with a molecular weight of about 10000 obtained by polymerizing a monomer acrylic material. The resinous polymer acrylic material is a high molecular weight acrylic material. We assumed that it would have a faster thermal curing speed than the monomer acrylic material and would be effective in controlling the shape of the black matrix.

With the BK ink using a resinous polymer acrylic material, the change in the shape of the black matrix before and after thermal curing was suppressed, enabling the formation of $4 \mu m$ fine lines (Fig. 8).

3. Conclusions and Outlook

By developing the new cardo resin mentioned above, applying the carbon dispersion to the dispersion resin, and improving the shape with a resin-like polymer acrylic material, we have succeeded in developing a BK ink that simultaneously achieves high light shielding, high resolution, and high insulation. By taking advantage of these characteristics, this BK ink is being adopted for CFs for small and medium-sized panels, mainly smartphones, as a material that can achieve high image quality in LCDs. Its adoption is expand-

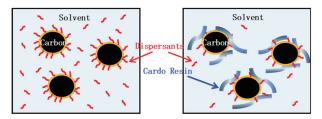


Fig. 6 Dispersant reduction by cardo resin dispersion

Table 3 Fine line formed by reducing dispersant

Dispersant amount relative ratio (%)		Fine line formation (μm)	
	100	10	
	60	7	
	40	6	
	20	Carbon agglomeration	

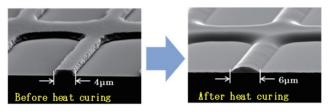


Fig. 7 Shape change during the heat curing process



Fig. 8 Shape change suppression effect

ing worldwide. We are currently developing a BK ink that can form fine lines of 2 μ m or less for head-mounted displays with 1500 ppi or more, which require even higher resolution.

The BK ink developed in this study can be applied not only to LCDs, but also to organic electroluminescence (OLED) displays. The market for the BK ink is expected to expand further. Recently, the color filter on encapsulation (COE) structure, in which the polarizer used for anti-reflection is replaced with the CF to achieve higher brightness and lower power consumption, has started to become more widespread for OLED displays. New functions such as low-temperature curing, low reflectance, and infrared (IR) transmission are required of the BK ink for the COE structure. We will continue our development efforts to improve the image quality of displays further.

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