Application of Diazo Complex with 18-Crown-6 to Visible Light Emission Film

Kieko HARADA*, Masahito KUSHIDA**, and Kazuyuki SUGITA**

Abstract Photosensitive p-N, N-dimethylamino-benzenediazonium chloride double salts (DZn) is applied to a visible light emission film—phototackifiable film—for multicolor phosphor screens. The emission intensity of the phosphor screen increased by addition of 18-crown-6. The coordination of 18-crown-6 to zinc ion was detected by FTIR spectrophotometry. The hygroscopic property of zinc chloride in the film was suppressed by coordination of 18-crown-6 to zinc ion. Therefore, zinc chloride was prevented from coloring and the emitted light was able to transmit so much increasingly through the phosphored matrix film. For these reasons, relative emission intensity of the film containing 18-crown-6 complex was larger than that of the film without 18-crown-6. Photolysis of DZn in the photo-tackifiable film with 18-crown-6 was accelerated at an elevated temperature, under which condition diazonium moiety was dissociated from the complex with the crown.

Key words: diazo compound, 18-crown-6, phosphor film, photolysis, coordination and dissociation

1. Introduction

Hygroscopic property of p-diazo-N, N-dimethylaniline chloride zinc chloride double salt (DZn) was applied to a visible light emission film—phototackifiable film—for multicolor phosphor screens. This process has a high resolution capability, and hence is especially suited for fabrication of finely patterned screens in color display tubes. The phototackifiable film forms by irradiation sticky zinc chloride to adhere the phosphor powders as shown in Formula (1) of Scheme.

Improvement of adhesion of phosphor powders and shelf life of the film was tried by addition of 18-crown-6. The stability of diazo com-
compound towards photodecomposition and thermal decomposition of diazo is greatly increased by complex formation with crown ether. The thermal stability is good for shelf life, but the stability towards photodecomposition is not favorable for imaging process on account of the decreased photosensitivity. Since heating of the diazo-crown complex causes dissociation of diazo moiety from the complex due to the entropic effects, photolysis was tried to be accelerated. The relative emission intensity of the phosphor film by addition of 18-crown-6 was increased. 18-crown-6 has appropriate size for coordinating to zinc ion, as the inner diameter of 18-crown-6 and zinc ion are 2.60 Å and 1.46 Å, respectively. The coordination of 18-crown-6 to zinc ion was followed by FTIR spectrum.

2. Experimental

2.1 Materials
p-Diazo-N, N-dimethylaminoaniline chloride was prepared from p-N, N-dimethylaminoaniline by usual diazotization with NaNO₂ and HCl at 0°C. The diazonium salt was complexed by adding an equimolar solution of zinc chloride. The precipitates were filtered, washed with water and dried. p-N, N-Dimethylamino-benzenediazonium tetrafluoroborate (DBF₄⁻) was obtained by adding aqueous hydrogen tetrafluoroborate to an aqueous solution of p-N, N-dimethylamino-benzenediazonium chloride. The precipitate were purified by recrystallization from methanol. A binder polymer was polyvinyl alcohol (PVA) obtained from Murakami Screen Co. under the name of Photo Emulsion Diazo Type (sp 1200). PVA for FTIR and transparency measurements film was from Yotsuya Sangyo Co. under the name of PVA L-05.

The phosphor powders were obtained from Nichia Kagaku Co. under the name of TV PHOSPHOR BLUE NP-2121. The wavelength of phosphorescence maximum is at 450 nm. The other materials used were of extra pure grade.

2.2 Formation method of phototackifiable film

A phototackifiable film (thickness: 0.6 μm) was formed on a glass plate by spin-coating a sensitizing solution containing DZn, 18-crown-6, PVA emulsion, and water, (0 or 0.2: 0.01: 0.2: 1). The film was exposed to light from a super high pressure mercury lamp Toshiba SHL-100UV at room temperature or 50°C, and then dusted with the phosphor powders. The films for FTIR spectrum and the transparency measurements were formed by spin-coating a sensitizing solution containing DZn, 18-crown-6, PVA, and water (0.3: 0.1: 0.3: 1.5) and DZn or DBF₄⁻, PVA and water (0.04: 0.3: 3), respectively. The content of DZn or DBF₄⁻ in the latter film is small, since the solubility of DBF₄⁻ in water is low.

2.3 Spectral measurements

Absorption spectra of DZn in aqueous solution and fluorescence spectra of the films on glass plates were measured by Shimazu UV-180 Spectrophotometer and Hitachi Fluorescence Spectrophotometer MPF-2, respectively. FTIR spectra of the films on the ITO glass plate were measured by Perkin Elmer 1600 Spectrophotometer.

3. Results and discussion

3.1 Effect of concentration of 18-crown-6

Phosphor weight was obtained from the weight increase after dusting. Effect of concentration of 18-crown-6 on phosphor weight is shown in Fig. 1(A). The film without DZn started to adhere the phosphor powders at 16% of
18-crown-6. The phosphor weight on the film without DZn approached a constant value above 50% of 18-crown-6. The film with DZn started to adhere the phosphor powders at 33% of 18-crown-6. The phosphor weight on the film with DZn was increased continuously by addition of 18-crown-6, but smaller than that on the film without DZn, because 18-crown-6 was used for complexation with to DZn. The relation between the concentration of 18-crown-6 and the emission intensity is shown in Fig. 1 (B). Although the phosphor weight of the film without DZn was smaller than that of the irradiated film with DZn, the relative intensity of the former was larger than that of the latter. The intensity of the unirradiated film with Dzn and 33-75% of 18-crown-6 was small and that of irradiated one was large. That is, the fog of this film is small.

It is considered the good additive weight for the visible light emission film of 18-crown-6 is 33%.

3.2 Effect of irradiation time
The DZn film without or with 33% of 18-crown-6 were irradiated and measured the phosphor weight and the relative emission intensity. Effect of irradiation time on phosphor weight and relative emission intensity are showed in Fig. 2(A) and (B), respectively. Phosphor weight of the DZn film with 18-crown-6 was smaller than that of the DZn film without 18-crown-6 after irradiation for 1 min. After three minutes, weight of the former was same as that of the latter. The photospeed of decomposition of the DZn film become lower by complexation with 18-crown-6 as shown in Formula (2).

The square plots in Fig. 2 (A), which were the DZn film with 18-crown-6 after irradiation at 50°C, were same as those (circles) of the Dzn film without 18-crown-6 after irradiation at room temperature. Photolysis of DZn in the phototakifiable film with 18-crown-6 was accelerated at the elevated temperature, under which condition diazonium moiety was dissociated from the complex.

3.3 Coordination of 18-crown-6 to zinc ion
The relative emission intensity of the DZn film with 18-crown-6 after irradiation at 50°C was larger than that of the DZn film without 18-crown-6 as shown in Fig. 2(B). The phosphor DZn film without 18-crown-6 became dirty pink after several hr in the air. The transmittance of the film with phosphor powders was...
measured by spectrophotometry. There was no absorption maximum in the broad absorption spectrum at 400-700 nm. The relations between irradiation time and transmittance of DZn films with or without 18-crown-6 at 500 nm are shown in Fig. 3. After irradiation for 3 minutes, the transmittance of the film with 18-crown-6 was larger than that without 18-crown-6.

In order to examine whether the decreasing of the transparency is due to the photoproduction of DZn or not, an irradiated film containing p-dimethyl-amino benzenediazonium tetrafluoroborate (BF₄) was compared with the irradiated film containing DZn without phosphor powders. Photolysis of DBF₄ is shown in Formula (3). The absorption spectra of these irradiated films had no maxima in the range of 400-700 nm. Although these films are very thin, the transmittance at 500 nm of the film with DBF₄ was much larger (4%) than that with DZn. Therefore, it is considered that the photo-product of diazo compound isn't the reason of the coloring film.

DZn is easy to decompose to form a phenol derivative in water as shown in Formula (1'), and the latter couples with remaining diazo compound to form azo dye as shown in Formula (4). During storage, DZn may couple with the thermal decomposition product. It is considered the coupled product is one of the reason for the decreasing transparency of the film.

The solids of 18-crown-6 and zinc chloride are transparent and white, respectively. When the
crystals of zinc chloride absorb the moisture, they become pink. It is considered that the hygroscopic property of the zinc chloride was suppressed by coordination of 18-crown-6 to zinc ion as shown in Formula (5). FTIR spectra were measured to confirm the coordination of 18-crown-6 to the zinc ion.

FTIR spectra of the films (PVA, DZn in PVA, photoproducts of DZn in PVA) were measured and shown in Fig. 4. The absorption band at 1220 cm\(^{-1}\) was assigned to (C-OH) of PVA. The absorption band at 1720 cm\(^{-1}\) was assigned to (C=0) of unsaponified vinyl acetate, remaining in the PVA. The bands at 2155 and 1392 cm\(^{-1}\) were due to \(-N^+=N\) and Ar-N stretching frequency of the diazo group. The spectrum of the DZn/PVA film after irradiation is same as that of PVA.

The spectrum of PVA added 18-crown-6 is shown in Fig. 5. The absorption band at 1150
cm\(^{-1}\) is assigned to the ether bond of 18-crown-6. The absorption band of ether bond of 18-crown-6 in PVA with DZn after irradiation is shifted to shorter wavelength than that of 18-crown-6 in PVA. From these results, it is confirmed that the zinc ion is coordinated by 18-crown-6.

The zinc chloride was prevented from coloring by coordination of 18-crown-6 to zinc ion and the emitted light was able to transmit so much increasingly through the phosphored matrix film. For these reasons, relative emission intensity of the film containing 18-crown-6 was larger than that of the film without 18-crown-6.

3.4 The storage stability of films

The photosensitive films were kept at 20°C and 75% of humidity. Remaining DZn in the film after various storage duration was dissolved in water and the solution was measured with a spectrophotometer. The effect of the addition of 18-crown-6 for the storage stability is shown in as Fig. 6. After 20–30 days, the remaining weight % of DZn with 33% of 18-crown-6 was larger than that without 18-crown-6. The weight of DZn with 50% of 18-crown-6 was smaller than that without 18-crown-6. When the DZn with 50% of 18-crown-6 is kept in air, part of 18-crown-6 makes the complex with DZn and the remaining part of 18-crown-6 absorbs the moisture during the storage. DZn is easy to thermally decompose in the presence of aqueous solution\(^{10,11}\). Therefore, it is thought that DZn with 33% of 18-crown-6 is suppressed to thermally decompose\(^{12}\).

4. Conclusion

When DZn with 18-crown-6 was applied to the visible light emission film, the fluorescence emission intensity of phosphor adhered film was improved by the coordination of 18-crown-6 to the remaining zinc ion. Photolysis of DZn in the photo-tackifiable film with 18-crown-6 was accelerated at an elevated temperature, under which condition diazonium moiety was dissociated from the complex with the crown. The photosensitive film was showed longer shelf life by complexation of DZn with 18-crown-6.

References
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