

Supporting information for

Preparation of Interference Pigment Using Black Graphite Nanosheet

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S.1 Characterization of hydrophobic polymer dispersants

The polymer dispersant poly(ST-2VP) (Scheme S1) was analyzed as follows. The composition of poly(ST-2VP) was estimated by $^1\text{H-NMR}$ spectroscopy (JEOL, JNM-ECX400P, 400 MHz) at room temperature. CDCl_3 was used as a solvent. The number-average molecular weight (M_n) of poly(ST-2VP) was estimated by gel-permeation chromatography (GPC) equipped with a multiangle light-scattering detector (GPC-MALLS/Shodex GPC-101; column: K-805L; detector: differential refractometer) and converted using calibration curves for standard polystyrene samples. CHCl_3 was used as an eluent to adjust the concentration to 0.1 mg/mL.

The yield of poly(ST-2VP), which was obtained as a white solid, was 16.5%. Figure S1 shows the $^1\text{H-NMR}$ spectrum. The ST:2VP ratio was calculated as 6.7:1 from the number of protons of the side chain, as determined from the $^1\text{H-NMR}$ spectrum. The M_n of poly(ST-2VP) was 89,000, as determined by GPC. From these results, the degree of polymerization of ST and 2VP was found to be 737 and 110, respectively.



Scheme S1. Synthesis of poly(ST-2VP) via free-radical polymerization

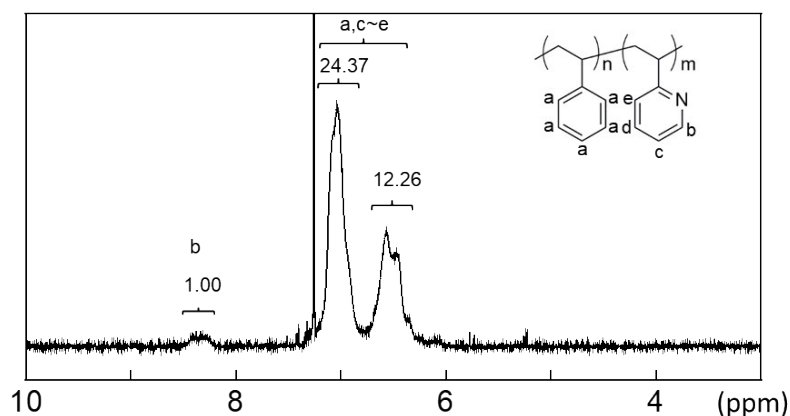


Figure S1. $^1\text{H-NMR}$ spectrum of poly(ST-2VP).

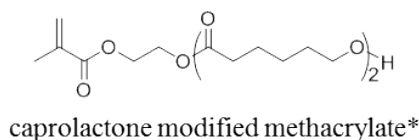
S.2 Preparation of acrylic urethane paint

Acrylic polyol was synthesized by free-radical polymerization in 104 g of methyl isobutyl ketone under a N₂ atmosphere, using 33 g of *tert*-butyl peroxy-2-ethylhexanoate (Nippon Oil & Fats Co., Ltd., PERCURE[®] O) as an initiator and acrylic monomers (Table A1). The reaction was conducted for 6 h at 110°C. Acrylic polyol with a hydroxyl content of 178 mg KOH/g was obtained. The acrylic polyol exhibited $M_n = 6400$ and $M_w/M_n = 1.9$, as determined by GPC.

To obtain acrylic urethane paint, 26 g of acrylic polyol and 10 g of 1,6-hexamethylene diisocyanate (Asahi Kasei Chemicals Corp., Duranate[™] TPA-100, NCO content of 23%) as a curing agent were mixed just prior to application. Toluene was added to reduce the viscosity. The isocyanate curing agent was reacted with the acrylic polyol in a ratio of 1.0 isocyanate groups per hydroxyl group.

Table A1. Sample specifications of acrylic polyol

Monomer	g
Methyl methacrylate	37.6
2-Hydroxyethyl methacrylate	53.1
Caprolactone modified methacrylate*	41.3
Styrene	33.0



S.3 Results of XPS investigation

Figure S2 shows raw data sets of high-resolution XPS spectra. Table 2 summarizes the fractions of carbon, oxygen, and sulfur derived from the evaluation of the C 1s, O 1s, and S 1s peaks.

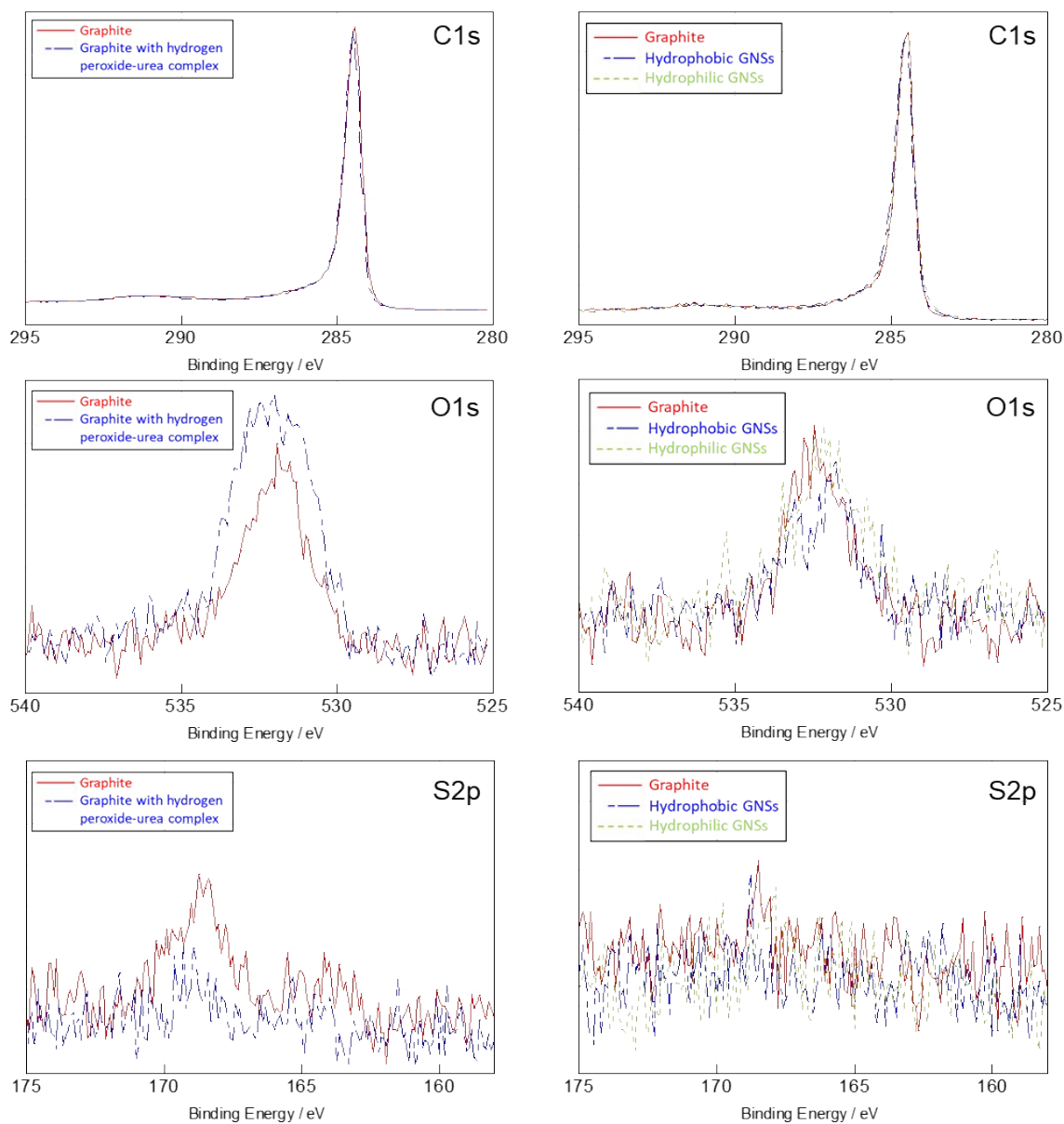


Fig. S2 High-resolution XPS spectra from which the data in Table 2 were extracted

S4. Model reflection spectrum

Interference at a thin film has been the subject of numerous publications^{1,2}. The thin-film interference model that we used is shown in Figure S3, where d_1 is the film thickness, ϕ_0 is the angle of incidence in medium 0, ϕ_1 and ϕ_2 are the angles of refraction in media 1 and 2, respectively, and n_0 , n_1 , and n_2 are the refractive indexes in media 0, 1, and 2, respectively. ϕ_1 , ϕ_2 can be calculated by Snell's law (1):

$$n_0 \sin \phi_0 = n_1 \sin \phi_1 = n_2 \sin \phi_2 \quad (1)$$

The basis on the interference theory is the Fresnel equations, which give the Fresnel reflection (r_{01} , r_{12}) coefficients as follows. The Fresnel reflection coefficients for the parallel and perpendicular polarized light at the planar interface between two linear isotropic media are represented by r_p and r_s , respectively:

$$r_{01s} = \frac{n_0 \cos \phi_0 - n_1 \cos \phi_1}{n_0 \cos \phi_0 + n_1 \cos \phi_1}$$
$$r_{01p} = \frac{n_1 \cos \phi_0 - n_0 \cos \phi_1}{n_1 \cos \phi_0 + n_0 \cos \phi_1}$$
$$r_{12s} = \frac{n_1 \cos \phi_1 - n_2 \cos \phi_2}{n_1 \cos \phi_1 + n_2 \cos \phi_2}$$
$$r_{12p} = \frac{n_2 \cos \phi_1 - n_1 \cos \phi_2}{n_2 \cos \phi_1 + n_1 \cos \phi_2}$$

λ is wavelength. β is the phase difference of multiply reflected wave inside medium 1 as it transverses once from one boundary to the other. The phase difference β is given by

$$\beta = \frac{2\pi n_1 d_1 \cos \phi_1}{\lambda}$$

The total reflected amplitude r is given by

$$r = \frac{r_{01} + r_{12}e^{-i2\beta}}{1 + r_{01}r_{12}e^{-i2\beta}}$$

The reflectance R is the squared magnitude of r :

$$R = |r|^2$$

The model reflection spectrum can be obtained by plotting R as a function of λ contained in β .

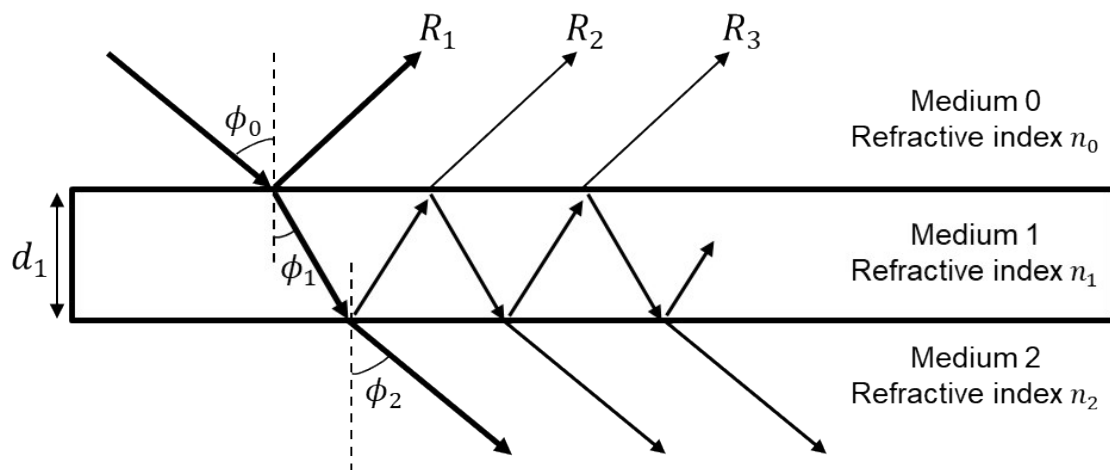


Fig. S3 Schematic of thin-film interference

1. R. M. A. Azzam, N. M. Bashara, "Ellipsometry and polarized light," North-Holland Pub. Co., New York, 1977.
2. G. Pfaff and P. Reynders, *Chemical Reviews*, 1999, **99**, 1963-1981.

S5. Cross-section SEM images of coating film

The GNS pigment was blended with acrylic urethane paint. The GNS pigment represented 5 wt% of the solid content of the entire paint. It was poured onto a chamber slide glass, left at room temperature for 24 h, and then cured at 140°C for 30 min. (Visual observation and recording of the reflection spectrum were carried out from the glass side; that is, the glass side was the top.) We expected pigment precipitated from paint to tend to orient with the flat GNS faces parallel to the top surface when the pigment was allowed to stand before curing. However, in practice, the GNS pigments were poorly oriented. Figure S4 shows typical cross-section SEM images of a coating film. The thickness of the coating film in the present study was between 100 and 150 μm . A GNS pigment-rich layer was observed near the top surface. The thickness of the GNS pigment-rich layer was between 30 and 40 μm from the top. The GNS pigment in the coating film was strongly disoriented.

Moreover, we attempted to orient the GNSs with their flat faces parallel to the surface by shrinking the films during drying and via shear forces generated by the coating method. However, this approach failed to control the orientation.

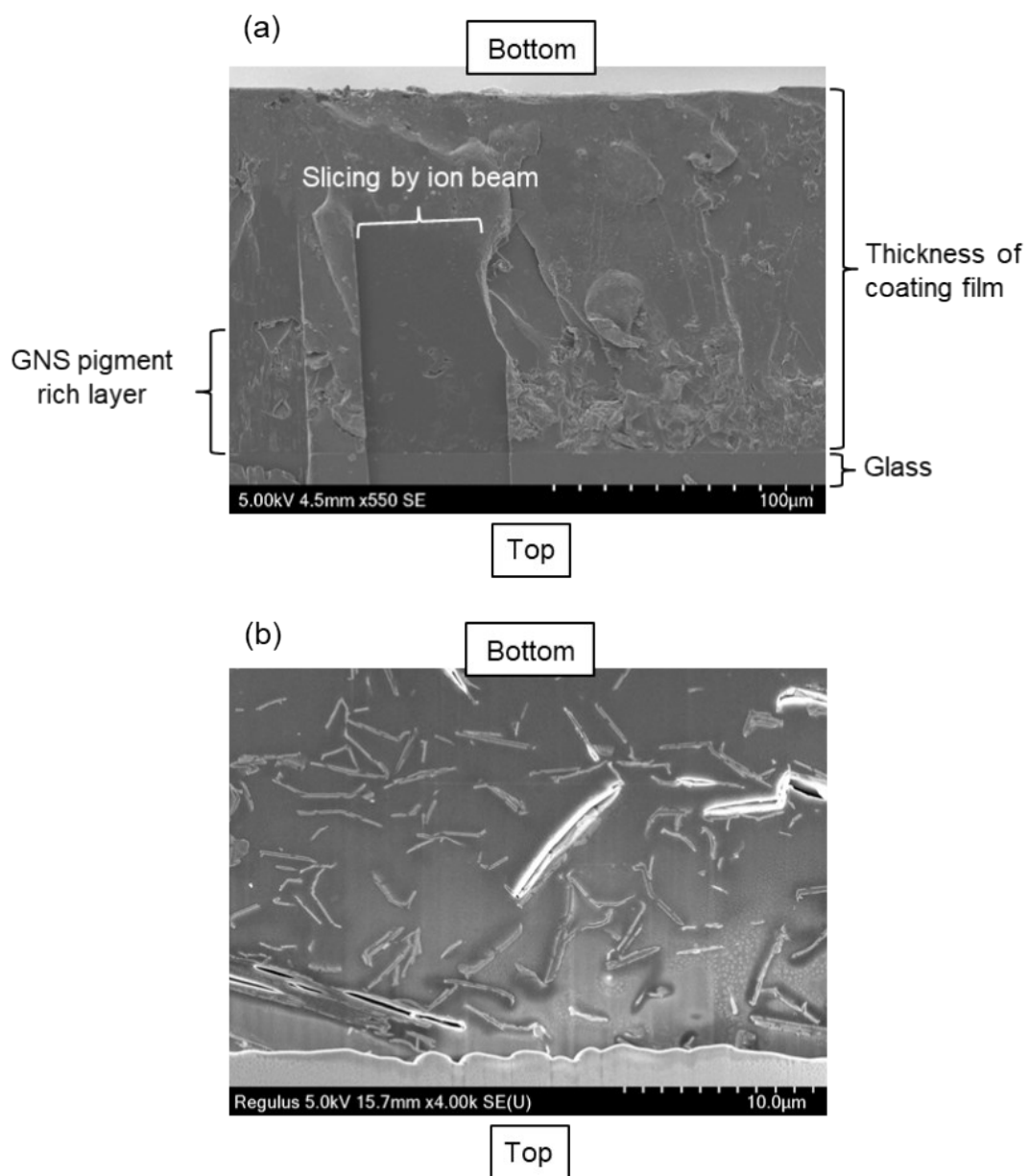


Fig. S4 Cross-section SEM images of a coated film with a GNS pigment-rich layer:
(a) the coating film and (b) the GNS pigment-rich layer