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LOW TEMPERATURE PLASMA OXIDATION TREATMENT OF SEVERAL ORGANIC PIGMENTS

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The modification of the surface of organic pigment by polarization applying the surface treating method by the low temperature oxygen plasma to several organic pigments were investigated.

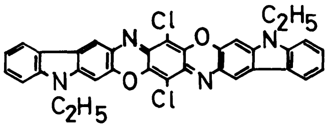
Generally, modern organic pigments of high qualities, for example, in sharpness, tinting strength, transparency, fastness, etc. are representative pigments of the poor miscibility with or dispersibility in polar vehicles such as water as the beginning. Because these organic pigments are non-polar at the surface of their particles, it is necessary to polarize the surfaces of the particles in order to overcome the above disadvantage. The most conventional method is a wet surface treatment procedure using a surface treating agent. In fact, many of the organic pigments in high qualities have been treated by this method. In this case, the derivatives correspond to the organic pigment are conventionally used as the surface treating agent. However, it is difficult to treat only the skin layers at the surfaces by such procedure. Thus, the favorable properties inherent to the organic pigment such as good fastness may be deteriorated.

Recently, rapid progress has taken place in the surface treating technology by the irradiation of low temperature plasma. The authors have investigated the treatment of carbon black by the low temperature oxygen plasma to improve the water dispersibility of it.[1)] The results indicated that the introduction of such polar groups as carboxyl and hydroxyl groups into the surface layer provided the polarity to it without deteriorating the original properties of the pigment. This paper describes the modification of the surface of pigment by polarization applying the surface treating method by the low temperature plasma to several organic pigments.

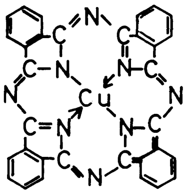
Dioxazine Violet (C.I. Pigment Violet 23 ; shortened to DV), γ type Quinacridone Red (C.I. Pigment Red 19 ; shortened to QR) and β type Cu Phthalocyanine Blue (C.I. Pigment Blue 15 ; shortened to CuPc) were used as the organic pigment. The chemical structures of these pigments are shown in Fig. 1.

The low temperature plasma treating method was carried out in almost the same way as for carbon black mentioned in the previous report.[1)] The procedure is as follows : 10 g of the organic pigment is put into the pyrex reactor which is evacuated for 1 hour under the pressure of 0.5 Torr. Oxygen is passed through the reactor while evacuating. The stirrer is revolving around and on its axis while high frequency is applied under the specified pressure. The conditions of plasma are kept to treat the sample. The number of revolution is constantly 10 rpm and the number of revolutions on its axis is 6 per a revolution.

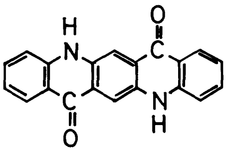
The measured results of specific surface area, pH and heat of wetting and the observed results of the water dispersion of DV, QR and CuPc after 24 h with the passage of time are shown in Table 1.



Dioxazine Violet



β type
Cu Phthalocyanine Blue



γ type Quinacridone Red

Fig. 1. Structures of pigments.

In the case of DV, comparing the pH values of the samples as the indicator of the treatment effect according to the conditions, the pH becomes lower as the high frequency output is increased under the constant conditions of the pressure of 1 Torr and the time of 3 h. And the pH treated by 20 W is lower than that treated by 10 W under the constant conditions of the pressure of 3 Torr and time of 3 h. Under the constant conditions of the output of 20 W and the time of 3 h, the higher the treatment pressure, the lower the pH is and the pH is the lowest under the highest pressure, 5 Torr. Under the constant conditions of the output of 20 W and the pressure of 5 Torr, the longer the treating time, the lower the pH value is and 5 h is the lowest. This value is the lowest among treated DV. These results indicate that the pH of DV treated by oxygen plasma is lowered with the increasing of output and/or pressure and/or time. But, to the contrary, when the output is too high (30 W), the pH is not lowered as much as that of the 20 W treatment. It is said, therefore, that the optimum output for treating DV by oxygen plasma is 20 W. The heat of wetting to water is closely related to the pH so that the former is increased as the latter is lowered in the same manner as for carbon black.[1)] The untreated sample is hardly dispersed in water, while the samples treated under any conditions are well dispersed in it.

In the case of QR, the pH is lowered with the increase of treating pressure and time in the same manner as in DV. Since the pH is lowered in such order of output as 30 W, 20 W, 5 W, and 10 W under the same conditions of pressure and time, the relatively lower output is effective for treating QR. The value of heat of wetting is raised as the pH is lowered. The untreated sample is hardly dispersed in water, while the samples treated under any conditions are well dispersed in it. No difference in the X-ray diffraction patterns can be detected between untreated QR and plasma treated QR.

In the case of CuPc, the value of pH is lowered with the increase of treating pressure and time and the decrease of output in the same manner as in DV and QR. When the heat of wetting is raised, the water dispersibility is more improved.

The decreasing rate of the pH for CuPc is, however, smaller than those for DV and QR and the pH is never lowered to 4 or less under any treating conditions shown in Table 1. The water dispersibility is, therefore, a little lower than those of DV and QR.

Figures 2 through 4 show the measurements from IR spectra of the untreated and treated samples, respectively, of DV, QR, and CuPc. The spectra of these treated samples give newly developed absorption bands near 3000 cm^{-1} to 3400 cm^{-1} and 1710 cm^{-1}, probably based on hydroxyl and carboxyl groups. It is revealed that hydroxyl and carboxyl groups were introduced on the surface of the sample by this plasma treatment. The strength of absorption bands becomes higher with the increase of the treating pressure and time in the same manner as that of the pH shown in Table 1.

The spectra of the treated samples of QR and CuPc give another newly developed absorption band near 1390 cm^{-1}, probably based on N-oxyd groups.

As shown in Fig. 1, QR and CuPc has respectively two imino groups and.four symmetric iso-indol rings connected with the nitrogen atom in a molecule.

Table 1. Plasma treating conditions and surface area, pH, heat of wetting and dispersion state in water

Pigment	Power	Pressure	Treatment time	Surface area	pH	Heat of wetting	Dispersion state$^{a)}$
	W	Torr	h	m^2g^{-1}		$J\ m^{-2}$	
DV	5	1	3	89.8	3.18	0.107	A
	10	1	3	88.7	3.04	0.110	A
	20	1	3	83.9	3.06	0.110	A
	10	3	3	86.7	2.92	0.112	A
	20	3	3	85.1	2.72	0.115	A
	20	5	1	91.4	3.17	0.107	A
	20	5	3	84.6	2.69	0.113	A
	20	5	5	80.1	2.56	0.118	A
	30	5	3	83.3	2.72	0.114	A
	Untreated			91.8	5.43	0.035	C
QR	5	1	3	26.8	4.14	0.296	A
	10	1	3	26.9	4.12	0.299	A
	20	1	3	27.3	4.25	0.289	A
	10	3	3	26.0	3.51	0.314	A
	20	3	3	25.9	3.55	0.311	A
	20	5	1	27.4	4.48	0.272	A
	20	5	3	24.5	3.20	0.320	A
	20	5	5	25.7	3.14	0.322	A
	30	5	3	25.1	3.33	0.318	A
	Untreated			28.5	8.81	0.215	C
CuPc	5	1	3	59.3	4.32	0.101	B
	10	1	3	62.6	4.36	0.100	B
	20	1	3	63.1	4.58	0.104	B
	10	3	3	61.1	4.12	0.099	B
	20	3	3	63.2	4.30	0.101	B
	20	5	1	63.8	4.44	0.104	B
	20	5	3	59.6	4.23	0.101	B
	20	5	5	61.6	4.18	0.103	B
	30	5	3	63.0	4.77	0.098	B
	Untreated			63.2	6.41	0.074	C

a) A:Dispersed well, B:Dispersed slightly, C:Sedimented.

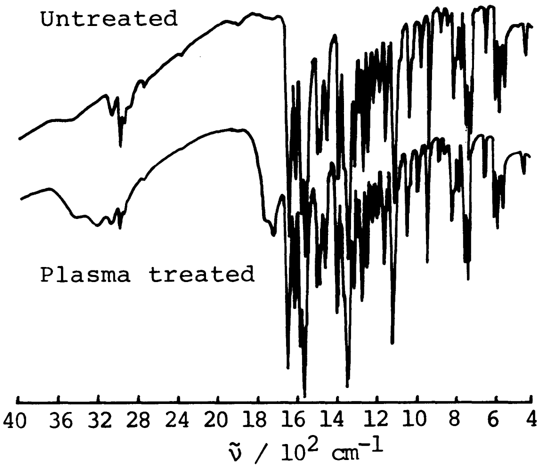


Fig. 2. IR spectra of DV.

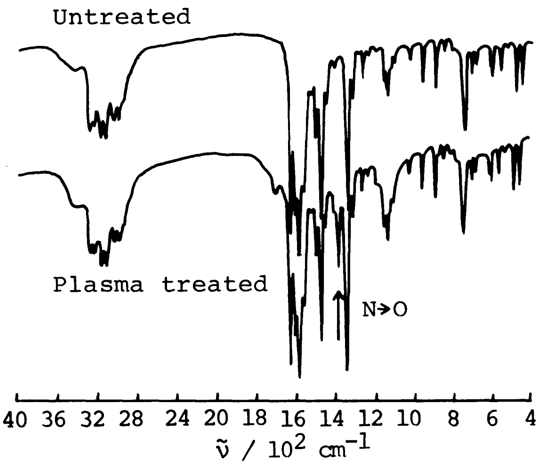


Fig. 3. IR spectra of QR.

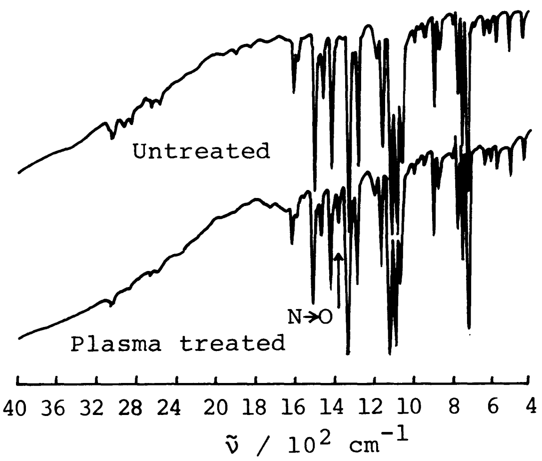


Fig. 4. IR spectra of CuPc.

Producing of N-oxyd groups indicate the oxidation of the imino group by the treatment of oxygen plasma in the case of QR. And it is considered in the case of CuPc that the bonds of nitrogen with four iso-indol rings are broken resulting in ring cleavage, these parts are oxidized to N-oxyd groups.

It is conceivable, therefore, that the decreasing rate of pH of CuPc treated by oxygen plasma is lower than and the water dispersibility is not so much improved as those of DV and QR, because carboxyl group is produced in a smaller quantity than those for DV and QR though N-oxyd group is mainly produced. Consequently, it is estimated that the water dispersibility is mainly caused by the formation of carboxyl group.

In order to investigate the properties of plasma treated pigments, baking type alkyd resin coating compositions were prepared, and the viscosity of these compositions and specular gloss at angle of 20° and sharpness of the coating films after compositions were coated on a tin plate and baked at 140°C for 30 minutes, it is recognized that the compositions comprising the plasma irradiated pigments showed a Newtonian flow, which is one of the preferred properties of a coating composition, giving the coating films better gloss and sharpness than original coating films containing untreated pigments. The influences on the weather resistance of these coating films by this plasma treatment are not appeared.

Reference

1) T. Ihara, S. Ito, T. Kuwahara, and M. Kiboku, Nippon Kagaku Kaishi, 1984, 1575.

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