Influence of Functional Group on the Electrification of Organic Pigments

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Electrification of phthalocyaninatocopper derivative-powders was investigated based on the measurement of contact potential difference (CPD) between the powder and reference gold electrode. The powder-introduced halogen substituents in the end group show negative CPD values. The value of CPD increases negatively as the number of chlorine substituents increases, while the value increases negatively as the number of bromine substituents increases. Powders having hydrogens in the end groups are initially positively electrified and tend to their respective CPD values as time elapses, while powders fully substituted by halogens are negatively electrified. It is found that the charge decay data are well represented by a sum of two exponential functions. Charge-decay speed depends greatly on the number of substituents. Molecular orbital calculation has showed that the measured contact potential difference changes linearly with the calculated Fermi level.

Introduction

In powder-handling processes, particles frequently come in contact with a wall of the equipment. During this contact, charge transfer between particles and the wall occurs. This brings about electrification of particles and sometimes causes particles to adhere to the wall, blockages in the pipeline, dust explosion, and other faults. On the other hand, electrification is utilized effectively in modern processes such as electrophotography and electrostatic powder coatings. In any applications, however, it is necessary to control the electrification of particles and to utilize the particles with optimized electrostatic and dynamic characterization. Elucidation of the electrification therefore has been an urgent subject of study. However, the electrification mechanism and electron configuration of particle surface have not been well defined.

First, it is necessary to give the so-called triboelectric series (Henikker, 1962) with numerical values. A contact-potential difference that shows the work function difference between two materials is the most direct physical property in relation to the particle electrification. We have developed a contact-potential measuring system and conducted many kinds of experiments (Itakura et al., 1995, 1996; Masuda et al., 1995; Nomura et al., 1997, 1998, 1999).

Hereafter, in order to use this system as a way of clarifying the electrification of several powders, we need to extend the investigation to the electrification of powders that are used in copy machines, printers, and the like. In particular, in order to develop these machines with high quality and high resolution, it is necessary to control the electrification of powders.

However, the electrification changes considerably according to particle size (Masuda and Iinoya, 1978), the kind of powder (Itakura et al., 1995, 1996; Masuda et al., 1995), and the environmental conditions, room temperature, and humidity (Nomura et al., 1997, 1998, 1999). It is still difficult to give the same specific charge for particles under the different operational conditions. Therefore, the electrification of powder usually has been controlled by adding a small amount of a charge-control agent (CCA). CCA is an additive powder of sub-micron size, which is utilized both for the polarity and amounts of charge control in tribo-electrification.

Because the market for color toner may expand dramatically in the near future, not only does the preceding CCA adding method increase the cost, but it is also difficult to keep up with the demand. In the literature, the electrification of CCA has been reported for the kind of species, the additive quantities, and the changeable end group (Anderson, 1996; Baur, 1997; Furuhata and Oguchi, 1995; Teshima and Itakura, 1993). However, there is no report that investigates the electrification of organic pigments in a toner without CCA. In particular, it is not well known how the molecular structure of the organic pigments in the toner influences

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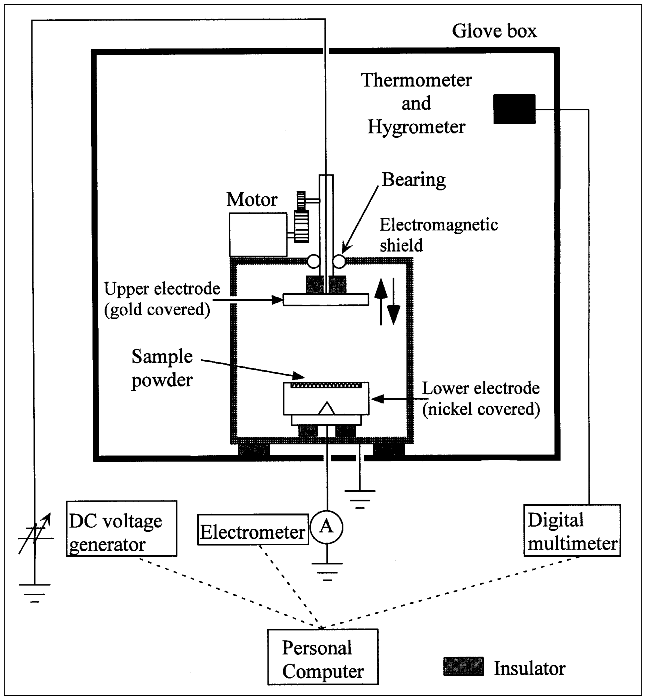

Figure 1. Experimental apparatus for CPD measuring system.

the electrification process. In addition, it also has not been shown how electrified powder keeps the charge. Although several charge-decay models of high-polymer powders (Cheever et al.; 1973; Golovoy and Colvin, 1975) have been suggested, it is not yet clear whether these charge-decay models are suitable for organic pigments.

In this article, we have studied how the electrification changes if halogen substituents with large electronegativity are introduced into the molecular structure of the organic pigment. Specifically, contact potential difference (CPD) and the charge decay with time have been measured for phthalocyaninatocopper derivative-powders that have been substituted by $-$Cl and/or $-$Br. Molecular orbital calculation also has been conducted, and the relationship between the calculated Fermi level and the CPD has been investigated.

Experimental Procedure and Molecular Orbital Calculations

CPD measuring system

The electrification of particles has been studied by blowoff charge (Anderson, 1996, 1999, 2000, Baur, 1997). However, the charge of the particles measured by this method is affected by both the operational condition and the environmental conditions, such as impact velocity, particle size, and relative humidity. In order to clarify the electrification of the particles, it is important to measure CPD directly.

Figure 1 shows the CPD measuring system that was developed in our laboratory to measure the CPD between a powder and a metal (Itakura et al., 1995). When voltage applied on the upper electrode is equal to the electric potential V between the powder and the electrode, the induced current becomes 0, even if the electrode moves up and down. Hereafter, we call such an applied voltage a null-current potential. The system consists of the main body, a voltage generator (Advantest R6144), an electrometer (Advantest TR8652), a digital multimeter (Advantest R6452), and a computer.

The triaxial cable with guard line is used between the lower electrode and the digital electrometer in order to cut off the external noise and measure the small current under stable conditions. To maintain the stable condition ($292\ \mathrm{K} < T < 294\ \mathrm{K}$, $8\% < \varphi < 12\%$), the main body is set up in a glove box. A sensor with a digital multimeter monitors both the temperature and relative humidity. The results are stored in the memory of a personal computer. All the equipment is controlled automatically by the computer through the GP-IB interface.

Sample powder is filled in the lower electrode under suitable vibration. The surface of the powder layer is smoothed off by rolling a polytetrafluoroethylene rod across it; contact with the rod electrifies the powder.

Two kinds of experiments—CPD measurements and the charge-decay measurements—were conducted. Because preliminary experiments showed that the charge decay took a very long time, CPD measurements were conducted as follows:

1. We prepared eight lower electrodes. Each of them was filled with a different powder sample. These samples were ground in a desiccator.
2. We placed a sample in the experimental apparatus and measured the null-current potential, V_0.
3. After the measurement, we returned the measured sample to the desiccator.
4. Next we measured the null-current potential, V_0, of the next sample.
5. We then repeated procedures 3 and 4 seven times. By repeating procedures 2 to 5, we saw that the null-current potential was the CPD when the deviation was within ± 10 mV/day of it. The null-current potential V_0 is expressed by the following equation (Itakura et al., 1996):

$$V_0 = V_{\mathrm{P/Au}} + \frac{a^2}{2\epsilon_a}\rho. \tag{1}$$

Charge-decay model

The most general model of charge decay is the following exponential law:

$$\rho = \rho_0 \exp\left(-\frac{t}{\tau_1}\right). \tag{2}$$

In this model, electrified material is replaced by the parallel combination of a capacitor and a resistor. As the time passes, the charge of the capacitor moves through the resistor to the ground and relaxes with time. The parameter τ_1 is the time constant for charge decay. It depends on the conductivity and permittivity of the material.

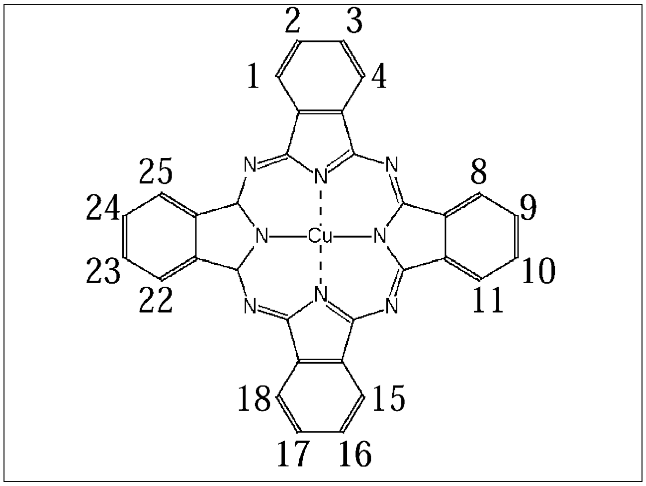

Figure 2. Structure of phthalocyaninatecopper.

Number in figure shows changeable end group.

Sample powder

Figure 2 shows the molecular structure of a phthalocyaninatocopper derivative. It has four benzene rings with sixteen hydrogen substituents, which are interchangeable with halogen substituents. In this work, we have prepared six kinds of phthalocyaninatocopper with chlorine and/or bromine substituents. The number of substituent of the end group, particle size (mass-median diameter), and the manufacturing methods are listed in Table 1.

Molecular Orbital Calculations

We can get the CPD values of the powder by directly using the system shown in Figure 1. These values are solely determined by powder materials and are not affected by the operational conditions, as in the blowoff method. Therefore we now can compare the CPD values with the molecular orbital calculations that can predict the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the material.

Table 1. Substituent of the End Group, Particle-Size and Manufacturing Methods for Phthalocyaninatocopper Derivatives

Sample No.	$N_{-\mathrm{Cl}}$	$N_{-\mathrm{Br}}$	$N_{-\mathrm{H}}$	$D_{p,50}$ [μm]	Manufacturing method
1.1	0	0	16	10	Micron dryer*
1.2	0	0	16	9.6	Spray dryer**
2.1	1	0	15	4.1	Tray dryer → Hammer mill*
2.2	4	0	12	2.9	Tray dryer → Hammer mill*
2.3	8	0	8	3.5	Tray dryer → Hammer mill*
2.4	16	0	0	4.5	Micron dryer*
3.1	8	8	0	2.6	Micron dryer*
3.2	2	14	0	3.0	Micron dryer*

* HOSOKAWA MICRON Corp.
** Niro Japan Co. Ltd.

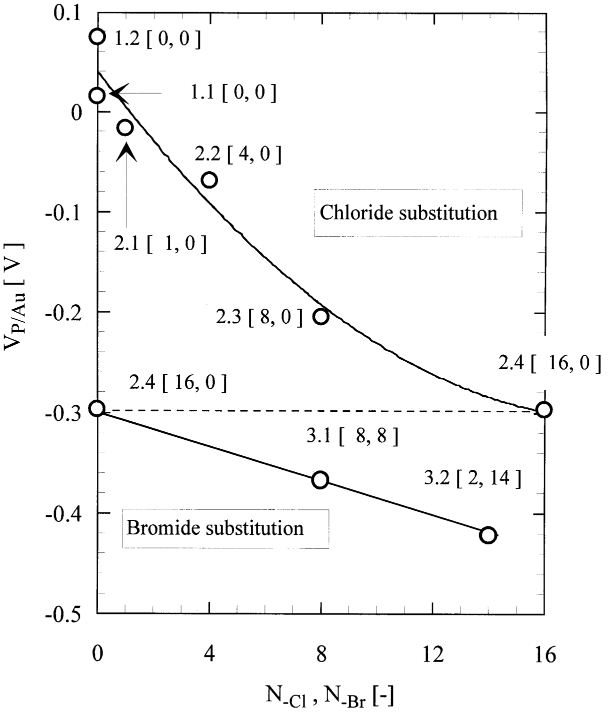

Figure 3. Influence of end group of phthalocyaninatocopper derivative on contact potential difference.

Number in figure shows sample number with number of substituents; [N-Cl, N-Br].

The molecular orbital calculations can be divided into two categories. The first is the AM1 method, which is quasi-empirical. Its special feature is that CPU time is relatively short. Calculations were made by using the MOPAC6.00 program (MOPAC CONSULTANT) on an Alpha 533-MHz computer (Visual Technology, Inc.). The second is the B3LYP/6-311G** method, which is nonempirical but needs lots of CPU time. Calculations were made by using the Gaussian 94 program (Gaussian, Inc.) on Origin SGI (Silicon Graphics, Inc.). The molecular structure was optimized by the molecular mechanics of Chem3D (Cambridge Soft. Corp.), and then by MOPAC6.00. We considered the optimized structure to be the basic one, and conducted the molecular orbital calculations of phthalocyaninatocopper derivative with the changeable end groups.

Experimental Results and Discussion

Results of CPD measurements

Figure 3 shows the relationship between the CPD $V_{P/\mathrm{Au}}$ and the number of phthalocyaninatocopper substituents. Table 2 shows the values of $V_{P/\mathrm{Au}}$ and W_P. It has been found that the CPD increases negatively as the number of chlorine substituents $N_{\text{-Cl}}$ increases.

Nonsubstituted phthalocyaninatocopper derivative shows positive CPD while the halogen substituted one shows negative CPD. We see that the CPD value disagrees with samples 1.1 and 1.2. This fact suggests that the different manufactur-

Table 2. Contact Potential Difference and Work Function of Sample Powder

Sample No.	$V_{P/Au}$ [V]	W_P [eV]
1.1	0.02	4.69
1.2	0.07	4.83
2.1	-0.02	4.72
2.2	-0.07	4.77
2.3	-0.21	4.91
2.4	-0.31	5.01
3.1	-0.37	5.07
3.2	-0.42	5.12

ing processes, shown in Table 1, can exhibit different electrostatic properties for the same materials.

The CPD becomes more negative if end groups of phthalocyaninatocopper are replaced with bromine substituents. For metal oxides, it has been reported that the specific charge decreased linearly when the electronegativity increased (Oguchi and Tamatani, 1982). In particular, the metal oxides with large electronegativity were electrified negatively. In our sample powders, the CPD for the bromine substitution products has a larger negative value than the chlorine substitution products. In other words, it was found that the CPD value changes with the number of substituents. However, the results are contrary to the order of Pauling's electronegativity ($x_H = 2.05$, $x_{Cl} = 3.0$, $x_{Br} = 2.8$). Therefore, we will discuss the reason for this after we investigate how the molecular orbital for these sample powders is formed. The section on the results of molecular orbital calculations describes this in detail.

Results of the null-current potential measurements

Figure 4 shows the measured null-current potential V_0 as a function of the time elapsed, t. Lines show calculated results that are mentioned later. If the hydrogen remains in the end group (samples 1.1, 2.2, and 2.3), the powders initially have a positive charge. On the other hand, if the end groups are fully substituted by halogens (sample 2.4, 3.1, and 3.2), the powders have a negative charge. The null-current potentials of all samples tend to the respective CPD. For both samples 2.4 and 3.1 shown in the inset, the initial potential is lower than for other samples. Here, the dashed lines show ±10 mV around the respective final value.

Golovoy and Colvin (1975) reported that the charge-decay process of acrylic powders can be described by the sum of two exponential functions. In the present work, we consider that the null-current potential degrades to the CPD after a long elapsed time; this process can be expressed by

$$V_0(t) = \alpha_1 \exp\left(-\frac{t}{\tau_1}\right) + \alpha_2 \exp\left(-\frac{t}{\tau_2}\right) + V_{P/Au} \qquad (3)$$

$$\alpha_2 = V_0(0) - \alpha_1 - V_{P/Au}, \qquad (4)$$

where, $V_0(0)$ shows an initial null-current potential. We investigate charge-decay characteristics through curve fitting of the experimental data. All parameters (α_1, α_2, τ_1, and τ_2) are determined by means of the nonlinear least-squares method (Marquadt method). If the experimental data can be expressed by a single exponential function, we assume it is $\alpha_2 \to 0$.

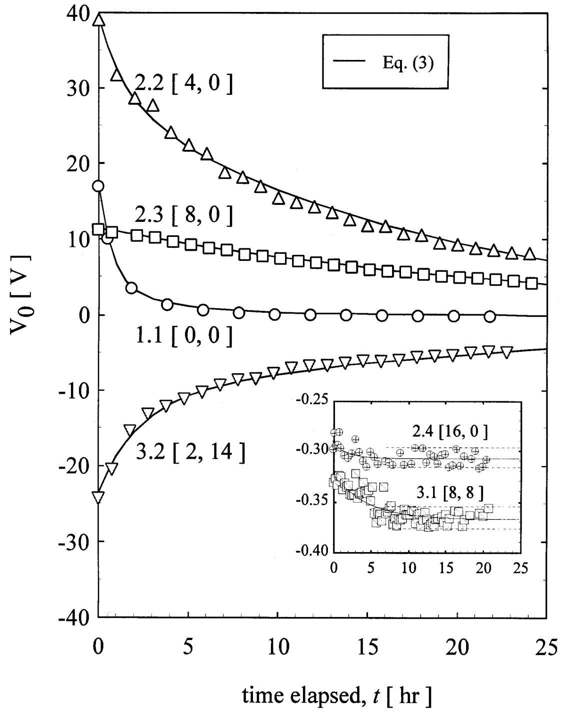

Figure 4. Influence of end group of phthalocyaninatocopper derivatives on charge relaxation.

Table 3 shows the curve-fitting results. The $\alpha_1/(\alpha_1 + \alpha_2)$ ratio decreased with the increasing number of chlorine substituents. For $N_{-Cl} \geqq 8$, the decay process can be expressed by a single exponential function. The maximum value of the charge-decay times τ_1 are at $N_{-Cl} = 8$ and $N_{-Br} = 0$. For samples with both bromine and chlorine substituents (samples 2.4, 3.1, and 3.2), the time τ_1 has its maximum value at $N_{-Br} = 8$. The time τ_2 increased as the number of chlorine substituents increased (samples 1.1, 2.1, and 2.2). Therefore, the charge-decay process of these samples depends mainly on the number of substituents. In other words, sample 2.3 is best able to show how powder can keep the charge, which is one of the important things in electrostatic powder coating and electrophotography.

These charge-decay times apparently depend on electric conductivity. We measured the intermolecular distance using XRD, which shows an index of the conductivity. However, we cannot clarify which peak shows the intermolecular distance,

Table 3. Substituents of End Group and Charge Decay Constants in Eq. 3

N_{-Cl}	N_{-Br}	Sample No.	$\alpha_1/(\alpha_1 + \alpha_2)$	$\tau_1/3600$ s	$\alpha_2/(\alpha_1 + \alpha_2)$	$\tau_2/3{,}600$ s	δ
0	0	1.1	0.773	0.751	0.227	3.94	0.03
1	0	2.1	0.773	0.949	0.227	10.6	0.03
2	14	3.2	0.531	1.90	0.469	21.7	0.06
4	0	2.2	0.275	1.51	0.725	18.2	0.05
8	0	2.3	1	25.6	0	0	0.02
8	8	3.1	1	4.52	0	0	0.03
16	0	2.4	1	1.78	0	0	0.03

because almost all the samples have many peaks near 0.328 nm (Brown, 1968).

Errors in the curve fitting of Eq. 3 were evaluated by Eq. 5 and listed in Table 3:

$$\delta = \sqrt{\frac{\Sigma\left(V_{0,\mathrm{Exp}} - V_{0,\mathrm{Cal}}\right)^2}{\Sigma\left(V_{0,\mathrm{Exp}}\right)^2}}. \tag{5}$$

Since δ is less than 0.06 for all samples, Eq. 3 can express well the experimental data as shown in Figure 4.

Results of Molecular Orbital Calculations

As mentioned in the section on the results of CPD measurements, the experimentally obtained CPDs $V_{P/\mathrm{Au}}$, were contrary to the order of Pouling's electronegativities of H, Cl, and Br. In order to explain these results, it is necessary to investigate the energy level of phthalocyaninatocopper derivatives further.

We first conducted the test calculation for phthalocyaninatocopper derivative that has no halogen substituents by using Gaussian94. We found that the atomic orbital of copper hardly affects the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of phthalocyaninatocopper derivative because the HOMO and LUMO of the derivative are the π-orbital.

In order to reduce the CPU time, we replaced the copper substituent in Figure 2 with two hydrogens and used the AM1 method to calculate the HOMO and LUMO of its halogen substituents. Because the Fermi level exists in approximately the central region of the bandgap (Wada and Nakano, 1971), we have considered the arithmetic mean of HOMO and LUMO to be the Fermi level. The HOMO, LUMO, and Fermi levels change with the atomic structures, that is, isomers. Therefore, we calculated them for some isomers and compared them with the experimental results. Table 4 shows the calculated results of the molecular orbital. For samples 2.1, 2.2, and 2.3, the values of the HOMO, LUMO and Fermi levels depend mostly on the neighboring group. In particular, the difference of the Fermi level between isomer 3 and 4 of Sample 2.3 is about 0.2 eV. On the other hand, these values scarcely change for Samples 3.1 and 3.2, which have only halogen substituents, even if the arrangement of the end groups switches. Figure 5 shows the relationship between the measured CPD, $V_{P/Vac}$, and the calculated Fermi level. The CPD, $V_{P/Vac}$, is based on the vacuum level and is calculated by

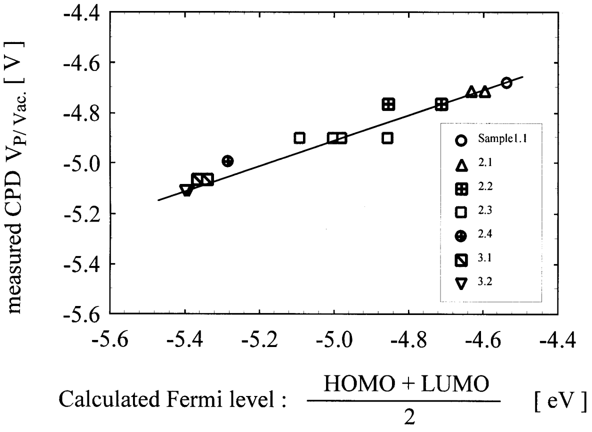

Figure 5. Relationship between measured contact potential difference based on the vacuum level and Fermi level by molecular orbital method.

$$V_{\mathrm{P}/Vac} = -W_P/e$$

$$= V_{\mathrm{P/Au}} - W_{\mathrm{Au}}/e, \tag{6}$$

where W_{Au} is the work function of gold, and is equal to 4.7 eV (Itakura, 1996). It was found that $V_{P/Vac}$ changes linearly with the Fermi level for these powders. Therefore, we can estimate the CPD, which is an index of triboelectrification, by the MO calculations with short CPU time, if we can know molecular structure of phthalocyaninatocopper derivative-powders.

Table 4. Molecular Orbital Calculations by AM1 method

Sample No. No.	Isomers	Substituted Position of − Cl (in Figure 2)	HOMO [eV]	LUMO [eV]	Fermi Level (HOMO + LUMO)/2 [eV]
1.1	1	—	−7.17	−1.90	−4.53
2.1	1	1	−7.30	−1.97	−4.63
	2	2	−7.26	−1.93	−4.60
2.2	1	1, 8, 15, 22	−7.49	−2.22	−4.85
	2	2, 9, 16, 23	−7.34	−2.08	−4.71
2.3	1	1, 2, 8, 9, 15, 16, 22, 23	−7.61	−2.35	−4.98
	2	1, 3, 8, 10, 15, 17, 22, 24	−7.63	−2.38	−5.00
	3	1, 4, 8, 11, 15, 18, 22, 25	−7.47	−2.23	−4.85
	4	2, 3, 9, 10, 16, 17, 23, 24	−7.71	−2.47	−5.09
2.4	1	-	−7.89	−2.68	−5.28
3.1	1	1, 2, 8, 9, 15, 16, 22, 23	−7.97	−2.74	−5.35
	2	1, 3, 8, 10, 15, 17, 22, 24	−7.97	−2.74	−5.36
	3	1, 4, 8, 11, 15, 18, 22, 25	−7.97	−2.76	−5.37
	4	2, 3, 9, 10, 16, 17, 23, 24	−7.98	−2.70	−5.34
3.2	1	1, 8	−8.02	−2.76	−5.39
	2	1, 15	−8.03	−2.77	−5.40

Conclusion

We have investigated the electrification characteristics of phthalocyaninatocopper derivatives using a contact potential difference (CPD) measuring system. The main results are summarized as follows.

1. The CPD of phthalocyaninatocopper derivatives with changeable end groups has a negative value, except when a sample has no halogen substituent. The value of the CPD increases negatively as the number of chlorine substituents increases. Bromine substituents cause a further increase in a CPD with a negative value.

2. Sample powders with hydrogens in the end groups are initially positively electrified. The charge-decay process can be expressed by the sum of two exponential functions by taking the contact potential difference into account. The process mainly depends on the number of chlorine substituents. In particular, if the number is larger than eight, the process can be expressed by the sum of an exponential function and CPD. The process's decay time is longest in all the samples if the number of chlorine substituents is the same as the number of hydrogens remaining.

3. The mean arithmetic value of HOMO and LUMO calculated by the AM1 molecular orbital method changes linearly with the CPD.

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Notation

a = thickness of powder layer
$D_{p,50}$ = mass median particle diameter, μm
e = elementary electric charge, C ($= 1.602 \times 10^{-19}$)
N = number of substituents
t = elapsed time, s
T = temperature, K
V = electrical potential, V
W = work function, eV
x = Pauling's electronegativity

Greek letters

α = coefficient of decay, V
δ = error defined by Eq. 5
ϵ_a = dielectric constant of powder layer, F/m
ρ = charge density, C/m^3
τ = time constant for charge decay, s
φ = relative humidity, %

Subscripts

0 = null-current
1 = charge decay 1
2 = charge decay 2
Au = gold
Br = bromine atom
−Br = bromine substituent
Cl = chlorine atom
−Cl = chlorine substituent
P/Au = between powder and gold
P/Vac = between powder and vacuum level

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