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Study on Electrochemical Behavior of Charge Control Agents (CCA) for Liquid Electrophotographic Development

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Charge control agents for liquid development were evaluated by electrochemical measurements, cyclic voltammetry and pulse voltammetry. Characteristics of charging were easily founded at high speed by these electrochemical methods. The NH standard potential of the charge control agent (versus NHE) was obtained and converted into an ionization potential. The control of charging in developing materials was adequately explained by the redox potential of the charge control agent. The present article reports that the best combination can be predicted by measuring redox potentials before formulating the toner.

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Introduction

Liquid electrophotographic developer consists of a developing agent of 0.1 - 20 μm particle size, and coloring materials, dispersed in a highly insulating liquid. The advantage of liquid development is superiority in resolution, for particle sizes of the color pigments are very small. Charge control agent (CCA) and resin are introduced for stabilization of the coloring agent.

Constitution of toner materials strongly relates to the characteristics of the developer. Gibson and Shinohara have measured the charging power in resin charging, and reported that quantity of charging is determined by resin chemical structure.[1,2]

Recently, it has been reported in dry development that charge-to-mass ratio (q/m) is important to controlling the quantity of charging.[3] Charging characteristics have also been evaluated by the photoelectron injection method,[4] hot electron injection method,[5] triboelectric charging method[6] and the electron trapping method.[7] However, the homogeneous surface states of toner without any electron traps are required by the above methods.

In these ways charging behavior has been elucidated for the dry process. However, these methods cannot be applied to liquid development. In evaluation of liquid developer, electrophoresis is the only common method. Evaluation of charging behavior in the wet process has not yet been established. In the wet process, it is not clear whether CCA controls polarity or quantity of charging.[8]

It is difficult to control charging of toner without knowing the role of the CCA.[9,10] No effective method has been reported for determining ionic state of charged toner quantitatively. In practice, the best combination is chosen by trial and error from various kinds of CCA and coloring agents.

The present authors intend to establish a new method of evaluating charging characteristics non-functionally. The redox potentials of materials adding to the liquid developer should provide important information for selecting the best combination of CCA and coloring agents. Cyclic voltammetry and pulse voltammetry were adopted to measure redox potentials.

Experimental

Devices and Materials

Schematic diagram of the apparatus for measuring redox potential is shown in Fig. 1.

Samples are introduced in 200 ml Pyrex H-cell, equipped with a flat optical window sufficiently large to illuminate of the entire area of the cell. The working electrode (WE) used is a platinum plate (20 × 10 × 0.3 mm). The counter electrode (CE) is a large platinum plate placed in a compartment separated from a standard Ag/AgCl electrode.

Acetonitrile (spectral grade, Wako Pure Chemical Industries) was used as the solvent. Lithiumperchlorate (best quality chemical reagent, Tokyo Kasei Co. Ltd.), 1.0×10^{-3} mol/l, was added as the supporting electrolyte. The CCA samples were introduced 5.0×10^{-5} mol/l concentration in the acetnitrile. Chemical structures of CCA are shown in Fig. 2. In the case of poor solubility of some CCA's in acetonitrile, dimethylformamide was added to improve solubility. The electrolyte was deacerated by purging with pure Ar gas.

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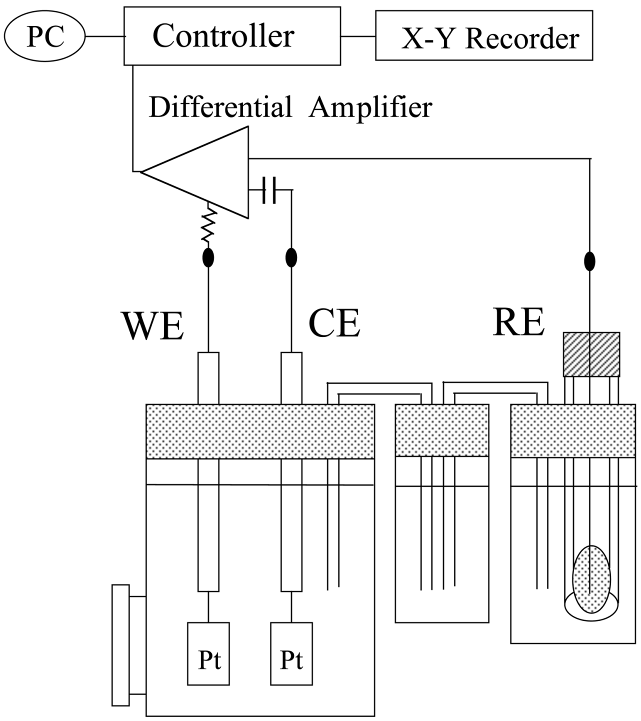

Figure 1. Schematic diagram of apparatus for measuring redox potential.

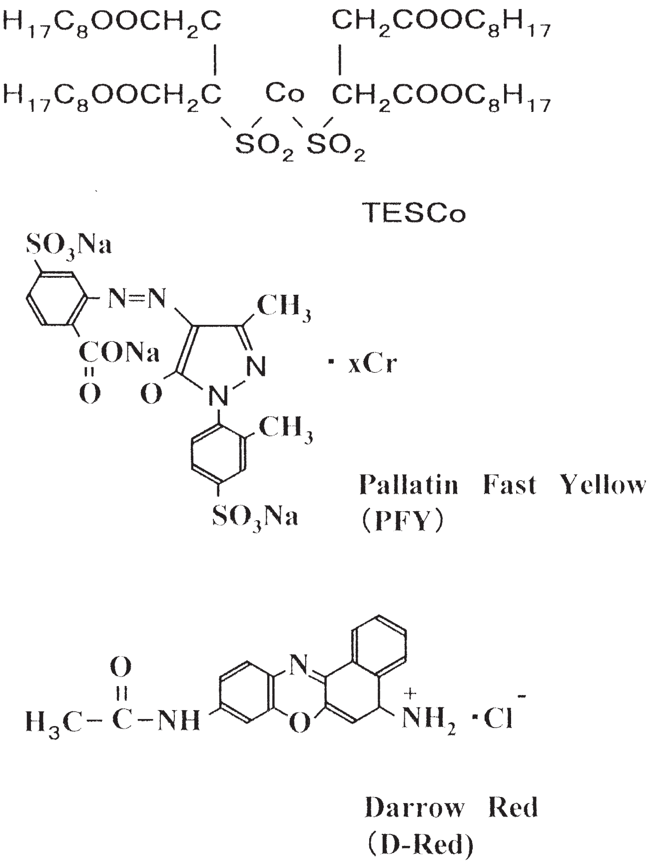

Figure 2. Chemical structures of CCA.

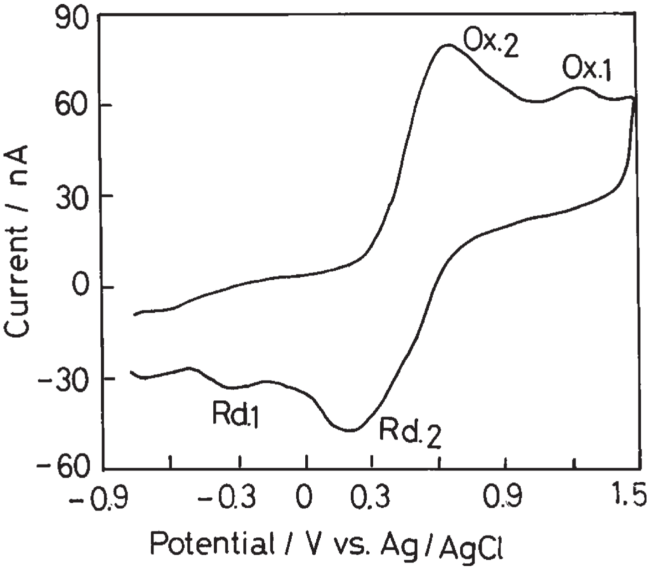

Figure 3. Cyclic voltammogram of dye A-1.

Electrochemical Measurement

The electrolyte was kept at 20°C; potentiostat (HA-501GS, HOKUTO Electrical Industry) and function generator (HB-105S) were used in measuring cyclic voltammetry. Chopping frequency of the triangle wave was 25 mV/second. Cyclic voltammograms were recorded an average of five repetitions (Fig. 3), by plotter (HP-7440a, YOKOKAWA) attached to a Personal Computer (PC-98, NEC). In order to detect currents of the order of nA, a differential amplifier was connected as shown in Fig. 1. The second oxidation wave was adopted as the redox potential for evaluation of sample in these experiments, as the first oxidation wave was not sensitive to addition of CCA.

Pulse voltammmetry was measured with sodium tetrafluoroborate as supporting electrolyte, in acetonitrile (Wako Pure Chemical Industries, spectrum grade) as solvent; 10 mV voltage step; 100 ms on-pulse, and 500 ms off-pulse, were applied in the measurement.

Liquid Developer

Sample of Liquid developer, A, were prepared as follows: tetrahydrofuran (THF), 100 ml, as solvent, tetra-2-ethyl sulfosuccinic acid cobalt salt (TESCo) 256 mg, as CCA, EVA (Evaflex™ 250 an ethylene-vinylacetate co-polymer, Mitsui DuPont Chemical Co.) 2.5 g, as binder, were mixed in a 200 ml round bottom flask. The solution, A, was heated with stirring at 150°C in an oil bath for one hour.

In another flask, B, coloring agents (A-1) (Mitsui Toatsu Chemicals), 0.1 g, was dispersed in poly-12-hydroxystearicacid (Itoh Oil Manufacturing Co., Ltd.), 90 mg, and Isopar™ G (Exxon-Mobil Corp.), 100 ml. The solution, B, was kept with stirring at 150°C. Then both solutions of A and B were mixed at 60°C. Isopar™ G at 5°C was rapidly introduced into the mixed solution for cooling. The deposited particles of resin were redispersed by a supersonic wave homogenizer. THF was removed from Isopar™ G by a centrifugal separator.

Measurement of Charging Properties of Liquid Developer

We formed various kinds of electrostatic image patterns by surface charging to 50 V - 150 V. We developed

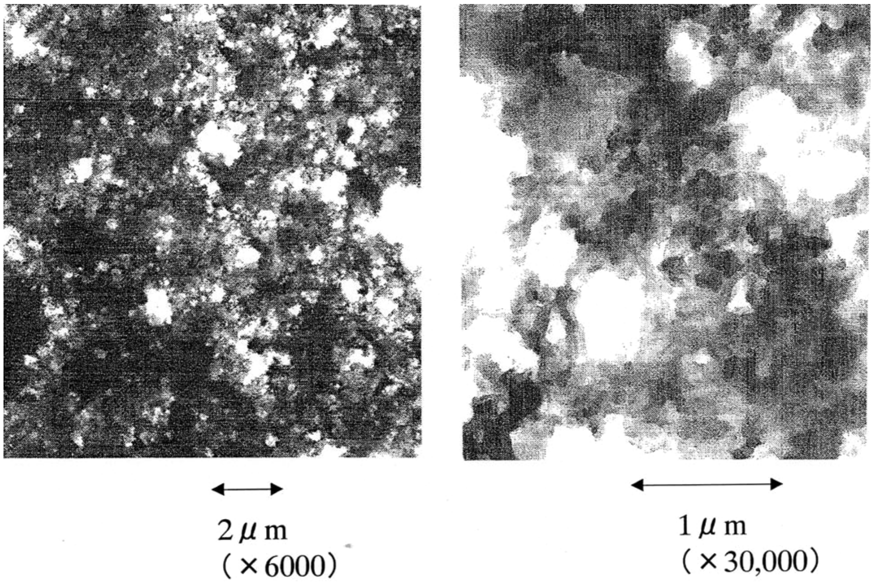

Figure 4. SEM picture of toner.

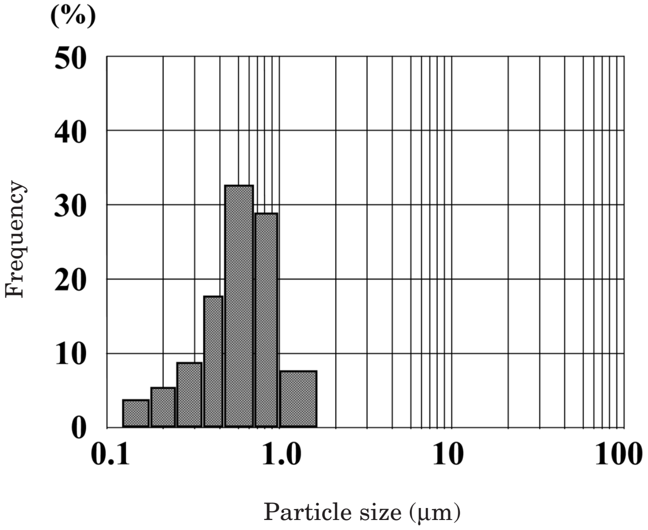

Figure 5. Grain size distribution of toner.

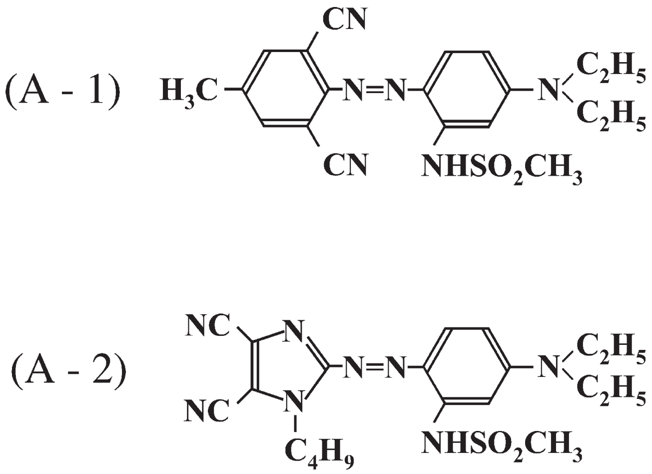

Figure 6. Chemical structure of dyes, A-1 and A-2.

them with the liquid toners and printed them on electrostatic sheets by means of a roller developing machine. The developing speed was set to 2.6 m/min. Liquid developer was introduced into an electrode cell, where a high voltage device (Keithly 237) was used to impose a potential across two electrodes, 4 cm × 4.5 cm, each. The initial electric current and speed of electrophoresis were measured. Potential ζ was measured by a potential analyzer (ESA-8000 Matic Applied Science).

Results and Discussion

Physical Characteristics of Liquid Developer

Liquid toners were obtained by mixing solutions A and B. An SEM picture of a typical resulting toner is shown in Fig. 4. The picture shows particles to have smooth spherical surfaces. Fine toner particles were confirmed by a grain size analyzer, Microtruck-2SRA (Nikkiso). Grain size distribution measured by the analyzer is shown in Fig. 5. A sharp distribution was found in the range of 0.12 - 1.5 μm, with an average particle size 0.7 μm.

Charging Characteristics of Toner

Chemical structures of dyes used for producing toner are shown in Fig. 6. Electrochemical behavior of azo dyes, (A-1 and A-2), were evaluated by the cyclic voltammetry (Fig. 7).

The results of the oxidation potential measurement are shown in Fig. 8. Redox potential versus Ag/AgCl was given directly by the voltammetric measurement. Potential versus NHE is obtained from the potential versus Ag/AgCl. Ion retransfer model (IRM) was proposed by Matsui[11] to describe interactions between toner surface and CCA. Applying this model to the present system, electron transfer between toner and CCA must be determined by the electrochemical redox potential.

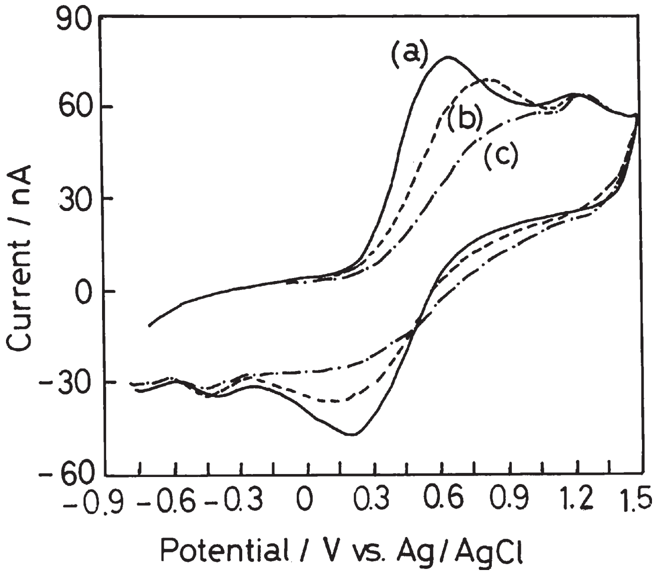

Figure 7. The result of the cyclic voltammogram of combinations of dye with CCA's: a) A-1; b) A-1 + TESCo (30%); c) A – 1 + TESCo (60%).

Sanders *et. al.*[12] have reported the relation between potential versus NHE and absolute ionization potential. On this scale both oxidation potentials of A-1 and A-2 are almost the same, -2.55 eV. The reduction potentials of both A-1 and A-2 are found to be -4.9 eV.

The oxidation potential of the CCA was measured in order to identify formation of a complex between CCA and A-1 or A-2. PFY or TESCo were used as CCA agents. The oxidation potentials of the CCA mixtures are shown in Fig. 9.

It is found in this figure that the oxidation potential depends on chemical structure of dye and also on the nature of the CCA. Combination of A-1 with TESCo shows the highest oxidation potential. The combination of PFY with A-2 gives an almost constant potential. It is recognized that the charge controlling ability of TESCo is higher than PFY.

The result indicates the best combination for toner to be A-1 and TESCo. A liquid toner was produced by this combination. Polarity of the produced toner was negative in charging experiments. In electrophoresis mesurement, the initial current of the toner was observed to be 850 nA and the current after 60 seconds was 240 nA. *Q*/*m* of the toner can be derived from the observed electric current and amount of toner deposited under conditions of electrophoresis. Potential ζ measured by the analyzer was 85 mV. Mobility was calculated on the basis of the potential by the equation of Schaffert.[13] Then, the mobility was estimated to be 3.9×10^{-10} m^2/s•V. The calculated mobility indicates the toner to be useful for high speed developing.

Similar measurements were performed for the toner comprising A-2 and PFY. In the electrophoresis measurement, an initial electric current value of the toner was 76 nA and the current after 60 seconds was 50 nA; *q*/*m* was 307 µC/g and potential ζ was measured to be 5 mV. These experimental values indicate poor charging under developing conditions; accordingly the toner cannot be applied to the high speed system.

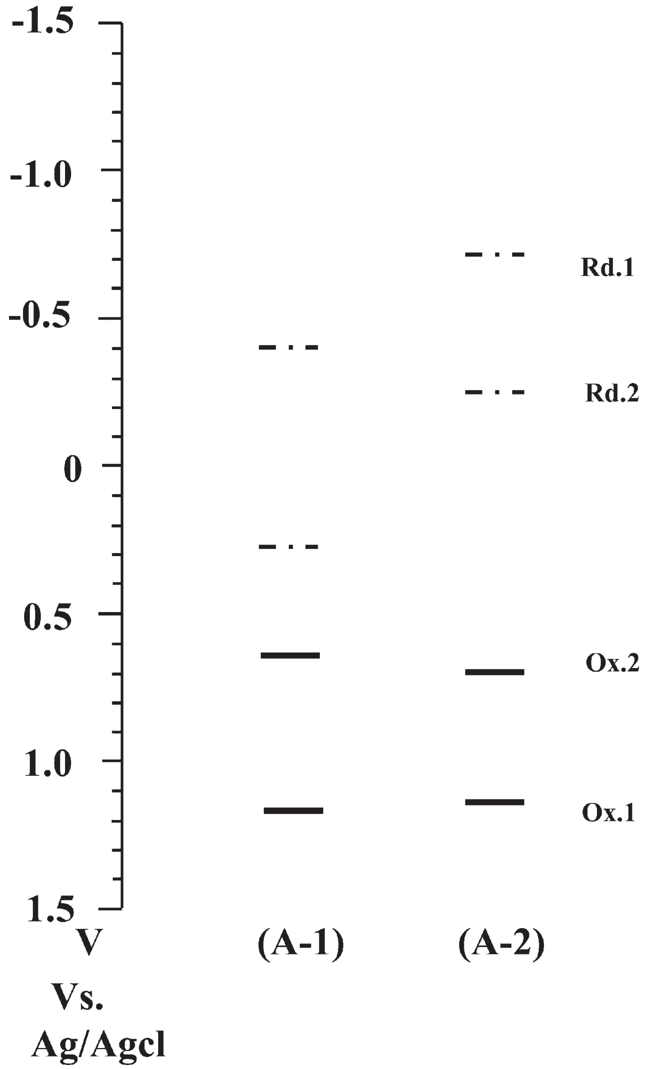

Figure 8. The results of the oxidation potential measurements.

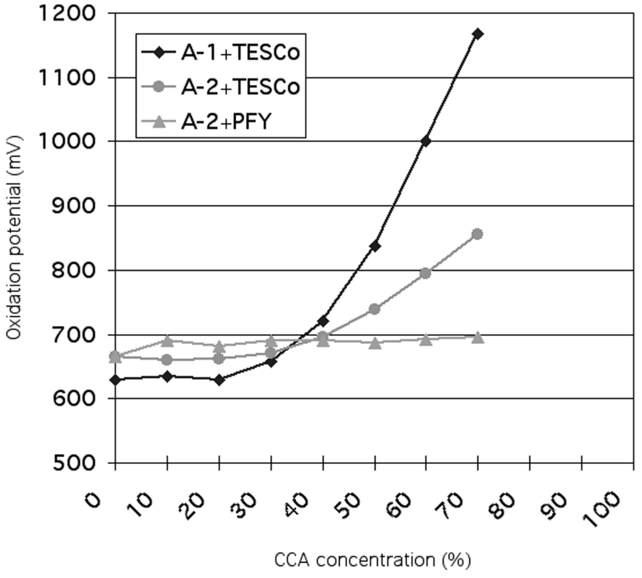

Figure 9. Relationship between CCA concentration and oxidation potential.

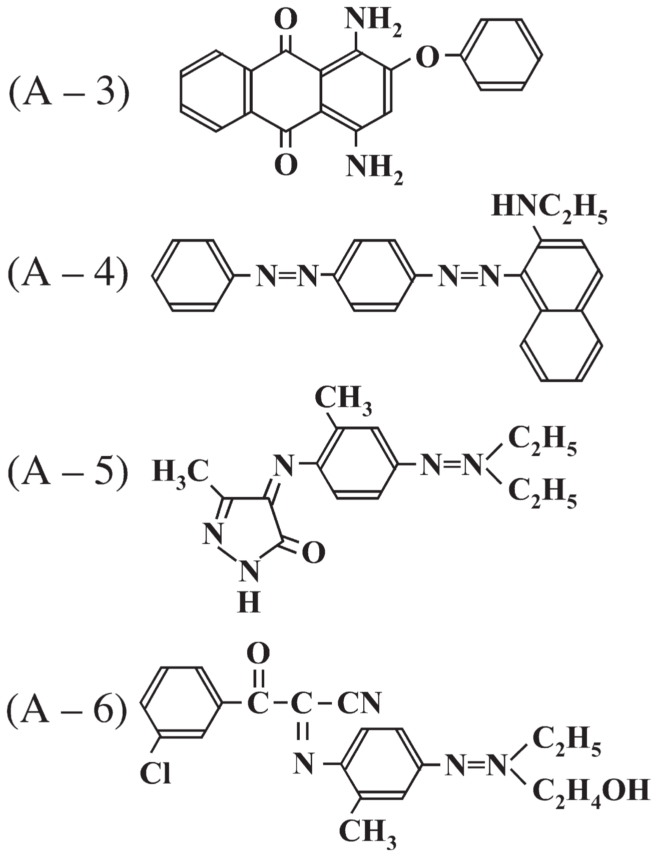

Figure 10. Chemical structures of dyes, a-3~6.

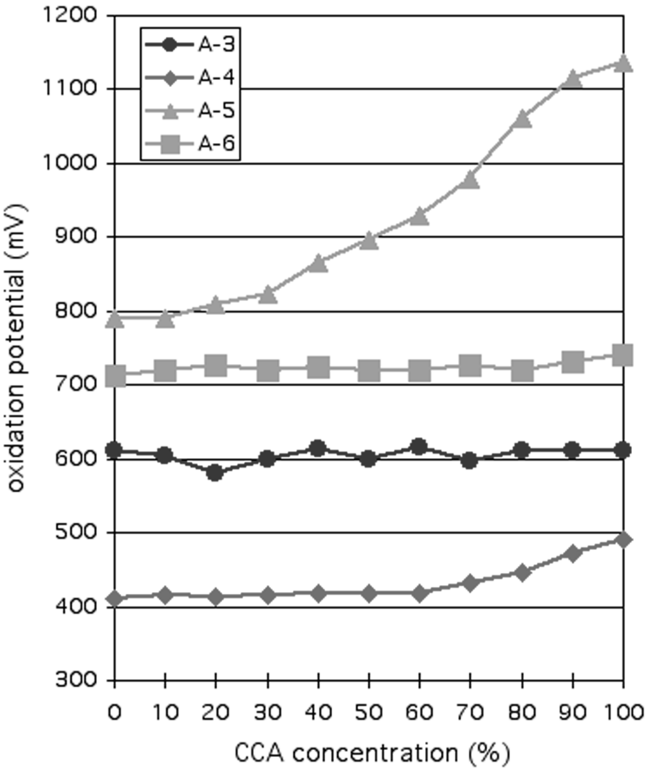

Figure 11. Dependence of oxidation potential on CCA concentration.

Charging Characteristics of Other Toners

Oxidation potential of other dyes were measured by cyclic voltammetry. Chemical structures of these dyes were shown in Fig. 10. The oxidation potentials of mixtures, TESCo and A-3~6, are shown in Fig. 11. Combination of A-5 with TESCo shows the highest oxidation potential among them. The result predicts that the best combination for toner should be A-5 and TESCo. A liquid toner was produced by this combination, and the toner charged negatively.

In electrophoresis measurements, an initial electric current value for this toner was 790 nA and the current after 60 seconds was 140 nA, q/m was 150 μC/g. Mobility was calculated on the basis of the ζ potential by the equation of Schaffert.[12] Potential ζ measured by the analyzer was 75 mV; then, the mobility was estimated to be 3.0×10^{-10} $m^2/s \cdot V$. The calculated mobility indicates the toner to be useful for high speed developing.

Similar measurements were performed for the toner comparing A-3 and TESCo. In the electrophoresis measurement, an initial electric current value of the toner was 34 nA and an electric current after 60 seconds was 10 nA; q/m was 18 μC/g. It was not possible to determine the ζ potential forth is combination. These experimental values show poor charging in developing and the toner cannot be applied to the high speed system.

It is shown by the above results that oxidation potential strongly reflects the charging characteristics of toner.

Pulse Voltammetry of Toner

Redox potentials of the dyes shown in Fig. 12 were measured by pulse voltammetry. Four kinds of dye (C-1~4)

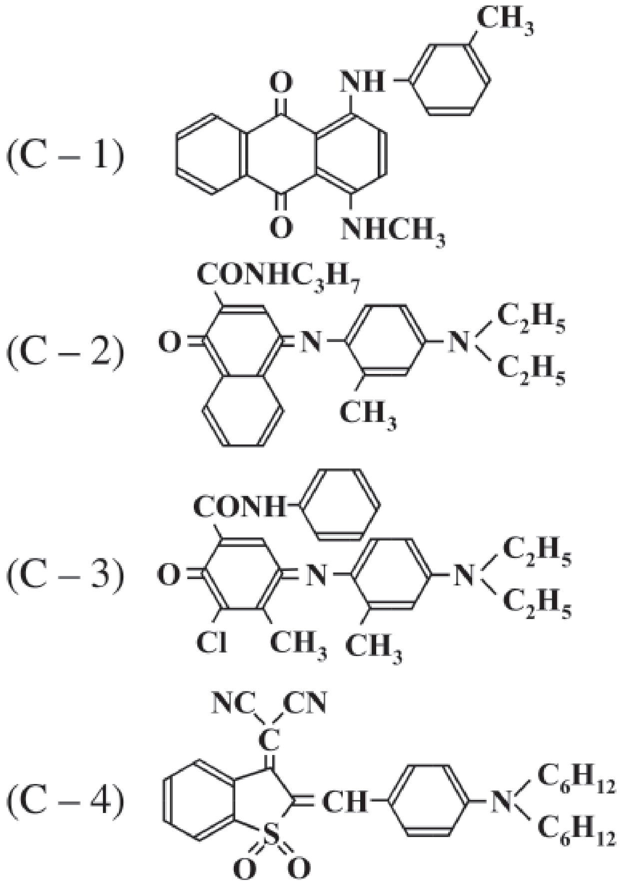

Figure 12. Chemical structures of dyes, C-1~4.

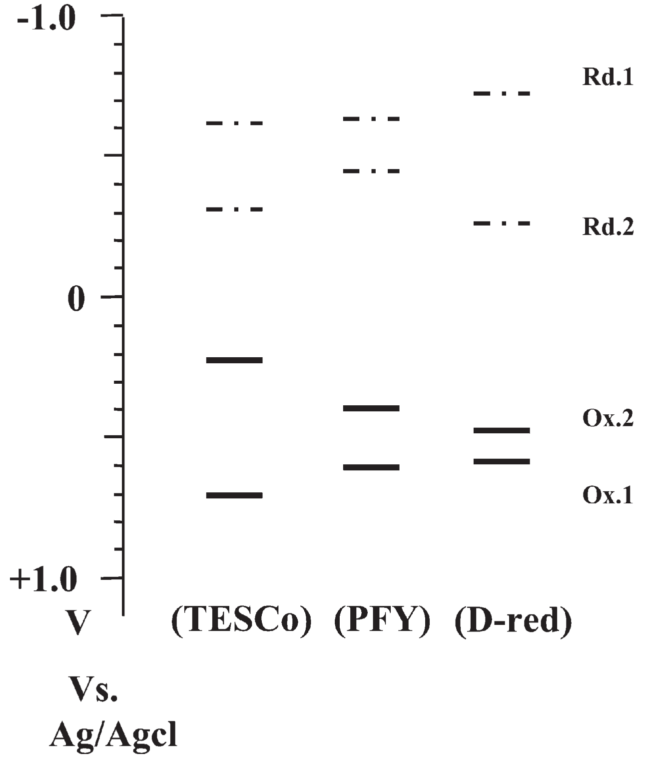

Figure 13. The results of the oxidation potential measurement.

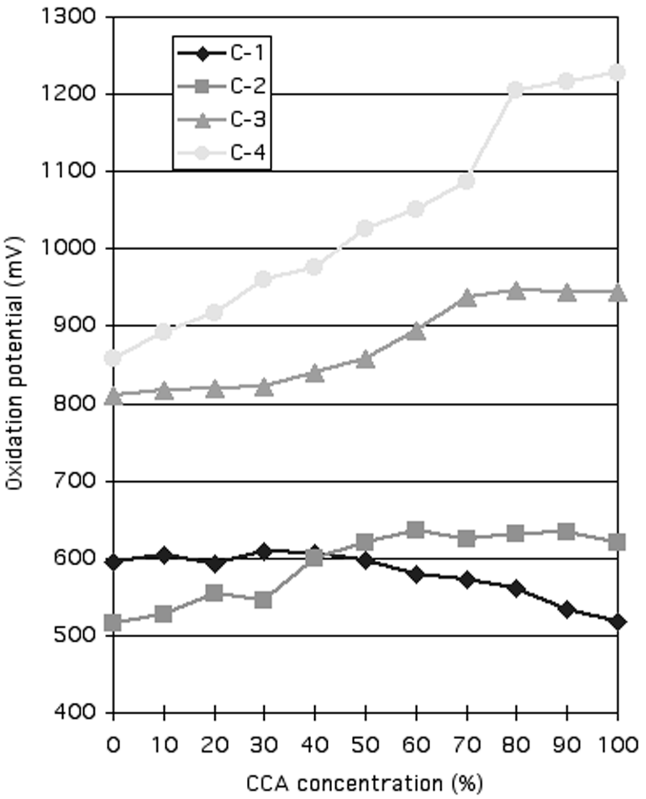

Figure 14. Dependence of oxidation potential on CCA concentration.

are sublimation dyes, and were refined by sublimation. The concentration of dye was 5.0×10^{-6} mol/l in electrolytic solution; 1.0×10^{-3} mol/l. Acetonitrile or tetrahydrofuran was used as the electrolytic solvent.

Redox potentials of TESCo, PFY and D-red measured by the pulse voltammetry are shown in Fig. 13. Both oxidation potentials of the CCA's, TESCo, PFY and D-red, are almost the same, -2.6 eV. The reduction potentials of TESCo, PFY and D-red are all found to be -5.0 eV.

Clear potential curves with high signal-to-noise could be obtained by pulse voltammmetry. Therefore, sensitivity of detection in pulse voltammetry is 10 times higher than that by cyclic voltammetry. Very low concentration, 7.0×10^{-9} mol/l of CCA in solution, is enough to obtain a potential curve in pulse voltammetry.

The oxidation potentials of mixtures, TESCo with C-1~4, are shown in Fig. 14. Combination of C-4 with TESCo shows the highest oxidation potential among them, which indicates that the best combination for toner to be C-4 and TESCo. A liquid toner was produced by this combination, which charged negatively.

In electrophoresis measurement, an initial current of 920 nA and the current after 60 seconds was 440 nA; q/m was 126 μC/g. Potential ζ measured by the analyzer was 70 mV. Then, the mobility was estimated to be 5.2×10^{-9} m^2/s•V. The calculated mobility indicates the toner is suitable for high speed developing.

Sublimination dyes, C-1~4, are not well dissolved in the electrolytic solvent however. These dyes are dispersed as fine powders in the solvent. Therefore, cyclic voltammetry is difficult to apply measuring redox potential for the sublimation dyes. Pulse voltammetry is quite effective to measure redox potential for the dispersed sample. The resulting potential obtained by pulse voltammetry provides a good explanation of charging characteristics of the toner.

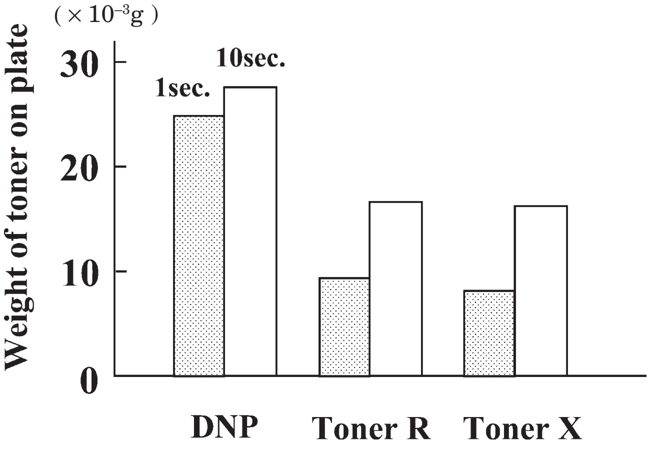

Figure 15. Developing characteristics of the produced toner (DNP).

Developing characteristics of this toner, DNP, were compared with commercial toners on the market. The results are shown in Fig. 15. Toners R and X are on the market for use in electrostatic printers. It is found that DNP toner has higher speed of development than either toner R or X. Utility of the combination of dye and CCA suggested from the electrochemical measurement was confirmed by comparing DNP with commercial toners.

Conclusion

Electrochemical potentials of charge control agent in liquid development were measured by cyclic voltammetry and pulse voltammetry. Charging characteristics of toner were predicted easily by the electrochemical method. The standard potential versus NHE of the charge control agent was observed and converted into ionization potential. The control of charging in the developing formulations was adequately explained by the redox potential of CCA. The best combination of CCA and dye in toner can be predicted by analysis of the electrochemical data.

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