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Dispersion Control of Liquid Toner by Dispersant and Analysis of Adsorption Structure

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Abstract

Dispersant which is effective for dispersion of liquid toner and adsorption structure of the dispersant were investigated. In order to disperse polyester toner particles in paraffin oil, a basic dispersant was examined. As the adsorbing unit, polyethyleneimine was selected, which can adsorb to carboxylic acid of polyester toner by acid-base interaction. Homopolymer of 12-hydroxystearic acid was selected as the dispersing unit because it has low polarity and it is easy to control molecular weight. Amide dispersants were synthesized by condensation reaction between adsorbing units and dispersing units of different molecular weight.

After the evaluation of liquid toner dispersibility with synthesized or commercially available dispersants, it was found that the dispersant with low molecular weight adsorbing units showed better dispersibility than one with high molecular weight adsorbing units. To compare the adsorption structure of dispersants, interaction force between surfaces adsorbed with each dispersant was analyzed by colloidal probe AFM. It was indicated that the adsorbing unit of high molecular weight forms train-loop-tail structure, while that of low molecular weight forms the brush-like layer. In the case of dispersant of high molecular weight, it was suggested that some of the adsorbing unit may adsorb to more than a single particle, which causes cross-linking between particles and leads to bad dispersibility.

Introduction

In the printing market, there is an expanding demand for digital printing systems that are capable of low-volume printing of a wide variety and high print quality. Liquid electrophotographic systems are attractive options for this printing market because the small particle size of liquid toner can allow very high image quality [1].

In liquid electrophotography, toner particles approximately 1-2 μm in size are dispersed in an insulating liquid and are developed to the photoconductor by electrophoresis. Because of the small particle size and narrow gap in the developing system, liquid electrophotography enables higher image quality printing. However, considering productivity and delivery time which is required for recent digital printing, printing speed in liquid electrophotography has room for improvement.

Based on the theory of electrophoresis, a liquid toner requires small particle size, low viscosity, and high electrical charge to achieve high speed printing [2]. In our previous investigation, it was necessary to add a lot of dispersant to make highly dispersed liquid toner of high toner concentration. The dispersant, however, had a negative influence on electrical properties and caused many problems in the developing and transfer process. Therefore it is essential to have a dispersant which can function at a low concentration to disperse particles in the toner.

In order to disperse particles in liquid, electrostatic repulsion and steric repulsion are important. As liquid toner includes solvent of low dielectric constant, it is difficult to utilize electrostatic repulsion. In previous studies, high molecular weight dispersant which can develop the steric repulsion is said to be effective to disperse organic microparticles in low-polar solvent.[2] It is also said that the preferable structure is a graft polymer dispersant consisting of an adsorbing unit which interacts with the particles and a dispersing unit which has affinity with the solvent (Figure 1).[2]

In this paper, we designed a dispersant having structure which is effective for dispersion of liquid toner. In order to clarify the cause of variations in dispersibility, adsorption structure of dispersants was analyzed.

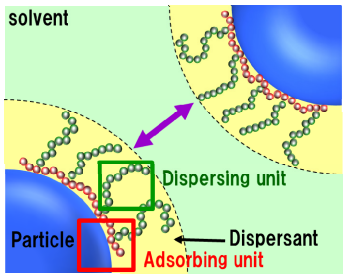

Figure 1. *Schematic illustration of the basic structure of dispersant.*

Experimental

Synthesis of dispersing unit (homopolymer of 12-hydroxystearic acid)

A 500-ml four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 12-hydroxystearic acid, xylene as a reaction solvent, and dibutyltin oxide as an esterification catalyst. The contents were heated to 190°C, the mixture was subjected to a reaction, and the reaction was terminated at a point that an acid value reached a value as listed in Table 1, to provide each of homopolymers A to E.

Table 1. Properties of the Experimental Dispersing Unit

Homopolymer	Acid Value[1)] [mgKOH/g]	Molecular Weight[2)] (Mn)
Homopolymer A	74	1600
Homopolymer B	35	2700
Homopolymer C	124	800
Homopolymer D	96	1100
Homopolymer E	53	2000

1) The acid value was measured according to ASTM D-1980-67.

2) The molecular weight (Mn) was measured by gel permeation chromatography (GPC) with THF.

Synthesis of amide dispersant

Dispersant A; A 100-mL three-necked flask was charged with Polyethyleneimine (PEI) 300, commercially available from JUNSEI CHEMICAL CO., LTD., number-average molecular weight: 1,500, and homopolymer A. The contents were heated to 150°C, and the mixture was subjected to a reaction until a reaction percentage reached 90%, to provide dispersant A. Here, a reaction percentage is a value calculated by [(acid value before the reaction – acid value after the reaction)/acid value before the reaction] x 100.

Dispersant B-H; Prepared in a similar method, except that polyethyleneimine and homopolymer were used as listed in Table 2, to provide each of dispersants B to H.

Dispersant I; Solsperse 13940, commercially available from Lubrizol Corporation, 40% active amide dispersant.

Table 2. Properties of the Experimental Dispersant

Dispersant	Mn of PEI[1)]	Mn of Homo-poly-mer	Dispersant	
			Ratio (PEI / Homo-poly-mer	Mw[2)]
Dispersant A	1500	1600	1/2	4500
Dispersant B	2580	1600	1/2	4700
Dispersant C	2640	1600	1/2	4900
Dispersant D	1500	2700	1/2	7800
Dispersant E	1500	800	1/2	2100
Dispersant F	189[3)]	1600	1/2	2900
Dispersant G	1500	1100	1/2	3100
Dispersant H	1500	2000	1/2	5800
Dispersant I	9400[4)]	1600[5)]	1/5[5)]	24000

1) The molecular weight (Mn) was measured by gel permeation chromatography (GPC) with a solution prepared by dissolving Na_2SO_4 in a 1% aqueous acetic acid solution.

2) The molecular weight (Mn) was measured by gel permeation chromatography (GPC) with a chloroform solution of FARMIN DM2098, commercially available from Kao Corporation.

3) Tetraethylenepentamine was used (Mn was calculated according to chemical formula).

4) Measured by gel permeation chromatography (GPC) with a mixed solution of chloroform and water, after amidolysis of dispersant

5) Value of NMR measurement

Preparation of polyester resin

A 10-L four-neck flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with bisphenol A propylene oxide adduct, bisphenol A ethylene oxide adduct, terephthalic acid, and dibutyltin oxide. The mixture was reacted at 230°C for 10 hours and further reacted at 8.3kPa for 1hour.

Preparation of toner

Polyester resin obtained above and pigment (Pigment Blue 15:3) were previously mixed, and the mixture was melt-kneaded. The kneaded product obtained above was cool-pressed with a cooling roller, and the cooled product was roughly pulverized with a hammer-mill, and then finely pulverized and classified with an air jet type jet mill, to provide toner particles having a volume-median particle size D_{50} of 10 μm.

Preparation of liquid toner samples

A 1-L polyethylene vessel was charged with toner particles obtained above, paraffin oil, and a dispersant listed in Table 2. The mixture was stirred, under ice-cooling at a rotational speed of 7000 r/min for 30 minutes, to provide a dispersion of toner particles having a solid content concentration of 37% by mass.

The dispersion of toner particles obtained above was subjected to wet milling with sand grinder using zirconia beads until a volume-median particle size D_{50} as listed in Table 3 was obtained. The beads were filtered off, to provide a liquid toner having physical properties as shown in Table 3.

Measurement of the particle size distribution of liquid toner

A volume-median particle size D_{50} was measured by Mastersizer 2000 (Laser diffraction/scattering particle size measurement instrument, Malvern Instruments, Ltd.), by charging a cell for measurement with Isopar G (Isoparaffin, Exxon Mobile Corporation).

Measurement of the viscosity of liquid toner

Viscosity was measured with VISCOMATE VM-10A-L (Torsional oscillation type viscometer, SEKONIC CORPORATION.) at 25°C.

Measurement of the heat storage stability of liquid toner

Each liquid toner sample (10 g) was placed in a glass sample vial and was allowed to stand at 40°C for 24 hours. The viscosities before and after storage were measured, to quantify heat storage stability from the calculation of the ratio of [viscosity after storage]/[viscosity before storage]. A value approaching 1 indicates excellent heat storage stability.

Measurement of force curve by atomic force microscopy (AFM)

AFM measurements were performed using Dimension V (Veeco Instruments Inc.). Colloidal probe made of polyester resin and a silicon wafer substrate spin-coated by polyester were soaked in 1.5wt% of dispersant solution in paraffin oil in order to adsorb the dispersant. After picking up, the substrate was fixed in glass petri dish filled with paraffin oil. Interaction force between the substrate and colloidal probe was measured. The speed of approach and retraction was fixed to 500 nm/s.

Results and discussions

Comparison of dispersibility of dispersants

As mentioned above, a liquid toner requires high dispersibility (small particle size, low viscosity, excellent heat storage stability) in high toner concentration to achieve high speed printing. Among the materials of liquid toner, dispersant has large influence on dispersibility.

We designed a dispersant for liquid toner which consisted of polyester toner particles as dispersoids and paraffin oil as the dispersion medium. As the adsorbing unit, polyethyleneimine was selected, which can adsorb to carboxylic acid of polyester toner by acid-base interaction [3]. Homopolymer of 12-hydroxystearic acid was selected as the dispersing unit because it has low polarity and it is easy to control molecular weight. By condensation reaction between adsorbing units and dispersing units of different molecular weight, amide dispersants were synthesized (Table 2).

In order to compare dispersibility of dispersants, liquid toner samples were prepared by wet milling method with same toner particles, same paraffin oil and same additive amount of dispersants. Physical properties of prepared liquid toner samples are shown in Table 3.

Table 3. Properties of Liquid Toner Samples

Liquid Toner	Disper-sant[1)]	D50 [μm]	Visco-sity [mPa·s]	Visco-sity (After heating) [mPa·s]	Heat Storage Stability
1	A	1.8	33	34	1.03
2	B	1.7	35	41	1.17
3	C	1.6	32	66	2.06
4	D	1.6	37	39	1.05
5	E	8	>1000	unmeasurable state	
6	F	2.8	37	212	5.73
7	G	2.3	132	158	1.20
8	H	1.9	42	45	1.07
9	I	1.9	25	45	1.80

1) Additive amount of dispersants is each 5 wt% towards toner particles, as active content.

Figure 2 shows comparison of viscosity before heating and heat storage stability by changing Mn of adsorbing unit, fixing Mn of dispersing unit and adsorbing unit (PEI) / dispersing unit (Homopolymer) ratio. If the dispersant has good dispersibility, the viscosity becomes low and the heat storage stability approximates 1. There was little difference in viscosity before heating, but liquid toner made of dispersant F which has minimum Mn, synthesized with tetraethylenepentamine showed bad heat storage stability. On the other hand, high Mn of adsorbing unit also led to bad heat storage stability. It was found that the dispersant having Mn of 1500 has the best heat storage stability.

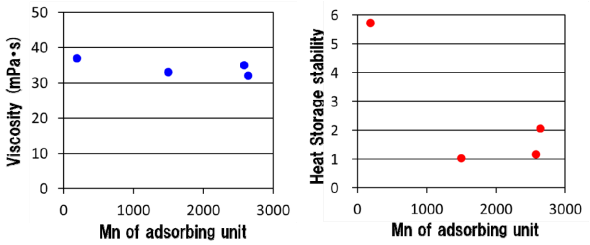

Figure 2. *Left: Viscosity of liquid toner made of different Mn of adsorbing unit. Right: Heat Storage stability of liquid toner made of different Mn of adsorbing unit.*

Figure 3 shows comparison of viscosity before heating and heat storage stability by changing Mn of dispersing unit, while fixing Mn of adsorbing unit and the ratio of adsorbing unit (PEI) / dispersing unit (Homopolymer). Dispersant having Mn of 1100 or less could not disperse toner particles effectively during wet milling, and the viscosity was high. The viscosity decreased and the heat storage stability approached 1 by increasing Mn, which means improvement of the dispersibility.

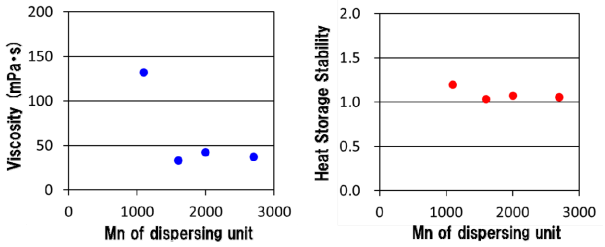

Figure 3. *Left: Viscosity of liquid toner made of different Mn of dispersing unit. Right: Heat storage stability of liquid toner made of different Mn of dispersing unit.*

Based on these results, dispersant A (Mn of absorbing unit =1500, Mn of dispersing unit = 1600, adsorbing unit / dispersing unit = 1/2) had the best dispersibility among synthesized dispersants (A-H). Dispersant A also had better dispersibility than dispersant I, commercially available and generally used for dispersion of liquid toner.

Figure 4 indicates the adsorbed amount of dispersant A and I with changing additive amount. It was found that dispersant A reached the saturated state of adsorption with a smaller amount.

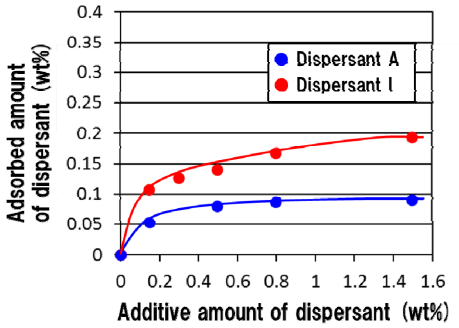

Figure 4. *Adsorbed amount of dispersant A and I*

Analysis of adsorption structure

As mentioned above, dispersant A had better dispersibility than dispersant I, a commercially available dispersant. The biggest difference between these dispersants is Mn of the adsorbing unit. It was assumed that the adsorption structure varied in accordance with Mn. In order to compare the adsorption structure, force curves of dispersant A and I were measured by colloidal probe AFM.

Substrates for AFM were prepared by spin-coating with polyester resin and soaking in a solution of each dispersant. A substrate without soaking was also prepared as a blank. Figure 5 shows force curve measured with a blank substrate. Weak attractive force was detected during both approaching and retracting process. Force curve measured with the substrate soaked in dispersant A is shown in Figure 6. During the approaching process, there was no attractive force between the substrate and the colloidal probe. It was suggested that the steric repulsive force arose due to the adsorption of dispersant. In the same procedure, a force curve with the substrate soaked in dispersant I was measured (Figure 7). Same as dispersant A, no attractive force was detected during the approaching process, and a repulsive force derived from adsorbed dispersant was detected. On the other hand, an attractive force was detected at a distance of 50-100 nm during the retracting process.

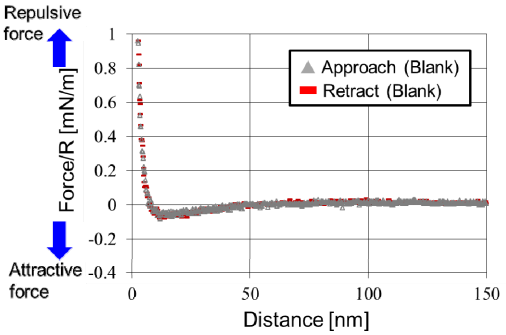

Figure 5. *Force curve between polyester resin surfaces in paraffin oil*

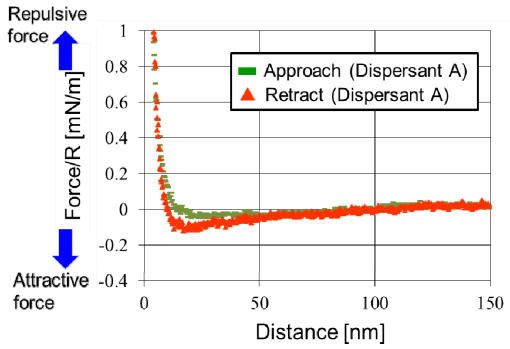

Figure 6. *Force curve between polyester resin surfaces with dispersant A in paraffin oil*

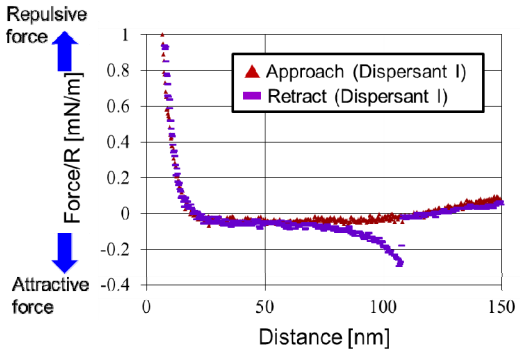

Figure 7. *Force curve between polyester resin surfaces with dispersant I in paraffin oil*

Figure 8 indicates force curve during the approach process measured with each substrate. Each force curve is the average of 10 measurements. The vertical axis of the graph is shown in a logarithm to clarify the difference. Starting points of repulsive force during the approach process were compared. Dispersant I showed repulsive forces from greater distance than Dispersant A. The point where repulsive force exceeded the base line (0.02 mN/m) was considered to be the starting point. The thickness of the adsorbing unit layer was estimated by deducting the starting point distance of the blank from the starting point distance of dispersant. The results are shown in Table 4. Adsorbing unit layer of dispersant I was thicker than dispersant A. Considering that the dispersing units of these two dispersants had the same Mn, it was suggested that adsorption structure of two dispersants was different.

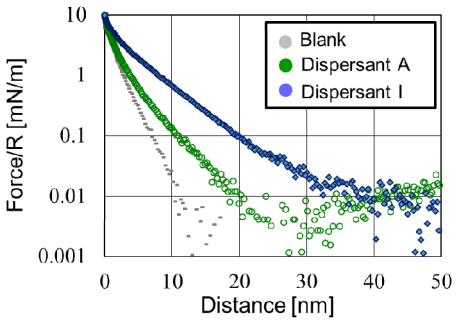

Figure 8. *Force curve during the approaching process between polyester resin surface with or without dispersant in paraffin oil*

Table 4. Thickness of adsorbing unit layer

Dispersant	Thickness (nm)
A	7
I	21

Based on the results above, the factors controlling dispersion are considered as follows. In the case of dispersant A which showed best dispersibility, no attractive force was detected during approach or retraction. During the approaching process, a repulsive force derived from adsorption of the dispersant was detected. This steric repulsive force led to the good dispersibility. On the other hand, in the case of dispersant I which showed worse dispersibility than dispersant A, strong attractive force was detected during the retracting process. This type of attractive force is described as "nano fishing" of polymer [4], and is caused by the pulling of polymer chains. Therefore, it is suggested that some of the adsorbing unit did not adsorbed because of its large Mn, and it caused cross-linking between particles during the approaching process. This cross-linking is considered to be the cause of agglomeration and bad dispersibility. Proposed structures of each dispersant in the adsorbed state are shown schematically in Figure 9. This force curve analysis indicates that the adsorbing unit of high molecular weight forms a train-loop-tail structure, while that of low molecular weight forms a brush-like layer.

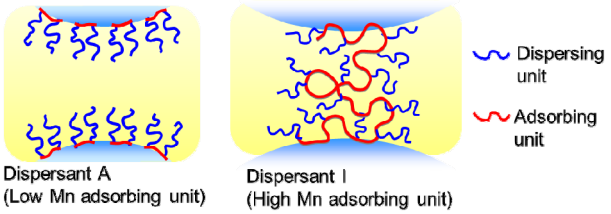

Figure 9. *Schematic illustration of the adsorption structure of dispersants*

Conclusions

In order to disperse toner particles consisting of polyester resin and pigments, amide dispersant consisting of adsorbing unit (PEI) and dispersing unit (homopolymer of 12-hydroxystearic acid) was synthesized, with various molecular weight and adsorbing unit / dispersing unit ratio. In this evaluation, the best dispersibility was achieved with a dispersant that consisted of an adsorbing unit with Mn of 1500, a dispersing unit with Mn of 1600, and a ratio of adsorbing unit / dispersing unit equal to 0.5. By analyzing the interaction force

using colloidal probe AFM, it was indicated that the adsorbing unit of high molecular weight forms train-loop-tail structure, while that of low molecular weight forms the brush-like layer.

Unlike dispersion in water, there is little electrostatic repulsion and weaker acid-base interaction in non-polar solvent such as paraffin oil. It was indicated that in the case of dispersant of high molecular weight, some of the adsorbing unit may adsorb to more than a single particle, which causes cross-linking between particles and bad dispersibility. It was demonstrated that adsorbing unit of low molecular weight was effective for dispersion in non-polar solvent.

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Author Biography

Mr. Tatsuya Yamada received his master degree in science and technology from Keio University in Japan in 2008. His research was based on organic synthetic chemistry through the academic studies. Since 2008, he has been working for Kao Corporation in the field of liquid toner based on polyesters.