The Material Design of the Polyester Color Toners

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Abstract

The color toner employing polyester resin is characterized by high transparent efficiency, excellent color reproduction, and long durability. These properties are due to the uniform colorant dispersion, the rheological properties, and the optimum toughness. As a result, polyester resin is indispensable for beautiful color prints and actually it has almost monopolized the color toner market. In this paper the characteristics and the material design of the polyester resin and toners are described. Furthermore, the trends of the development of the color toners are also described, i.e. the single component toners, the developers for "Print-On-Demand", and the color toners which can be fixed without oil.

Introduction

Color toners must melt well in the fusing process. Therefore the average molecular weight of the resin must be low and the distribution must be narrow. In the case of the styrene/acrylic copolymer for the color toners, the toner will be too brittle. Typical example of color toner with styrene/acrylic copolymer is the toners of XEROX 6500. To maintain the durability, the average molecular weight of the XEROX 6500 toner is set to be 60,000 ~ 70,000. Then the transparency of the pictures of XEROX 6500 is not enough to be accepted to today's market. At present all color toners are made of polyester resins except RICOH 5006 toner made of the epoxy resin.

Properties and Advantages of the Polyester Color Toners

Monomer Design and Molecular Weight Distribution of the Color Toners

Physical properties of various color toners are shown in Table 1. The softening points of all toners are in the range from 95 to 110ºC except of HP Color Laser Jet toner. The glass transition temperatures of the color toners are lower than that of the black toners for the mono-color printer (Tg = ca.60-70ºC).

These thermal properties depend on the molecular weight and the monomer composition of the binder resin. If the monomer composition is the same, the softening temperature and the glass transition temperature are simply dependent on the average molecular weight of the polymer. In the case of polyester resins, as the acid value of the polymer increases, the glass transition temperature becomes higher, because the apparent molecular weight become larger by increasing the number of the hydrogen bonds.

In the case of styrene acrylic copolymer, styrene is a hard segment and acrylic acid esters are soft segments. The thermal properties can be controlled by changing the ratio of the hard and soft segments. In the case of polyester resins the representative monomers are shown in Table 2. Terephthalic acid is a hard segment. Maleic acid, fumaric acid, succinic acid derivatives, ethylene glycol, and propylene glycol are soft segments.

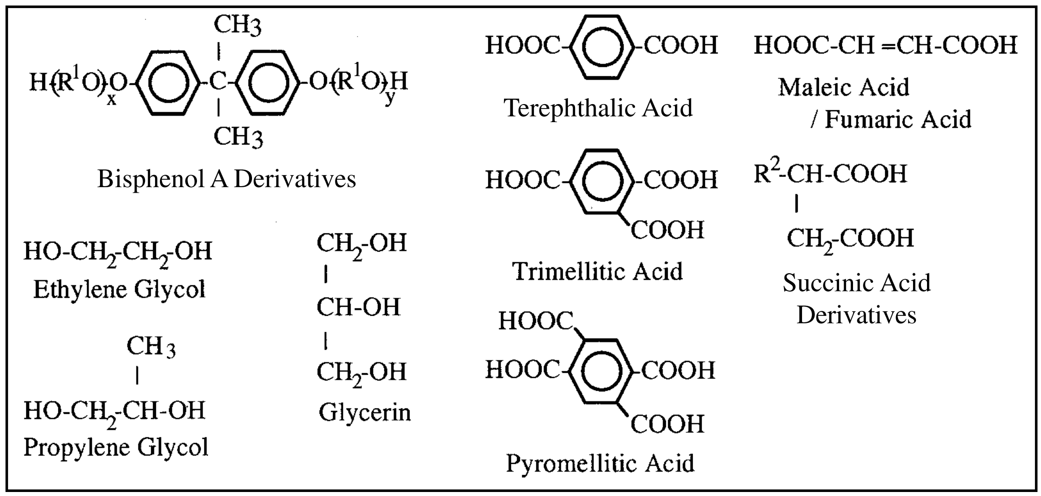
Table 1. Physical Properties of Color Toners

	Yellow			Magenta			Cyan			Black		
	D50 µm	T1/2 °C	Tg °C	D50 µm	T1/2 °C	Tg °C	D50 µm	T1/2 °C	Tg °C	D50 µm	T1/2 °C	Tg °C
CANON CLC-500	8.3	101.1	60.8	8.4	98.1	61.1	8.5	98.4	61.0	10.2	101.1	60.9
XEROX 5760	7.8	102.8	67.6	8.1	102.2	65.1	7.9	101.9	64.8	9.8	101.1	65.3
RICHO 506	7.1	99.3	52.4	7.1	98.5	57.7	7.1	97.6	57.5	7.1	97.7	57.7
QMS Magicolor	10.0	95.2	60.3	10.0	95.9	59.8	9.9	98.5	60.3	10.1	100.2	60.3
XEROX 4920	7.3	98.6	60.1	6.8	99.2	60.3	7.2	97.6	59.8	7.0	101.4	59.7
HP Color Laser Jet	16.0	126.2	55.5	15.3	127.9	57.9	16.0	126.7	59.5	11.8	124.8	56.5
Tektronix Phaser 540	8.9	105.0	65.3	8.7	105.0	66.0	9.3	105.0	66.0	8.9	103.0	65.0
Apple Color Laser Writer	8.9	107.3	62.3	9.1	104.8	61.6	8.8	105.2	61.6	8.9	105.1	61.7

D50 = Median particle diameter measured by Coulter Multisizer
T1/2 = Temperature at which half the sample has been extruded. (measured by SHIMADZU FLOW TESTER)
Tg = Measured by DSC.

Table 2. The representative monomers of the polyester resins.

Alcohol monomer | Acid monomer



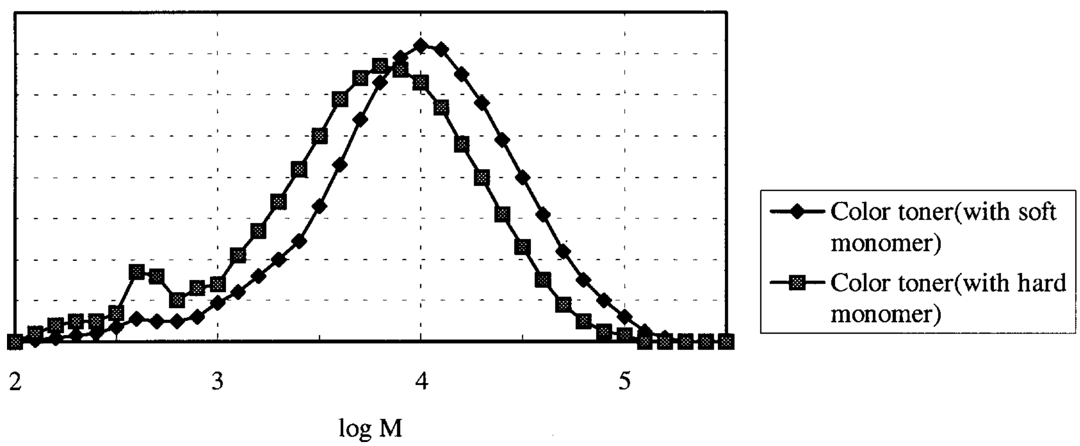


Figure 1. The molecular weight distribution of the color toners.

T1/2 of polyester resin for the color toner must be low, as shown in Table 1. However if the average molecular weight is too low, the durability of the toner cannot be satisfied. Then T1/2 of polyester for the color toner must be low with keeping the enough molecular weight. For that purpose, the ratio of soft segments will be increased within the limit which the Tg of polyester does not become too low. The molecular weight distributions of two polyester toners which have the same softening temperature (T1/2 = 98-100ºC) are shown in Figure 1. When T1/2 is same, the average molecular weight of polyester toner with the soft segment is higher than that with the hard segment. Consequently the durability of the color toner with the soft monomer is better than that with the hard monomer.

Bisphenol A derivatives are very excellent monomers for color toner, because they have both the soft and hard segment in one molecular unit. Accordingly they give both optimum toughness and good thermal properties for polyester toners.[1] Therefore the polyester with Bisphenol A derivatives and fumaric acid is most popular for the design of the color toners.

The molecular weight distribution of the polyester is important to control the fixing strength and the gloss of the fixed images. The molecular weight distributions of three typical color toners are shown in Figure 2a and the corresponding gloss values with various fusing temperatures are shown in Figure 2b. Type -1 toner has the typical molecular weight distribution of the color toner. In Type-2 toner the fraction of the higher molecular weight is increased and Type-3 toner has the similar distribution of the black toner for the mono-color printer. Generally, as the fraction of the high molecular weight components is smaller, the gloss of the pictures becomes higher by supplying the enough fusing energy. However when the fraction of the high molecular weight components becomes large, the gloss of the pictures will be kept low even if the fusing temperature is high. The toner layer including the high molecular weight components will be distorted by its elastic strain and the surface of the toner layer will be rough. Therefore, the gloss level of the color print is dominated by the molecular weight distribution of the polymer as well as by the fusing condition of the printer.

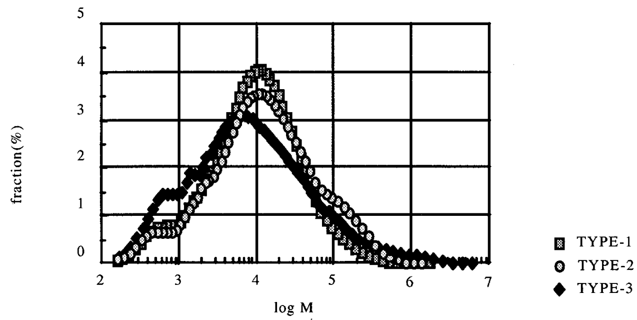


Figure 2a. The molecular weight distributions of the various kinds of color toners.

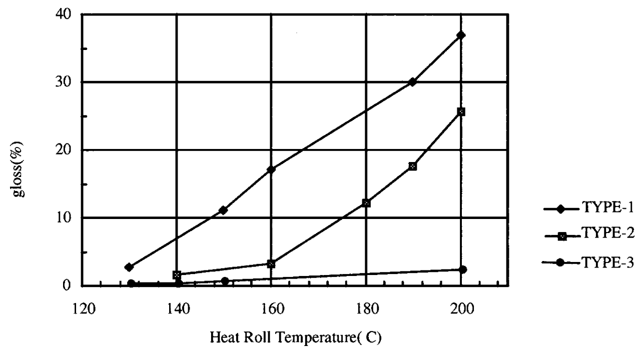


Figure 2b. The gloss of the various toners.

Effect of the Acid Value of Polyester Resin

Acid value is one of the most important properties of polyester resins. In general, by using the polyester with the high acid value, the uniform dispersion of organic pigments can be obtained compared with the polyester with the low acid value. It is said that the polar substitutents of polyester resin develop affinity between the resin and the pigments easier, because most of the pigments have polar functional groups.

Q/M of the toners depend on the acid value of polyester, as shown in Figure 3. The polyester with the high acid value allows the color toners to charge well. Additionally, as described above, the hydrogen bonding gives enough toughness to the toners.

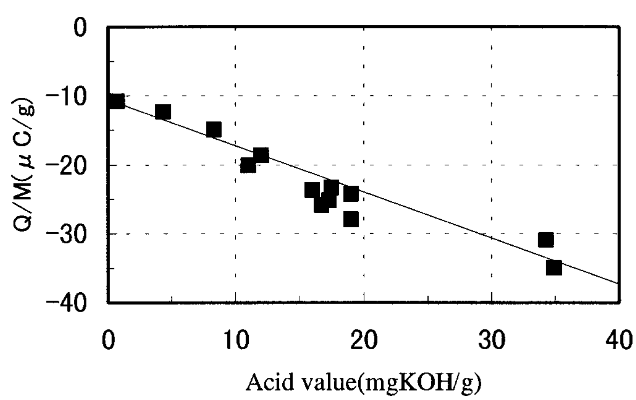


Figure 3. Dependence of Q/M of the toners on Acid Value of polyester.

It is said that Q/M of the toners with high acid value polyester tends to depend on the humidity.[2] However, since the polyester with the high acid value has many advantages, the humidity dependence of Q/M of the polyester with the high acid value should be compensated by optimizing other components, for example, charge control agents, surface additives, coated carrier, and so on.

Charge Control of the Polyester Color Toners

Organic pigments have various functional groups, therefore they strongly affect Q/M of the color toners. An example of the charge-up behavior of the color toners is shown in Figure 4.

The black pigment, carbon black, has the role to stabilize the charge of the toner by its electronic conjugation. However because of the conductivity of carbon black, Q/M of the black toner tends to be lower than that of other color toners. It is not so easy to control the Q/M of the black toner to the same level of the color toners.

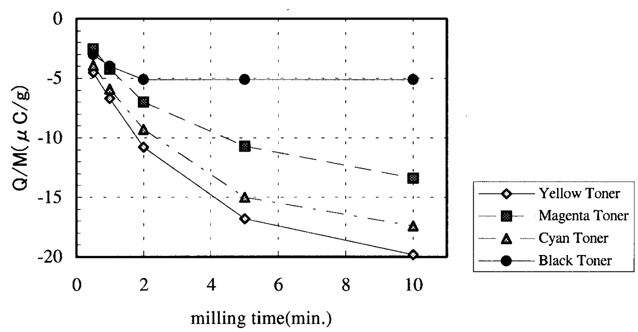


Figure 4. Charging-up behavior of the color toners.

Copper phthalocyanine is usually used as the cyan pigment, which has the charge stabilization effect because it has electronic conjugation and it is not conductive. Therefore Q/M control of cyan toner is generally the easiest among four different color toners.

As magenta pigments, 2,9-dimethylquinacridone and Carmine 6B are popular. In Figure 4, Quinacridone was included in the magenta toner. Quinacridone tends to charge positive because the amino groups are included in the molecule. Carmine 6B tends to charge negative, but it is humidity sensitive because of its ionic structure and the existence of the water soluble by-products.

Diazo-type yellow pigment is the most popular among yellow pigments. They are strongly charged negative. Therefore the charge of the yellow toners has the tendency to be charged up by mixing with the carrier.

To adjust the charge properties of four different color toners, special efforts are required. For the color toners, ditertiarybutyl salicylic acid complexes are the most popular as the Charge Control Agent.[3] Further the new charge control agents, for example boron compounds[4,5] and the polymer type charge control agents[6] are proposed.

The polyester resin has high negative Q/M level, so the polyester toner without CCA also has high Q/M level, although the charging rate is not so fast. By including CCA to the toner, the saturation level of Q/M will be decreased, and the charging rate of the developer will become fast as shown in Figure 5.

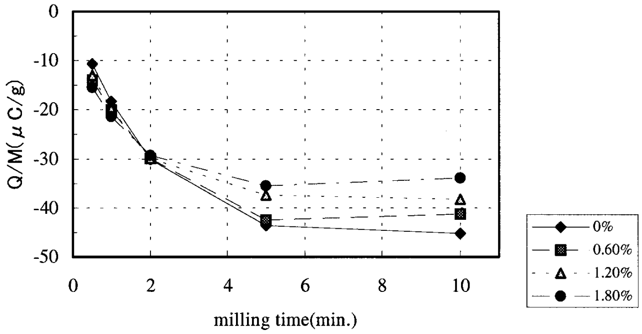


Figure 5.The charge-up behavior of the toners with the various amounts of CCA.

Some surface additives are also useful to charge control such as those used in XEROX 5760 toners.[7] Because of the external addition of specially prepared titanium dioxide, XEROX 5760 toners have very small humidity dependency of Q/M.

For the case of the two component developer, there is a possibility to control the charging-ability from the carrier side. If the charging-ability is different from one color to another, an appropriate carrier should be selected to each color, such as XEROX 6500. In general, the styrene/acrylic coated carrier gives high and quick charging-ability to polyester color toners. The styrene/acrylic coated carrier are used in CANON CLC-series and XEROX 5670.

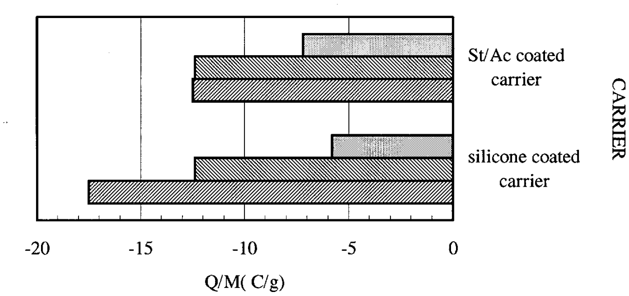


Figure 6. The ambient dependency of Q/M of the developer, Toner: Cyan Toner.

Trends of the Development of the Color Toners

Non Magnetic Single Component Toners

By using the non magnetic single component development system, the size of the desk top color printer can be diminished. Because there is no need to use the carrier, defects from the carrier, the edge effects, the white spots, and the brush marks, can be eliminated. Furthermore since the opposite electrode can be placed close to the photoconductor, the uniformity of solid pictures is excellent.

On the other hand, in the single component development apparatus, toners must be charged quickly between the metering blade and the development roll. Therefore the charging-ability of the toners is more important to obtain the excellent print quality compared with the case of the two component development system. Moreover the flow-ability of the toners is also important. Q/M of the single component toners strongly depends on the flow-ability of the toner more than the two component developer. If flow-ability is usually excessive, the retention time within the nip between the blade and the roll becomes small and Q/M of the toners becomes low. For example, from the elemental analysis of Tektronix Phaser 540 toner the extremely large amount of the charge control agent is known. Q/M of this toner is higher than other color toners (see Figure 7). It seems that a charge control agent is selected, which can enhance Q/M of the toner. In this toner only 0.3wt% of silica is included, accordingly, it is supposed that the flow-ability of the toner is kept low to scrub the toners effectively by the metering blade.

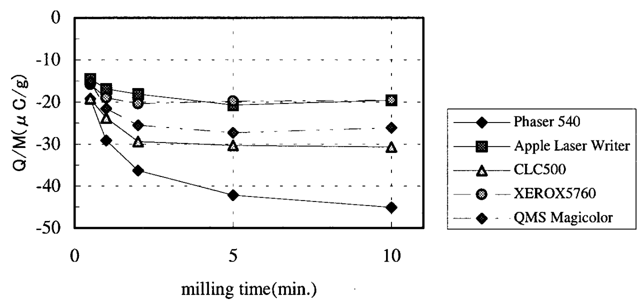


Figure 7. The charge-up behavior of the various color toners. Carrier: Silicone coated ferrite (T/D =3%).

In the case of the single component toners used in the jumping development, such as Apple Laser Writer, Q/M of the toners must be kept low optimum level. Excess Q/M level causes poor jumping and unacceptably low image density. Therefore the adhesive force of the toner surface must be decreased to obtain good jumping. Thus a large amount of the surface additive is required. But if a large amount of silica is used, Q/M of the toner becomes too high. Then the low charging surface additives are required for the jumping toners. In the case of the Apple toners, a large amount of titanium dioxide is observed at the surface of the toners by the SEM photography.

On the other hand, to obtain enough durability in the single component developer, the stress to the toners at the nip between the metering blade and the development roll must be diminished. By addition of a large amount of silica the mobility of the toners within the nip is enhanced and the stress will be diminished. However the charging efficiency will also be decreased. Then the amount of the surface additives will be decided to compromise both requirements.

Due to the stress in the nip, surface additives tend to be smeared into the toners. Then in the process of volume printing, the flow-ability of the toners will become poor. Therefore to avoid the change of the flow-ability, larger size silica is often used.[8]

Color Developers for "Print-on-Demand"

The first released developer for "Print-on-demand" is Chromapress developer. Since Q/M behavior of this developer is decreased with milling time, this developer seems to have the excess charging speed. It is because this developer was designed to have the good print quality when the pictures having high image coverage are printed. In such a case, much amount of toner is supplied to the developer and the quick charging speed is required. Considering its thermal properties (T1/2 = ca.98°C, Tg = ca.54°C), the standard linear polyester is used as the binder resin. Then it seems that the toughness of the toners is not enough to maintain the long durability.

Hence, in this area, the design of polyester resin becomes more and more important to satisfy both the good reproduction of the color tone and the long durability.

Color Toners for the Oilless Fuser

One of the obstacles to decrease the volume of the printer is the fuser oil tank. To decrease the amount of oil, many efforts are carried out. For that purpose, the softening temperatures of HP Color Laser Jet toners are higher than other color toners as shown in Table 1. The cohesive force inside the toner layer becomes large and the surface of the fixed image of toner is not smooth. Also the cohesive force of the toner layer becomes large and the adhesive force between the toner layer and the fuser roll becomes small. Therefore, the amount of the fuser oil can be decreased.

However, because of the rough surface of the fixed images, enough transparency of the image on the transparent film cannot be obtained. It is very difficult to decrease the amount of fuser oil while maintaining the excellently transparent pictures.

Hence to obtain the oilless color fusing the adhesive force must be decreased between the smooth surface of the toner layer and the fuser roll. It can be achieved by controlling the adhesive force of the surface of the toner layer and the cohesive force in the toner layer.[9] (but the detail cannot be described here).

Conclusion

Polyester resin gives the excellent color reproduction and the long durability.

- The optimum gloss level of the print can be obtained by designing the molecular weight distribution of the polyester resins.
- The polyester with the high acid value gives the uniform dispersion of the pigments.
- By including the optimum amounts of CCA, the desired charge level of the polyester toners can be obtained.

The single component toner and the toner's fixing ability without fuser oil are being developed to decrease the volume and the cost of the desk top printers.

Finally it is becoming more and more popular that electrophotography is applied to Print-on-Demand. For this application, toughness of the toners will be required to attain the long life of developer as the print speed is increasing.

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