

New Polyester Resin for Electrophotography Toner Having Excellent Fixing Properties

Koji Nakayama
Tomoegawa Paper Co., Ltd.
Shizuoka, Japan

Abstract

This present research relates to a toner comprised the new polyester resin for electrophotography which is used in copiers, printers, fax machines or multifunction devices utilizing heat-roll fixing.

This polyester resin was prepared by synthesizing a linear polyester resin having low molecular weight peak top in a range of 1×10^3 to 1×10^4, and then cross-linking with dicarboxylic acid component having long chain structure and polyol component having four hydroxyl groups.

This resin has a low molecular weight peak top and widened molecular weight distribution. The toner comprised this resin showed excellent fixing properties at low temperature without losing anti-offset up to 220°C. Then, it was concluded that the polyester resin is an useful toner binder for the contact heated fixing process.

Introduction

With the recent spread of the copiers, printers, fax machines and multifunction devices which are based on electrophotography, these machines have come to be required not only to be energy-saving (diminish power consumption) mainly for the purpose of environmental protection, but also to be operable at higher speed. There also is a desire for the machine, which can be operated at lower rolling pressure and thinner diameter of the roll for the purpose of fixing-roll simplification for attaining machine cost reduction. [1)]

In addition, since copiers having a double-side-copying function or equipped with an automatic document feeder has spread widely with the trend toward shifting to higher-grade copiers. The electrophotographic toners for use in such copiers and printers etc. are required to have a low fixing temperature, to be less apt to cause offset, and to be excellent in fixing strength to receiving paper so as to avoid smearing during both-side copying or in the automatic document feeder.

To meet the requirements described above, the following techniques including a binder resin having an improved molecular weight or improved molecular weight distribution, have been proposed.

Specifically, an attempt has been made to employ a binder resin having a reduced molecular weight to attain a lower fixing temperature. However, the reduction in molecular weight has also resulted in a reduced viscosity besides the lowered melting point, and this has caused a problem of offset to the fixing roll. To avoid this offset phenomenon, a technique of widening the molecular weight distribution of the binder resin has been proposed. For obtaining a polyester resin having a widened molecular weight distribution, a technique of using a polyfunctional monomer having a functionality of three or higher as a crosslinking ingredient has been employed. However, this technique has a problem that the increased crosslink density results in an increased melt viscosity and impaired fixiability, although it's effective in preventing the offset phenomenon. Another drawback is that the glass transition temperature (Tg) of the resin should be lowered so as to impart sufficient fixiability and this unavoidably impairs the storage stability of the toner.

An object of the present research is to provide a toner for electrophotography which is fixiable at a low fixing temperature, has no problem concerning the anti-offset properties, and is excellent in the fixing strength to receiving paper and in the image characteristics.

Experimental

Preparation of Polyester Resins[2,3,4)]

(1) Composed Polyester Resin Comprised Linear And Cross-Linked Polyester Resins Prepared By Two Steps Polymerization

The Preparation of Linear Polyester Resin

498.8g(1.45mol) of polyoxypropylene bisphenolA (2,2'-bis[4-(2-hydroxypropyleneoxy)phenyl] propane), 216.6g (1.305mol) of isophthalic acid and 650mg of dibutyltin oxide as a catalyst were put into a round bottom flask having four inlet portions. The linear polyester resin (P1) was obtained by reacting the mixture while introducing a nitrogen gas into the inlet, heating the mixture at 200°C; and after an outflow of water being completed, raising the temperature gradually to 230°C for 1hour; and stirring for 2 hours maintaining this temperature in the melted state.

Preparations of Polyester Resin Comprised Linear and Cross-Linked Polyester Resins

Next, 120g of the obtained linear polyester resin (P1) was put into a round bottom flask having four inlet portions

provided with an agitator, a condenser, and an inlet for nitrogen gas. The polyester resins (A,B,C) were obtained by reacting the mixture while introducing a nitrogen gas into the inlet, heating and stirring it at 200°C for 30minutes, simultaneously inputting 0.025mol of pentaerythritol, 0.0155mol of long chain aliphatic dicarboxylic acid [hexanedioic acid, dodecandioic acid, eicosandioic acid], and 0.3g of di-butyltin oxide as a catalyst; raising the temperature to 200°C, stirring the mixture while maintaining this temperature for 2 hours, and raising the temperature to 220°C, stirring for 2 hours, and reducing the pressure in the flask, and stopping the reaction when the resin wound the agitator.

These composed polyester resins (A,B,C) are obtained through two steps polymerization process. The flow of the polymerization is shown in Figure 1.

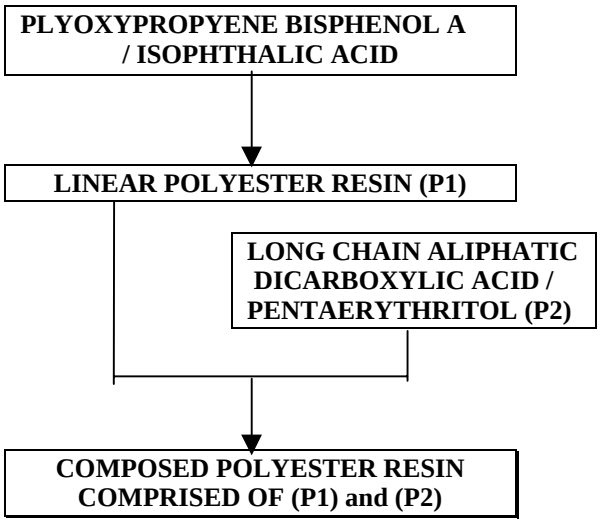


Figure 1. Process of polymerization

Table 1. The Monomers Used in the Preparation of Polyester Resins

Resin No.	Aliphatic Dicarboxylic Acid n=	Cross-linking Agent	Polymerization Step
A	4	Pentaerythritol	Two
B	10	Pentaerythritol	Two
C	18	Pentaerythritol	Two
D	18	Pentaerythritol	One
E	18	Trimethlolpropane	One

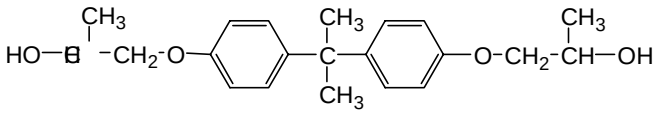
Aliphatic Dicarboxylic acid: HOOC-$(CH_2)_n$ –COOH
Hexanedioic acid ; n=4
Dodecandioic acid ; n=10
Eicosandioic acid ; n=18

(2) The Polyester Resins Prepared by One Step Method

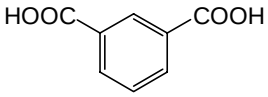
The polyester resin D was prepared using the same weight of the same raw materials used in polyester resin C. However, one step reaction was employed in the preparation of resin.

The polyester resin E was prepared in the same manner in the polyester resin D, namely, one step polymerization, except that pentaerythritol as a cross-linking agent was changed into trimethlolpropane.

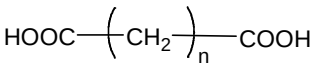
These polyester resins from A to E are characterized in Table 1. The structures of monomer used are given in Figure 2.



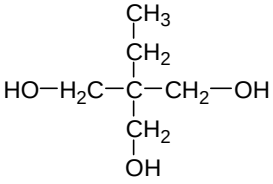
Polyoxypropylene Bisphenol A



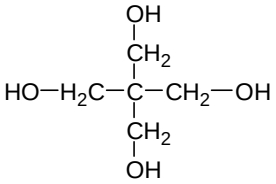
Isophthalic Acid



Aliphatic Dicarboxylic Acid



Trimethlolpropane



Pentaerythritol

Figure 2. The structures of monomer used

Preparation of Toner

The polyester resins and other component were mixed with a mixer at the following composition (Table 2).

Table 2. The Composition of the Toner

Material	Ratio (parts)
Polyester Resin	97.0
Carbon Black	6.5
Metallic Dye containing Chromium	2.0
Polypropylene	3.0

After melting and kneading the mixture, the particles having an average particle diameter of 8μm were obtained by classifying. The negatively charged toner particles were prepared by staining 0.3 parts of hydrophobic SiO_2 to the surface of the obtained classified particles, using a mixer.

Evaluation Tests

The following evaluation tests were performed on the obtained toners.

(1) The Properties of the Polyester Resins

The melt starting temperature and flow softening points were measured using flow tester CFT-500C manufactured by Shimazu corporation, the measured conditions are as follows:

Plunger: 1cm^2
Diameter of the die: 1mm
Length of die: 1mm
Load: 20kgF
Preheating temperature: 80°C
Preheating time: 30sec
Heating rate: 6°C/min

The melt starting temperature (Ti) was designated to be the temperature at the time when the plunger's descent began. Similarly, the flow softening point (Tm) was designated to be the temperature at the time when the plunger had traversed half the distance between the points where it began its descent and the bottom of the apparatus.

The acid values (AV) are measured in accordance with Japanese Industrial Standard K0070. The glass transition temperature (Tg) is measured by DSC. The Tg was designated to be the temperature at the middle point through the second scan.

The molecular weight of the resin was measured by GPC.

Mp; Peak top molecular weight
Mn; Number average molecular weight
Mw; Weight average molecular weight
Mw /Mn; molecular weight distribution

(2) Non-offset Temperature Range

Two component developers were obtained, which is comprised of 4 parts of obtained toners and 96parts of non-coated ferrite carrier. The obtained developers were used in a commercially available copier to form unfixed rectangular images each having a width of 20mm and a length of 50mm on A4 size receiving paper.

The unfixed toner images thus formed on the receiving paper were then fixed using a fixing device having a thermal fixing roll with the diameter of 30mm, whose roll surface is covered with fluorine-contained resin, and a press fixing roll whose surface is covered with silicone rubber. This fixing device was operated at a rolling speed 200mm/sec, while gradually varying the surface temperature of the heated roll 5°C by 5°C to 230°C. The copies thus obtained at each surface temperature of the heated roll were examined for toner smears in the margin. The range of temperature at which smear-free copies were obtained is referred to as the non-offset temperature range.

(3) Fixing Strength

Using the fixing device described above, the unfixed toner images described above were fixed to the receiving paper at the surface temperature of the heated roll of 150°C, 170°C,and 190°C. The image densities of the fixed test patterns were measured, after rubbing them with an eraser under a constant rubbing pressure. The image densities were measured with a reflective densitometer. The fixing strength, in %, was determined according to the following mathematical expression.

Fixing strength (%) = Density of fixed image after rubbing / density of fixed image before rubbing ×100

Results and Discussion

The Properties of the Polyester Resins

The results evaluated for the polyester resins are summarized in Table 3 and Table 4.

The linear polyester resin (P1) has the low peak top molecular weight and low melt starting temperature. Thus, it's suitable for the fixing at low temperature.

The number of carbon atom in the long chain aliphatic dicarboxylic acid affects on the Tg, Ti and Tm of the composed polyester resin, and these values are falling down with increasing number of carbon atoms.

As compared with the polyester resins of D and E prepared by one step polymerization, the composed polyester resins from A to C have broad molecular distribution.

Table 3. The Properties of the Polyester Resins

Resin	Tg (°C)	Ti (°C)	Tm (°C)	AV (mgKOH/g)
P1	62.1	83	99	21.6
A	69.5	109	134	1.5
B	66.3	104	131	1.0
C	62.9	103	129	1.0
D	65.0	104	125	6.4
E	63.7	106	129	1.4

Table 4. The Molecular Weight of the Polyester Resins

Resin	Mp ($\times 10^3$)	Mn ($\times 10^3$)	Mw (1×10^5)	Mw /Mn
P1	3.70	1.70	0.40	2.4
A	5.02	3.09	2.17	70.2
B	4.76	3.52	2.14	60.8
C	4.35	3.31	2.16	65.3
D	4.84	3.94	1.42	36.0
E	11.6	6.12	1.45	23.7

On the polyester resin D and E prepared by one step polymerization, the number of hydroxyl groups in the cross-linking agent affects on the molecular weight distribution and peak top molecular weight, namely, the resin D with pentaerythritol having four hydroxyl groups possesses more broad molecular weight distribution and lower peak top molecular weight than the resin E with trimethlolpropane having three hydroxyl groups.

As compared the composed polyester resin C prepared by two steps polymerization with the polyester resin D prepared by one step polymerization, the resin C has more broad molecular weight distribution and lower peak top molecular weight than the resin E.

The molecular weight distributions of a typical resin are shown in Figure 3.

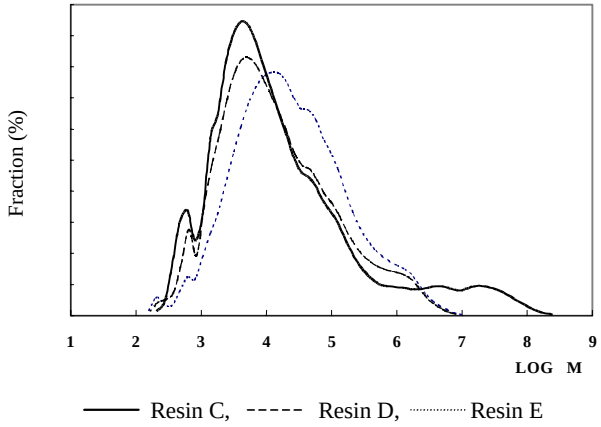


Figure 3. Molecular weight distribution

The Fixing Properties of the Toner

The results of the fixing strength for the toner prepared with the polyester resin are shown in Table 5.

Table 5. The Fixing Properties of the Toner

Toner (Resin) No.	Non-offset Temperature Range (°C)	Fixing Strength(%) 150°C	170°C	190°C
A	140 – 230	50.2	64.9	77.4
B	140 – 230	59.4	74.9	83.4
C	130 – 220	65.9	80.3	89.0
D	135 – 195	59.6	75.8	86.5
E	140 – 200	46.1	58.2	73.2

The toners prepared with the polyester resin from A to C have wide non-offset temperature range. The width of offset temperature range is 90°C, while the toners comprised of the resin D or E have narrow width of 60°C.

The fixing strength depends on the number of carbon atom in the long chain aliphatic dicarboxylic acid, and is improved with increasing number of carbon atoms.

Particularly, the toner C, that is, the composed polyester resin C prepared using eicosandioic acid has excellent fixing strength of 65.9% at 150°C and anti-offset temperature range from 135°C to 220°C, consequently, its fixing properties are especially improved in comparison with the common toner E which is in a market.

The toner C has excellent fixing properties, while, the toner D comprised the polyester resin D prepared using the same weight of the same raw materials used in the polyester resin, has poor anti-offset property because of low Mw and narrow molecular weight distribution.

Consequently, the polyester resin C is the best as a toner binder having the excellent fixing properties at low temperature.

Conclusion

This polyester resin was prepared by synthesizing a linear polyester resin having low molecular weight peak top about 4×10^3, and then crosslinking with dicarboxylic acid components having long chain structure and polyol components having four hydroxyl groups.

1. The polyester resins prepared by two steps polymerization have more broad molecular weight distribution and lower peak top molecular weight than the polyester resins prepared by one step polymerization.
2. The toner comprised of this composed resin shows excellent fixing strength at low temperature and widens anti-offset temperature range.
3. The number of carbon atoms in the long chain aliphatic dicarboxylic acid affects the fixing strength, therefore, the long chain structure is suitable for improving the fixing strength at low temperature.
4. In order to obtain broad molecular weight distribution and low peak top molecular weight, it is preferable to select polyol components having more than four hydroxyl groups as a cross-linking agent.

Then, it was concluded that the composed polyester resin having exellent fixing property at low temperature and anti-offset property is a useful toner binder for the contact heated.

References

1. Koji Nakayama, *J. Electrophotography*, **30**(2), 30 (1991).
2. Japanese Patent, First Publication 9-251216.
3. Japanese Patent, First Publication 10-60104.
4. Japanese Patent, First Publication 10-69126.

Biography

Koji Nakayama received his B.E. in Industrial Chemistry from the Tokyo University of Agriculture and Technology in 1977. He joined Tomoegawa Paper Co., Ltd. in 1977 working on research and development of papers in the Technical Research Laboratory. He was transferred to Chemicals Division (Toner Plant) in 1983 working on development of toners. He has worked on research and development of functional materials in the Technical Research Laboratory since 1995. His current interests are resins for toner.