

# A Hybrid Resin for Toner

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## Abstract

Hybrid Resin was prepared by hybridizing polyester and styrene-acrylic with bi-reactive monomer such as fumaric acid to utilize advantages of both resins for toner binder. This paper describes the development of Hybrid Resin that was stabilized in charge at high temperature in polyester by hybridizing styrene-acrylic through considering dielectric constant ( $\epsilon$ ). Further, thanks to low molecular weight and low glass transition temperature of styrene-acrylic part, lower temperature fixing for toner was also achieved.

## Introduction

Important technological requirements for electrophotographic toner in these days, are low temperature fixing ability, developer long life, and quick chargeability. Especially, low temperature fixing ability is one of the most important technologies in the field of low end as well as high speed copier or printer, because it brings minimization of consumed energy of the overall machines and less trouble in paper feed or paper burning, and so on. From this point of view, it is well known that polyester resin have been widely used for electrophotographic toner.<sup>1,2</sup> Since polyester can be designed to have wide molecular weight distribution and good affinity to paper, low temperature fixing is achieved. Particularly toner using polyester having high acid value (AV) shows good fixing ability, because of large cohesive energy caused by its many polar groups such as COOH or COOR groups with OH group. Furthermore, polyester toner has potentially long life in developer by its mechanical strength and quick chargeability.

It is well known that toner using polyester with soft side chain such as long alkyl or alkenyl group shows further low temperature fixing.<sup>1</sup> Since the side chain can move at under glass transition temperature, which is called  $\beta$  dispersion, much lower temperature fixing was achieved. However, it is not so easy to get charge stability, especially at high-temperature and high humidity, by using toner formulated with polyester having high AV and large amount of soft side chains. The tribo electric charge ( $q/m$ ) of the toner undesirably rises at high-temperature and declines at high-humidity. In case of dual developing system, appropriate carrier or toner formulation could be selected to overcome charge problem above mentioned. On the other hand, in case low AV polyester, the toner shows excellent charge stability even under severe environmental conditions<sup>3</sup> but decreased fixing ability compared to that of toner using high AV polyester. It was not so easy to get both low temperature fixing and charge stability by polyester resin itself.

Styrene-acrylic has been most widely used as toner binder resin, because of reasonable price and charge stability at high-temperature and high-humidity. On the contrary, styrene-acrylic resin seems not to fulfill both low temperature fixing and developer long life because mechanical strength of the resin is inferior to that of polyester. Furthermore it has a lack of quick chargeability because of high resistivity.

In order to solve above problems, many approaches have been proposed by blending or coupling polyester with styrene-acrylic.<sup>4-11</sup> However, since polyester has inherently poor compatibility with conventional styrene-acrylic by considerable difference in solubility parameter, mere mechanical blending of the component might result in poor dispersion of both resin themselves and additives in the resin. This may lead in turn to cause a lack of uniformity in charge distribution of toner. Consequently it often causes deterioration images like background. By the way, graft polymerization of considerable amount of styrene-acrylic monomers with unsaturated polyester often causes gelation.

Now, in the study of tribo electric charge ( $q/m$ ), dielectric constant ( $\epsilon$ ) is considered as a parameter which affects toner chargeability. Concerning the charge stability of toner in high-temperature, we will also indicate the temperature dependency of  $\epsilon$  in this paper.

In this study, we have synthesized a new resin hybridized polyester with styrene-acrylic, we call Hybrid Resin, to get both low temperature fixing and charge stability at high temperature.

## Experimental

### The Preparation of Resins:

To take advantage of low temperature fixing of polyester, large amount of polyester monomers was used compared to those of styrene-acrylic.

Polyester monomers including bi-reactive monomer such as fumaric acid were placed in a vessel. Styrene-acrylic monomers and radical polymerization initiators were mixed and placed into a dropping funnel. After the mixture of polyester monomers was heated to the temperature addition polymerization starts, the styrene-acrylic monomer mixture was added dropwise from the dropping funnel to the vessel. Followed by completing addition polymerization reaction, the reaction temperature was elevated to polymerize other monomers. The degree of polymerization was monitored by a Ball & Ring softening point (Tsp) according to ASTM E28-67. Measurement machine was ASP-MGK2 (MEITEC Corporation). Polymerization reaction was stopped at desired Tsp.

**Table 1. Monomer compositions of resins**

Entry	Monomers		
	Polyester	Styrene -acrylic	Bi-reactive monomer
Hybrid Resin A	BPA-PO,TPA,TMA OSA(large amount)	St,2-EHA	Fumaric acid
Hybrid Resin B	BPA-PO,TPA,TMA OSA(large amount)	St,2-EHA	Maleic anhydride
Hybrid Resin C	BPA-PO,TPA,TMA OSA(large amount)	St,2-EHA	Fumaric acid
Polyester A	BPA-PO,BPA-EO, TPA,TMA OSA(large amount)	-	-
Polyester B	BPA-PO,BPA-EO, TPA,TMA OSA(small amount)	-	-
Styrene -acrylic	-	St,2-EHA, DVB	-

BPA-PO :Bisphenol A propylene oxide adduct  
 BPA-EO :Bisphenol A ethylene oxide adduct  
 TPA :Terephthalic acid  
 OSA :Octenyl succinic anhydride  
 TMA :Trimelitic anhydride  
 St :Styrene  
 2-EHA :2-Ethyhexyl acrylate  
 DVB :Divinyl benzene

**Table 2. Physical Properties of Resins**

Entry	Styrene-acrylic Mpt	Domain particle size	Tm °C	Tg °C	AV (KOHmg/g)
Hybrid Resin A	35,000	0.5µm	133.5	62.5	8.5
Hybrid Resin B	10,000	2.0µm	135.0	61.0	10.5
Hybrid Resin C	8,000	1.5µm	136.0	59.5	9.5
Polyester A	-	-	125.0	63.0	20.5
Polyester B	-	-	134.0	62.0	2.0
Styrene -acrylic	-	-	133.0	62.5	-

Tm :Softening point by Flow Tester  
 Tg :Glass transition temperature  
 AV :Acid value  
 Mpt :Peak top of molecular weight distribution

The monomer compositions and physical properties of Hybrid Resins with reference resins are listed in Table 1 and Table 2, respectively. Polyesters were prepared by condensation polymerization, and styrene-acrylic was prepared by addition polymerization in o-xylene. Softening point (Tm) of resin was measured by Flow Tester (Model CFT 500, Shimazu), and glass transition temperature (Tg) was obtained by DSC (DSC Model 200; Seiko Instruments, Inc.) according to ASTM D3418-75. Acid value (AV) was measured according to ASTM D1980-67.

### The Measurement of Gel Permeation Chromatography:

The molecular weight of resin was measured by Gel Permeation Chromatography (GPC). The resin was dissolved at room temperature in chloroform in concentration from 0.05 to 0.5 wt%. The solution was filtered through membrane filter with pore sizes of 0.5 µm to remove insoluble part.

### The Preparation of Toners:

91.5 wt% of resin, 5.5 wt% of a carbon black, 1.8 wt% of a polypropylene wax and 0.9 wt% of charge control agent (CCA) were added, and they were compounded by twin-extruder, micronized and size-classified to 11 µm in volume median diameter. All toners for test were treated with 0.3 wt% of hydrophobic silica to get efficient flow for test operation.

### The Measurement of the Dielectric Constant (ε) of Resin and Toner:

The resin or toner were melt and pressed to form thin pellets. After heating at 135°C for 5 min, they were cooled to room temperature by degree applying the pressure. The thickness of pellet obtained was about 2 mm. The ε of each sample was measured according to JIS K6911 5.14 at several temperatures. Each sample having several ε (in Figure 1) was obtained from toner by using the polyester resins having different AV ( 2.0, 20.5, 35.0, 54.5 KOHmg/g).

### The Measurement of the Tribo Electric Charge (q/m) of Resins and Toners:

Polyester resins for measuring q/m were micronized and size classified to 11µm in volume median diameter. Each resin having different AV (in Figure 2) was obtained by changing monomer ratio. The tribo electric charge was measured with a blow-off method using a Faraday cage, a capacitor and an electrometer. For the test, resin/developer or toner/developer mass ratio (T/D) was set at 3% using non-coated ferrite carrier whose average diameter was 100 µm.

### Actual Copy Test:

2 kg of developer above mentioned were placed in a single roll development housing set to operate against a selenium alloy photoconductor drum, and image development was set to occur at 7% of black/white ratio for a image cycle. The T/D was maintained at 3% by magnetic sensor in the housing. The running speed was set at 500 mm/sec. Small samples of the developer were removed from the developer roll for measurement of q/m. Image density (ID) was also measured for each sampling point at a black solid area on the paper with Macbeth Densitometer The climate condition was kept at 23±3 °C and 55±10 % RH.

### The Evaluation of Fixing Ability:

The fixing ability was evaluated by determining the lowest fixing temperature. The lowest fixing temperature used herein was the temperature of the fixing roller at which the fixing ratio of the toner exceeds 70%. This fixing ratio of the toner was calculated from the image density change before and after loading of sand-rubber eraser. The image density was measured with Macbeth Densitometer. Heat-roller diameter was 40 mm. Nip width and nip pressure was set 2 mm and 2.0 kg/cm, respectively. Process speed was at 160 mm/sec.

## Results and Discussion

### The Relation Between Tribo Electric Charge ( $q/m$ ) and Dielectric Constant ( $\epsilon$ ):

At first dielectric constant ( $\epsilon$ ) was observed to realize chargeability of toner or resin. As shown in Figure 1, tribo electric charge ( $q/m$ ) increased with increasing  $\epsilon$  of toner in negative charge. Generally  $\epsilon$  is affected by induced dipole moment and permanent dipole moment. Especially in studying  $\epsilon$  of polar polymer, permanent dipole moment is very important.  $\epsilon$  of polar polymer is affected by permanent dipole moment orientation of polar groups such as carboxylic group. Generally polyester shows higher  $\epsilon$  than that of conventional styrene-acrylic because polyester has larger amount of polar groups than the latter. On the other hand,  $q/m$  of resins having several acid value (AV) was measured, as shown in Figure 2. It is apparent that  $q/m$  increased with increasing AV. It is assumed that the resin having high AV shows high  $\epsilon$  because of many permanent dipole moments originated from carboxylic group. Therefore, carboxylic group seems to be one of the factors that affect level of  $q/m$ .

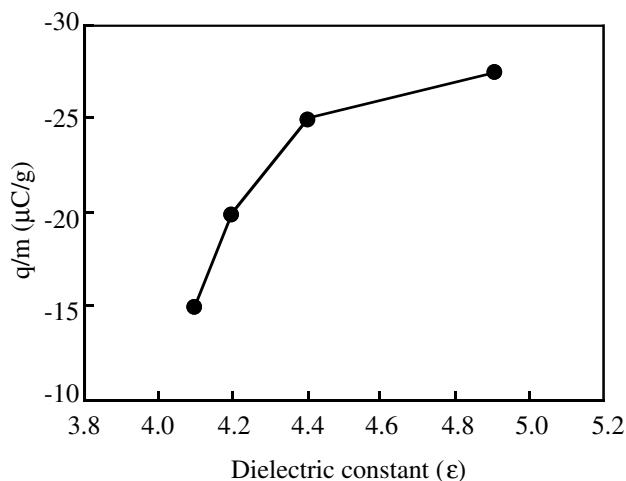


Figure 1. Triboelectric charge ( $q/m$ ) vs dielectric constant ( $\epsilon$ ) of toner.

Considering triboelectric property above mentioned, temperature dependency of  $\epsilon$  of resin and toner were measured. Results are shown in Figure 3. Though polyester A having high AV and using large amount of soft monomer such as octenyl group in side chain brought much lower temperature fixing as shown in Figure 7, the  $\epsilon$  of the resin itself increased at high temperature as well as in toner. On the contrary,  $\epsilon$  of polyester B having low AV and small

amount of soft monomer was independent of temperature change. However low temperature fixing was not satisfied with the toner using polyester B (data not shown). It is supposed that the long side chain of soft monomer can move under  $T_g$  and it may help orienting the dipole moment at that condition. Therefore, this might be a reason that the  $q/m$  of Polyester A toner increased at high-temperature. On the other hand,  $q/m$  of conventional styrene-acrylic toner did not change even at high-temperature because  $\epsilon$  of this resin is stable in such condition. But conventional styrene-acrylic has poor fixing ability compared to that of polyester.

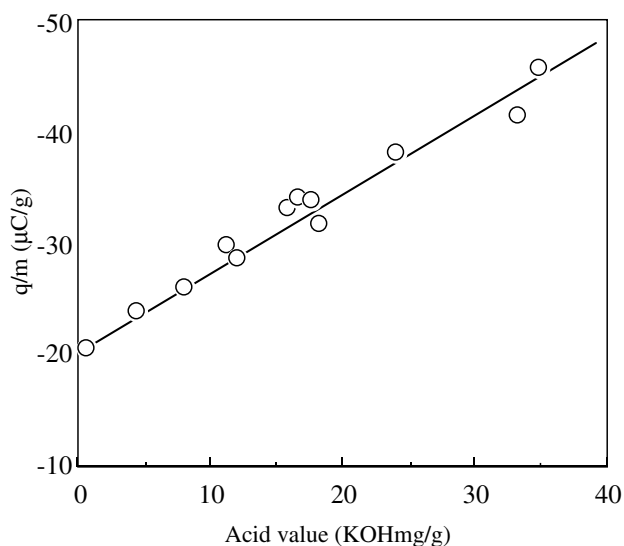


Figure 2. Triboelectric charge ( $q/m$ ) vs acid value of polyester resin.

In actual copy test,  $q/m$  of toner using polyester having high AV and with large amount of soft side chain increased with rising temperature of developer in running machine as shown in Figure 5. Then, we tried to control temperature dependency of  $\epsilon$  of polyester having high AV and using large amount of octenyl group by introducing styrene-acrylic having low  $\epsilon$ . To disperse uniformly resin itself and toner additives in producing toner, it was necessary to disperse styrene-acrylic finely in polyester. Thus, we tried to get both low temperature fixing and stable chargeability at high-temperature.

### The Characterization of Hybrid Resin:

To disperse styrene-acrylic in polyester uniformly, we have developed a technique where both polyester monomers and styrene-acrylic monomers are concurrently polymerized in a same reaction vessel. In addition, to obtain resin uniformity, bi-reactive monomer that has both C=C double bond and carboxylic groups such as fumaric acid or maleic anhydride was used. It is also confirmed that these bi-reactive monomers could bring the polyester partially grafted with styrene-acrylic. The obtained Hybrid Resins showed an islands-sea structure formed by styrene-acrylic dispersed in polyester, and had a single peak of glass transition temperature ( $T_g$ ). The average domain size of styrene-acrylic was not larger than 2  $\mu\text{m}$ . The diameter was measured by a transmission scanning electron microscope (TEM). It was changed dependent of the amount of bi-

reactive monomer. The key of excellent dispersion was caused by existence of the chemical species hybridized two types resins with bi-reactive monomer unit.

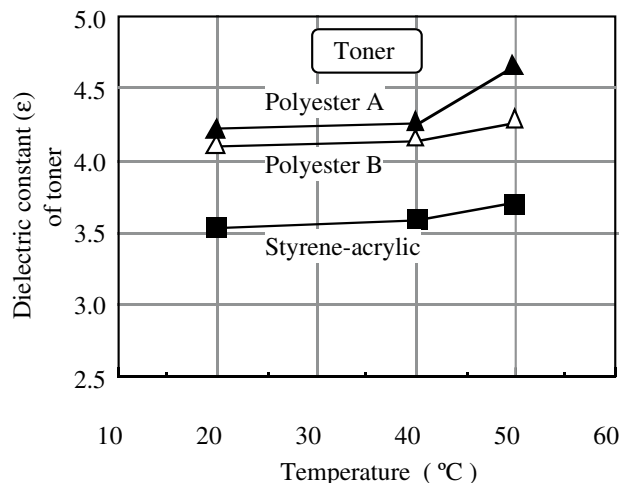
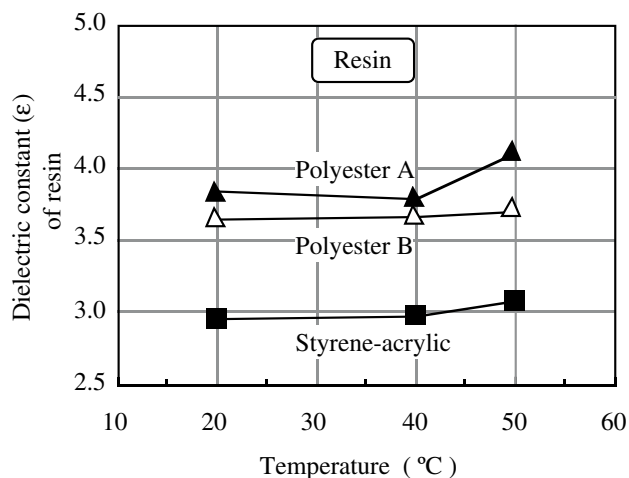


Figure 3. Dielectric constant ( $\epsilon$ ) vs temperature of resin and toner

Table 3. Dielectric constant ( $\epsilon$ ) of resins

Resin	$\epsilon$ ( at 20 °C )
Hybrid Resin A	3.56
Hybrid Resin C	3.60
Polyester A	3.82
Polyester B	3.65
Styrene-acrylic	2.92

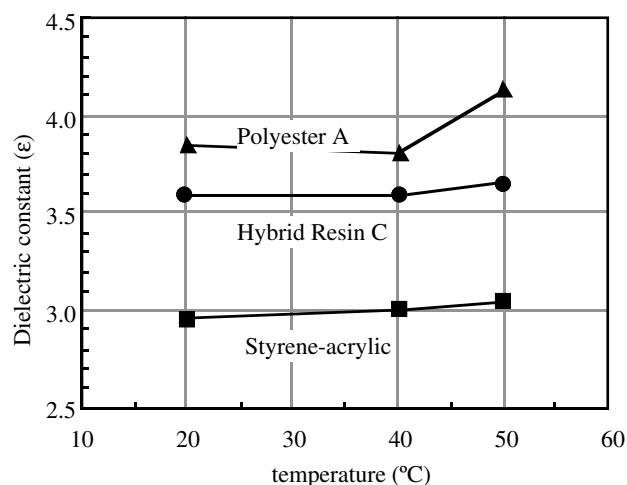


Figure 4. Dielectric constant ( $\epsilon$ ) of resin vs temperature.

The  $\epsilon$  of resins are listed in Table 3. These data show that the  $\epsilon$  of Hybrid Resin became lower than those of polyesters. The temperature dependency of  $\epsilon$  of resin is shown in Figure 4. The  $\epsilon$  of Hybrid Resin C became stable at high-temperature because the dipole moment orientation in polyester might be inhibited by introduced styrene-acrylic. Further, in actual copy test, as shown in Figure 5,  $q/m$  of the toner using Hybrid Resin did not increase with increasing developer temperature. It can be seen that the  $q/m$  change of low temperature fixable polyester toner at high-temperature was stabilized by controlling temperature dependency of  $\epsilon$ .

Further, by decreasing  $\epsilon$ , water adsorption of toner using Hybrid Resin decreased and so  $q/m$  of the toner did not decline even at high-humidity (data not shown).

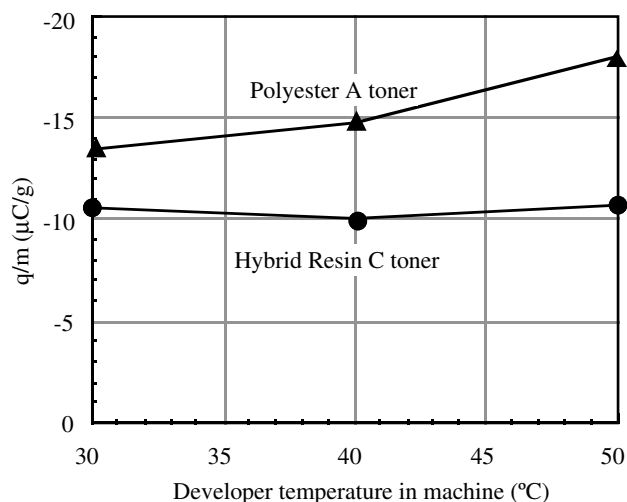


Figure 5. Tribo electric charge ( $q/m$ ) of toner vs developer temperature in machine.

#### The Evaluation of Fixing Ability of the Toners:

In respect of the toner for heat-roll fixing, it is very important to control molecular weight of binder resin besides the cohesive energy or  $\beta$  dispersion. It is well known that low melt viscosity part, in other words low molecular weight part affords low temperature fixing and high mo-

lecular weight part gives hot-offset resistance. Because of its wide molecular distribution, cross-linked polyester is suitable to balance both requirements. Figure 6 shows a general idea of crosslinked polyester.

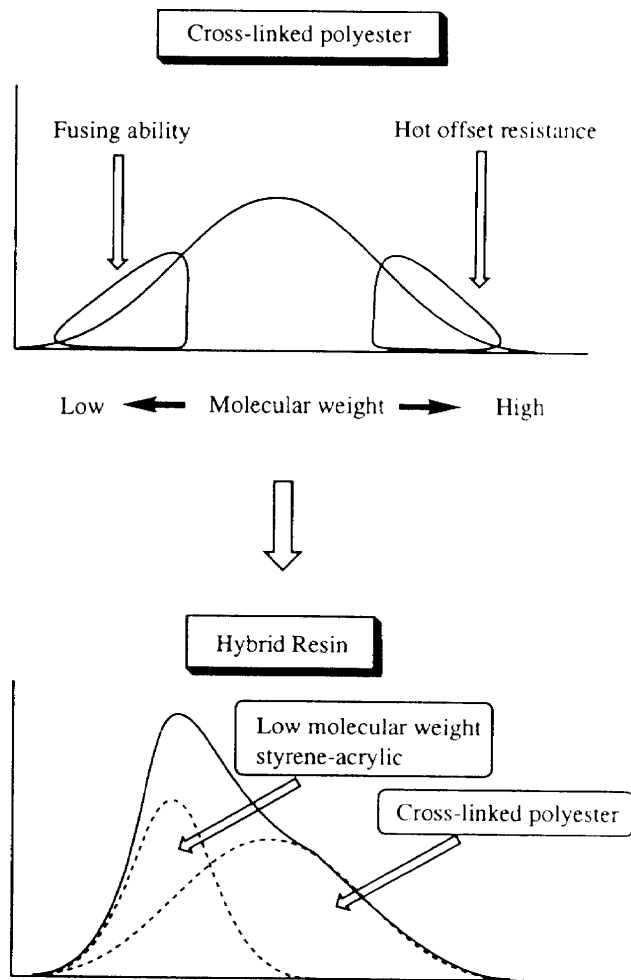


Figure 6. Molecular weight distribution design of Hybrid Resin.

For low temperature fixing of toner, the molecular design of styrene-acrylic part of Hybrid Resin is important, especially design of molecular weight and Tg. Its molecular weight is controlled by the amount of polymerization initiator or reaction temperature. Figure 6 also shows a concept of molecular design of Hybrid Resin. The suitable peak top of molecular weight distribution (Mpt) of styrene-acrylic sampled after completing addition polymerization is from 5,000 to 40,000. If it is smaller than 5,000, blocking of toner happens at 50°C. If larger than 40,000, low temperature fixing is interfered. On the other hand, Tg of styrene-acrylic is estimated by generally calculating with composition of the monomers in advance. The suitable estimated Tg is from

50 to 70°C. If lower than 50°C, blocking of toner happens. If higher than 70°C, low temperature fixing is interfered. The fixing test results are shown in Figure 7. Lower temperature fixing of toner using Hybrid Resin designed suitable for low temperature fixing in styrene-acrylic part was achieved than that of reference polyester (polyester A) toner.

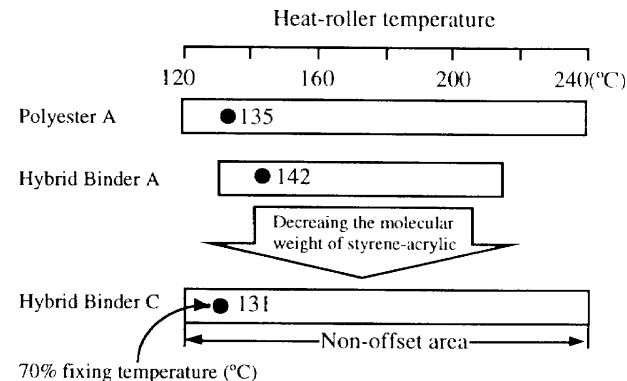


Figure 7. The evaluation of fixing ability of toner.

## Conclusion

Progressing in low temperature fixing, the charge stability of toner was achieved by hybridizing polyester with styrene-acrylic with bi-reactive monomer in the view point of temperature dependency of dielectric constant ( $\epsilon$ ). The  $\epsilon$  of Hybrid Resin was stabilized by inhibiting the dipole moment orientation in polyester even at 50°C. Consequently, the tribo electric charge ( $q/m$ ) of the Hybrid Resin based toner became stable at high-temperature. Further, a lower temperature fixing has been achieved for toner by introducing the styrene-acrylic part with both low molecular weight and low calculated Tg. This resin, we think, is one of a new generation of toners binder.

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