

Eco-friendly Aqueous-based Polyester Chemically Prepared Toner including Crystalline Polyester

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Abstract

In the full color laser printers and copiers, the performance features of high print speed, fine image quality and environmental friendliness are required. Therefore the special toner also has been required for high speed printing and fine image quality. Recently many chemically prepared toners (CPTs) have been proposed, and these toners are suitable to achieve small and narrow particle size distribution. But most of these toners use styrene acrylic resin, and only a few toners use polyester which is superior to styrene acrylic resin in low-energy fusing. But due to the use of organic solvents in the manufacturing process, environmental friendliness remains a matter for improvement in polyester CPTs.

We reported a novel PES CPT without using any solvent in the manufacturing process at NIP27 and NIP28.

In this study, three technologies for advanced PES CPT were described.

1) To develop polyester chemically prepared toner which has larger fusing latitudes for full color printers, we developed a technology to cross-link polyester with oxazoline polymer.

2) To develop eco-friendly polyester chemically prepared toner for low-energy fusing, we tried to introduce crystalline polyester by emulsification in aqueous phase. It was found that crystalline polyester could be emulsified successfully in the presence of amorphous polyester which makes crystalline part soluble with amorphous part.

3) We have found it is possible to make a toner having core-shell structure in which the core contains crystalline polyester for low-temperature fusing and the shell uses seed polymerization of styrene for storage stability. In this seed polymerization process, styrene monomer was reacted and cross-linked with the polyester of surface of the toner particles. The shell made by seed polymerization is suitable to be insoluble with polyester core.

From this study, we could obtain a toner having core-shell structure in which the core contained crystalline polyester and the shell contained amorphous polyester cross-linked by styrene. Furthermore, the toner provided improved performance in storage stability and low-temperature fusing.

Introduction

In recent years, environmental issues have received a considerable amount of attention. As part of that focus, it has been required to have electrophotographic toners that are fusible at lower temperature for the purpose of saving energy. In addition, it

has been required that the toners should have small particle size and narrow particle size distribution for fine image quality.

To develop toner for low energy fusing and high image quality, there are several methods to manufacture polyester chemically prepared toner [1]. But there are still concerns due to the use of organic solvents that are required in the CPT manufacturing process. It has been desired to manufacture polyester chemically prepared toner without any organic solvent.

We previously described at NIP27 a completely solvent-free CPT process using nonionic surfactant instead of organic solvent [2]. And at NIP28, we reported better storage property with the reduction of the amount of surfactant by using a combination of anionic surfactants and nonionic surfactants. And we reported improved non-offset resistance by using a buffer solution (pH8) as the neutralizing agent to prevent hydrolysis of the polyester resin [3].

We developed an advanced, eco-friendly polyester chemically prepared toner for full color printers and copiers which has larger fusing latitudes and contains crystalline polyester introduced by aqueous phase emulsification.

Experimental

Preparation of amorphous polyester resins

APES-1; A 10L four-neck flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with bisphenol A propoxylate and ethoxylate, terephthalic acid, and dibutyltin oxide were reacted at 230°C for 10 hours and further reacted at 8.3kPa for 1 hour. Then, fumaric acid and hydroquinone were added, and reacted at 210°C for 3 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

APES-2; The above alcohols, terephthalic acid, trimellitic anhydride, dodecenylsuccinic acid anhydride and dibutyltin oxide were reacted at 230°C for 5 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

APES-3; The above alcohols, the above acids, and dibutyltin oxide were reacted at 230°C for 5 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained.

APES-4; The above alcohols, terephthalic acid, trimellitic anhydride, adipic acid and dibutyltin oxide were reacted at 230°C for 5 hours. Thereafter ingredients were reacted at 8.3kPa until the desired softening point was attained. The thermal properties of reacted amorphous resins are listed in Table 1.

Table 1. Properties of the Experimental Polyester Resin

	Acid value ¹⁾ (mgKOH/g)	T 1/2 ²⁾ (°C)	Tg ³⁾ (°C)
APES-1	24	108	64 ⁴⁾
APES-2	21	121	63 ⁴⁾
APES-3	18	117	56 ⁴⁾
APES-4	20	84	47 ⁴⁾

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

2) The softening point (T 1/2) was measured according to ASTM E-28-67.

3) The glass transition temperature (Tg) was measured by a differential scanning calorimeter (DSC).

4) Tg was read by the tangential way.

Preparation of crystalline polyester resin

C-PES; A 10L four-necked flask equipped with a nitrogen inlet tube, a dehydration tube, a stirrer, and a thermocouple was charged with 100 weight parts of 1,9-nonanediol as alcohol and 100 weight parts of sebacic acid. Dibutyltin oxide and hydroquinone were used to control the reaction. Then, the ingredients were reacted at 190°C and held for 5 hours in a glass flask. Thereafter, the temperature was raised to 210°C, reacted for 5 hours, and further reacted at 8.3kPa for 1 hour. The thermal properties of the crystalline polyester are listed in Table 2.

Table 2. Properties of the Experimental Crystalline Polyester Resin

	T1/2 (°C)	Mp ⁵⁾ (°C)	AV ⁶⁾ (KOHmg/g)
C-PES	83	78	16

5) Mp was read by the peak top. This value is called melting point.

6) The acid value was measured according to ASTM D-1980-67 solvent chloroform

1) Experimental for improvement of fusing latitudes; Preparation of cross-linking polyester emulsions with oxazoline polymer

Em-A; A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with APES-1, APES-2, nonionic surfactant (polyoxyethylene oleyl ether), anionic surfactant (sodium dodecylbenzene sulfonate), and aqueous sodium hydroxide solution (concentration: 5% by weight) as a neutralizing agent. The ingredients were stabilized at 95°C for 2 hour. Subsequently, deionized water was added dropwise to the mixture. During the addition, the temperature of the system was kept at 95°C. Emulsion containing finely prepared APES-1 and APES-2 was obtained through a wire mesh.

Em-B; In a similar method, emulsion containing APES-3 and APES-4 was obtained.

Em-A1 to A4; A 2L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with Em-A at room temperature. Next, acrylic polymer containing oxazoline groups (Epocros WS-700; Nippon Shokubai) was added dropwise to Em-A, and the mixture was stirred for 10 minutes at 25°C. Amount of the oxazoline-functional polymer is

listed in table 3. After that, the mixture was heated to 95°C, and kept at 95°C for 1 hour. Finally, polyester emulsion cross-linked with oxazoline polymer was obtained through a wire mesh after cooling.

Table 3. Properties of the cross-linked polyester emulsions

	polyester	Oxazoline Polymer (Eq.) ⁷⁾
Em-A	APES1/APES2	0
Em-A1	APES1/APES2	0.063
Em-A2	APES1/APES2	0.125
Em-A3	APES1/APES2	0.250
Em-A4	APES1/APES2	0.500

7) Amount of oxazoline polymer (WS700) was represented by equivalent (Eq.) to the acid values of the polyester resin.

Preparation of A-PES toners

Toner-A; The resulting polyester emulsion (Em-A), colorant (Pigment Blue 15:3) dispersion, and wax emulsion containing carnauba wax were mixed in a 2L four-neck flask at room temperature (25°C). Next, an ammonium sulfate aqueous solution was added to the mixture as a coagulant. Thereafter the mixture was heated up to 55°C, and held at 55°C, and stirred for 4 hours to form aggregated particles.

Thereafter, the mixture was heated to 80°C, and stirred for 3 hours to unify the aggregated particles. Subsequently, the suspension was filtered, washed with deionized water and dried to give a fine colored resin particle powder, particle size of 5.0µm. Each toner was blended with fumed silica as fluidizing agent. In similar method, Toner-B, Toner-C, and Toner-D were prepared from polyester emulsion Em-A2, Em-A3, and Em-A4, respectively.

2) Experimental for lower energy fusing; Preparation of cross-linking crystalline polyester emulsions with oxazoline polymer

Exp-1; A 5L four-necked flask equipped with a dropping tube, a cooling tube, a stirrer, and a thermocouple was charged with CPES, nonionic surfactant (polyoxyethylene lauryl ether), anionic surfactant (sodium dodecylbenzene sulfonate), and aqueous sodium hydroxide solution (concentration: 5% by weight) as a neutralizing agent. The ingredients were stabilized at 98°C for 2 hour. Subsequently, deionized water was added dropwise to the mixture. During the addition, the temperature of the system was kept at 95°C. Emulsion containing prepared CPES was obtained through a wire mesh.

Exp-2-6; In a similar method, emulsions containing CPES and APES-1, APES-3 or APES-4 were obtained (Exp2-6). The combination ratio of CPES and APES is listed in table 4.

Em-B1, In a similar method to cross-linking polyester emulsion as above mentioned, crystalline polyester emulsion (Exp-6) was cross-linked with oxazoline polymer. The amount of oxazoline polymer was 0.125 Eq for the acid values of the polyester resin.

Table 4. Combination ratio of CPES and APES

	Combination ratio of polyester resin	
Exp-1	CPES	100
Exp-2	CPES/APES1	50/50
Exp-3	CPES/APES1	30/70
Exp-4	CPES/APES3	50/50
Exp-5	CPES/APES3	30/70
Exp-6	CPES/APES3/APES4	15/50/35

Measurement of the particle size distribution of emulsions and toners

The particle size distribution of emulsions was measured by LA-920 (Laser scattering particle size analyzer, HORIBA Co., Ltd.). The particle size distribution of toners was measured by Multisizer II (Beckman Coulter, Inc.) with the 50 μ m size aperture.

Measurement of the glass transition temperature of emulsions and the melting point of neutralized crystalline polyester containing amorphous polyester in emulsification process

Glass transition temperature (T_g) of emulsions and melting point (Mp) of neutralized polyesters containing CPES at emulsification were measured by a differential scanning calorimeter (DSC). Samples were prepared by vacuum freeze dryer. The T_g was measured at the temperature heating from 0 °C to 160°C, and was read by the tangential way. Mp was measured at the condition as follows, first, heating to 98°C by 50°C/min, then, keeping at 98°C for 5 minutes, after that, cooling down from 98°C to 0°C by 10°C/min. The amount of energy output for re-crystallization was measured. The melting point of emulsions was read by the peak top of the energy output of re-crystallization.

Toner preparation containing crystalline polyester

Toner-E; The resulting polyester emulsion (Em-B1), colorant (Pigment Blue 15:3) dispersion, and wax emulsion containing carnauba wax and paraffin wax were mixed in a 2L four-neck flask at room temperature (25°C). Next, an aqueous solution containing ammonium sulfate as a coagulant was added to the mixture. Thereafter the mixture was heated to 55°C, and kept at 55°C, and stirred until the aggregate particles grew up to 4.3 μ m. Then polyester emulsion (Em-A) was added dropwise to aggregate particle dispersion, and the temperature of the mixture was kept at from 55°C to 60°C to form encapsulate particles. Thereafter, the mixture was heated to 70°C, and stirred for 2 hours to unify the aggregated particles. Subsequently, the mixed dispersion was subjected to a suction filtration step, a rinsing step, and drying step, to give a fine colored resin particle powder, particle size of 5.0 μ m. Each toner was blended with fumed silica as fluidizing agent.

3) Experimental for lower energy fusing and higher storage stability; Preparation of core-shell CPES toner grafted by styrene seed polymerization

Toner-F; The resulting polyester emulsion (Em-B1), colorant (Pigment Blue 15:3) dispersion, and wax emulsion containing carnauba wax and paraffin wax were mixed in a 2L four-neck flask at room temperature (25°C). Next, an aqueous solution containing

ammonium sulfate as a coagulant was added to the mixture. Thereafter the mixture heated to 55°C, and kept at 55°C, and stirred until the aggregate particles grew up to 4.3 μ m. Then, polyester emulsion (Em-A) was added dropwise to aggregate the particle dispersion, and the temperature of the mixture was kept at from 55°C to 60°C to form encapsulated particles. Next, styrene monomer was added dropwise to encapsulate particles dispersion, and the mixture was stirred for 30 minutes at 60°C. Amount of styrene is listed in table 5. After that, the mixture was heated by 70°C. Then, initiator (ammonium persulfate) and reducing agent (sodium ascorbate) were added dropwise to the mixture, and the temperature of the mixture was kept at 70°C for 3 hours. Finally, core shell toner containing crystalline polyester whose shell was grafted by styrene was obtained through a wire mesh after cooling.

Table 5. Amount of styrene for seed polymerization

	PES(Em-B1)/PES(Em-A)/Styrene (wt)
Toner-E	100/30/0
Toner-F	100/30/3

Evaluation of fusing property

Fusing performance was evaluated using an off-line fuser. (Hot roll & Pressure roll), oil free type.

At first, each toner sample was developed and transferred on the paper so that the mass per area (M/A) was 1.5 mg/cm². This M/A is comparable to three toner layer (maximum M/A of full color printer/copier). The paper was J-paper by Xerox Corporation. Then the paper was passed through the fuser. The line speed was 160 mm/sec.

The upper limit of the fusing temperature was defined as the upper temperature limit at which the hot-offset was not observed. And the fusing temperature was defined as the lower temperature limit at which the cold-offset was not observed and the fusing ratio of the toner exceeds 80%. The fusing ratio of toner was calculated as the change in image density before and after Scotch tape (3M) stripping.

The fusing latitude was defined as the temperature difference between the fusing temperature and the upper limit of fusing temperature.

Evaluation of storage stability by heat

Each toner sample (20 g) was placed in a polyethylene bottle (capacity: 100 mL) and was allowed to stand at 55°C for 12 hours. Heat storage stability was determined by the amount of blocked toner and aggregated toner observed in the sample. In the case of good storage stability, blocking and aggregating of toner was not observed.

Results and discussions

1) Evaluation of toners prepared from cross-linking polyester emulsions with oxazoline polymer for improvement of fusing latitudes

The polyester emulsion can be prepared in aqueous phase by using nonionic surfactant and anionic surfactant, and polyester chemically prepared toner has been obtained. But there are a few constraints on emulsification of polyester in aqueous phase. It is difficult to emulsify the polyester resin that has high molecular weight and high softening point over 100°C because phase

inversion emulsification should proceed at below boiling point. To remove this concern, we tried to cross-link the emulsified polyester resin which is easily emulsified.

Table 6 shows the emulsion diameter (D50), the softening point (T1/2), and glass transition temperature (Tg) of the emulsified polyester after cross-linking by oxazoline polymer. The D50 and Tg did not change after cross-linking, but the T1/2 of the emulsified polyester became higher than before cross-linking. This higher T1/2 indicates that the carboxyl groups of the polyester chain reacted with oxazoline groups and that the molecular weight of the polyester chain increased by cross-linking by the amide ester bond.

Table 6. Properties of polyester emulsions

	Oxazoline Polymer(Eq)	D50 (nm)	T1/2 (°C)	Tg (°C)
Em-A	0	141	104	60
Em-A1	0.063	140	105	59
Em-A2	0.125	138	117	59
Em-A3	0.250	142	142	58
Em-A4	0.500	148	190	58

The fusing latitudes of the toners using polyester emulsions cross-linked by oxazoline polymer were investigated and the results are shown in Figure 1. The fusing latitudes of toner cross-linked by oxazoline polymer (Toner-B, C, and D) were expanded compared with that of Toner-A (not cross-linked). By cross-linking emulsified polyester resin, the toner's resistance to hot-offset was improved. On the other hand, the performance of low energy fusing became worse as the amount of oxazoline polymer increased.



Figure 1. Fusing property of toner

Toner-A was prepared from Em-A, Toner-B was prepared from Em-A2, Toner-C was prepared from Em-A3, Toner-D was prepared from Em-A4,

2) Evaluation of emulsification of the crystalline polyester in the presence of amorphous polyester

CPES was emulsified in the presence of amorphous PES by aqueous emulsification process. Ratio of CPES/APES, Mp of CPES and emulsion D50 are summarized in Table 7. CPES itself was not emulsified well, however, crystalline polyester could be emulsified in the presence of amorphous polyester resin. As shown in Table 7, when the ratio of amorphous polyester resin was increased, it was much easier to emulsify the crystalline polyester in aqueous phase. The melting points of neutralized crystalline polyester resin containing amorphous polyester in emulsification process became lower as the ratio of amorphous polyester increased. Figure 2 shows that a relationship between the

difference of Mp and emulsion diameter. The difference of Mp means the difference between the melting point of neutralized pure crystalline polyester (at Exp-1; CPES =100) and the melting point of neutralized crystalline polyester containing amorphous polyester. It is found that crystalline polyester could be emulsified more easily as the difference of Mp became larger. The difference of Mp relates to the state of crystalline sites in polyester. Larger difference of Mp indicates lower crystallinity of crystalline sites. The reason that crystalline polyester could be emulsified in the presence of amorphous polyester is assumed to be that the amorphous polyester works as a plasticizer. The addition of amorphous polyester reduces crystallinity of the crystalline sites.

Table.7 Properties of CPES emulsions containing APES

	Combination ratio of polyester resin		Mp (°C)	Emulsion diameter D50 (μm)
Exp-1	CPES	100	49.5	Not emulsified
Exp-2	CPES/APES1	50/50	48.7	2.172
Exp-3	CPES/APES1	30/70	40.7	0.348
Exp-4	CPES/APES3	50/50	44.5	0.318
Exp-5	CPES/APES3	30/70	36.9	0.354

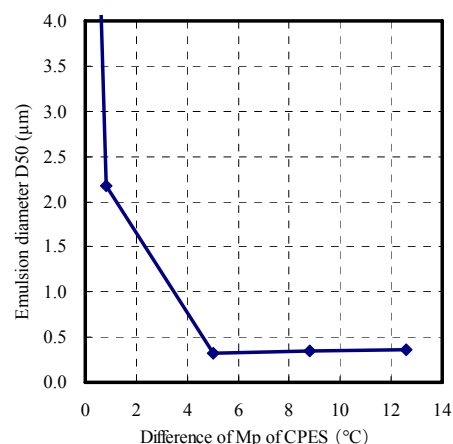


Figure 2. Relationship between difference of Mp and emulsion diameter

Thermal properties of cross-linking CPES emulsion and APES emulsion

Table 8 shows the T1/2 and Tg of polyester emulsions for core and shell. Em-B was prepared from CPES, APES-3 and APES-4. Em-B1 was cross-linked Em-B by oxazoline polymer. After cross-linking, Tg of Em-B1 was not changed from Em-B, but T1/2 of Em-B1 was slightly increased by cross-linking.

Table 8. Properties of cross-linked polyester emulsions

		Oxazoline Polymer (Eq.)	D50 (nm)	T1/2 (°C)	Tg (°C)
Core	Em-B (Exp-6)	0	143	78	34
	Em-B1	0.125	138	81	35
shell	Em-A	0	141	104	60

Thermal properties of toner containing crystalline polyester

Table 9 shows the Tg of toner-E made from Em-B1 core and Em-A shell (high Tg). In the test of heat storage stability of Toner-E, blocking occurred even though high Tg polyester was encapsulated on low Tg core. The reason for the bad storage ability was assumed to be that the low Tg core polyester and the high Tg shell polyester were miscible in each other during the coalescing process.

Table 9. Properties of polyester resin and toner

		T1/2 (°C)	Tg (°C)	Heat Storage stability
Core	Em-B1	81	35	-
Shell	Em-A	104	60	-
Toner-E		88	35	Bad(12.0g)

3) Evaluation of core-shell CPES toner grafted by styrene seed polymerization for lower energy fusing and higher storage stability

In order to reduce the miscibility of core and shell polyesters, seed polymerization of polyester emulsion for the shell was examined.

In this seed polymerization process, styrene monomer was reacted and grafted with the polyester of surface of the toner particles. There are two important technical points to cross-link the polyesters on the surface of toner. One is to use polyester resin containing fumaric acid which has unsaturated double bonds which can react with styrene for shell particles (Em-A). The degree of polymerization can be regulated by the amount of styrene and fumaric acid. Secondly, the condition of seed polymerization between styrene and polyester should be carefully selected. In the case of manufacturing polyester CPT by emulsion aggregation method, aggregation and encapsulation should be performed below the melting temperature of wax because wax emulsion particles will bleed out from the surface of the toner particles if the temperature in aggregating or coalescing process is higher than the melting point of wax. Consequently, the temperature of seed polymerization should also be controlled under the melting point of wax.

Table 10 shows the thermal property of core-shell toner grafted by styrene seed polymerization. The T1/2 and Tg were slightly increased compared to Toner-E. In the test of heat storage stability of Toner-F at 55 °C, Toner-F showed better heat storage stability than Toner-E.

Table 10. Properties of polyester resin and toner

		T1/2 (°C)	Tg (°C)	Heat Storage stability
Core	Em-B1	81	35	-
Shell	Em-A	104	60	-
Toner-F		92	42	Good(0.2g)

The improvement in storage ability was attributed to the reduced miscibility of polyesters for core and shell by seed polymerization in the shell polyester particles, Figure 3 shows the T1/2 of polyester by seed polymerization to Em-A against the amount of styrene monomer. It was observed that the T1/2 of polyester became higher as the amount of styrene monomer increased. This indicated that the polyester grafted by styrene had higher degree of polymerization by seed polymerization.

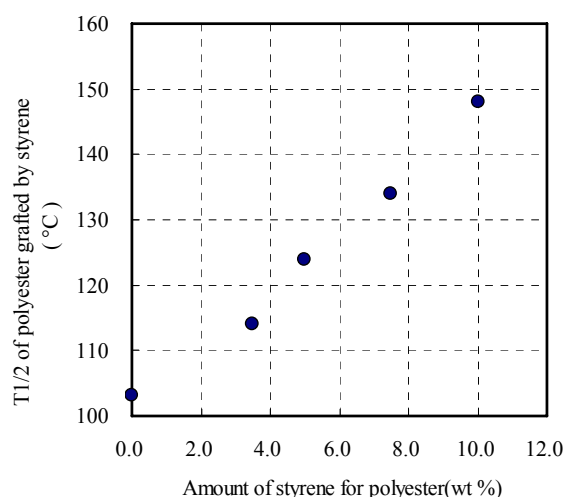


Figure 3. The relationship between T1/2 of polyester grafted by styrene and the amount of styrene monomer

It is well known that miscibility between heterogeneous polymers depends on both parameter χ to take account of the energy of interdispersing polymer and the degrees of polymerization of the polymers in Flory-Huggins theory (Eq (1)).

$$\delta G_{mix} / NRT = (\phi_1/m_1 \ln \phi_1 + \phi_2/m_2 \ln \phi_2) + \chi_{12} \phi_1 \phi_2 \quad (1)$$

δG_{mix} ; Gibbs free energy change for mixing polymers,

N ; the number of moles of polymers

R ; gas constant

T ; absolute temperature

ϕ_1, ϕ_2 ; volume fraction of polymer 1 and 2

m_1, m_2 ; degree of polymerization of polymer 1 and 2

χ_{12} ; parameter of interdispersing polymer 1 and 2

Therefore, it is expected that high molecular polyester for shell reduced the miscibility between the high Tg shell and the low Tg polyester core.

Evaluation of fusing property

The fusing latitudes of the toners were investigated and the results are shown in Figure 4. The fusing property of Toner-F was nearly equivalent to that of Toner-E (previous method). By inhibiting miscibility of the polyester resins for core and shell, high T_g of the surface on the toner was kept, so the low energy fusible toner with good storage ability can be obtained.

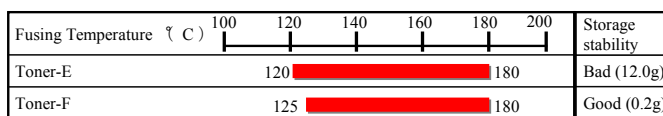


Figure 4. Fusing property of toner

Conclusions

The investigation of the eco-friendly aqueous-based polyester chemically prepared toner including crystalline polyester has led to the following conclusions:

1) Cross-linking polyester resin by oxazoline polymer improves the toner's resistance to hot-offset.

2) During emulsification, crystalline polyester can be finely emulsified in the presence of amorphous polyester as plasticizer.

3) Seed polymerization by styrene to the surface of polyester toner improves the performance of both storage stability and low-energy fusing property.

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Author Biography

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