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Preparation of Suspension Polymerized Color Toners and Correlation Between Ingredients and Rheological Behavior

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Syntheses and technology for preparation of cyan toner for dual component development by means of a suspension polymerization method is described. In this study, the organic phase, containing styrene monomer, n-butylacrylate, divinylbenzene, azo-*bis*-diisobutyronitrile, paraffin and Phthalocyanine Blue, was first dispersed into the aqueous phase, containing polyvinyl alcohol and sodium dodecylsulfate as suspension dispersants. Then dispersion was performed by a rotor-stator homogenizer, and subsequently the dispersion system was transferred to a three-orifice flask with a paddle stirring blade, where the polymerization reaction occurred. Correlations between amount of crosslinking agent and molecular weight of insoluble proportion in toners, and between gel content and some rheological behavior, such as viscous flow temperature, and melt index are discussed. Effects of Phthalocyanine Blue on charge-to-mass ratio and the interaction between resin in toners and Phthalocyanine Blue were studied. It was suggested that gel formation rather than increasing the molecular weight of the insoluble portion of the toner resulted in a change in rheological behavior according to the measured data of gel content, GPC, DSC, softening point and melt index. The Phthalocyanine Blue cause a notable increase in charge-to-mass ratio. The related infrared spectra suggested that the interactions between Phthalocyanine Blue T and resin mainly involved physical forces.

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Introduction

Conventionally, toners for development of electrostic charge patterns have been manufactured by fusion-mixing colorants into thermoplastic resins, to be dispersed uniformly therein, followed by pulverization and classification into desired particle sizes by means of micropulverizers and a classifier. Such a preparation method is capable of producing excellent toners, but is limited in certain respects, namely, in the scope of choice of materials for the toner and because the resin-pigment dispersion must be sufficiently friable for really high speed pulverizing, a large proportion of minute particles are contained. Furthermore, this is a batch process which tends to be slow, expensive, noisy and dusty. In order to remove the drawbacks of the pulverization method as described above, we propose to provide a process which will directly produce a colored particle in the particle size range of about 10 μm useful in the electrophotographic reproduction system. In summary, possible methods could be classified into (1) encapsulated toner processes[1–10]; (2) coalescence process[11]; suspension process[12–21]; and dispersion polymerization.[22]

The suspension polymerization process is an economical preparation of toners which does not resort to the conventional pulverization and classification methods and which manufactures toner particles with an average volume diameter of from about 1 to 25 μm. This method directly provides toners by dispersing a composition comprising a monomer, a polymerization initiator, a colorant and other components in water. Since no pulverization step is included, no fragility for the materials is necessary, and a toner is obtained in a spherical shape with correspondingly excellent free flow properties.[15] It was also reported to be possible to obtain a toner excellent in heat fixing characteristic by crosslinking.[10,18,19,21,23–25] It was noticed however that some reports suggested that polymerized spherical toners may not give the best final image compared to fine quasispherical toner.[13]

In this study a cyan toner for dual component development was prepared by the suspension polymerization method, in which styrene and N-butylacrylate were employed as the polymerization monomers, divinylbenzene as the crosslinking agent, and paraffin as release agent. In addition, we selected Phthalocyanine Blue not only as colorant but also as charge control agent. The influences of crosslinking agent, release agent on the melt rheological behavior of toner, and interaction between Phthalocyanine Blue and resin were explored. Although kinds and amount of initiator, and ratio of amount of styrene to n-butylacrylate have significant effects on fixing behavior, related discussion is not included in this article insofar as those effects are relatively straightforward and apparent.[26–27]

Experimental

Materials, styrene and divinylbenzene, were purchased from Beijing Xinguang Chemicals. N-butyl acrylate was purchased from Shanghai Chemicals. Azo-*bis*-diisobutyronitrile and methylene blue were products of Beijing

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TABLE I. Analytical Data of the Polymerized Toner

Name	Crosslinking agent, % w Monomer Base	paraffin, % w Monomer Base	Gel Content (%)	Glass Transition Temperature T_g, °C	Viscous flow Temperature T_f, °C	Softening point, °C	Melt Index ($ml.s^{-1}$)
A	0	0.3		55.97–61.88	135.17–140.85	98	1.202
B	0.9	0.3	5.2	68.36–72.03	143.49–171.01	107	0.880
C	1.1	0.3	8.3	60.64–70.37	156.27–179.05	110	0.818
D	0	0		62.78–70.95	142.47–151.65	105	1.003

Chemicals. Phthalocyanine Blue T was from Shanghai Dyestuff Plant No. 8. Paraffin, with a melting point of 52°C, was from Tianjing Chemicals No. 1. Polyvinyl alcohol 1788 was purchased from Sichuan Vinylon Plant. Sodium dodecylsulfate was from Tianjin Nankai Chemicals. All agents were reagent grade and used as received. Distilled water was prepared in the laboratory as required.

Preparation of Cyan Toners

The organic phase, containing 44.0 g styrene monomer, 6.0 g n-butylacrylate, 0.15 to 1 g divinylbenzene, 1.35 g dissolved azo-*bis*-diisobutyronitrile, 0.15 g paraffin and approximately 2.5 g Phthalocyanine Blue T, was first dispersed into the aqueous phase, containing 1.47 g polyvinyl alcohol 1788 and 0.103 g sodium dodecylsulfate as suspension dispersants in 295 g distilled water. In order to reduce the solubility of monomer in the aqueous phase and to inhibit monomers from polymerization in aqueous phase, respectively, 0.52 g KCl and 0.04 g methylene blue were dissolved in the aqueous phase. Dispersion was performed by a rotor-stator homogenizer (manufactured by Qidong Changjiang Mechanical Plant).[1] The dispersion mixture was agitated at 3000–4000 rpm for 20 minutes at room temperature. Subsequently, it was transferred to a three orifice flask with a paddle stirring blade, where the monomers were polymerized at 70°C for about 7 hours. After cooling to room temperature, the reaction product was washed repeatedly with water until the aqueous phase was clear, and the product was then dried under ambient conditions for 24 hours.[28]

Extraction

The process for extracting Phthalocyanine Blue T out of polymerized toner particles consisted essentially of (1) dissolving 2 g polymerized cyan toner particles in 10 ml xylene, (2) subsequently pouring 100 ml methanol into the solution, (3) separating the precipitate and solution by filtration, (4) repeating the extraction-precipitation process 6 times, and (5) thereafter getting a white precipitate.

Measurement

Measurement of Molecular Weight

The molecular weight of the toner was determined by gel permeation chromatography (Waters: 515 HPLC Pump, 717 Plus Autosampler and 2410 Refractive Index Detector), tetrahydrofuran (THF) as a solvent at a flow rate of 1 ml per minute. Columns were stabilized in a chamber at 32°C. Standard polystyrene samples were used for the preparation of the calibration curve.

Determination of Gel Fraction

Polymerized toner was weighed (W_0) and then dissolved in THF. Then the solution was left to stand overnight, and thereafter filtered with a 0.45 μm polytetrafluoroethylene film filter. The residue of THF-insoluble matter on the film was weighed (W_1). The gel fraction percentage was determined as:

$$\text{gel fraction (\%)} = (W_1)/(W_0) \times 100\%$$

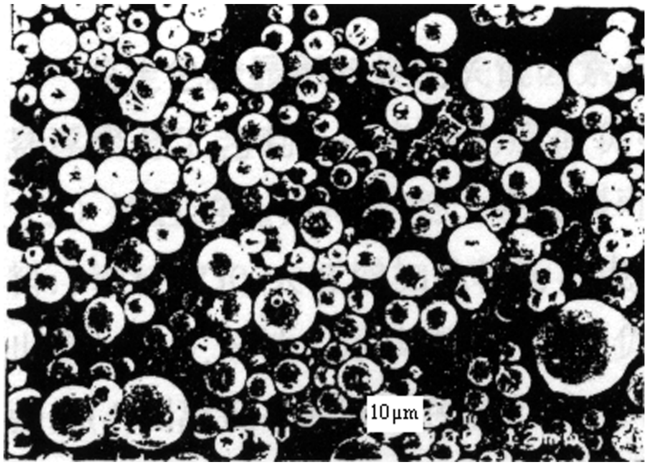

Figure 1. SEM Photograph of suspension polymerized toner (1,000×)

Measurement of Melt Index and Softening Point

The melt index and softening point were measured using a Shimadouzu Flowtester (CFT-500). Toner, which had been molded in advance into the shape of a cylinder with a diameter of 10mm and a height of 10 mm, was pressed through a capillary with a diameter of 1.00 mm under a load of 20 kgF. The sectional area of the plunger was 1.00 cm^2. Preheat time was 300 seconds. Melt index was the flow rate of the toner melt through the capillary at the fixed temperature of 150°C. The softening point was the temperature at which the height of remaining toner cylinder was decreased by one-half when temperature was raised from 80°C to 160°C at a rate of 6.0 degrees per minute.

Scanning electron microscopy (SEM) data were collected using a JSOM 6301 SEM by Hitachi. Particle size was determined with a Coulter Counter (Hialeah, Florida USA). The charge on the toner was generated by tumbling toner particles and polymer-coated ferrite carrier inside a 100 ml bottle on a roll mill. The toner charge thus generated was determined using the standard blow-off procedure with a blow-off power charge measuring apparatus from Toshiba Chemical Products Co., Ltd., Japan. Transition temperature of viscous flowing of toners was determined using SDT 2960 simultaneous DTA-TGA thermal analyzer by TA Instruments; infrared spectrum data were collected using a Fourier transform infrared spectrophotometer (FTIR) by Bio-Rad Win-IR.

Results and Discussion

The toner prepared by the suspension polymerization method described in this paper was spherical with a smooth surface as shown in Fig 1.

Crosslinking Agent

Data in Table I and Table II describe cyan toners with different amounts of DVB added during polymerization. Without having been able to evaluate the retarding effect

TABLE II. GPC Data for Insoluble Portion of Toners with Content of Crosslinking Agent

Name	`Mn	Mn	Mp	Mz	Mv	Polydispersity
A	11575	35698	18541	303259	27561	3.084026
B	10945	24799	17427	82309	31491	2.265844
C	10419	29478	15333	208706	23693	2.829246

Table III. Data Concerning Charging Effect of Phthalocyanine Blue

Phthalocyanine Blue T, %w Monomer Base	Mean Particle size, μm	charge-to-mass, μC/g
0	16	− 6.7
2.4	12.4	−7.3
3.0	13.5	−11.7
3.5	14.3	−16.0
4.0	12.7	−20.7
5.0	10.2	−22.1

of Phthalocyanine Blue on the polymerization reaction quantitatively, we could not obtain a copolymer resin with the exactly desired molecular weight distribution simply through changing amounts of initiator or dyestuff added to the monomers. The GPC data showed (comparing data for B and C with that for A in Tables I and II) that the molecular weight distribution corresponding to the insoluble portion of the toner did not increase with the amount of crosslinking agent, which was apparently different from what was reported elsewhere.[22,27] The gel content data indicated that gel content increased significantly with the amount of crosslinking agent. The data also showed that viscous flow temperature increased, the viscous flow transition temperature region broadened, and the melt index decreased with the addition of crosslinking agent and its increasing amount, respectively, although the molecular weight distribution of the insoluble portion did not alter simultaneously. So we reached the conclusion that change in rheological behavior of toner melt was mainly caused by gel formation.

Release Agent

Paraffin dissolved into the organic phase completely and was used as release agent to avoid smudges on the fixture roll and hollow character defects.[29] Experimental data on rheological behavior of polymerized toners, showed that the paraffin had a strong plasticizing effect, sharply decreasing the viscous flow temperature and the softening point temperature, and increasing the melt index with addition of paraffin, as shown in Table I (compare A with D). It was also noted that the glass transition temperature decreased with addition of paraffin.

Phthalocyanine Blue

In these experiments, the Phthalocyanine Blue was dissolved in the organic phase during polymerization; it functioned both as colorant and charging agent.[31–35] Increasing the amount of Phthalocyanine Blue T clearly resulted in increase of the charge-to-mass ratio, as shown in Table III.[36]

Figure 2 illustrates the FTIR spectra of Phthalocyanine Blue T (a), suspension polymerized particles with same compositions as described above without added Phthalocyanine Blue T (b), and precipitate from which Phthalocyanine Blue T had been extracted (c). Comparing spectrum (b) with (c), it was found that the two spectra were almost identical, which suggested that the interactions between Phthalocyanine Blue T and copolymer molecules of styrene and butylacralate must be mainly physical forces.

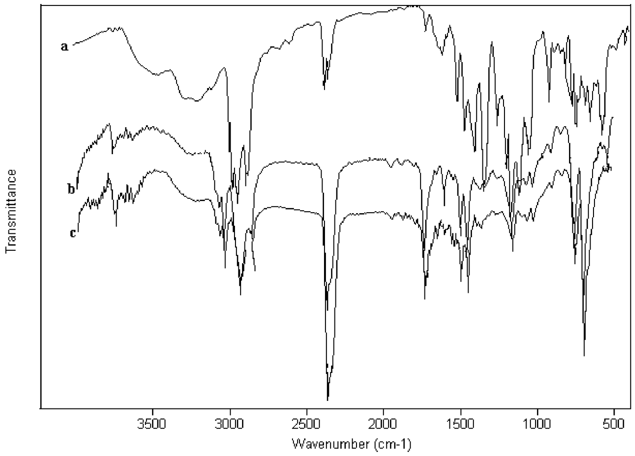

Figure 2. Infrared spectra of Phthalocyanine Blue T(a), suspension polymerized particles without addition of Phthalocyanine Blue T (b), and precipitate of polymerized cyan toners from which Phthalocyanine Blue T had been extracted (c).

Conclusion

In this study, a kind of cyan toner for dual component development was prepared through the suspension polymerization method. The GPC data showed that molecular weight distribution of the insoluble portion in toners did not change with addition of a crosslinking agent, while gel content in toners increased significantly with amount of crosslinking agent. So the main cause of melt rheological behavior changes of the toner, such as increasing viscous flow temperature, broadening of viscous flow transition temperature region and decreasing melt index of toners, with the addition of crosslinking agent and increasing of its amount, was gel formation. DSC data, softening point and melt index, showed that paraffin had a heavy plasticizing effect on polymerized toners, evidenced by sharp decrease of the viscous flow and softening point temperatures, and increase in the melt index, all with the addition of paraffin. The Phthalocyanine Blue functioned both as a colorant and as a charging agent, increasing amount of Phthalocyanine Blue resulted in a significant increase of charge-to-mass ratio. The related infrared spectra suggested that the interactions between Phthalocyanine Blue T and copolymer molecules of styrene and butylacralate mainly involved physical forces. ▲

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