

# Synthesis of Trimellitic Anhydride Microcapsule Toner by Liquid-Phase Separation

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**ABSTRACT:** A microcapsule toner containing trimellitic anhydride for use as a foam inhibitor in printing applications was synthesized by liquid-phase separation in organic solvents. It is possible to determine materials appropriate for the microencapsulation of trimellitic anhydride from solubility parameters calculated on the basis of the molecular structures of raw material candidates. Considering solubility parameters of various polymers, the polyethylene/methacrylic acid copolymer was selected for the microcapsule wall material. In addition, two kinds of solvents, toluene [solvent (a)] and isoparaffin [solvent (b)], were employed. It was necessary for the microcapsule materials to meet the following conditions: (1) the wall material must completely dissolve in solvent (a); (2) the core material must

disperse well, but not dissolve in solvent (a); and (3) the wall and core materials must not dissolve in solvent (b). By using mixtures of either lecithin and basic barium petronate or lecithin and basic calcium petronate as charge control agents, the trimellitic anhydride microcapsules could be charged either positively and negatively, respectively. The microcapsule toner fabricated in this method was successfully applied in commercial printing machines, where it inhibited foaming effectively enough to satisfy product requirements in the printing industry. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3822–3826, 2003

**Key words:** microencapsulation; phase separation; compatibility

## INTRODUCTION

Microcapsules are minute heterogeneous containers that are usually either spherical when enclosing a fluid or roughly shaped when enclosing a solid and generally consist of a core material enclosed within a wall material. Animal and plant cells are well-known examples of naturally occurring microcapsules. Artificial microcapsules were first produced in the 1950s for carbonless copying paper.<sup>1,2</sup> Microencapsulation is very useful for modifying chemical and mechanical properties of a core material. Presently, microcapsules are widely used to control a core material's release characteristics, to improve its stability by protecting it from environmental stimuli, and to modify its surface properties.<sup>3–8</sup> Performing such roles, they are employed in numerous products including drugs,<sup>9–13</sup> cosmetics,<sup>14</sup> foods,<sup>15</sup> and printing toners.<sup>16–22</sup> A variety of techniques are commonly used to fabricate microcapsules such as liquid-phase separation,<sup>16</sup> interfacial polymerization,<sup>23,24</sup> emulsion polymerization,<sup>6</sup> solvent evaporation,<sup>7</sup> and spray drying.<sup>15</sup> Among these techniques, liquid-phase separation, a kind of physicochemical technique, is very convenient and can produce microcapsules even without water. Furthermore, this technique is suitable for preparation of

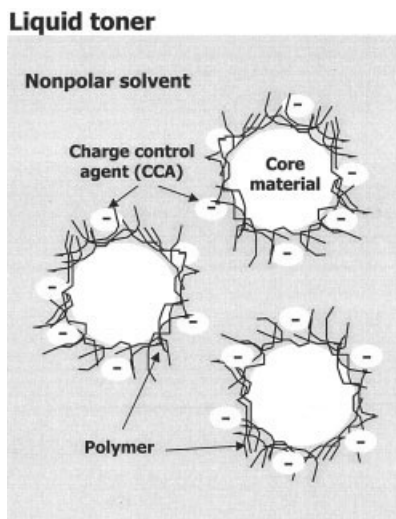
small particles because they can be formed in a nonpolar solvent.

One of the many applications of microcapsules is in liquid toner for digital printing. Toners have been widely studied in the field of electrophotography<sup>16–22</sup> and can be categorized into solid and liquid types. Figure 1 shows an illustration of microcapsules in a liquid toner. They consist of a core material, a polymer enclosing the core material, and a charge control agent (CCA). Concerning a liquid toner, the microcapsules must be dispersed in a nonpolar solvent and charged either positively or negatively. A liquid toner is most suitable for high-resolution printing because its particles are much smaller than those of a solid toner. Furthermore, this industrial field demands a functional toner displaying various characteristics necessary for multi-item, on-demand, and small-lot printings. In this article, we report the synthesis of a microcapsule toner by liquid-phase separation in organic solvents, with a special focus on the microencapsulation of trimellitic anhydride (TMA) for use as a foam inhibitor.<sup>25</sup>

## EXPERIMENTAL

We synthesized microcapsules of TMA (Mitsubishi Gas Chemicals, Japan) by liquid-phase separation in organic solvents. In this method, the following two kinds of solvents are employed: (a) a "good" solvent and (b) a "poor" solvent. A good solvent dissolves a

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**Figure 1** Illustration of microcapsules in a liquid toner.

wall material; however, a poor solvent does not. This difference in solubility is exploited to deposit a wall material on the surface of a core material. Therefore, solubility is the key to the success of this method. In this method, solubility parameters (SPs) were used to determine an appropriate wall material and appropriate good and poor solvents.

On this basis, a copolymer was selected for a wall material. SPs of polymers are generally good indicators of their compatibilities. Considering a degree of solubility between a homopolymer and a solvent, if a difference between their SPs is small, the solubility is high, and if it is large, the solubility is correspondingly low. In this study, SPs of homopolymer were calculated from the molecular attraction constants ( $G$ ) of their constituent functional and atomic groups and their molecular volume ( $V$ ) by the formula<sup>26,27</sup>:

$$\delta_p = \sum G/V$$

SPs of solvents were obtained from the force of attraction between molecules on the basis of Hildebrand-Scatchard's theory of solutions, as follows<sup>27-29</sup>:

$$\delta_s = (\Delta E_v/\Delta V_1)^{1/2}$$

where  $\Delta E_v$  is the vaporization energy,  $\Delta V_1$  is molecular volume, and  $\Delta E_v/\Delta V_1$  is the cohesive energy. A wall material used in this study has to meet at least two criteria. First, it must include a first-monomer component with poor affinity to an electrically insulating dispersion medium (i.e., a poor solvent) to form portions that are insoluble in a poor solvent. Second, it must include a second-monomer component with good affinity to a poor solvent so as to form portions that are soluble or swell in a poor solvent. The former component is necessary for formation of the wall,

whereas the latter ensures that microcapsules disperse well in a poor solvent. If we let  $\delta_{p1}$  be the SP of a homopolymer composed only of the first monomer of a copolymer,  $\delta_{p2}$  be the SP of a homopolymer composed only of the second monomer of a copolymer, and  $\delta_{s2}$  be the SP of a poor solvent, then the following three relations are empirically maintained:

- (a)  $|\delta_{p1} - \delta_{s2}| \geq 1$
- (b)  $|\delta_{p2} - \delta_{s2}| \leq 1$  and
- (c)  $|\delta_{p1} - \delta_{p2}| \geq 0.5$

Additionally, concerning a poor solvent, the volume resistivity must usually be at least  $10^{10}$   $\Omega\text{cm}$ . The material chosen for the microcapsule core, that is, TMA, should not dissolve in the good solvent at all, or at least only with difficulty. Therefore, we selected the following materials (Fig. 2):

- good solvent: toluene ( $\delta_{s1} = 8.9$ );
- poor solvent: isoparaffin ( $\delta_{s2} = 7.3$ , Isopar-L<sup>TM</sup>);
- and
- wall material: polyethylene ( $\delta_{p2} = 8.1$ )-methacrylic acid ( $\delta_{p1} = 9.4$ ) copolymer

They satisfy the three conditions mentioned above, as the following calculations show:

- (a)  $|\delta_{p1} - \delta_{s2}| = |9.4 - 7.3| = 2.1 \geq 1$
- (b)  $|\delta_{p2} - \delta_{s2}| = |8.1 - 7.3| = 0.8 \leq 1$ ; and
- (c)  $|\delta_{p1} - \delta_{p2}| = |9.4 - 8.1| = 1.3 \geq 0.5$

In the copolymer, the proportion of the second-monomer component to the first-monomer component (2nd : 1st) is 10 : 90 by weight. Its melting point is 95°C and its melt flow rate (MFR) as defined by ASTM D-1238 is 500 dg/min. This MFR is equivalent to a weight-average molecular weight of about 250,000.

Furthermore, lecithin, basic calcium petronate (BCP) (calcium sulfonate, 45 wt %; calcium from calcium hydroxide and calcium carbonate, 3 wt %; and mineral oil, 52 wt %), basic barium petronate (BBP), and neutral calcium petronate (NCP) were employed as CCAs so that TMA toners would be positively or negatively charged.

By using these above-mentioned materials, microcapsules were synthesized by liquid-phase separation, namely, solvent displacement method. The synthesis method was as follows: the core material (3.6 g), the copolymer (3.6 g), and CCA (0–1.2 g) were added to toluene (80 g), and the mixture was dissolved and/or dispersed for 3 h with a dispersing machine. Next,

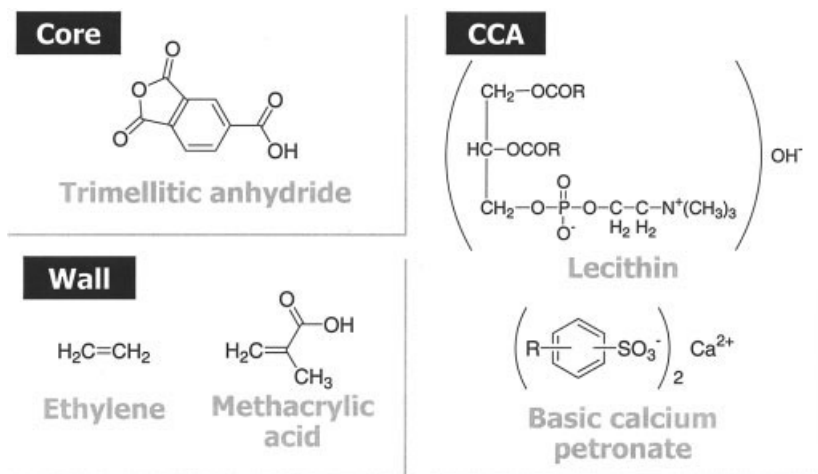


Figure 2 Chemical structures of the raw materials employed in the microcapsules.

isoparaffin (360 g) was added, and the solution was exposed to ultrasonic waves. The toluene was then gradually removed from the solution with an evaporator, yielding the master toner. Finally, the master toner was diluted with the isoparaffin so that its solid portion comprised 4%.

Charge polarity and amount of the TMA toner were measured by electrophoresis of the toner in the following manner. Two electrode plates, each of which was made of brass and had a dimension of 5.0 cm in length and 4.5 cm in width, were set in a cell for current measuring, which was filled with the liquid toners, and those electrode plates were made to face to each other with distance of 1.0 cm. Then, 1000 V of voltage was impressed between both the electrodes by means of high-voltage generator (Keithley, Type 237), and electric current was consequently measured from a start time of electricity supply to a time when 60 s had passed since the start time. TMA microcapsule sizes were measured by laser-Doppler method and their structures were observed by scanning electron microscope (SEM: Hitachi, S-5000H). Finally, the syn-

thesized TMA liquid toners were applied in commercially available printers and their inhibition effects to foaming were evaluated by observing a difference between a thickness of the foamed portion and that of the nonfoamed portion.

## RESULTS AND DISCUSSION

An SEM image of the TMA microcapsule toner is shown in Figure 3. The solvent was evaporated from the toner to conduct SEM observation. As can be clearly seen, aggregates of TMA microcapsules occurred because of the removal of the solvent. In the liquid toner, aggregates of the microcapsules were never observed. This aggregation is thought to have occurred because of the deposition of the copolymer component that dissolved and/or swelled in the solvent. Figure 4 shows the diameter distribution of the TMA microcapsules in the liquid toner. Their sizes were very uniform, with a diameter ( $D_{50}$ ) of about 2.3  $\mu\text{m}$ . The microcapsule size depends in a large part on the size of the raw core material (about 1–2  $\mu\text{m}$ ), because the polymer wall is very thin.

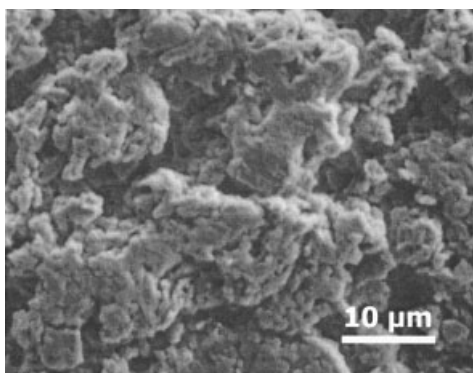


Figure 3 SEM image showing the TMA toner after evaporating the solvent.

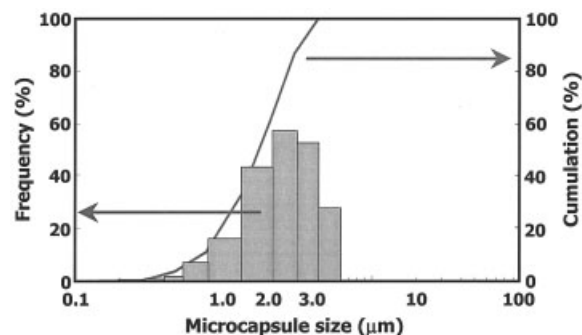


Figure 4 The diameter distribution of the TMA microcapsules in the liquid toner.

TABLE I  
Dependence of Polarity of Microcapsule on CCA

CCA	Polarity	CCA	Polarity
(1) Lecithin	±	—	—
(2) Basic barium petronate	+	(1) + (2)	+
(3) Basic calcium petronate	+	(1) + (3)	-
(4) Neutral calcium petronate	±	(1) + (4)	-

Various kinds of CCAs were tested to control the polarity and amount of charge on the microcapsules. The charge polarity of the TMA microcapsule toner obtained for various CCAs is listed in Table I. The CCAs tested provided good polarity control. Because lecithin contains both a hydrophobic aliphatic glyceride group and a hydrophilic phosphate ester group or (2-hydroxyethyl) amino group, it yields a bipolar charge for TMA microcapsules. In this study, a mixture of lecithin and BCP was employed as the CCA to negatively charge the TMA microcapsule toner, because negative-charged toners can be used in our printing system. Figure 5 shows the dependence of the initial current on the CCA amount. Toner electrification was evaluated by using an initial current value measured by the electrophoresis method. In the CCA used, the proportion of BCP to lecithin (BCP : lecithin) was 1 : 1 by weight. Without the CCA, the TMA microcapsules were charged neither positively nor negatively. The initial current increased linearly with an increase in the amount of the CCA. It is very important to adjust an appropriate toner charge to the printer used, as this greatly affects printing properties such as density and resolution. As shown in Figure 5, the optimal toner charge for a particular printer can be obtained easily by controlling the amount of CCA added.

Figure 6 shows changes in the initial current with storage time. The charge of the TMA toner gradually decreased with an increase in storage time. The reason for this decrease is that TMA, which has a high reac-

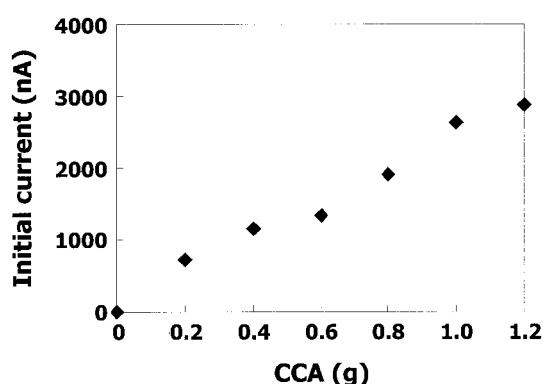


Figure 5 Dependence of the initial current on the amount of CCA.

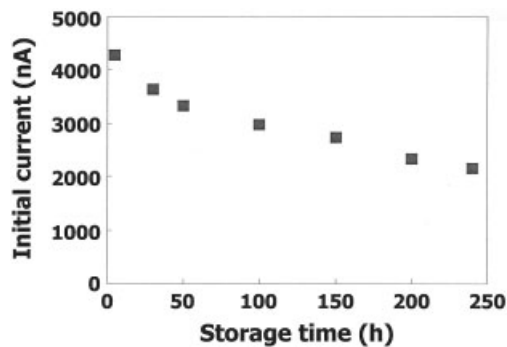


Figure 6 Change in the initial current with storage time.

tivity, is thought to easily react with the CCA because the microcapsule walls synthesized by this method are often very thin because of the low copolymer concentration during toner preparation or TMA surfaces might be partially disclosed in the toner. Therefore, the toner charge is thought to be stabilized by thickening the microcapsule wall, preventing reaction between TMA and the CCAs.

The TMA toners synthesized in this study can be readily applied in commercially available printers. Figure 7 shows the pattern printed on a poly(vinyl chloride) sheet containing a foaming agent. The print was heated at 120°C for 3 min to induce foaming. As this image demonstrates, foaming was successfully inhibited by controlling the print density of the TMA toner. The foam inhibiting effects provided by the TMA toner are sufficient to meet the requirements of the printing industry.

## CONCLUSION

A method for selecting an appropriate wall material and solvent based on solubility parameters has been suggested for the synthesis of microcapsules by liquid-phase separation in organic solvents. Our results indicate that, without conducting screening experi-

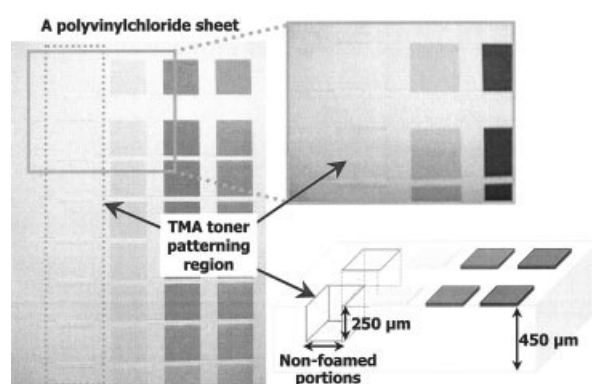


Figure 7 Foam inhibition pattern printed using the TMA toner.

ments, it should be possible to select appropriate materials for the microencapsulation of functional core materials based on calculations involving parameters related to the molecular structures of raw materials. Employing this method, a functional liquid microcapsule toner, that is, the foam inhibitor toner, has been successfully synthesized for the first time. The TMA toner was applied in commercially available printers. It showed good printing characteristics and inhibited foaming well enough to satisfy the demands of high-resolution professional printing. Finally, our synthesis method proved useful for producing copolymer microcapsules, and microcapsules synthesized in this way should have a wide range of applications in many industrial fields.

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