THE SYNERGISTIC EFFECT OF MIXED XEROGRAPHIC TONER AGGLOMERATION

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Agglomeration phenomena of two mixed xerographic toners were investigated using 1-octadecanol as the agglomeration agent and a cationic surfactant as the co-agglomeration agent. One toner carrying no surface charge agglomerated well under most conditions, while the other toner carrying a negative surface charge performed worse. It was found that when mixing these two toners together during pulping and when using 1-octadecanol as the agglomeration agent alone, there was an additive effect on agglomeration. On the other hand, addition of a small amount of cationic surfactant dramatically enhanced the mixed toner agglomeration efficiency and generated an obvious synergistic effect. The particle number after agglomeration was significantly reduced, and the particle size was greatly increased compared to the single toner agglomeration. The optimal amount of the cationic surfactant was close to the optimal cationic surfactant demand of the negatively charged toner. Based on these findings it can be recommended that the cationic surfactant should be added during agglomeration of the mixed office waste paper, and its optimal dosage needs to be chosen to reach the best performance.

Keywords: Mixed toner; 1-octadecanol; Cationic surfactants; Agglomeration; Synergistic effect; Surface charge

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INTRODUCTION

As part of an effort to reduce impacts on the natural environment, reductions in the amount of virgin fiber for paper making have been undertaken in many countries. This had led to the increased use of recycled paper as raw material for paper making. For countries that are short of wood resources, this is even more important for the paper industry. Among all recycled papers, office recovered paper is an important grade, noting that it contains quite a lot of bleached fiber. To regenerate suitably pure and clean fiber, contaminants in the recovered paper have to be separated out of it. One of the main contaminants in office recovered paper is toner ink. Toners are plastic-based ink used in xerographic copying processes or laser-printing processes (Chen *et al*. 2004). The plate-like shape and wide size distribution of toner particles detached from fibers makes deinking by the conventional methods of washing, flotation, centrifugal cleaning, and screening ineffective or inefficient (Zabula and McCool 1988; Odada and Urushibata 1991). These difficulties have led to the development of the agglomeration process, by which toner is agglomerated into larger particles using a combination of chemicals, heat treatment, and mixing (Snyder and Berg 1994; Chang *et al*. 1996; Chen *et al*. 2004). The larger, more spherical agglomerated particles can be separated from the fiber easily by screening and centrifugal cleaning, yielding a clean, high quality pulp (Borchardt *et al.* 1997).

Among all agglomeration chemicals, 1-octadecanol has been known as a highly effective agglomerating agent for toner ink. However, it had been found that the agglomeration process can be ineffective when furnish contains highly sized fibers or starched paper (Snyder and Berg 1994). Cationic starch was specifically proposed as an interfering material if the toner is negatively charged. It will generate a negative effect on the 1-octadecanol agglomeration. A positively charged surfactant CTAC (cetyl-trimethyl ammonium chloride) was shown to eliminate the negative effect in a model system (Chen *et al*. 2004). However, the system did not work on conventional printing papers.

Our previous study showed that certain xerographic toner carrying no surface charge agglomerated much better than another toner having a negative surface charge under either neutral or alkaline conditions. Actually, the negatively charged toner did not agglomerate at all under alkaline conditions. The addition of a cationic surfactant greatly improved the agglomeration of the negatively surface charged toner but had a relatively negative effect on the toner carrying no surface charge (Wang *et al*. 2011). Other work by the research team confirmed that some negatively charged laser toner agglomerated well under neutral conditions, but it was not agglomerated under alkaline conditions. Adding the proper type of cationic surfactants was able to greatly improve the agglomeration efficiency (Jiang *et al*. 2012).

It is thus clear that different toners have different agglomeration characteristics and that neutral pulping conditions generate less agglomeration problems. Since available sources of post-consumer office paper contain many different types of toners, it was of interest to examine the results of 1-octadecanol agglomeration performed with more than one toner present. Although an effective co-agglomeration system had been proposed by using nonylphenol polyethylene glycol ether (HLB = 8.9) together with 1-octadecanol to agglomerate the combinations of two different type of toners, the mixed toner agglomeration system has not been studied thoroughly (Welf and Venditti 2001). The effect of cationic surfactant use for mixed toner agglomeration has not been studied before.

This study mainly focused on the agglomeration effect of cationic surfactants when added to a mixed two-toner system. The aim is to give more understanding and help to improve some agglomeration problems in mixed office waste de-inking systems.

EXPERIMENTAL

Materials

The copy paper used in the study was a commercial product "GOLD BALL", made by APP Co., China. Photo-copied paper was printed from the same original by using two different Japanese xerographic copy machines and copied with toners made by the same company: Kyocera KM-1635 (Toner A) and Canon iR 6000 (Toner B). Toner A carried no surface charge and Toner B carried a slightly negative charge. All other chemicals were purchased locally. Detailed information for these materials is listed in Table 1.

Pulping

These two photo-copied papers were torn to 1 cm × 1 cm pieces separately and mixed with different weight percentages before pulping. A homemade stainless steel pulper (cylindrical vat, 1.0 L, 10 cm diameter) with a screw type rotor driven by a variable speed motor was used for pulping and agglomeration.

Table 1. List of Materials

Materials	Names (or grades)	Source
Paper	APP copy paper, 70 g/m^2, AKD sized, dual purpose for xerographic, laser, bubble jet and offset printing	APP Co., China
Toner A	Kyocera KM-1635	Kyocera Co., Japan
Toner B	Canon iR 6000	Canon Inc., Japan
1-octadecanol	Pure chemical	Shanghai Jiu Yi Chemical Reagent Co.
CTAB	Cetyl trimethyl ammonium bromide, cationic surfactant, pure chemical	Shanghai Ling Feng Chemical Reagent Co.
LDBAC	Lauryl dimethyl benzyl ammonium chloride, cationic surfactant, pure chemical	Shanghai Jin Wei Chemical Co. Ltd.
Poly-DADMAC	Poly-diallyldimethyl ammonium chloride, cationic standard titrant	BTG Mütek GmbH
PVSK	Potassium sulfate ester of polyvinyl alcohol, anionic standard titrant	BTG Mütek GmbH

Before pulping, 465 mL of distilled water was added to the pulper and heated up to 70^{o}C by partially submerging the pulper in a water bath maintained at a little bit higher than 70 ^{o}C. 1-octadecanol (0.6 g, 2% based on O.D. paper) and different amounts of surfactants (based on O.D. paper) were added and mixed at 300 rpm for three minutes to ensure that the 1-octadecanol was molten. To the pulper, 30 O.D. grams of mixed photo-copied paper was added and disintegrated at 800 rpm for 15 minutes at the consistency around 6.0%. After 15 minutes, the rotor speed was reduced to 440 rpm for 45 minutes for toner agglomeration. All experiments were conducted under the same conditions. After pulping, the pulp slurry was transferred to a plastic bag and cooled down in tab water. Six handsheets, each with a basis weight of 60 g/m^2, were made according to TAPPI Standard Method T205 OM-8. The handsheets were air dried for 24 hours and evaluated by an image analysis system with a Canon LiDE100 Scanner. The software used was Autospec V4.0 Image Analysis System (State Key Laboratory of Pulp and Paper Engineering; South China University of Technology). The size range of specks detected was set from 0.01 mm^2 to 10 mm^2. The resolution was set at 600 dpi. Each experiment was conducted twice to verify the experimental error.

Surface Charge of Toners

Blank transparency films were copied through Kyocera KM-1635 and Canon iR 6000 copiers to transfer their toner onto the film surface. The printed toner was then scraped and collected from the film surface by a stainless steel perpendicular scraper. The collected toner was then screened to sizes between 50 and 100 mesh. Screened toner (0.1 g) was added to a 150 mL glass beaker with 40 mL of distilled water. The beaker was then put on an electric heater with automatic temperature control and mixed with a speed-controlled Teflon rotor for 60 minutes at 70 ^{o}C.

After cooling to room temperature, 5 mL of cationic polyelectrolyte (0.001 Eq./L Poly-DADMAC) was added to the mixture and allowed to react for 30 minutes. After the reaction, the filtrate was separated from the slurry with a 200 mesh ceramic filter to collect the filtrate. The filtrate was then back-titrated using an anionic polyelectrolyte titrant (PVSK) to determine the surface charge of each toner. The endpoint was determined by a streaming current device (PCD-03 Mütek, BTG).

RESULTS AND DISCUSSION

Single Toner Agglomeration

Experiments for single toner agglomeration were conducted to understand each toner's agglomeration performance and characteristics. Toner A and Toner B had quite different agglomerating performance, as shown in Table 2. When using 1-octadecanol as the agglomeration agent, Toner A performed well. The number of ink particles per square meter (NPM) was reduced by more than 96% (from 491,000 to 19,000), and the average particle size was increased by seven times, from 0.03 mm^2 to 0.23 mm^2. Toner B, on the other hand, agglomerated poorly. The reduction of NPM value was only 54% (from 433,000 to 197,000) and the reduction of PPM was 57% (from 29,201 to 12,689). Since both the NPM and PPM had a similar reduction rate, the average ink particle size was almost unchanged. Furthermore, visual observation clearly showed that not only the particle size but also the particle shape were different between these two agglomerated toners. After agglomeration with 1-octadecanol, the ink particles of Toner A were spherical, whereas those of Toner B were flat. These differences in size and shape can greatly affect the screening efficiency (Carr 1991; Borchardt *et al*. 1997). These results are also consistent with earlier studies (Chen *et al*. 2004; Wang *et al*. 2011).

From previous studies, it is clear that chemically-aided toner agglomeration is influenced by toner charge characteristics (Chen *et al*. 2004; Wang *et al*. 2011; Jiang *et al*. 2012). A charge titration test was conducted to determine the surface charge of the toners. It was found that Toner A has non-detectable surface charge; whereas Toner B has a slightly negative surface charge of -0.002±0.001 mEq./g. These results were consistent with the agglomeration performance of each toner (Table 2).

It was also shown in our previous studies that addition of some cationic surfactant such as CTAB can greatly improve the agglomeration of the toner carrying a negative surface charge. As shown in Figs. 1 and 2, CTAB was very effective for Toner B's agglomeration, dramatically reducing the NPM number and enlarging the average ink particle size. When the dosage of CTAB reached 0.08%, the value of NPM reached the minimum value (41,000) and the average ink particle size reached to the maximum value (0.22 mm^2). When the dosage of CTAB exceeded 0.08%, the agglomeration efficiency became lower. In the case of Toner A, the story was different. Adding CTAB as the co-agglomeration agent had an adverse effect on both the NPM value and the average ink particle size. Although the adverse effect happened to Toner A, the agglomerated ink particle shape still remained spherical and most of them were able to be screened out by use of a 0.15 mm slot screen. This phenomenon has been found and discussed in detail in previous reports (Wang *et al*. 2011; Jiang *et al.* 2012).

Thus, it is clear that different types of toners have different agglomeration performance. For Toner A, 1-octadecanol alone was sufficient to achieve good agglomeration. But the addition of CTAB was needed for Toner B to get a similar result.

Table 2. Performance of 1-Octadecanol Agglomeration

Toner	1-octadecanol (%)	NPM (number/m^2)	PPM (mm^2/m^2)	Average particle size (mm^2)
A	0	491414	15361	0.0313
	2.0	18940	4459	0.2351
B	0	432749	29201	0.0675
	2.0	197225	12689	0.0643

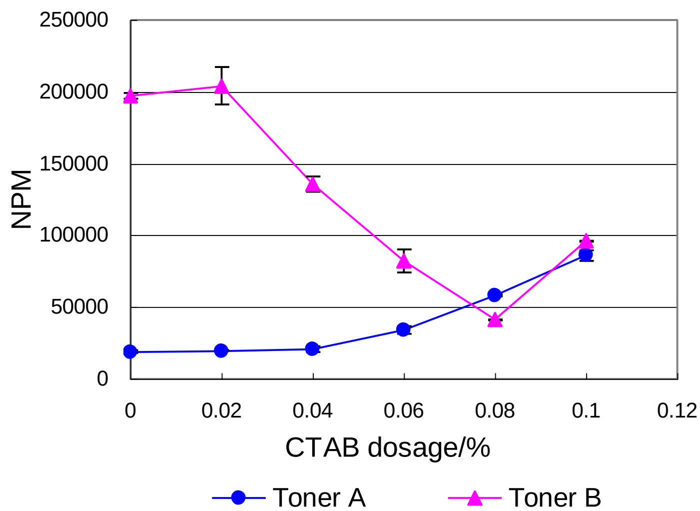

Fig. 1. Effect of CTAB on NPM after agglomeration with 2.0% 1-octadecanol

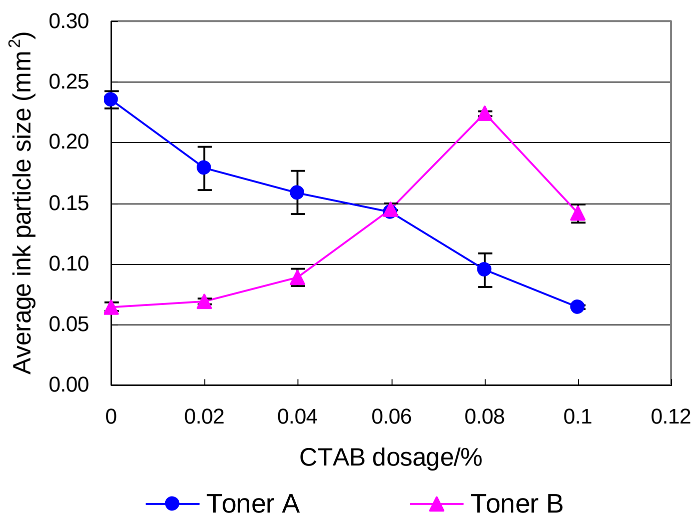

Fig. 2. Effect of CTAB on average ink particle size after agglomeration with 2.0% 1-octadecanol

Agglomeration of the Two-Toner System via 1-Octadecanol

Experiments were conducted to explore the effect of 1-octadecanol on agglomeration in the case of a combination of two different toners. This was achieved by agglomerating a pulp stock that contained paper printed with Toner A and paper printed with Toner B mixed with different weight percentages. The results are shown in Figs. 3 and 4. In these figures the measured actual NPM and average ink particle size after pulping are defined as actual value (AV for short). The theoretical values of different paper toner combination (TV for short) were calculated according to the following equations:

$$NPM(TV) = \frac{NPM\ of\ Toner\ A * weight\ of\ paper\ A + NPM\ of\ Toner\ B * weight\ of\ paper\ B}{weight\ of\ paper\ A + weight\ of\ paper\ B}$$

$$PPM(TV) = \frac{PPM\ of\ Toner\ A * weight\ of\ paper\ A + PPM\ of\ Toner\ B * weight\ of\ paper\ B}{weight\ of\ paper\ A + weight\ of\ paper\ B}$$

$$Average\ ink\ particle\ size\ (TV) = \frac{PPM(TV)}{NPM(TV)}$$

In these equations, the term “NPM of Toner A or B” means the NPM value of pure Toner A or B agglomeration. Likewise, “PPM of Toner A or B” means the PPM value of pure Toner A or B agglomeration. As can be seen in both figures, there was an additive effect of the two toners relative to agglomeration. As shown in Fig. 3, the NPM was slightly higher than the theoretical value when the percentage of Toner A paper was lower than 60%. This might be caused by the reduction of the effective number of collisions between Toner A and 1-octadecanol when the highly dispersed ink particles of Toner B were present. Although the negative interference existed, the impact on the system was small. As shown on Fig. 4, the agglomerated ink particle size was almost not affected and was consistent with the theoretical value.

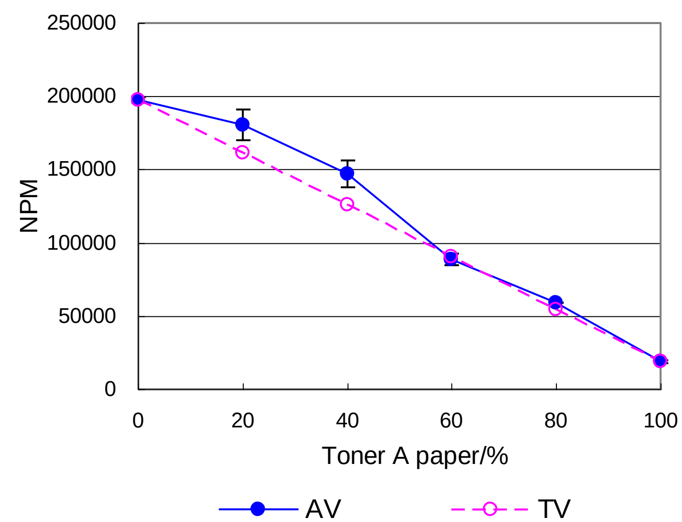

Fig. 3. Effect of 2.0% 1-octadecanol on NPM after agglomeration of two toners mixed with different percentages

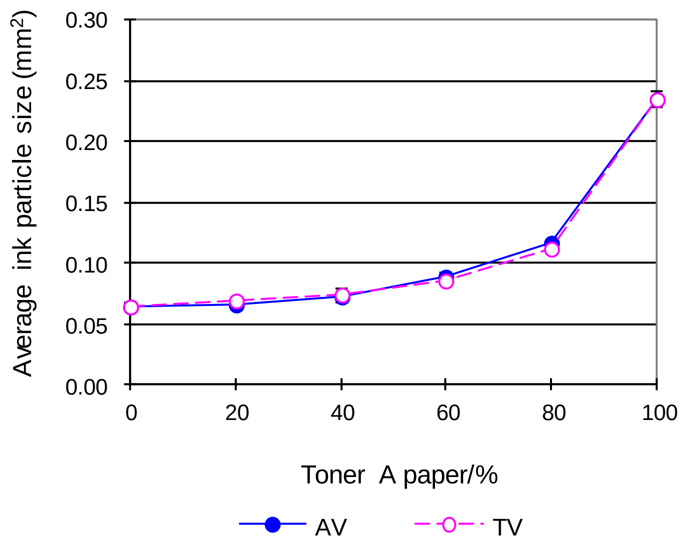

Fig. 4. Effect of 2.0% 1-octadecanol on average ink particle size after agglomeration of two toners mixed with different percentages

It is clear that when two different toners were present during the agglomeration stage, the presence of a second toner, which possessed different agglomeration characteristics, had very little influence on each other. An additive effect of the agglomeration was basically observed.

The Effect of Cationic Surfactant on the Two-Toner System

In order to investigate the effect of the cationic surfactant on agglomeration efficiency of the two-toner system, a small amount of cationic surfactant, 0.08% CTAB, was added together with 2.0% 1-octadecanol. The results are shown in Figs. 5 and 6. The theoretical values of mixed toners agglomeration based on single toner agglomeration results with the same amount of 1-octadecanol and CTAB were also plotted in the same figures for comparison.

Figure 5 shows the effect of the addition of CTAB on NPM after agglomeration of two different toners mixed with different weight percentages.

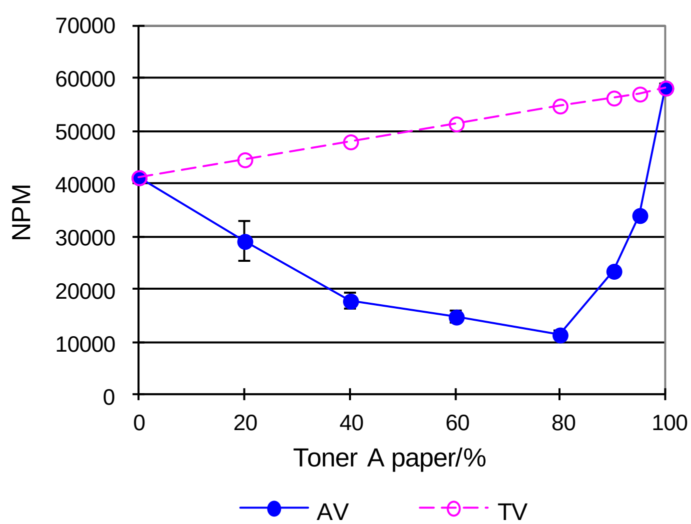

Fig. 5. Effect of 0.08% CTAB on NPM after agglomeration of two toners mixed with different percentages at 2.0% 1-octadecanol

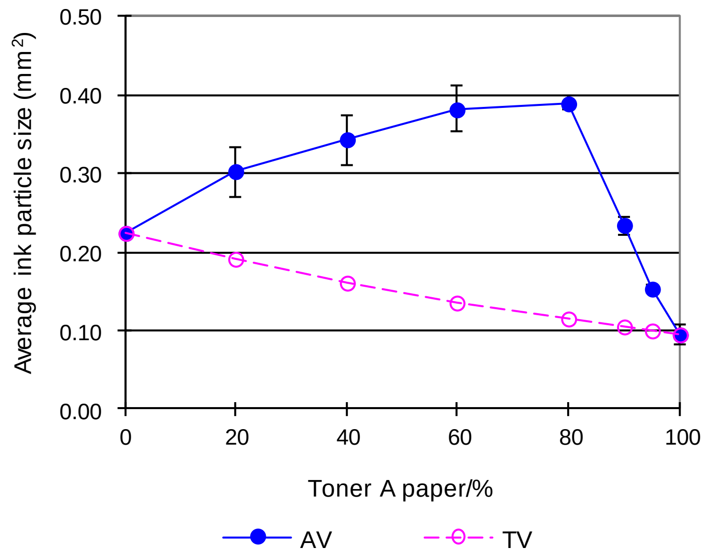

Fig. 6. Effect of 0.08% CTAB on average ink particle size after agglomeration of two toners mixed with different percentages at 2.0% 1-octadecanol

As shown in Fig. 5, the NPM after pulping was much lower than the theoretical value throughout the range of mixing ratio. When increasing the percentage of the Toner A paper in the mixed paper, the NPM gradually decreased and appeared to reach a minimum (11,000). Compared to the theoretical value of the percentage of Toner A paper at 80%, the NPM reduction was 80% (from 55,000 to 11,000). Above this percentage, the NPM value appeared to increase. It should also be noted that the minimum NPM value is even better than the best agglomeration result of single toner agglomeration either with or without the cationic surfactant (Fig. 1).

The effect of the CTAB on agglomeration of the two-toner system was further manifested by the average ink particle size, as shown in Fig. 6. The average ink particle size increased from 0.22 mm^2 to a maximum of 0.39 mm^2 when an optimal percentage (80%) of the Toner A paper was added. Above this percentage, the average ink particle size was rapidly reduced from 0.39 mm^2 to 0.09 mm^2. Although the average ink particle size was reduced quickly, the size was still bigger than the theoretical value. Furthermore, the optimal average particle size of 0.39 mm^2 was more than three times larger than the theoretical value of 0.11 mm^2 and was also much larger than that of single toner agglomeration (Fig. 2).

Thus, it is clear that the 1-octadecanol and the cationic surfactant CTAB can form a synergistic agglomerate system for deinking of papers printed with different toners. Even though adding CTAB as the co-agglomeration agent had an adverse effect for Toner A, it seemed the 1-octadecanol and the surfactant CTAB system induced agglomeration of all the toner particles and thus formed the largest ink particle size. Actually, adding a small amount of Toner B paper would generate this synergistic effect and made the agglomeration efficiency higher. Although the reason is unclear, it was hypothesized that with the help of CTAB the agglomerated Toner B had very high agglomerating ability and thus promoted the overall agglomeration efficiency.

Amount of Cationic Surfactant

The charge of surfactant relative to the OD paper weight also impacts agglomeration performance. It was interesting to determine whether a different amount of CTAB would affect the synergistic effect of the mixed toners agglomeration. Levels of 0.04%, 0.08%, and 0.10% CTAB were added by pulping two mixed toners paper at the weight ratio of 1:1 with 2.0% 1-octadecanol, respectively. The results are shown in Figs. 7 and 8. As shown in Fig. 7, when 0.04% CTAB was added, the agglomeration efficiency was poor. The NPM after pulping (79,000) was close to the theoretical value (78,000), and thus only an additive effect was observed. When increasing the dosage of CTAB to 0.08%, the agglomeration reached to its best performance. The NPM after pulping was reduced by 67% comparing to the theoretical value (from 50,000 to 16,000). It should be mentioned that this dosage was also the best agglomeration condition for the pure Toner B. When CTAB dosage was further increased to 0.10%, the NPM after pulping was reduced by 69% compared to the theoretical value (from 91,000 to 28,000). Although the synergistic effect remained similar to that of 0.08% CTAB, the agglomeration efficiency became worse (from 16,000 to 28,000).

The results shown above were further manifested by the agglomerated ink particle size (Fig. 8), which had a very similar trend. Thus, it could be concluded that the agglomeration efficiency was affected by the amount of the cationic surfactant added. The optimal amount of the cationic surfactant was close to the optimal cationic surfactant demand of the negatively charged toner.

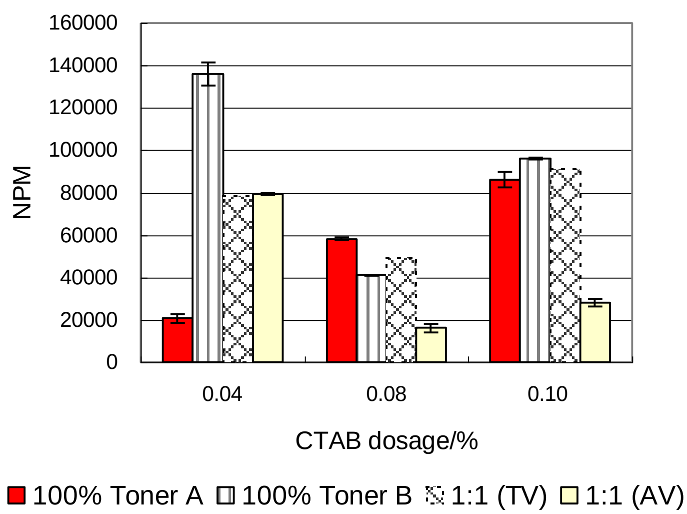

Fig. 7. Effect of CTAB on NPM after agglomeration of two toners mixed by the ratio of 1:1 with 2.0% 1-octadecanol

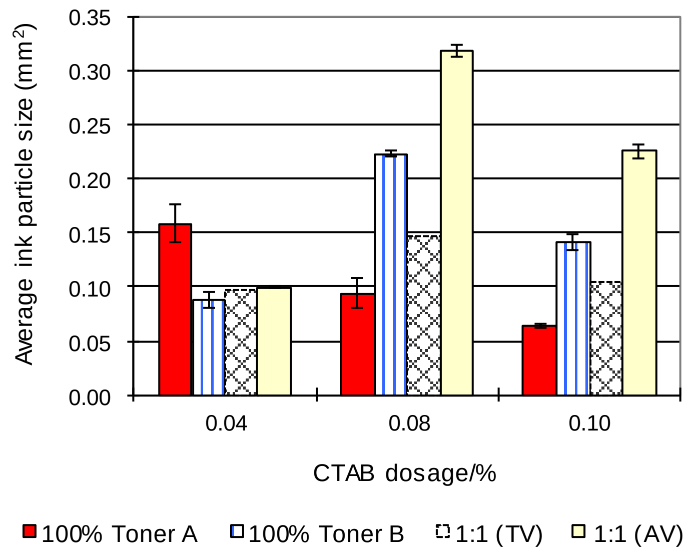

Fig. 8. Effect of CTAB on average ink particle size after agglomeration of two toners mixed by the ratio of 1:1 with 2.0% 1-octadecanol

Different Type of Cationic Surfactants

In order to further examine the effect of different cationic surfactants on agglomeration of mixed toners, another cationic surfactant, LDBAC, was used. LDBAC contains a C12 alkyl group and carries a phenol group. The pulping conditions were the same as described earlier, with mixing of two toners paper at the weight ratio of 1:1 with 2.0% 1-octadecanol. Since the best agglomeration performance of LDBAC occurred at 0.06% for Toner B (data not shown), we choose this condition to compare with the dosage of 0.08% CTAB. As shown in Figs. 9 and 10, not only CTAB but also LDBAC could generate the synergistic effect. Actually, the NPM synergistic effect of LDBAC (from 59,000 to 19,000, 67%) was close to that of CTAB (from 50,000 to 16,000, 67%), and the agglomerated ink size synergistic effect of LDBAC (from 0.08 to 0.24, 3 times) was higher than that of CTAB (from 0.15 to 0.32, 2 times). Thus, the synergistic effect of LDBAC was better than CTAB, and it can be concluded that the synergistic effect is valid for more than one type of cationic surfactant.

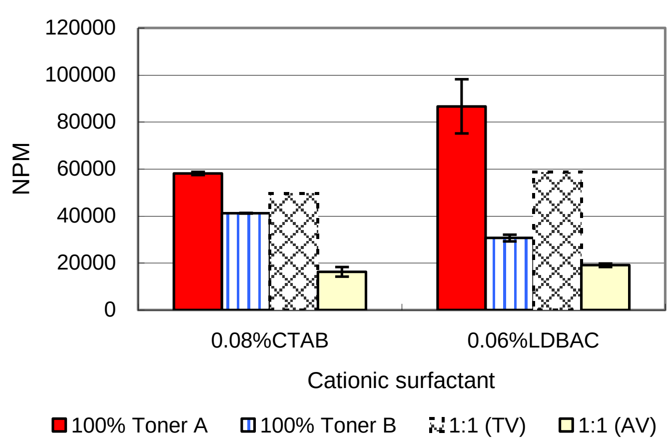

Fig. 9. Effect of LDBAC and CTAB on NPM after agglomeration of two toners mixed by the ratio of 1:1 with 2.0% 1-octadecanol

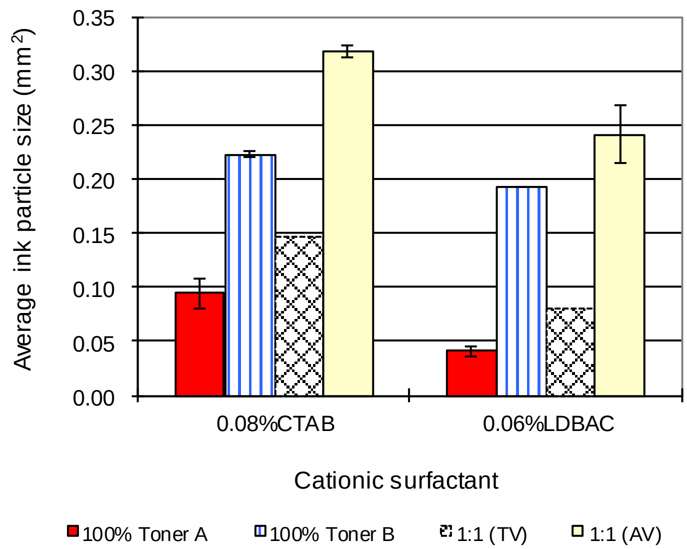

Fig. 10. Effect of LDBAC and CTAB on average ink particle size after agglomeration of two toners mixed by the ratio of 1:1 with 2.0% 1-octadecanol

CONCLUSIONS

1. When repulping paper sheets printed with just one type of xerographic toner, adding a small amount of cationic surfactant together with 1-octadecanol will greatly improve the agglomeration of the toner carrying a negative charge but will have a slightly negative effect on that of the toner carrying no surface charge.
2. An additive effect of the mixed toner agglomeration existed when only 1-octadecanol was used for the agglomerative deinking of a mixture of paper sheets printed with two different kinds of toner.
3. Adding a small amount of cationic surfactant together with 1-octadecanol will enhance agglomeration efficiency and generate a significantly synergistic effect in a mixture of some paper sheets xerographically printed with different toners.
4. The synergistic effect is affected by the amount of the cationic surfactant added. The optimal amount of the cationic surfactant is close to the optimal dosage for the agglomeration of just the negatively charged toner by itself.
5. It is recommended that agglomerative deinking of mixed office waste paper with 1-octadecanol should be carried out with the addition of an appropriate amount of the cationic surfactant.

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