THE EFFECT OF OFFSET PRINTING INK ON LASER TONER INK AGGLOMERATION UNDER NEUTRAL PULPING CONDITIONS

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1-octadecanol is known to be a highly effective agglomerating agent for laser toner ink. However, the office waste paper used in the actual production often contains various types of inks. The effect of the offset ink and types of surfactants with different charge characteristics were studied relative to the agglomeration of the laser toner ink under neutral pulping conditions. It was found that the addition of a small amount of the offset ink printed waste paper was beneficial for the agglomeration of the laser toner ink. The optimal percentage of addition is 12.5% to 25%. The offset printed ink had a positive charge of 0.001±0.0005 mEq/g when the offset ink was treated by 70˚C water at neutral conditions. Addition of a proper amount of cationic surfactant was beneficial to improve the agglomeration at any ratio of the mixed laser printed and offset waste papers. When the percentage of offset waste paper was less than 50%, the addition of anionic surfactant and nonionic surfactant was harmful for agglomeration, and there was no significant effect at higher offset content.

Key words: Laser toner ink; Offset printed ink; Deinking; Agglomeration; Surfactant

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INTRODUCTION

The utilization of secondary fiber has been increased tremendously during recent years. It has become an important source of fibers in papermaking due to the shortage of the forest resources (Olson *et al.* 1993). Office waste paper, which mainly consists of laser printed paper and xerographic paper, is a fast growing source of secondary fiber due to the increase in the utilization of office photocopiers and computer printers. Recycled office waste paper also contains a certain amount of the offset printed papers other than the non-impact printed paper and computer printouts, as well as non-acceptable materials such as brown grade, file folder, and plastic wrap.

Contaminant removal is the major objective of wastepaper recycling. The efficiency of contaminant removal determines the quality and yield of the final product. And, ink is considered to be one of the major deleterious contaminants due to its dark color. Inks normally vary in composition and presents in different forms depending on the printing processes. The quality of the recycled fiber is normally determined by the extent of ink removal.

The ink used in laser printers is different from traditional ink, such as solvent-based ink. It is thermoplastic, and it is electro-statically placed on a page, where it gets fused in place. The bond between the ink and the fiber is normally strong, and the size of the released ink particles during the pulping stage are larger in comparison to the conventional oil-based ink, which makes the laser printed waste paper often difficult to deink by conventional deinking methods such as washing, flotation, centrifugal cleaning, and screening (Vidotti *et al.* 1992). The difficulty has led to the development of agglomeration processes, which function according to the liquid bridge principle, by which the toner agglomerates into larger particles using combinations of chemicals, heat treatment, and mechanical mixing (Snyder and Berg 1994; Chang *et al.* 1996; Chen *et al.* 2004). The larger, more spherical agglomerated particles can then be readily separated from the fiber slurry by screening and centrifugal cleaning (Ferguson 1992; Borchardt *et al.* 1997). Such approaches usually handle the laser printed waste paper effectively, allowing high-grade fibers to be recovered.

Among agglomeration chemicals, 1-octa-decanol has been known to be a very effective chemical. It has also been found that the addition of a small amount of cationic surfactant can help agglomeration of some negatively charged xerographically copied ink in both alkaline and neutral conditions in the presence of 1-octadecanol (Wang *et al.* 2011).

The ink used in offset printed waste paper is normally oil-based ink. The binder of oil-based ink is vegetable and/or mineral oil. After pulping, the ink particles are small and the characteristics are different from the laser-printing ink. These types of ink particles are lipophilic and they are often separated from the wastepaper pulp by flotation with a collection agent (Wasilewski 1987). However, the consumption of the water is too high and the dyes and pigments are difficult to remove, which cause environmental pollution. Furthermore, another difficulty in deinking is the ink re-deposition. When deinking is carried out under neutral conditions, the ink may redeposit onto the fiber surfaces more than under the alkaline conditions, even though some surfactants were added. That is because the higher pH value in the alkaline condition could promote the ionization of carboxyl groups, thus giving rise to a strong electrostatic force of repulsion (Galland *et al.* 2000).

To summarize, the waste paper used in actual production often contains several types of inks. Different inks have their own suitable deinking conditions. The objectives of this research were to find the effect of the offset printed ink on agglomeration of the laser toner ink under neutral pulping conditions, and to find the effect of surfactants on agglomeration of mixed toners.

MATERIALS AND EXPERIMENT

Materials

The laser printed paper used for experiments was a commercial product "GOLD BALL", made by APP Co. Ltd, China. This paper was printed with HP LaserJet 1010. The offset paper used for experiments was a commercial product from Shangdong Bohui Co. Ltd, China. The ink used was EXCEL ST-2000, made by Sunsure Ink Co., Ltd.

All other chemicals were purchased locally. Detail information for these materials is listed in Table 1.

Table 1. List of Materials

Material	Names(or grades)	Source
Paper A	APP copy paper, 70g/m^2, AKD sized, filled with $CaCO_3$, dual purpose for xerographic, laser, bubble jet and offset printing	APP Co. Ltd, China
Paper B	Offset printing paper, 70 g/m^2, AKD sized, filled with $CaCO_3$	Shangdong Bohui Co. Ltd, China.
Ink A	HP1010	Hewlett-Packard Co., America
Ink B	EXCEL ST-2000	Sunsure Ink Co., Ltd
1-octadecanol	Chemical pure	Shanghai Jiu Yi Chemical Reagent Co.
SDBAC	Stearyl dimethyl benzyl ammonium chloride, Cationic surfactant, chemical pure	Shanghai Jin Wei Chemical Co., Ltd.
SDBS	Sodium dodecyl benzene sulfonate, Anionic surfactant, Chemical pure	Shanghai Jiu Yi Chemical Reagent Co.
NP-10	Emulsifier (NP-10), Chemical pure	Shanghai Jiu Yi Chemical Reagent Co.

Pulping and Analysis

All pulping conditions were set at the neutral pH. Two sources of printed papers were weighed in proportion in advance. These papers were then shredded to 1 cm x 1 cm pieces and mixed together. A homemade 1.0 L stainless steel pulper with a screw type rotor driven by a variable speed motor was used for pulping and agglomeration. Before pulping, 402 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 (0.525 g, 1.5% based on paper) and different amounts of surfactants were added and mixed with water at 300 rpm for three minutes to ensure that the 1-octadecanol was solublized. To the pulper, 35 O.D. grams of mixed waste paper was added and disintegrated at 813 rpm for 15 minutes. After 15 minutes, the rotor speed was reduced to 443 rpm for another 45 minutes for toner agglomeration.

The deionized water with pH of 6.51 was used for waste paper pulping at neutral conditions. After pulping, the pH was 7.03, which was measured after the pulp slurry was cooled down to room temperature.

After pulping, the pulp slurry was transferred to a plastic bag and cooled down in tap water. Six handsheets, with 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 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 results were repeated 3 times, and the average data was used for analysis.

RESULTS AND DISCUSSION

The Effect of 1-Octadecanol Agglomeration on Different Inks from Different Waste Paper

Evaluation experiments of the agglomeration performance of 1-octadecanol were executed for deinking of two different types of waste papers. Paper A was printed with laser toner ink (Laser) and paper B was printed by the offset printed ink (Offset), respectively. The handsheets were made from the pulping slurry, and followed by image analysis. The results are shown in Figs. 1 and 2.

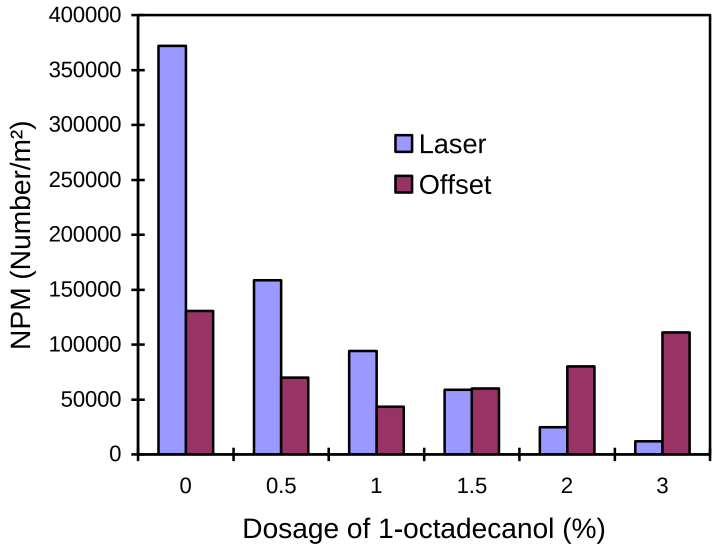


Fig. 1. Effect of 1-octadecanol on the ink particle number per square meter (NPM) after agglomeration of different inks

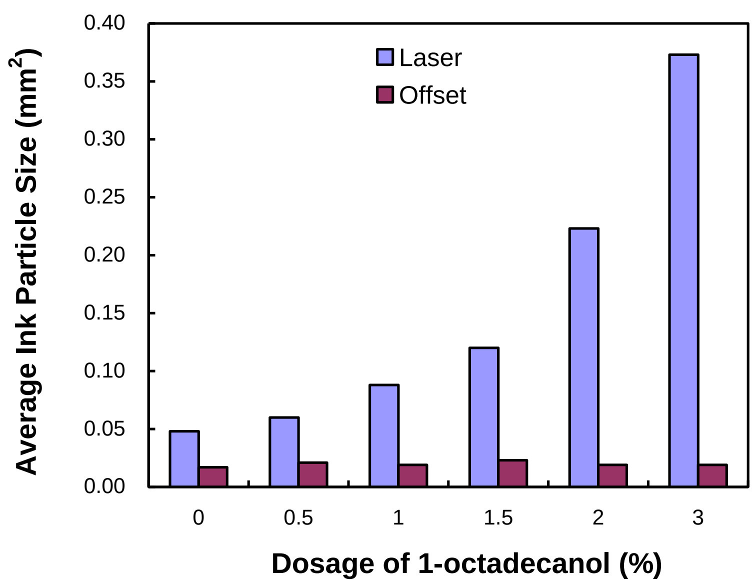


Fig. 2. Effect of 1-octadecanol on the average ink particle size after agglomeration of different inks

As shown in Figs. 1 and 2, the laser toner ink agglomerated well under neutral pulping conditions, while the offset printed ink did not agglomerate. For laser toner ink, the number of ink particles per square meter (NPM) was reduced by more than 96%, and the average ink particle size was increased more than seven times, from 0.05 mm^2 to 0.37 mm^2, after agglomeration with 1-octadecanol.

For the case of offset printed ink, the NPM was reduced along with the addition of 1-octadecanol, and it reached its minimum value at one percent of addition. The minimum NPM was 43,000, and the reduction of NPM was only 67%. When the dosage was above 1.0%, the NPM was increased obviously. However, the average ink particle size almost did not change. It is known that during the offset printing, one of the most important things is to keep the ink-water balance. The wetting agent used in the offset print is alcohol. The surface tension is about 23 N/cm^2. The wetting agent promoted ink emulsification and reduced the lipophilicity of the ink that it can be printed on the paper B with proper functionality. During the agglomerating deinking, a small amount of 1-octadecanol, which is very hydrophobic, would help the release of the oil-based offset inks out of the paper surface, causing a reduction of NPM value. However, when the dosage of 1-octadecanol was increased over 1.0%, the scattered offset ink particles with the excess 1-octadecanol were deposited on the fiber surface. Thus, a small amount of 1-octadecanol could help the ink to be removed from the fiber surfaces, but it could not agglomerate the offset printing ink.

The Effect of Offset Printed Ink on Agglomeration of Laser Toner Ink

Actual waste paper production often contains several different types of waste papers with different printed inks. When the waste papers from various sources have been mixed, the influence of different ink types during the deinking process has been rarely discussed. In order to verify the influence, the effect of 1-octadecanol on a mixture of two different kinds of waste paper by 1:1 was studied. The results are shown in Fig. 3.

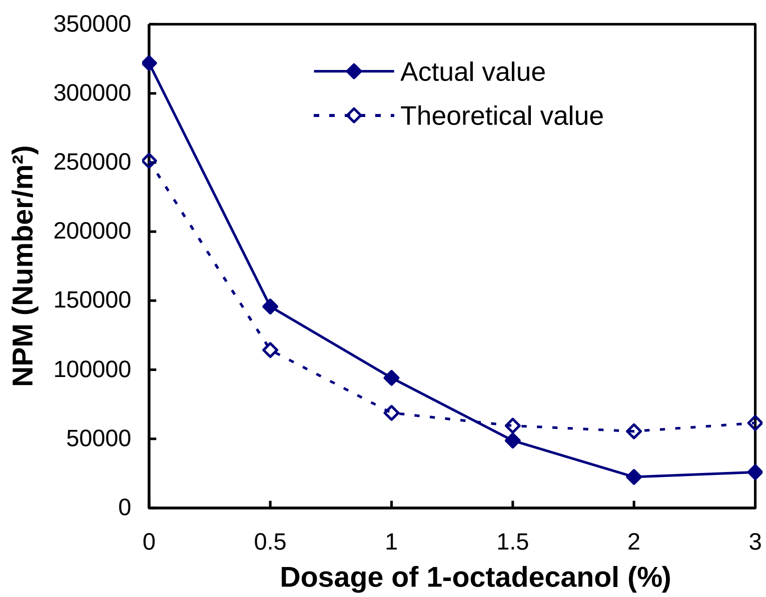


Fig. 3. Effect of 1-octadecanol on two kinds of waste paper mixed by the ratio 1:1

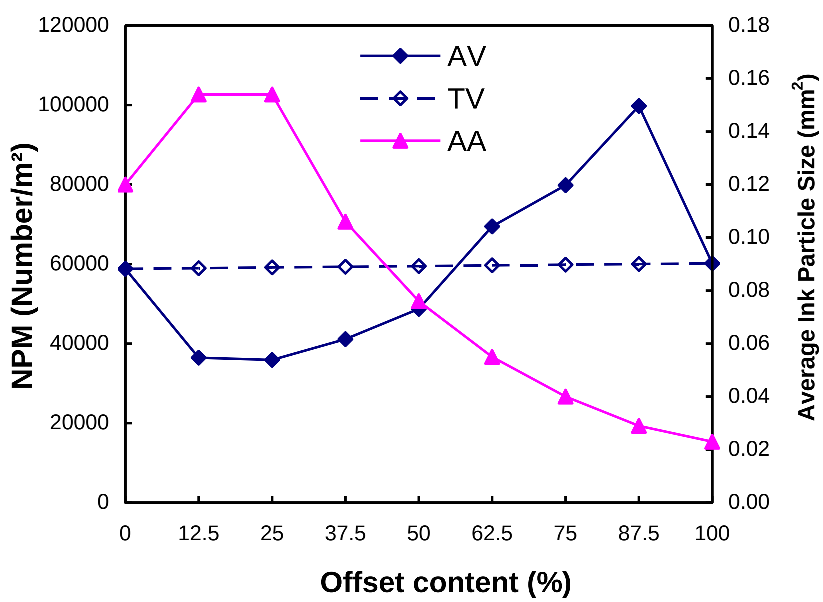
As shown in Fig. 3, there are two curves. One of them indicates the actual value obtained from the experiments, and another one is the theoretical value obtained from calculation. When two different waste papers were mixed by the ratio 1:1, it is first hypothesized that the two different inks react with the 1-octadecanol separately, and they do not affect each other. Thus, the theoretical NPM was half of the NPM summation of two inks which were shown in Figs. 1 and 2.

The actual NPM was reduced when the 1-octadecanol dosage was increased. The theoretical value was lower than the actual one when the 1-octadecanol dosage was less than 1.5%. Two values were different, but they met approximately at the point of 1.5% of 1-octadecanol dosage. At this point, the influence of 1-octadecanol dosage between the theoretical value and the true value were same; the corresponding conditions were selected for the subsequent experiments.

Figure 4 shows the effect of offset printed ink on agglomeration of laser toner ink under neutral conditions. The dosage of 1-octadecanol was 1.5%, and two different kinds of waste papers were mixed with different proportions.

The NPM was reduced from 60,000 to 38,000, and the ink particles were at the maximum average size when added with 12.5 to 25% offset waste paper. However, when adding more offset ink printed waste paper, the average ink particle size was reduced promptly, and the NPM was increased. When the proportion of the offset printed waste paper was above 60%, it was harmful for laser toner ink agglomeration.

The charge titration method was used to determine the charge of offset printed ink. The offset printed ink had a positive charge of 0.001±0.0005 mEq/g when the offset ink was treated with 70°C water at pH 7. It is possible that offset printed ink works as a cationic surfactant, which can promote laser toner ink agglomeration during the deinking process and exhibits a synergistic effect.



(AA− Average Area; TV− Theoretical value; AV− Actual value)

Fig. 4. Effect of offset printed ink on agglomeration of laser printed toner with 1.5% 1-octadecanol

Effect of Surfactants on Agglomeration with Different Inks

In order to further investigate the agglomeration ability of 1-octadecanol together with a surfactant, which is normally used during the deinking process, three different surfactants were studied. The cationic surfactant (SDBAC), anionic surfactant (SDBS), and nonionic surfactant (NP-10) were added into the slurry with 1.5% 1-octadecanol separately. The results are shown in Figs. 5 and 6 for the laser toner ink, and Figs. 7 and 8 for the offset printed ink.

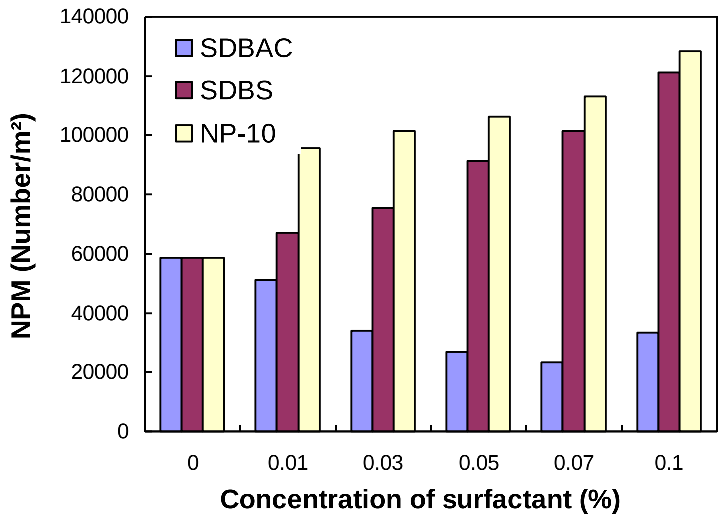


Fig. 5. Effect of surfactants on NPM after agglomeration of laser toner ink with 1.5% 1-octadecanol

Figure 5 shows the effects of different surfactants on NPM after the agglomeration of laser toner ink with 1.5% 1-octadecanol. For the laser toner ink, the NPM was 60,000 when no surfactant was added. The NPM value was reduced when adding a small amount of SDBAC. When the dosage of the SDBAC reached 0.07%, the NPM decreased to approximately 23,000. The reduction of NPM was about 60%. If the dosage of the SDBAC was more than 0.07%, a negative effect appeared. The effects of the addition of SDBS and NP-10 were identical, which were all in the opposite direction relative to the effect of SDBAC.

The effect of different surfactants on agglomeration of laser toner ink was further manifested by the average ink particle size of the agglomerated toner, as shown in Fig. 6. The average ink particle size increased from 0.12 mm^2 to 0.27 mm^2 for laser toner ink with addition of 0.07% SDBAC. Above and/or below the optimum dosage, the particle size was reduced. However, addition of SDBS and NP-10 had a negative effect on the particle size. Cationic surfactant not only reduced the NPM value but also enlarged the size of agglomerated toner ink. The maximal particle size was 0.27 mm^2, and the minimum of the NPM was 23,000 with addition of 0.07% SDBAC. The SDBAC has a similar chemical structure of long chain as 1-octadecanol. It was produced by 1-octadecanol, hydrobromic acid, and dimethylamine. Thus, it has synergistic effect with 1-octadecanol.

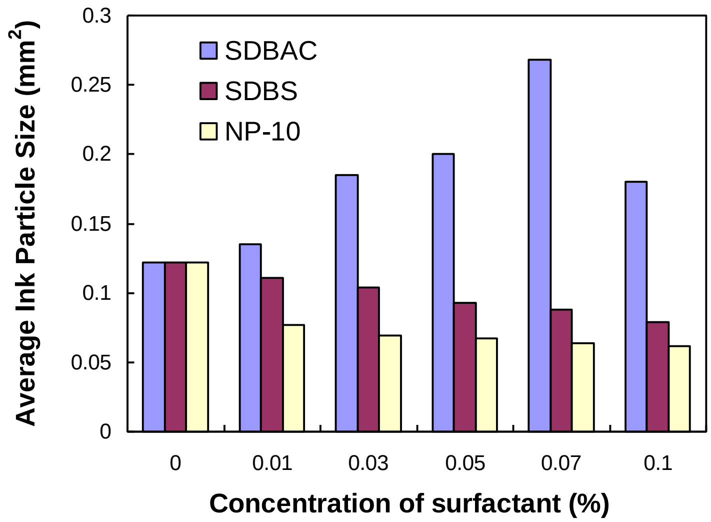


Fig. 6. Effect of surfactants on the average ink particle size after agglomeration of laser toner ink with 1.5% 1-octadecanol

The anionic surfactant (SDBS) and the nonionic surfactant (NP-10) are often used as dispersants. Their HLB values are higher; thus they showed stronger hydrophilic properties. The HLB values of SDBS, NP-10, and 1-octadecanol are 31, 14, and 0.83, respectively. The lipophilicity of 1-octadecanol is much stronger than that of SDBS and NP-10, respectively. When the surfactant (SDBS or NP-10) was added with 1-octadecanol, the surfactant could disperse the 1-octadecanol to small particle size and reduce the lipophilic character of 1-octadecanol. Since the laser toner ink was thermoplastic, the effects of SDBS and NP-10 were negative on NPM and particle size.

The same experiments were carried out for offset printed ink, and the results are shown in Figs. 7 and 8.

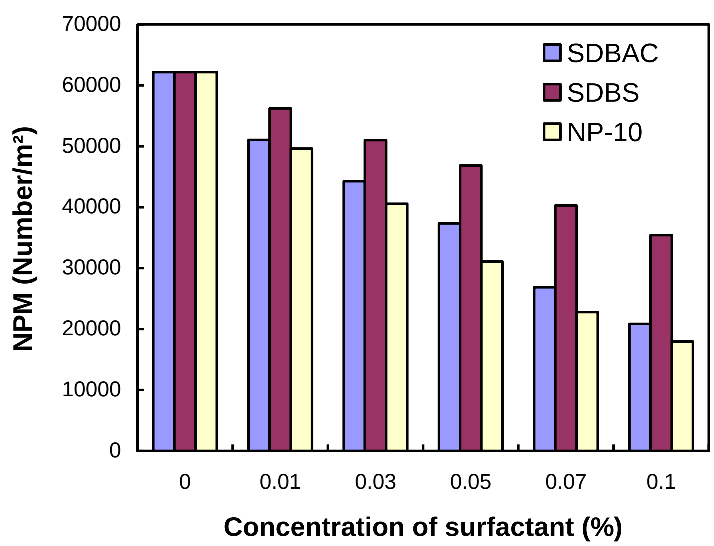


Fig. 7. Effect of surfactants on NPM after agglomeration of offset printed ink with 1.5% 1-octadecanol

According to the results, three kinds of surfactants with different charge characteristics were all effective for NPM and gave positive results. The surfactants could make the ink separate from the fiber easily. The NPM was reduced rapidly with the increased amount of the surfactants. The nonionic surfactant was the most effective one. The minimum of NPM was 18,000 at the dosage of 0.1%. The reduction was nearly 70%. The effect of anionic surfactant was the mildest.

The effect of surfactants on the average ink particle size after agglomeration of offset printed ink with 1.5% 1-octadecanol is shown in Fig. 8. It was clear that the value of the particle size was maintained at 0.02 mm^2. It could be concluded that these surfactants were ineffective for enlarging the particle size.

Thus, the surfactants used for the offset ink deinking had no effect on agglomeration with 1-octadecamol, but they had a synergistic effect with 1-octadecamol on removing the ink particles from the fiber surface easily.

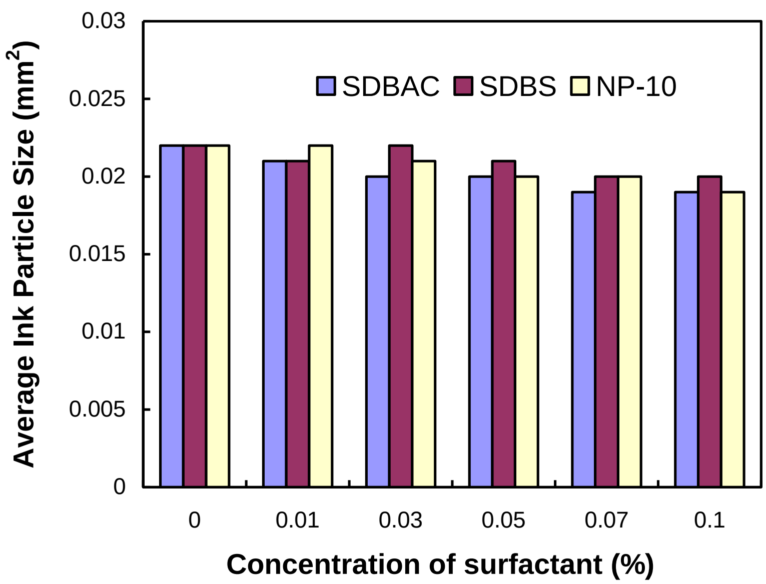


Fig. 8. Effect of surfactants on the average ink particle size after agglomeration of offset printed ink with 1.5% 1-octadecanol

Effect of Surfactants on Agglomeration with Different Inks of Mixed Waste Papers

Figures 9 and 10 showed the effect of different surfactants on the agglomeration of mixed waste paper with 50% offset waste paper and 50% laser printed paper. All three types of surfactants had a trend of positive effect on the agglomeration, but all with an optimal point. And the optimum dosage of each surfactant was different. The optimum dosage of cationic surfactant (SDBAC) was 0.05%, NPM was 38,000, and the size of the average ink particle was 0.1 mm^2. Meanwhile, the optimum dosages of SDBS and NP-10 were 0.03% and 0.01%, respectively. Below and/or above the optimum dosage, the NPM was larger, and the size was smaller, respectively.

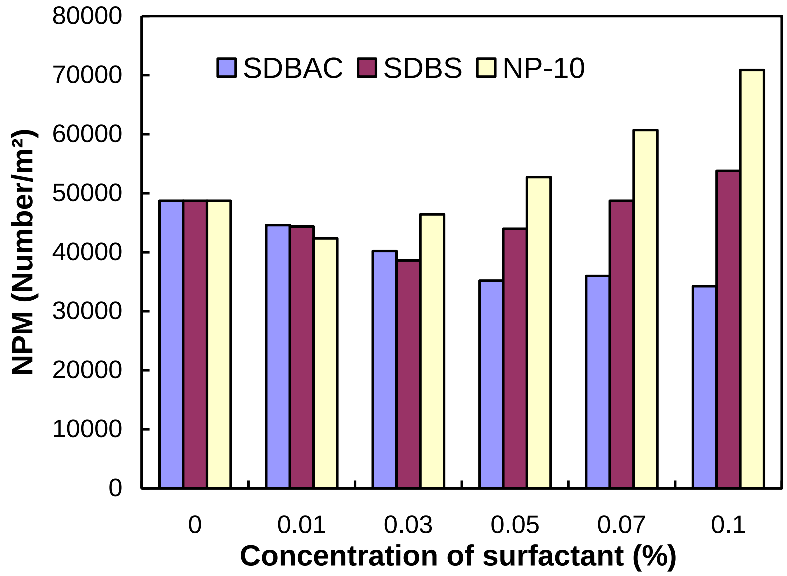


Fig. 9. The effect of different surfactants on NPM after agglomeration with 1.5% 1-octadecanol of mixed waste paper with 50% offset and 50% laser printed paper

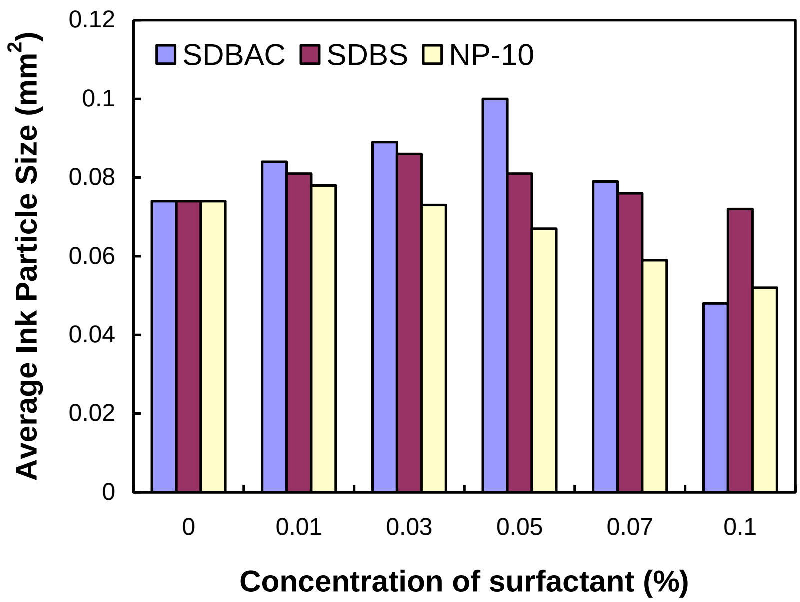


Fig. 10. The effect of different surfactants on average ink particle size after agglomeration with 1.5% 1-octadecanol of mixed waste paper with 50% offset and 50% laser printed paper

In Figs. 11 and 12, line A represents the inks with 1-octadecanol only; lines B, C, and D represent the inks mixed with SDBAC, SDBS, and NP-10, respectively. The dosages were 0.05%, 0.03%, and 0.01%, respectively, which were their optimum dosages.

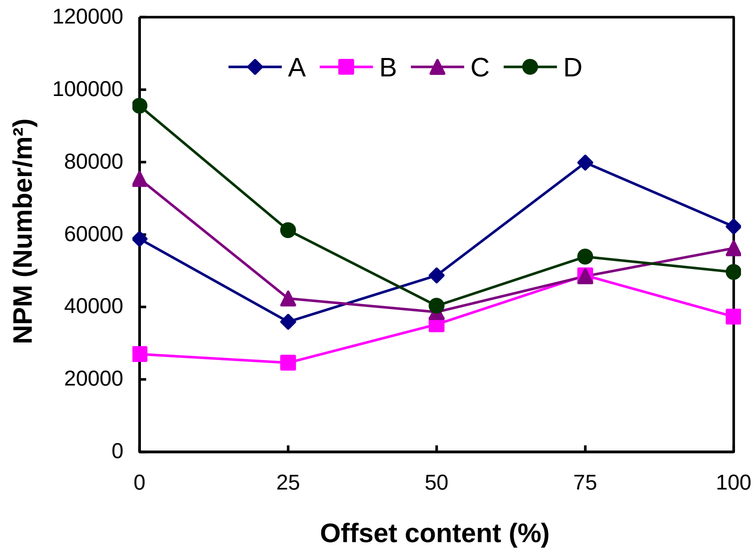


Fig. 11. The effect of different surfactants on NPM after agglomeration of different percentage of offset with 1.5% 1-octadecanol

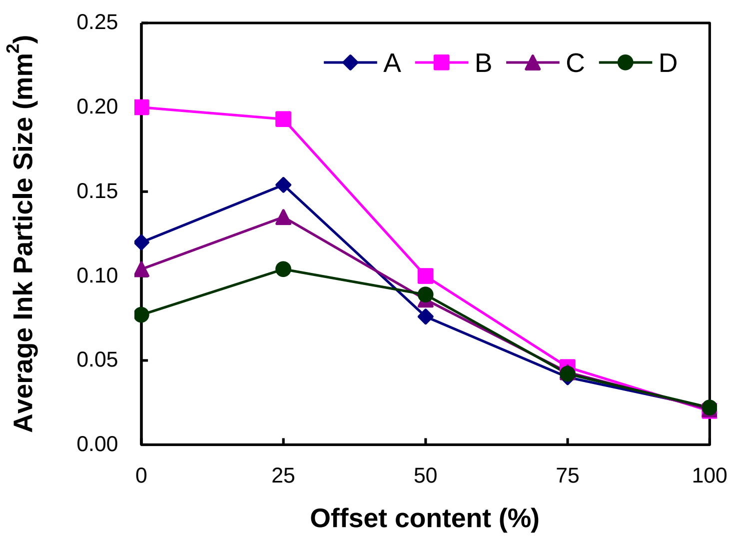


Fig. 12. The effect of different surfactants on average ink particle size after agglomeration of different percentage of offset with 1.5% 1-octadecanol

It was found that the addition of cationic surfactant was beneficial to reduce the NPM and enlarge the average ink particle size at any percentage in comparison to the condition of no surfactant. When the percentage of offset waste paper was less than 50%, the addition of anionic surfactant and nonionic surfactant was harmful for agglomeration. When the percentage of offset waste paper was more than 50%, the NPM was reduced a little, and the average ink particle size was enlarged very slightly. It seems that there was no significant effect during the high content of offset waste paper. Thus, the addition of anionic surfactant and nonionic surfactant was harmful for agglomeration at lower offset content, and it showed no significant effect at higher offset content.

CONCLUSIONS

1. 1-octadecanol is a very effective agglomerating agent for laser toner ink under neutral pulping conditions. But 1-octadecanol cannot agglomerate the offset printed ink. A small amount of 1-octadecanol can remove the ink from the fiber surfaces easily. But the particles can re-deposit with 1-octadecanol onto the fibers, and the NPM is increased when the dosage is more than 1.0% during deinking of the offset printed ink.
2. Addition of a small amount of the offset waste paper (about 12.5 to 25%) can be beneficial to improve the agglomeration of the laser toner ink during the deinking process. The offset printed ink showed a positive charge of 0.001±0.0005 mEq/g when the offset ink was treated by 70^{o}C water at neutral conditions. It may act in the same way as a cationic surfactant in the deinking process.
3. For laser toner ink, the cationic surfactant has a positive effect with 1-octadecanol on agglomeration. However, addition of SDBS and NP-10 has a negative effect on the particle size. For offset printed ink, three kinds of surfactants with different charge characteristics are all effective for NPM and give positive results, and the nonionic surfactant is the most effective.
4. Adding a proper amount of cationic surfactant was beneficial to reduce the NPM and enlarge the average ink particle size at any ratio of the paper mixture. When the percentage of offset waste paper was less than 50%, the addition of anionic surfactant and nonionic surfactant was harmful for agglomeration.

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