Liquid bridge agglomeration: a fundamental approach to toner deinking

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ABSTRACT: An alternative agglomeration technique for deinking toner-printed furnishes has been investigated. This technique requires only the addition of an immiscible hydrocarbon oil dispersed in water at dosages of approximately 1% by weight on fiber. The addition is made during repulping. The process appears to be effective at all temperatures of interest (23° C and 70° C are tested) and requires no surfactants or additional chemicals. The result of the oil addition is the agglomeration of the toner particles into spheres of 1 mm to 1 cm in size. These spheres contain the added oil which acts as a binder, holding the toner particles together by liquid bridges. The process is ineffective when the furnish contains highly sized fibers or starched paper, and future work seeks to address these crucial problems.

KEYWORDS: Agglomeration, deinking, liquids, oil, toners, waste papers.

Toners are thermoplastic-based inks which are electrostatically placed on a page and then fused in place. They are used in all copy machines and laser printers, and therefore are major contaminants of secondary fiber from mixed office waste. The continued innovations in the printing process have also made toner-printed papers a growing segment of all post-consumer paper, as both copy machines and laser printers become faster and cheaper.

Toner-printed furnishes are often difficult to handle with conventional deinking methods. One solution may be to agglomerate the toners with suitable chemicals *(1)*. In this process, such chemicals are added to the repulper while a certain temperature and good mixing are maintained. Typically, agglomerates form within 15 to 45 min. Conventional methods, such as centrifugal cleaning and screening, then remove these agglomerates downstream.

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Unlike flotation or washing, agglomeration is a deinking process that a mill can add without significant capital investment. In addition, it usually handles toner-printed furnishes effectively, allowing high-grade fibers to be recovered. These factors combine to make the process attractive.

However, current agglomeration processes rely on proprietary chemical formulations and require elevated temperatures (40–70°C) *(2, 3)*. We believe these processes chemically fuse the toners to one another, and therefore produce very strong agglomerates. This paper presents the results of a program directed at using a different technique to agglomerate the toners. We call this technique "liquid bridge agglomeration." It requires only cheap commodity chemicals, like fuel oil, and can be done at any convenient temperature. The agglomerates that result are not chemically bound together, but held together by liquid bridges between the toner particles. These agglomerates are undoubtedly weaker, and the presence of highly sized fibers and starch disrupt the process, but we anticipate further work can minimize these problems.

Background

To separate the toner particles from the fiber slurry, liquid bridge agglomeration uses the difference in the toner and fiber wettability. In

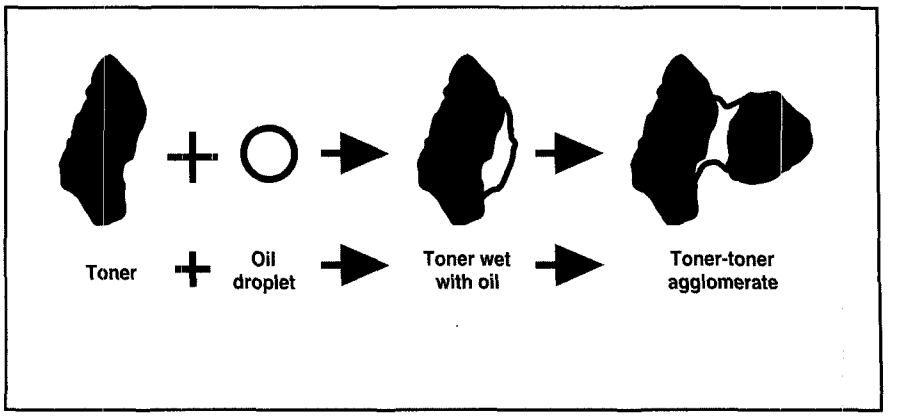
this respect, the process is similar to flotation. In flotation, the toner particles attach to the bubbles because they are hydrophobic while the fibers do not attach because they are hydrophilic. Likewise, in liquid bridge agglomeration, the added oil droplets stick to the toner particles because they are hydrophobic but not to the fibers because they are hydrophilic. The toner particles then become coated with oil droplets. When two toner particles collide, the oil droplets form a liquid bridge between them, holding them together. The process continues until many toner particles are collected into a large, spherical agglomerate (up to 1 or more cm in diameter) which is then removed by centrifugal cleaning or screening. The process is depicted in **Fig. 1.**

References *(4–8)* outline liquid bridge agglomeration as a separation technique, and general information is also contained in reference *(9)*. "Liquid bridge agglomeration" is our term, and refers to the underlying mechanism; in the literature, the technique is often called "spherical agglomeration" or "oil agglomeration."

Liquid bridges are formed when a small amount of wetting liquid occurs between two solids. The liquid, because it adheres to the solids and develops a curved interface, exerts a force that pulls the solids together. A standard feature of liquid bridges is that the smaller they are, the stronger they are *(6)*. Thus, very large toner particles are not held together as well as small toner particles in liquid bridge agglomeration. However, it appears that liquid bridges are strong enough for the toner particles produced on repulping.

The process has aroused the greatest interest in separating coal from ash. The coal particles are hydrophobic like the toner particles, and the ash is hydrophilic like pulp fibers. Just as flotation was adapted to deinking from the mineral processing field, liquid bridge agglomeration may also find use in deinking. In fact, one process for deinking newsprint that uses liquid bridge agglomeration was recently described *(10)*.

1. Liquid bridge agglomeration process



Experimental procedure

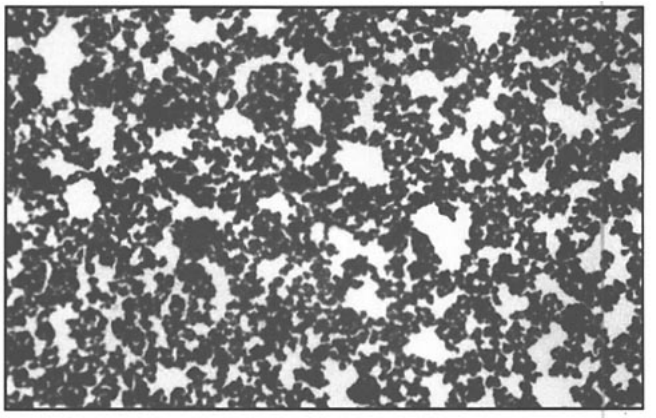
For the experiments on toner powders without the presence of fiber, the desired amount of the agglomerating oil, *n*-hexadecane, was volumetrically measured and added to 200 mL deionized water. The mixture was blended at high speed on a VirTis® "23" homogenizer for 2 min to disperse the oil into small droplets. The dispersion was put into a 500-mL beaker and agitated by a magnetic stirbar. While stirring, 0.067 g of a toner from an Apple Laser Writer laser printer was added, initiating agglomeration. After 2 min, the run was stopped (it was found that no further agglomeration occurred after this time for these runs). Samples of toner particles were observed and photographed through a Bausch & Lomb light field optical microscope, yielding the pictures shown in **Figs. 2–6.**

For the experiments with both fibers and toner present, a different apparatus was used. It consists of a Cole-Parmer StirPak® 23–2300 rpm 1/10 hp laboratory mixer mounted over a 4-L cylindrical glass vessel, shown in **Fig. 7.**

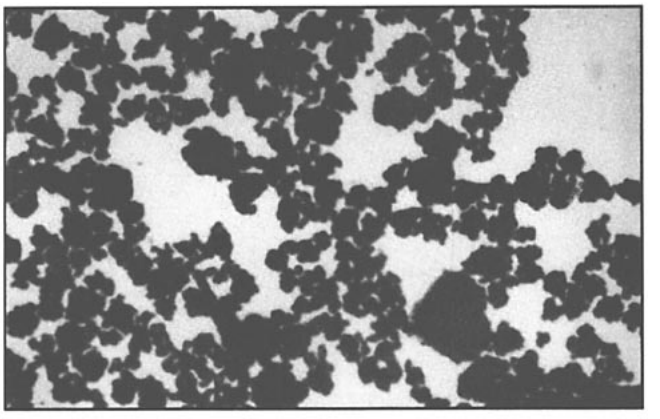
For a typical experiment, the type of paper was selected, weighed out, and torn into pieces. The pieces were added to a 3.8-L (1 gal), 3-hp Waring blender. The desired amount of an Apple Laser Writer toner was then added as an unprinted powder. Lastly, 1 L of deionized water was put in and blended at 15,000 rpm for 2 min. The resulting pulp was added to the 4-L agglomeration vessel and set stirring at approximately 180 rpm. Separately, the desired amount of *n*-hexadecane was volumetrically measured and added to 200 mL of deionized water and homogenized on the VirTis® "23" homogenizer at high speed for 2 min. The resulting dispersion of hexadecane in water was added to the agglomeration vessel, starting agglomeration. Visual observations were made during the run, which normally lasted for 30 min. Sometimes small samples were taken from the vessel and examined under the Bausch & Lomb microscope.

At the beginning of the agglomeration experiments, the pulp was gray and had only very small visible toner specks in it. If the process was successful, the pulp became white and several 1–10-mm toner spheres were formed. Thus, visual observation allowed an effective assessment of agglomeration performance. In unsuccessful runs, the pulp remained gray and no agglomerates were formed. For these runs, examination under a microscope showed many 10-μ toner particles mixed in the fibers.

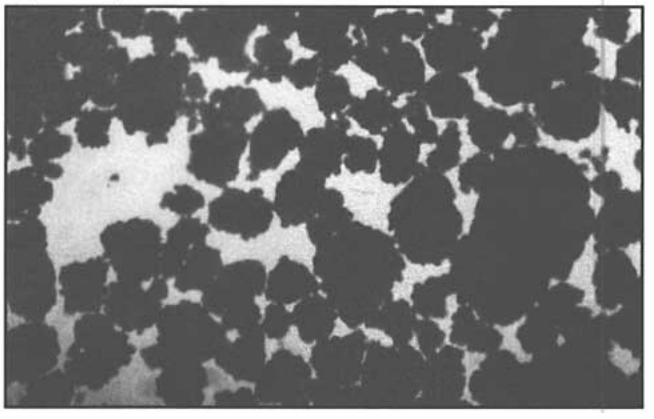
2. Toners agglomerated with 0.09 oil/toner volume ratio. One cm equals 220 μ.



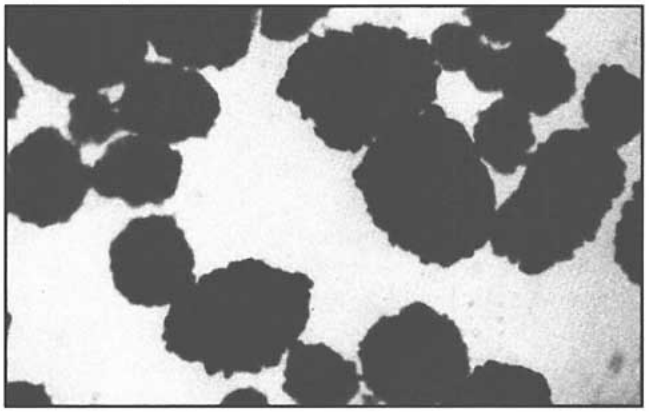
3. Toner agglomerated with 0.28 oil/toner volume ratio. One cm equals 220 μ.



4. Toner agglomerated with 0.46 oil/toner volume ratio. One cm equals 220 μ.



5. Toner agglomerated with 0.69 oil/toner volume ratio. One cm equals 220 μ.



For the experiment with filler, $CaCO_3$ equal to 20% of the fiber weight was added to the blender and blended with the fiber and toner.

For the experiments with starch, starch equal to 1% of the fiber weight was separately dissolved in 200 mL of deionized water and boiled on a hot plate for 20 min. After cooling for 10 min, the starch solution was added to the agglomeration vessel before the dispersed oil. To ensure that the starch was adsorbing only on the fibers initially, in one experiment the starch was added to the fibers in the blender and repulped with them before the toner was added. The two methods of adding starch gave identical results, however.

For the experiment on the effect of pH, the deionized water added to the blender for repulping had 0.001 moles of sodium hydroxide added, making its pH = 11.

For the 70°C runs, the standard agglomeration experiment procedure was followed, except hot water was added to the blender for repulping and the agglomeration apparatus was immersed in a constant temperature water bath at 70°C. All other runs were done at 23°C.

The agglomeration runs were done at 1% consistency, with 14.3 g weighed fiber (assumed 6% moisture content) added to 1.35 L of water. Since 14.3 g of paper equals three of our standard copy paper (8.5 in x 11 in.) sheets, these were printed on an Apple Laser Writer with a standard pattern, and the weight difference before and after printing was determined to calculate the amount of toner on the sheets. The result was 0.114 g per sheet, so 0.342 g of toner was added to the blender to simulate a realistic quantity of toner. For the runs where printed sheets were used, no additional unprinted toner was added. It was found that whether the toner was added in unprinted form or added as printing on the paper did not matter; either agglomeration occurred in both cases (when filter paper was the paper) or in neither case (when 8.5 in. x 11 in. copy paper was the paper). The runs at 5% consistency were identical to those at 1% except for the increase in the amount of toner, fiber, and oil.

n-hexadecane was used as the agglomerating oil because it is nonvolatile (boiling point 287°C), relatively nontoxic, forms a high interfacial tension with water (50 mN m^{-1}) *(11)*, and represents a typical fuel oil or diesel fuel, which would be cheap sources of an agglomerating oil. The interfa-

cial tension is important because the strength of the agglomerates depends on it *(8)*, and hydrocarbons with significant aromatic contents have lower interfacial tensions with water (about 35 mN m^{-1}) *(11)*. If a mill were to use liquid bridge agglomeration, a dosage of about 20 lb/ton of fiber would be needed, costing approximately US$ 2 (assuming a wholesale price of US$ 0.50/gal for diesel fuel and 4 gal used per ton).

It is important that the oil be added in dispersed form (so that it can reach and contact the toner particles), and this is the purpose of dispersion in the VirTis® "23" homogenizer. It has two sets of knife-edge blades that rotate at speeds up to 23,000 rpm, producing a dispersion with many 1–5-μ size hexadecane droplets (as observed under the microscope). Note that the dispersion is not stabilized by any surfactants, as these would lower the oil–water interfacial tension. Thus, the dispersion can be expected to coalesce and separate over the course of hours.

The 8.5-in. x 11-in. copy paper was a nonrecycled Hammermill paper, while the filter paper was grade 415 VWR® Qualitative. The starch was STA-LOK® 400 manufactured by the A. E. Staley Co., Decatur, IL, and is a cationic potato-derived starch.

Agglomeration experiments were run for 30 min. In general, if agglomeration occurred, it happened within the first few minutes after the dispersed oil was added. Several of the experiments were run longer to observe any further changes (for up to 3 h), and neither for runs with agglomerates nor for unsuccessful runs was any change after the first 15–30 min observed.

Results and discussion

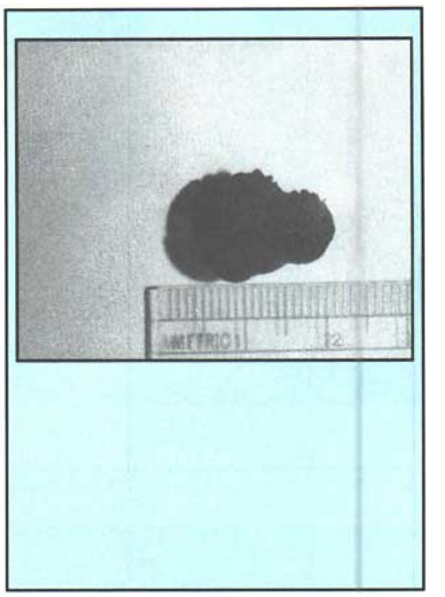
Experiments on toners without fiber

The agglomeration literature on coal and other hydrophobic minerals suggested that adding a dispersed nonpolar and immiscible liquid ought to agglomerate the hydrophobic particles in a slurry, including toners. To verify that indeed this is the case, we first attempted to agglomerate toner particles in water in the absence of fiber or other materials. A concentration of toner in water was selected based on our calculations of a typical amount of toner in a repulper (about 0.25 g/L for a 1% consistency pulp). We varied the oil dosage to observe how this influenced the agglomeration.

As given in references *(8, 9)*, the oil dosage affects the type of agglomerates formed. Normally, four states are observed (in order of increasing oil dosage): funicular, pendular, capillary, or liquid–liquid particle transfer. In the funicular and pendular states, the agglomerates are becoming larger, more spherical, and stronger, until a maximum is reached in the capillary state. This state is reached when the dosage of oil is equal to that which exactly fills the pore volume between the toner particles. For example, if the toners are equally sized spheres, the closest packing yields a 0.26 void volume, or an oil/toner volume ratio of 0.35. Further oil addition causes liquid–liquid particle transfer, where the particles disperse in the oil phase. This results in a sharp reduction in strength and soft, spongy agglomerates. The ideal level of oil addition is therefore that which leads to the capillary state.

Figures 2–6 show the results of varied oil dosage on toner particle agglomeration. In Fig. 2, the ratio of oil volume to toner volume is 0.09. The individual toner particles show some clumping and appear to be in the funicular or pendular state. In Fig. 3, the oil/toner volume ratio is 0.28. In Fig. 4 it is 0.46, and in Fig. 5, 0.69. As is apparent, the size and sphericity of the toner agglomerates increases dramatically with the level of oil addition. By Fig. 6, the volume ratio is 0.92. The agglomerate formed is about 1.5 cm in diameter,

6. Toner agglomerated with 0.92 oil/toner volume ratio, the ideal.



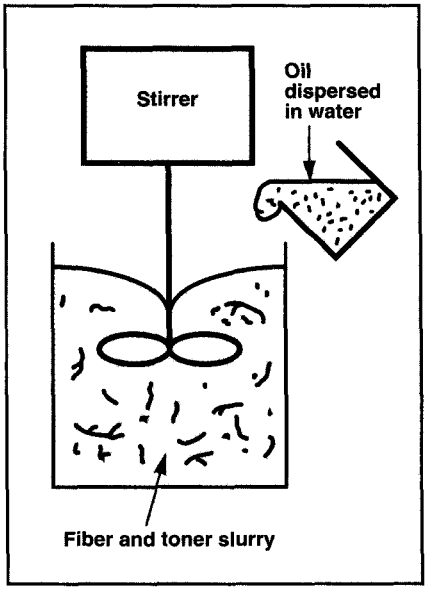
and the capillary state has been reached. Further oil dosages continued to form centimeter-sized agglomerates, but, as expected, the agglomerates became softer and more oily.

These experiments indicated that oil agglomeration works on pure toners and with hexadecane as the agglomerating oil. Also, we know the toners pack more openly than spheres, requiring an oil/toner volume ratio of about 0.9 for the largest and strongest agglomerates. With this information, we moved on to agglomerate toners in the presence of fibers.

Experiments on toners and repulped fiber

When unprinted toner particles were added to repulped blank copy papers at 1% consistency, the toner particles no longer agglomerated. If the same amount of toner particles were added to copy papers at only 0.1% consistency, then a modest amount of agglomeration occurred. This consistency was far too low for practical use. Why was the presence

7. Diagram of agglomeration apparatus



of the copy paper fiber disrupting agglomeration? Further experiments answered this question.

If instead of copy papers, filter paper was repulped, agglomeration was successful, even up to 5% consistency. This indicated that something present in the copy papers but not in the filter papers was responsible. After talking to the manufacturer of the filter papers, we discovered that the filter paper was 70% cotton and 30% wood derived, and had only 0.06% ash content. Also, the filter paper had no filler, starch, or size added. So we began to examine the effects of each of these additives.

Working with a dissolving pulp (ultra-pure-wood cellulose used for making rayon, cellophane, and other materials), we obtained successful agglomeration. This meant that the low wood-fiber content of the filter paper was not responsible. Adding $CaCO_3$ equal to 20% of the filter paper weight also did not prevent agglomeration in this system, eliminating the filler as responsible.

For investigating the effect of size 8.5 in. x 11 in. sheets with no size and sheets with 5-lb/ton alkenyl succinic anhydride (ASA) size were tested. The sheets were prepared at the Weyerhaeuser Technical Center in Federal Way, WA, and otherwise were typical paper. On the sheet with no size, a small amount of agglomeration occurred. The slurry became significantly less gray, but not white as was the case with the filter paper fibers. Also, the agglomerates were numerous and small. However, when the 5 lb/ton-size papers were used, the agglomeration process was completely disrupted. No agglomerates at all were formed, and the slurry remained dark gray. These experiments thus showed that size has a highly deleterious effect on agglomeration, but even without any size, agglomeration is not very effective.

The effect of the starch was decisive. When added to the filter paper fibers, agglomeration was entirely prevented. Therefore, in addition to difficulties with highly sized sheets, starch appears to completely block the agglomeration process.

The effect of the size is probably explained by the highly hydrophobic patches on the fiber surfaces present from the sizing agent. These patches, like the hydrophobic toners, attach to the oil droplets and then "agglomerate" with toner particles. This produces the undesirable effect of binding the toner particles to the fibers. Examination of the pulps after attempted agglomeration supported this explanation: toner particles were found spaced along the lengths of the fibers.

The reason for the disruptive role of the starch is unclear. We hypothesize that the starch adsorbs at the oil–water interface and stabilizes the oil droplets against coalescing on the toner particle surface. We have observed the stabilizing effect of starch on oil-in-water dispersions. These stabilized oil droplets probably flocculate with fibers, since cationic starch adsorbs strongly to fibers *(12)*. This keeps the oil then unavailable for coating and agglomerating the toner particles. With an understanding of the mechanism, it is possible that an additive can be used to block it.

Experiments on the range of effective conditions

Since agglomeration was successful with the repulped filter paper, we attempted to probe its sensitivity to temperature, pH, and consistency. For a temperature of 70°C, agglomeration was very slightly worse than at 23°C, indicating that it is not temperature sensitive. Also, the copy paper continued to be unagglomerated at 70°C, showing that the starch and size maintain their inhibitory effects at this temperature.

Although all experiments were carried out without the presence of caustic (at a pH of 5–7), agglomeration was unaffected by adding caustic to raise the pH to 11. Note that both the lack of a strong temperature effect and a pH effect are consistent with the mechanism of liquid bridge agglomeration. The method depends only on the oil droplets sticking to the toner particles, and neither the temperature nor the pH are expected to affect this strongly.

Experiments at 5% consistency showed that agglomeration worked as well as it did at 1% consistency. This is despite the very poor mixing we had in our apparatus at this consistency. Our equipment did not allow us to attempt any higher consistencies, but as long as the fiber–fiber shearing is not so strong as to break up the agglomerates that are forming and that sufficient mixing is available to bring the oil droplets into contact with the toner particles and the toner particles with each other, higher consistencies will probably work.

Summary

The study shows the effect of an exceedingly simple method of deinking toner-printed furnishes. The method requires only 1% by weight on fiber of an inexpensive fuel oil added as a

dispersion in water to repulping. Caustic, temperature, and moderate consistencies do not affect the process significantly. In less than 15 min, a great majority of the toner is collected into 1–10-mm agglomerates that can easily be removed with conventional downstream processing equipment, such as screens and centrifugal cleaners. The added fuel oil is relatively nontoxic: negligible vapor pressure, and easy either to reuse or to dispose of by combustion.

However, starch is found in virtually all stocks, and this interrupts the agglomeration process. Further work is directed to clarifying why this is and how it can be counteracted. A second concern is that the proper dose of oil is added for the repulper, which requires knowing how much toner is present. This would vary with the particular load of office recovered paper repulped and may have to be adjusted from time to time. This would present a problem if the total amount of toner-printed papers repulped varied erratically and drastically throughout the day. Another difficulty is working with highly sized fibers. For these, the wettability difference between the toner and fiber is lost, preventing the process from operating.

However, suitable chemistry may inhibit the effect of the starch and properly chosen surfactants can control the fiber wettability, hopefully overcoming these obstacles. Further work that successfully addresses these issues would yield an effective and economical method of deinking office waste. ■

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CORRECTION

Pia Wågberg, coauthor of "Surface profilometry—a comparison between optical and mechanical sensing of printing papers," notes the following corrections should be made in the paper published on p. 115 of the December 1993 *Tappi Journal*:

1. There should not be a "dx" in equation no. 2.
2. In **Fig. 4**, the lower curves for both "cast coated" and "coated fine paper 2" depict the mechanical stylus and should have been depicted with filled circles.
3. In **Fig. 8** the unfilled square symbol is supposed to depict LWC, not SC, while the filled square symbol should depict SC, not LWC.