

# Model deinking studies: carbon black removal by oil-coated plastic pellets

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**ABSTRACT:** *Plastic pellets coated with either silicone or paraffin oil were used to remove carbon black dispersed in water. Silicone oil was found to be a more effective coating; the viscosity of the oil and thickness of the coating were not important factors. With sufficient collecting surface area and contact time, the coated pellets were able to remove all of the carbon black from the dispersion.*

**KEYWORDS:** *Agglomeration, carbon black, deinking, deposition, pellets.*

In 1976, Sparks and Puddington (1) described a novel newsprint deinking process in which plastic pellets containing iron cores were added to repulped newspapers. The key step was the deposition of dispersed newsprint ink onto the plastic pellets, which were then separated from the pulp by magnets. In their patent, Puddington *et al.* (2) described a variety of collector particles to remove ink, including solid or porous pellets, flakes, or short rods. If the particles were not softened at deinking temperatures, they were coated with a sticky or viscous substance such as oil, gum, or wax to improve adhesion between the carrier particles and the contaminating particles. In a similar application, Rubio and Holberg (3)

have reported the use of polypropylene pellets coated with oleic acid to remove fine and ultra-fine mineral particles from mineral pulp suspensions.

We believe that Sparks and Puddington's work is interesting from two perspectives. First, it is an alternative to flotation or wash deinking, which could offer advantages. Second, plastic pellets can be considered to be a model for air bubbles in flotation deinking. Pellets have the advantage that their size and surface chemistry can be controlled, perhaps leading to more fundamental information about flotation deinking. Specifically, we were interested in the effects of the type of pellet and pellet surface treatment on ink removal. This work describes

the deposition of carbon black suspensions onto plastic pellets. The carbon black was dispersed with sodium laurate and subsequently aggregated with calcium chloride. This is similar to fatty acid flotation deinking chemistry.

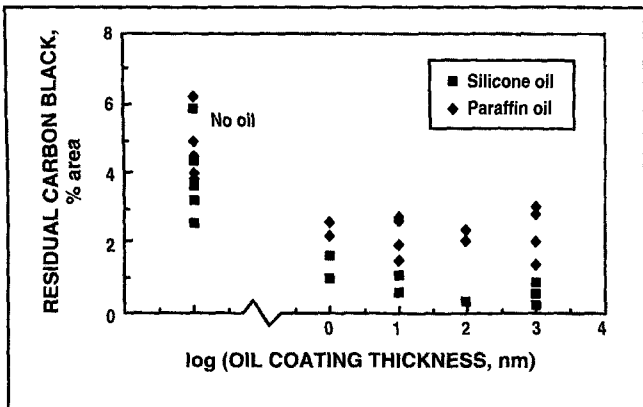
## Experimental

Aqueous dispersions of carbon black were used as a model for newsprint ink. REGAL™ 991 (Cabot) containing about 1.0% volatiles was used as received. The following method was used to produce a 40-mg/L carbon black dispersion containing  $4.0 \times 10^{-5}$  M sodium laurate (99% purity, Sigma) and  $1.0 \times 10^{-3}$  M NaCl.

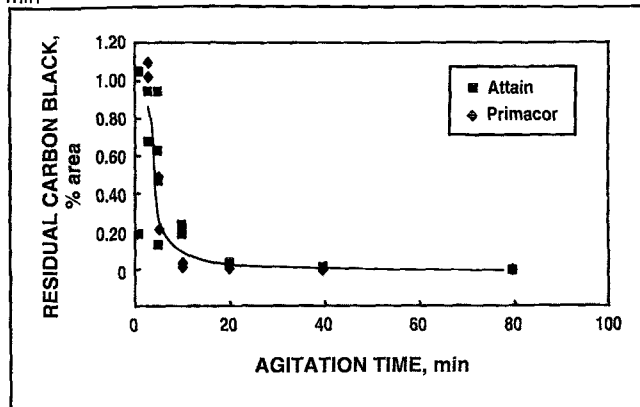
To prepare a 500-mL dispersion, the carbon black was stirred for 15 min in about 400 mL of Milli-Q™ water, which had been pH adjusted to 9.5 with NaOH. Next, 20 mL of a 1-mM solution of sodium laurate was added, and stirring was continued for an additional five minutes. The wetting process was followed by dispersion by sonification with a Branson Ultrasonics model 450 Sonifier (flat-tipped horn). The sonification process was performed for five minutes at 50% power with a 0.5-second pulse duration. Finally, 0.25 mL of a 2-M NaCl solution was added to the dispersion, which then was transferred to a 500-mL volumetric flask and filled with water previously adjusted to pH 9.5 with sodium hydroxide. The dispersion

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1. Relative area on filters covered by carbon black after the dispersion was treated with oil coated pellets during 5 min of agitation. The lowest areas of residual ink corresponded to the highest deposition. Oil coating thickness ranged from 1 nm to 1000 nm.



2. Relative area on filters covered by residual carbon black after the carbon black dispersion was treated with silicone oil (100 cp), coated PE (ATTANE™), and PE-CO-AA (PRIMACOR™) pellets (1-μm coating thickness) for agitation times ranging from 1 min to 80 min



was shaken, then placed in a Branson Ultrasonics model 2200 bath for five minutes. The operating range of the ultrasonic horn is best suited for volumes of less than 500 mL. Freshly prepared carbon black dispersions were required for each experiment to obtain reproducible results.

An ultralinear low-density polyethylene (PE), ATTANE™ 4001 (Dow Chemical), was chosen as the substrate because it is free of additives such as slip or antiblock, which could alter the surface chemistry of the pellets. To determine the effect of a more hydrophilic substrate (PE-co-AA), PRIMACOR™ 3440 (Dow Chemical), a copolymer of polyethylene and acrylic acid containing about 9.5 mol% acrylic acid, was examined. PE-co-AA also is free of slip and antiblock additives.

Twenty measurements of the length, width, and height were made with a micrometer for each type of pellet. To estimate the surface area of PE pellets an oval rod was used as an approximate shape, and for PE-co-AA pellets the shape was approximated by half an ellipsoid. The areas corresponding to these geometries are given below. In both equations, the length is equal to  $2a$ , the width to  $2b$ , and  $h$  is the height.

PE Pellets

$$A = 2\pi \left( ab + h\sqrt{(a^2 + b^2)/2} \right)$$

PE-co-AA Pellets

$$A = \pi \left[ ab + b^2 + \frac{a^2 b \sin^{-1} \left[ \frac{\sqrt{(a^2 - b^2)}}{a} \right]}{\sqrt{(a^2 - b^2)}} \right]$$

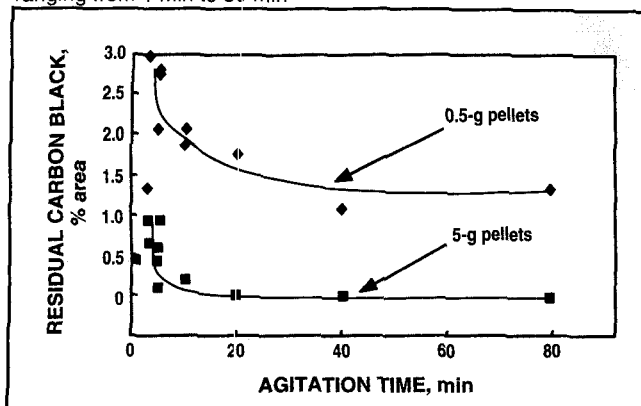
The average surface area for PE pellets was found to be 76.6 mm<sup>2</sup> per pellet, with a standard deviation of 3.63 mm<sup>2</sup>; the area for PE-co-AA pellets was found to be 36.3 mm<sup>2</sup>, with a standard deviation of 3.45 mm<sup>2</sup>. The corresponding specific surface areas were  $2.28 \times 10^{-3}$  m<sup>2</sup>/g for PE and  $1.27 \times 10^{-3}$  m<sup>2</sup>/g for PE-co-AA.

The plastic pellets were coated with two types of oils: paraffin oil (BDH) and trimethyl terminated polydimethylsiloxane (Petrarch). The paraffin oil was available in two viscosities: light oil at about 20 cp and heavy oil at about 150 cp. Three viscosities of the silicone oil were examined: 10, 100, and 10,000 cp. The pellets were coated with the various oils by dissolving a known amount of oil in a suitable solvent, adding the pellets to form a slurry, then removing the solvent by roto-evaporation. The paraffin oil was dissolved in n-

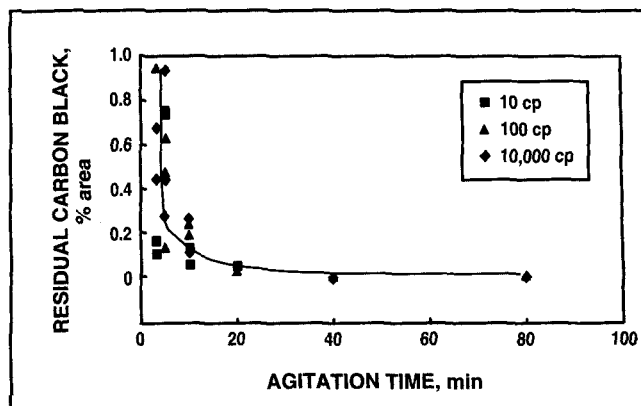
heptane, 10- and 100-cp silicone oils were dissolved in acetone, and toluene was used to dissolve 10,000-cp silicone oil. In the coating procedure, 1 mL of coating solution was used per gram of pellets, which was sufficient to submerge the pellets. The amount of oil used to coat the pellets was determined by choosing a desired thickness of the oil layer and estimating the surface area of the pellets based on measurement of the length, width, and height of the pellets. For polyethylene (PE) pellets with a 1-μm-thick oil layer, 2.2 μL of oil were used per gram of pellets.

Because the total surface area of the pellets was relatively low ( $2.2 \times 10^{-3}$  m<sup>2</sup>/g and  $1.3 \times 10^{-3}$  m<sup>2</sup>/g), it was possible that the amount of residual oil found on the flask wall after the coating process could be significant. To determine the amount of oil successfully transferred to the pellets' surface in the coating step, the amount of oil remaining in the vessel was measured. An oil-soluble dye, Oil Red O (Aldrich), was dissolved in the oil-solvent coating solution at 10% by weight of the oil. The dyed oil was used to coat the pellets. After removing the dry, coated pellets, the residue in the coating vessel was dissolved (in acetone for silicone oil and in heptane for paraffin oil), and the concentration of Oil Red O was de-

3. Relative area on filters covered by residual carbon black after the carbon black dispersion was treated with different amounts of silicone oil-coated pellets (1- $\mu$ m coating thickness) for agitation times ranging from 1 min to 80 min



4. Relative area on filters covered by residual carbon black after the dispersion was treated with silicone oil coated pellets (1- $\mu$ m coating thickness) for three different viscosities of oil

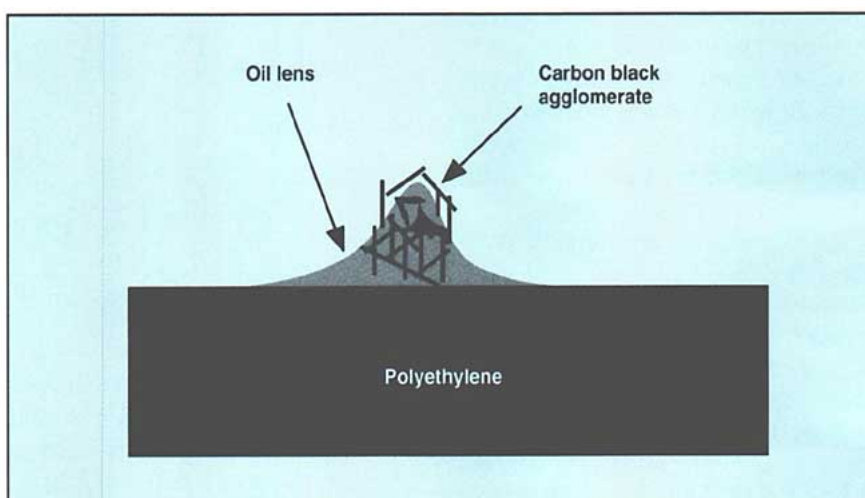


terminated by ultraviolet analysis at 510 nm. Approximately 95% of the oil used in the coating process was retained on the surface of the pellets.

The deposition experiments were performed at room temperature and  $\text{CaCl}_2$  was added as the collector chemical. In a typical experiment, 5 g of oil-coated pellets were added to an Erlenmeyer flask containing 50 mL of the carbon black dispersion and 2 mL of 0.1-M  $\text{CaCl}_2$ . The flask was fitted with a ground-glass stopper and then placed on a Burrel Wrist Action Shaker at 30% shaking intensity. After the required agitation period, three 1-mL aliquots of the clarified dispersion were quickly removed and diluted to 25 mL with Milli-Q water. These samples were filtered on Millipore mixed ester membrane filters having an average pore diameter of 3  $\mu$ m.

Filters obtained from the deposition experiments described above were examined by transmitted light microscopy and digitized image analysis to measure the surface area covered by the carbon black. Two different techniques were used to prepare the samples for analysis. The first technique has been described by Nguyen *et al.* (4). In this method, a filter is treated with a mixture of organic solvents followed by acetone vapor, rendering the filter invisible and fixed to the microscope slide.

5. Oil lens bridging deposited carbon black agglomerate. The interfacial tension between the oil and the water contributes to the adhesion of the carbon black to the PE.



This method provides excellent contrast between the carbon black particles and the background and is suitable for high magnifications. A second method, modified from the method described by Blain *et al.* (5), consists of wetting the filter with a 10%/90% by volume methanol/water solution and covering the filter with a cover slip during the analysis to keep it wet. The advantage of this method is that it is simple, quick, and nondestructive.

Image analysis was performed with a Kontron IBAS image analysis system, Zeiss AXIOPLAN microscope, and Hamamatsu model C2400 black and white, NTSC microscope video camera with a one-inch SIT

tube. Images 480 x 440 pixels were obtained from eight positions on each filter. These images were analyzed with transmitted light, and the total area covered by carbon black particles was measured. Analyses of solvent treated filters were performed at 400X magnification; filters treated with methanol/water were analyzed at 100X magnification.

PE-co-AA and PE pellets were pressed into disks to obtain flat, smooth surfaces for contact angle measurements. Approximately 10 g of pellets were placed between Teflon™ discs in a 1.5-in.-diameter, preheated, hardened tool steel die. The pellets were heated in the die in an oven for three hours at 110°C for

|                       | PE   |                    | PE-co-AA |                    |
|-----------------------|------|--------------------|----------|--------------------|
|                       | Mean | Standard deviation | Mean     | Standard deviation |
| Milli-Q water         | 81   | 4.2                | 78       | 6.3                |
| Paraffin oil (150 cp) | 32   | 3.3                | 30       | 3.8                |
| Silicone oil (100 cp) | 10   | 3.1                | 17       | 7.2                |

PE-co-AA pellets and 130°C for PE pellets. Finally, the pellets were pressed at 5500 psi until a stable load was achieved, and then the disc was removed from the die.

Prior to analysis the disks were washed with detergent, followed by acetone and then by Milli-Q water. Advancing sessile drop contact angle measurements were performed with a Ramé-Hart NRL contact angle goniometer. The liquids used included Milli-Q water, heavy paraffin oil, and 100-cp silicone oil. The data reported are the average of 20 measurements except for silicone oil on PE (6 measurements) and on PE-co-AA (8 measurements).

## Results

Carbon black was colloiddally dispersed in water using sodium laurate as a dispersant. The resulting dispersions did not aggregate and did not deposit onto the plastic pellets. The carbon black dispersions were destabilized by calcium chloride (0.004 M) addition resulting in the formation of carbon black aggregates. PE pellets (5 g) were mixed with 50 mL of aggregated carbon black, and the amount of carbon black not deposited (residual carbon black) was determined by image analysis. The quantity of residual ink is shown as the relative area of carbon black on the surface of the Millipore filter used to trap dispersed carbon black particles. **Figure 1** shows residual carbon black as a function of the thickness and type of oil coating on the PE pellets. With-

out oil treatment, there was essentially no deposition, whereas significant carbon black removal occurred with pellets having an average coating as thin as 1 nm.

Silicone oil appeared to give greater carbon black removal at 5 minutes than did mineral oil (**Fig. 1**). However, given enough time and pellets, both types of oils could remove all the suspended carbon black. Examples of the kinetics of carbon black removal are shown in **Fig. 2**. Most of the carbon black particles are deposited in the first 10 minutes. There was no evidence of detachment of deposited carbon black after 80 minutes of agitation. The effect of oil was more extreme at longer exposure times. After about 40 minutes exposure essentially all the carbon black deposited onto oil-coated pellets, whereas there was essentially no deposition on the pellets not treated with oil (oil-free pellet data not shown).

The role of pellet surface chemistry was investigated by comparing removal with oil-coated PE pellets (ATTANE) to removal with oil-coated poly(ethylene-co-acrylic acid) pellets (PRIMACOR). The experiments were conducted under conditions of constant total pellet surface area. The kinetic results in **Fig. 2** suggest that there was no observable difference in deposition rates. Untreated pellets were pressed into sheets, contact angles of water and oils were determined, and the results are summarized in **Table I**. In spite of the fact that the PRIMACOR pellets contained 9.5 mole% acrylic

acid groups, the contact angle results were similar on the two surfaces. Spreading experiments indicated that the oils spread more quickly on the PE surface than on the PE-co-AA surface. Solvent was used when oil-treating the pellets for the deposition experiments, and observation of pellets treated with dyed oils suggested that our procedure gave uniform coatings.

The effects of pellet surface area are illustrated in **Fig. 3**. With only 0.5-g pellets, the rate of removal and the maximum amount removed was lower. At the end of the experiment the 0.5-g pellets were much blacker than the 5-g samples. Thus, the pellets appeared to have a finite capacity to collect carbon black.

PE pellets were coated with a 1- $\mu$ m-thick coating of silicone oil at three different viscosities: 10, 100, and 10,000 cp. Experiments were performed with 5 g per 50 mL of carbon black dispersion. The results of image analysis (water/methanol treated filters) are shown in **Fig. 4**. The rate of removal of agglomerated carbon black did not appear to depend upon oil viscosity.

## Discussion

The presence of an oil coating on the pellets was a prerequisite for efficient carbon black removal. In related work, Rubio and Holberg (3) used polypropylene pellets coated with emulsified oleic acid as a carrier substrate to separate fine particles from mineral pulps. They also found that the coating was necessary for the process to occur efficiently, but they did not minimize their use of coating material.

The oil can serve two roles. First, it could increase the deposition rate, perhaps by lowering electrostatic barriers to repulsion. Second, oil could increase the adhesion of deposited carbon black agglomerates, which in turn would retard detachment during mixing. Increased adhesion could occur because the oil formed a lens or bridging liquid in a

## Recycling

manner analogous to spherical agglomeration (5-7). This mechanism is illustrated in Fig. 5. We predict that the strength of oil bridges should be enhanced by increasing the oil viscosity or increasing the quantity of oil. Neither parameter seemed significant in our results.

Calcium ions were required to induce carbon black aggregation and deposition. Calcium is known to form insoluble salts with sodium laurate, so the effect of the calcium ions was to reduce electrostatic repulsion between carbon black particles and the pellet surface.

Blain and co-workers at ICI Canada have described a recycling technology in which newsprint ink is not removed but is agglomerated to a size that minimizes the optical impact of the ink in paper (5). In their process, dispersed ink particles agglomerate into large spherical particles. The carbon black particles in the agglomerates appear to be bound by oil, which originates from the ink or is added during pulping. Therefore, the main difference between ICI's technology and our work is the presence of the plastic beads, which act as a carrier for the oil and ultimately for the carbon black.

If we consider pellets used in this work as models for air bubbles in flotation deinking, we would predict that oil addition should improve deinking efficiency. Oil has been shown to improve some types of mineral flotation (8,9). Currently, we are investigating the potential for oil to improve conventional flotation deinking.

## Conclusions

The main conclusions from this work were:

- The presence of oil on the surface of the pellets was essential for collection of the carbon black; however, the thickness of the oil layer did not have a significant effect on the ability of the coated pellets to collect carbon black.
- Silicone-oil-coated pellets removed carbon black more efficiently than paraffin-oil-coated pellets.
- There was no difference between the ability of PE and PE-co-AA pellets to remove carbon black.
- The viscosity of the coating oil did not affect the carbon black

removal in the viscosity range of 10 to 10,000 cp.

- We speculate that the coating liquid acts as a lens or bridging liquid in a manner similar to spherical agglomeration. ■

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This work was supported by the Mechanical and Chemimechanical Wood Pulps Network of the Canadian Network of Centres of Excellence program. The authors appreciate the insight and advice offered by Gilles Dorris and Maureen O'Neill of Paprican, Jeanette Grant of ICI Canada, and Ivan Miletic of McMaster University.

Received for review Jan. 5, 1994

Accepted Feb. 20, 1994.