Deinking flexographic-printed papers: Destabilization of flexographic ink dispersions with copper compounds

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ABSTRACT: Flexographic printing inks form electrosterically stabilized colloidal dispersions in water that display extreme stability at the alkaline pH values of most wastepaper deinking systems. A significant amount of U.S. newspapers are now printed using water-based flexographic inks, and the residual inks from these sources are problematic to remove in deinking plants. A successful flocculant for flexographic ink particles used in deinking plant filtrate streams requires that both the electrostatic and steric components of colloidal stabilization be eliminated simultaneously. The present study shows the advantageous characteristics of cupric chloride in achieving rapid flocculation of flexographic inks. Flocculation experiments were performed with a model ink as well as a mixture of offset and flexographic inks from recycled newspapers. The critical coagulation concentration of cupric chloride has been compared to other chloride, nitrate, and copper salts. Copper(II) chloride has been found to be significantly more effective than other such salts in achieving destabilization and aggregation of flexographic ink particles. A possible flocculation mechanism of flexographic ink particles by cupric chloride is presented.

Application: The results of this study describing the colloidal properties of flexographic ink particles can point the way to further research into commercially viable approaches to deinking.

The move in the early 1990s toward printing using water-soluble inks has resulted in larger amounts of recycled paper printed with such inks entering industrial deinking plants. Water-based inks have been developed for flexographic, offset, and rotogravure printing systems. In particular, the printing of many newspapers has moved from the traditional lithographic offset process to the flexographic process. Such water-based ink formulations can eliminate issues with volatile organic compounds and are viewed as being more environmentally friendly; when these papers enter the recycle stream, however, they can have significant detrimental effects on deinking processes, such as those for recycled old newsprint (ONP). In the deinking plant, problems with flexographic inks in recycled newspapers involve at least three major issues: (1) their hydrophilic particles resist removal by standard alkaline flotation; (2) the particles are very small and can redeposit on fiber surfaces and in pores, where they remain irreversibly attached [1]; and (3) if a washing process is employed (with or without flotation), process water will become severely contaminated with ink.

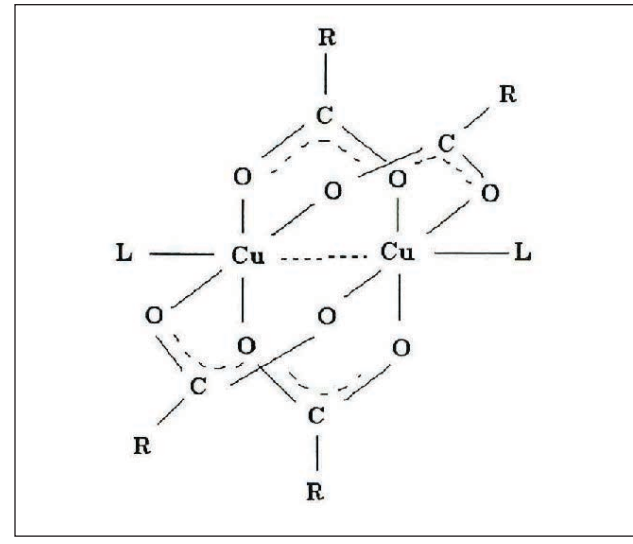
Water-based flexographic printing of newsprint has increased dramatically over time [2,3]. With the exception of old corrugated containers, ONP is recovered in the United States at the highest level of any type of secondary fiber grade—73% as of 2011 [4]. Thus, the recycled paper industry must process a massive amount of ONP, much of it now printed with water-based flexographic ink systems. In many industrial situations, any more than a 10%–15% concentration of flexographic-printed newspaper entering an ONP deinking plant can lower deinked pulp brightness to unacceptable levels [3,5]. Colloidal dispersions (such as water-based flexographic inks) with both a steric and electrostatic component represent the most robustly stable sols for these types of materials. This robust stability is most desirable in many situations, such as in paper coating colors (i.e., pigmented dispersions for one or two-sided coatings); in water-based latex paints; and in paper sizing dispersions, such as alkyl ketene dimer or alkenyl succinic anhydride. In the case of deinking of flexographic ONP, however, the formation of highly stable ink dispersions can be very problematic. The exact particle size range of such inks is somewhat variable, in some studies reported to be between 0.1 and 1 μm [6,7], and in another significantly smaller (50–100 nm) [8]. It has been found that dispersed air flotation in general is not effective for particles smaller than about 10 μm [9]. Earlier work in our laboratory found that flexographic ink particles simulated using Cabot carbon black were in the range of 200 nm under alkaline conditions [10]. For most inks containing carbon black particles, the *primary* particle size is on the order of 30–40 nm; however, when present as actual inks they are always aggregated to some extent into a larger size. The exact composition of the binder and the specific dispersion medium properties (e.g., pH, ionic strength) will ultimately determine average

particle size. It has been shown in many previous studies [6,10-13] that flexographic newsprint inks are indeed electrosterically stabilized under the moderately alkaline conditions typical of ONP deinking plants (pH 9–10). This stability is provided by polyacrylic acid-type polymers (such as sodium polyacrylate), which are used in the original ink manufacturing process to stabilize the ink particles as well as function as binders in the printing process.

The inability to adequately aggregate flexographic ink particles into larger sizes, combined with their hydrophilic nature in typical alkaline deinking systems, prevents their effective removal from wastepaper fiber by either conventional dispersed air deinking or by dissolved air flotation for clarification of the resulting residual process water from washing deinking [14]. Several research studies have focused on ways to somehow modify dispersed air flotation to handle flexographic newsprint inks, such as lowering pH to acid conditions [7]; using an acidic or neutral prewash stage [12]; using novel collector chemicals [3,6]; or using double flotation schemes, with or without an additional washing stage [8]. A particularly novel approach was that used by Shemi and Hsieh, where an electric field was combined with a standard flotation cell [15]. While some limited success was achieved, in some cases the gains realized were very small; in others it would be problematic to implement them commercially.

Because of the previously mentioned properties of flexographic newsprint particles and deinking difficulties using conventional flotation, the objective of the present study was to instead focus on the situation in which a washing process would be used to remove the particles. Limitations on water usage and discharge require a more or less closed water loop in plants; thus, it is necessary to be able to sufficiently clarify the washing filtrate for a deinking process to be feasible. It would be advantageous, then, to be able to identify one or more compounds that may accomplish successful aggregation of flexographic ink particles under alkaline conditions. The aggregation mechanism of these compounds could then potentially be replicated so as to clarify the washing filtrate.

Divalent ions such as calcium at high concentrations have been found to successfully aggregate flexographic ink particles under certain conditions [6,16]. These ions can form complexes with the polyacrylic acid groups present in flexographic ink dispersions [17]. Zinc sulfate has been used as a coagulant in alkaline water clarification from flexographic deinking with some success [18]. It is also possible to effectively remove flexographic ink particles from a water dispersion physically, as in the use of ultrafiltration [19]. In this study, we have investigated the use of copper-containing compounds and have found that such compounds can be very effective flocculating agents for flexographic ink particles. Copper compounds are known to have a high affinity for carboxylic acid groups that are present in flexographic ink stabilizers [20]. The interaction of copper with both adsorbed and free polyelectrolytes can be understood in the formation of a coordination compound [21].



1. Dimeric structure of copper with carboxylic groups.

A coordination compound can be defined as the combination of one or more central metal atoms within a larger molecule. Common examples of coordination compounds are vitamin B12, hemoglobin, and the common chelating agent EDTA (ethylenediaminetetraacetic acid). Copper complexes are known to be generally more stable than other divalent and trivalent metal ion complexes, such as nickel, cobalt, zinc, iron, manganese, and magnesium. Copper(II) chloride, or cupric chloride ($CuCl_2$), also possesses a higher affinity for carboxylic acid groups as compared to other divalent metals of the first transition series [22,23]. This higher affinity appears to be due in part to the stability of the dimeric structure shown in **Fig. 1** [20]. We sought to show that copper compounds can simultaneously (1) reduce or eliminate particle charge and (2) remove the steric component to stabilization imparted by adsorbed polymeric stabilizers. In addition, copper ions may interact with any free polyacrylic acid present in solution and tie up this additional source of potential stabilizing material.

Reducing the pH of the system can also result in a reduction of particle charge (for example, as measured by zeta potential) but, as noted earlier, lowering the pH to this extent in a commercial ONP deinking plant is not usually feasible. These complexation properties of copper compounds could potentially result in making copper-containing compounds excellent flocculating agents for flexographic ink dispersions. Regarding the dimeric copper structure in Fig. 1, the axial ligands L consist of undissociated carboxylic acid molecules [21]; or, in the absence of excess carboxylic groups, they may consist of water molecules [23]. Subramanian and Natarajan [24] have shown that the chelation of poly(acrylic acid) with copper(II) increases with increasing pH. At pH of approximately 2.5, however, most of the polyelectrolyte is in the protonated free acid form and chelation with cupric ions is minimal. Thus, acidic conditions would not likely be viable for flocculation with copper.

In a higher pH range (between 4 and 6), maximum chelation occurs, leading to the dimeric structure shown in Fig. 1. Above pH 6, chelation is still strong, but it is not further increased due to the coulombic interactions between ionic atmospheres of the surrounding molecules. Thus, copper compounds can effectively complex with polyacrylic acid groups at the mildly alkaline pH values that are typically employed in ONP deinking plants.

MATERIALS AND METHODS

Model flexographic ink

A model ink was made by ultrasonification of 0.44 g of carbon black in 750 mL of deionized water for a period of 2 h. A total of 2 min of mixing was done every 30 min during this time. An acrylic resin (Flexo F, S.C. Johnson & Son; Racine, WI, USA) was precipitated from the stabilizing/binder solution by lowering the pH to 1. It was then washed with deionized water until no further pH variation of the washing water was observed. The electrolyte-free acrylic resin was air dried for 24 h and then dissolved in a solution of 0.1M sodium hydroxide (NaOH). After 2 h, the precipitated acrylic resin in caustic solution was mixed with the ultrasonified carbon black according to the recipe shown in **Table I**. This is a typical composition used to prepare commercial flexographic inks for printing applications.

Black Pearls 420 carbon black was supplied by Cabot Corp. (Boston, MA, USA). Flexo F was used as the stabilizing acrylic resin (ammonium salt—3 wt%/monoethanolamine salt—27 wt%). The molecular weight of the acrylic resin was given as 50,000 g/g-mole with an acid number of 197 (the acid number represents the moles of NaOH necessary to reach the equivalence point).

Residual ink dispersions

Residual ink dispersions were obtained from laboratory washing deinking of flexographic/offset newsprint mixtures. The sources of ONP were the *San Francisco Chronicle*, a publication known to be printed with flexographic ink, and *The Daily* of the University of Washington, a publication known to be offset printed. The washing procedure was as follows: using a blender as a pulper, 70 g o.d. newspaper was weighed, torn into 25x25-mm strips, and placed into a stainless steel container. A total of 1930 mL of water and a specific recipe of deinking chemicals were added (chemicals used in repulping were NaOH, 2.2% [J.T. Baker Chemicals; Phillipsburg, NJ, USA]; sodium oleate, 1.0% [J.T. Baker Chemicals; Phillipsburg, NJ, USA]; and sodium silicate, 3.0% [Sigma-Aldrich; Milwaukee, WI, USA]). All percentages are based on o.d. fiber. These chemicals and dosages are typical for commercial repulping and washing deinking of ONP.

Carbon Black	Black Pearls 420
Polymer Concentration (g/L)	0.10
Volume of Flexo F in NaOH (mL)	0.89

I. Model ink composition. Total volume of (acrylic resin + NaOH + carbon black + water) = 1000 mL.

The entire mixture was agitated for 20 min at low velocity. Two 571-g samples of this fiber suspension were weighed exactly and diluted to reach a volume of 1400 mL and then thoroughly mixed. The actual washing process was simulated by applying hand pressure to the fiber lightly on a 150-mesh screen over a collecting container until a press cake was formed.

Turbidity

Turbidity was measured with a RATIO/XR turbidimeter (model 43900, HACH Company; Loveland, CO, USA). This turbidimeter is capable of measuring turbidities from 0.001 to 1999 nephelometric turbidity units (NTU). The reading of this apparatus is the ratio of the nephelometric signal (90°) to the sum of the transmitted light and forward-scattered light.

Critical coagulation concentration

To determine the critical coagulation concentration (CCC), concentrations (logarithmically scaled) of electrolytes were added to test jars with a model flexographic ink. The jars were shaken vigorously for 20 s and poured into turbidity cells. The cells were left to stand for 30 min. A control (no salt) was included for comparison. The salt concentration necessary to reach a turbidity of approximately 200 NTU was considered to be the CCC.

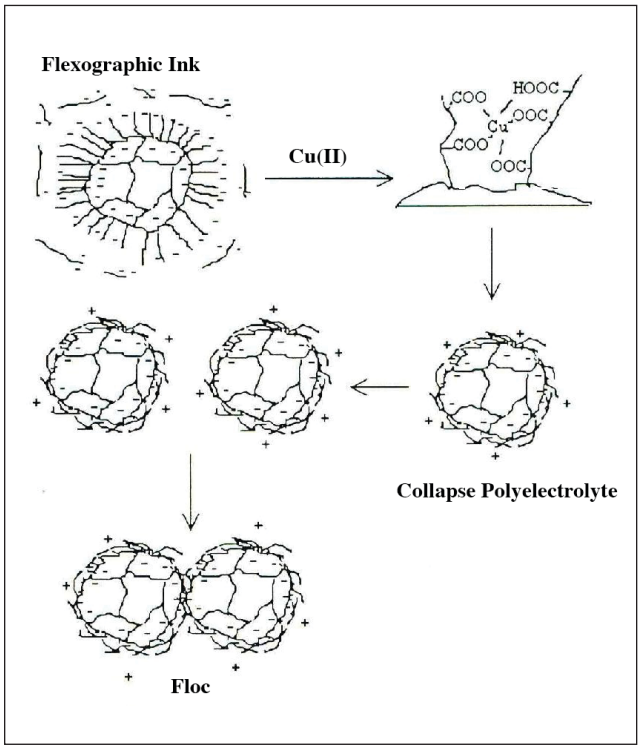
Zeta potential

Zeta potential was obtained with a Zetasizer 4 (Malvern Instruments; Southborough, MA, USA). It operates by the application of an electrical field that makes particles move through fringes created by two helium-neon laser beams. Scattered light from the particles is received by a photo multiplier where it is analyzed to give particle velocity. This particle velocity is converted to zeta potential with the Smoluchowski equation.

RESULTS AND DISCUSSION

A compound that will successfully flocculate electrosterically stabilized dispersions must be able to eliminate both particle charge and the steric component to stabilization simultaneously. It was found in this study that copper(II) chloride likely possesses this dual destabilization action on flexographic ink dispersions. A depiction of this destabilization mechanism by $CuCl_2$ for such colloidal sols is shown in **Fig. 2**.

The capacity of copper ions in inducing flocculation of flexographic inks can in part be attributed to the hydrophobization of the adsorbed polyelectrolyte. Indeed, the introduction of the sodium salt of acrylic acid into a solution of copper chloride has shown to immediately create water-insoluble fibers [20]. Other divalent cations (e.g., Ca+2) are



2. Destabilization mechanism by copper(II) for electrosterically stabilized dispersions such as flexographic newsprint inks.

known to form strong complexes with carboxylic groups [6]. This complexation may reduce charge and possibly cause the precipitation of the acrylic resin adsorbed onto flexographic ink particles [16]. To verify the effectiveness of copper and other divalent salts in flocculating flexographic inks, the CCC of $CuCl_2$, barium chloride ($BaCl_2$), and calcium chloride ($CaCl_2$) were measured and compared as shown in **Table II**.

Calcium chloride, $BaCl_2$, and $CuCl_2$ are all divalent salts that should have a similar effect on the flocculation of electrosterically stabilized systems based on charge reduction by the divalent cation. The CCCs of $CaCl_2$ and $BaCl_2$, as shown in **Table II**, are both approximately four orders of magnitude higher than the CCC of $CuCl_2$. The large difference in the CCC of $CaCl_2$ and $BaCl_2$ as compared to $CuCl_2$ should be attributable to the effect of the copper ion on the solubility of the polyelectrolyte in water because the anion is the same in all cases. In fact, as the flexographic particles are negatively charged at alkaline pH values, the cation is the relevant species for charge reduction and/or elimination. This large difference in CCC is an important piece of evidence in the ability of copper(II), as in $CuCl_2$, to flocculate flexographic inks.

This unusual effectiveness of $CuCl_2$ in destabilizing flexographic ink systems may be due to both the capacity of the Cu+2 divalent cation to rapidly collapse the particle electric double layer and its effect on the solubility of the acrylic resin, which would affect the steric stability component. Zeta potential was measured to compare the effect of copper and calcium ions on particle charge. The concentration of $CuCl_2$ and $CaCl_2$ necessary to reach a constant zeta potential value of -20 mV was on the same order of magnitude: 1.17E-4 moles/L and 5.03E-4 moles/L, respectively. This result implies that the more important characteristic of $CuCl_2$ is probably its effect on the steric stabilization component of flexographic inks and not simply reduction of particle charge. In recent work on the process known as electroflotation (where a current is applied to metal electrodes), it was clearly seen that using a copper electrode resulted in superior coagulation of flexographic ink particles [25]. In earlier work by the same authors using electroflotation, deinking of flexographic waste was also examined, but the type of metal electrode was not identified in the paper [7]. The present work presents for the first time a detailed mechanism that provides the understanding of exactly how copper compounds destabilize electrosterically stabilized flexographic ink particles. While the previous work cited reports vaguely on this effect, there was no attempt made to present a fundamental mechanism by which this phenomenon occurs.

The large difference between the CCC of $CuCl_2$ and $CaCl_2$ shown in Table II indicates a specific interaction between copper and flexographic inks. As previously pointed out, this interaction is likely attributable to the dimeric structure shown in Fig. 1. The formation of this structure was verified by measuring the ratio of carboxylic groups to copper ions at the CCC. The total number of ionized carboxylic groups in a 0.1g/L model flexographic ink can be calculated as 3.9E-4 mole/L. This value is approximately 3.3 times the concentration of copper ions necessary to reach the CCC of flexographic inks. It is also in accord with the ratio of carboxylic groups to copper ions (3:1) of the divalent copper structure shown in Fig. 1.

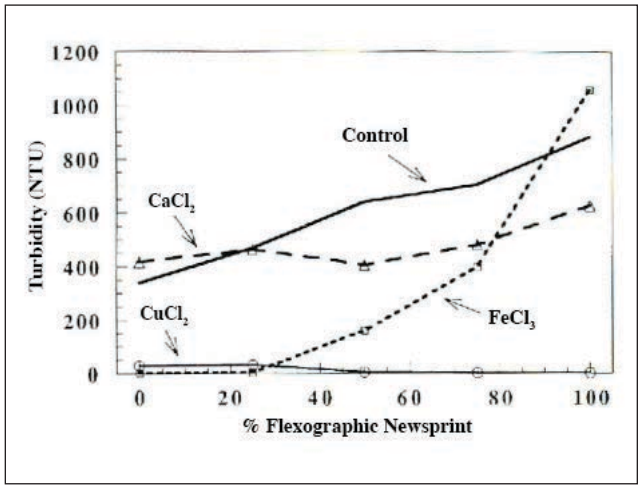
The effect of different copper salts in inducing flocculation of model flexographic inks at pH 10 was compared to

Salt	CCC (mole/L)
$CaCl_2$	9.53E-1
$BaCl_2$	9.42E-1
$CuCl_2$	1.17E-4

II. Critical coagulation concentration of a model flexographic ink upon addition of various salts.

Salt (mole/L)	CCC	CCC/CCC of $CuCl_2$
$CaCl_2 \times 2H_2O$	9.53E-1	8150
CuCl	1.01E-2	86
$Cu(NO_3)2 \times 3H_2O$	7.02E-4	6
$CuCl_2 \times 2H_2O$	1.17E-4	1

III. Critical coagulation concentration of a model flexographic ink upon addition of various salts at pH 10.



3. The effect of cupric chloride, calcium chloride, and ferric chloride (all three salts at a concentration of 3.9 E-3 mole/L) in the clarification of filtrate water after washing deinking of flexographic-offset newsprint at pH 10.

$CaCl_2$ via the measured CCC. Critical coagulation concentrations of copper(I) chloride (CuCl), $CuCl_2$, copper(II) nitrate ($Cu(NO_2)_2$), and $CaCl_2$ were compared as shown in **Table III**.

The molecular solubility of CuCl in water (0.0062 g/100 mL = 6.26E-4 mole/L) is lower than that of the other salts in Table III. This may be the cause of the inferior performance of this salt. Copper(I) chloride, however, was still about 100 times more effective than $CaCl_2$. The best flocculant was $CuCl_2$. The difference in the CCC between $Cu(NO_2)_2$ and $CuCl_2$ may be attributed to the larger size of the nitrate salt. The volume per mole of $Cu(NO_2)_2$ is 104.12 mL/mole and the volume per mole of $CuCl_2$ is 67.92 mL/mole. The larger size of the nitrate salt may prevent close approach to the ink surface as compared to the smaller copper salt. The closer the approach, the better the interaction to reduce charge and eliminate the steric effect.

An effective coagulant for the clarification of ONP washing deinking wastewater in commercial applications must be able to flocculate mixtures of flexographic and offset washing deinking inks simultaneously. The flocculation capacity of $CuCl_2$ and two other chloride salts of different valences were analyzed at the same concentration (3.9E-3 mole/L) on residual ink mixtures of flexographic-offset newsprint (**Fig. 3**). The control sample is the residual ink without any added salt.

As can be seen in Fig. 3, $CuCl_2$ was particularly effective (turbidity less that 50 NTU) in the clarification of water contaminated with flexographic-offset inks in all mixtures of flexographic and offset newsprint. It is interesting to note that very slightly lower turbidities were obtained with ferric chloride ($FeCl_2$) as compared to $CuCl_2$ for low concentrations of flexographic newsprint (<25%). Ferric chloride, however, leaves an unsightly yellow color after particle settling. At higher concentrations of flexographic ink, however, $CuCl_2$ is a far superior flocculant. It would not be surprising that offset ink particles would be stabilized by a different mechanism than flexographic ink particles.

Calcium ions may also form strong complexes with the carboxylate groups of the electrolyte stabilizer in flexographic inks under alkaline pH conditions [16]. This complexation may reduce particle charge as well as cause the precipitation of the acrylic resin onto carbon black. Increasing amounts of calcium ions may also change the aggregation kinetics of flexographic ink particles and the density of their aggregates considerably. In the presence of sodium oleate, calcium may cause flexographic ink particles to aggregate and become hydrophobic. This could happen when unstable ink particles would either coagulate (homocoagulate) to form larger ink particles, or form a deposit (heterocoagulate) making calcium soap particles. Such structures can vary from less than 50 µm for homocoagulates to more than 300 µm for heterocoagulates [16]. Apparently, the electrostatic charge of the ink particles is negated by calcium ions. Under these conditions ink particles will aggregate and be prone to precipitate with calcium soaps. This will render flexographic ink particles hydrophobic. However, on the basis of much prior work in attempting to use dispersed air flotation to remove flexographic ink particles with calcium chemistry, the formation of these calcium complexes may not be very significant because dispersed air has never been found to be effective in such situations. In our work, destabilization of ink particles by copper(II) was always seen to be significantly more effective than that produced by calcium-based flocculants.

The flocculation mechanism that we propose here between flexographic inks and $CuCl_2$ begins with the formation of a hydrophobic chelate between copper ions and the carboxylic groups of the polyelectrolyte. This hydrophobization reduces charge, causes the polyelectrolyte to collapse onto the particle surface, and facilitates agglomeration during particle collisions. Copper ions also precipitate the free polyelectrolyte in solution, preventing further polyelectrolyte adsorption upon reduction of particle charge. Once the steric contribution to stabilization has been significantly decreased, particle aggregation occurs. An important characteristic of the flocculation mechanism of flexographic inks with cupric chloride is that the chelation of the carboxyl groups of the polyelectrolyte by copper ions is not pH dependent in the range where most deinking plants operate (pH between 8 and 10).

A few final comments on the ramifications of this research are important to make.

First, hydrogen peroxide (H_2O_2) and/or sodium hydrosulfite ($Na_2O_4S_2$, also known as sodium dithionite) bleaching stages are commonly used for the production of deinked ONP. It is well known that heavy metal ions such as Mn+2, Fe+2 and Fe+3, and Cu+2 or Cu+3 will rapidly decompose H_2O_2 and render it ineffective for bleaching of fiber [26]. Thus, it is essential to use a chelating agent such as pentetic acid (DTPA) or ETDA in the bleaching stage to prevent this

from occurring. However, if a copper-based flocculation step were proposed for water clarification in a commercial ONP deinking process, it would be essential in process design to isolate the water loops between bleaching and water clarification to prevent this decomposition from occurring. Interestingly, it has been claimed that the magnesium ion Mg+2 actually stabilizes H_2O_2 in a pulp bleaching stage [27]. In the case of sodium hydrosulfite bleaching, heavy metal ions are also known to destabilize the bleaching liquor [28,29]. Thus, the same comments mentioned earlier regarding peroxide bleaching would also apply to using $Na_2O_4S_2$.

Second, were copper-based compounds to be used for deinking water clarification, there would be important considerations if effluent containing copper were to be sent on to a water treatment plant. Again, in this case it would be crucial to isolate the water streams to prevent any significant amounts of copper compounds being sent on to effluent treatment.

However, with regard to the previous two points, it is not the purpose of this work to propose or advocate the commercial use of copper salts in commercial flexographic deinking plants because of the earlier described effects of copper on effluent/remediation or bleaching with hydrogen peroxide and sodium dithionite. Rather, this work clearly identifies a successful flocculation mechanism of flexographic ink particles by $CuCl_2$. This discovery of this mechanism might then be a strategy to design new chemicals or processes to destabilize flexographic inks in ONP recycling plants without the previously mentioned limitations.

CONCLUSIONS

Cupric chloride is almost four orders of magnitude more effective than other divalent chloride salts such as $CaCl_2$ and $BaCl_2$ in inducing flocculation of model flexographic inks. The reduction of the steric component of flexographic inks by chelation of copper ions with carboxylic groups of the polyelectrolyte, along with charge reduction, is the most likely cause of this difference. In addition, $CuCl_2$ has been found to be more effective in flocculating flexographic inks than other copper salts and calcium salts, such as $Cu(NO_3)_2$, CuCl, and $CaCl_2$.

A possible flocculation mechanism of flexographic inks and copper (II) has been proposed. In this mechanism, a dimeric copper (II) complex with carboxylic groups eliminates both the electrostatic and steric factors that are responsible for the robust stability of flexographic ink dispersions. **TJ**

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We were interested in the exceptional stability of flexographic ink dispersions found in newsprint deinking plants, which caused process water contamination problems. This research identifies a particularly effective coaglulant for flexographic ink dispersions. It also corroborates related research with flexographic inks and copper metal done in 2011.

One of the biggest challenges in our work was developing a realistic laboratory model of actual flexographic ink dispersions. We needed a similar carbon black particle used in these inks, a flexographic ink stabilizer, and the correct dispersion methodology.

It was quite surprising that copper(II) compounds were so effective on a very robustly stable dispersion; this was not known in the literature at the time of this study. If the mechanism of stabilization we discovered could be used in a more environmentally friendly compound, a commercial product for destabilizing flexographic ink process water could be offered to deinking plants. The next step is use of this knowledge for product development by a chemical supplier to the paper industry.

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