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Investigation of Recycled Paper Deinking Mechanisms

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INVESTIGATION OF RECYCLED PAPER DEINKING MECHANISMS

by

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Veronika Husovska, Ph.D.

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The use of water-based inks is on the rise. Sub-micron pigment particles are used for flexographic and inkjet water-based inks. Conventional deinking eliminates larger particles than those from these new ink systems. Therefore, water-based inks represent recycling difficulty.

Deinking experiments of water-based inks are carried out. The deinking strategy initially investigated elimination of pressure sensitive adhesive due to similar acrylic polymer chemistry used in water based inks. The impact of pH on stickies and ink agglomeration during deinking is studied. Experiments in acidic regions show growth of acrylic inks and stickies agglomerates, simplifying elimination.

Pre-recycling of water-based inks is explored. Exceptional cleanliness of acidic circuit waters compared to alkaline is demonstrated.

Conventional wisdom claims an alkaline environment is needed for ink detachment from paper. It is found that the benefit of acidic milieu is the agglomeration of the pigment – resin complex of water-based ink. Further, flotation deinking of model inks is performed. Agglomeration and flotation of inkjet inks using surfactants is

performed to better understand ink behavior during deinking while limiting its re-deposition.

Three types of food grade soybean oils are tested for utilization in the paper recycling industry. Fatty acids extracted from oils are utilized in one loop flotation deinking of offset printed paper. Extracted fatty acids “A”, “B” and “C” had varied acid and saponification number. The effect of each of the soy-oil fatty acid on deinking is studied. Deinking results are compared to INGEDE 11p procedure, using oleic acid. It is discovered that fatty acids “C” and “B” have better deinking performance than oleic acid. Lower acid number acids perform better.

Acid “C” and bentonite clay is used in one loop - flotation deinking of inkjet printed-paper. Fatty acid “C” is compared against oleic acid. It is determined that fatty acid “C” has positive effects on deinkability.

The surface of the bentonite clay is altered by coating it with fatty acid “C”. Bentonite clay is successful in removing sub-micron hydrophilic inkjet ink pigment particles. Clay has a positive effect on the discoloration of recycled water.

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CHAPTER I

INTRODUCTION

Our society is striving to be more efficient and sustainable. The paper and printing industries are following this trend as well. Therefore, it is very important to recycle paper coming from all types of sources. Recycled paper is further used to produce different paper grades such as cardboard, packaging grades, office paper, newsprint and hygiene paper [Retner, 2008]. In the U.S. alone, the overall recovery of paper and paperboard was 66.8% in 2011, according to 2013 statistics done by American Forest and Paper Association [Anon, 2013]. It is forecasted that in the future, the trend for recycling and recovery will significantly increase. In addition to all of these recycling efforts, the goal is to produce light colored products out of recycled waste. In order to achieve this goal, ink has to be removed. A deinking process achieves ink removal. With the above-mentioned green attempt, deinking should be as gentle as possible and should not harm the environment. Another criterion posed on deinking is the production of high quality products [Retner, 2008].

Currently, the repulpability of tprinted office waste material is being evaluated by use of an industry-accepted laboratory "INGEDE Method 11p" [Fischer, 2010, Fischer, 2013], where a Hobart mixer is used for waste processing. However, in this work a MicroMaelstrom™ Laboratory Pulper type of slush–maker was used. A modified INGEDE method has already been proposed and adapted at Western Michigan University [Buitrago, 2011]. The main reason to use the laboratory MicroMaelstrom pulper is its resemblance of industry slush-makers. It is believed that this instrument mimics the commercial recycling process more than a Hobart type mixer. In this project, the INGEDE method will be modified to test various soy oil byproducts in their ability to replace oleic acid with the aim to help soy oil producers to find additional applications of their products. A flowchart for the INGEDE Method 11p [2009] is given in the Table 1.1.

Table 1.1 Repulping, storage and disintegration process parameters

Re-pulping recipe	Sodium hydroxide	0.6%
	Sodium silicate	1.8%
	Hydrogen peroxide	0.7%
	Oleic acid/Acid from soy oil #1 or #2 or #3	0.8%
Re-pulping conditions	Water hardness adjusted to	128mg Ca^{2+}/L
	Temperature	45°C
	pH	9.5±0.5
	Consistency	6%
	Mixing speed	500 RPM
	Re-pulping time	10 min
Storage	Consistency	5%
	Duration	60 min
	Temperature	45°C
Disintegration	Consistency	4%
	Duration	1 min
	Temperature	45°C
2 Filter pads and 10 handsheets were formed from undeinked pulp		
Flotation	Consistency	0.8%
	Duration	12 min
	Temperature	45°C
	Aeration flow rate	1L/min
2 Filter pads, 10 handsheets were prepared from deinked pulp, 2 membrane filters were prepared from water obtained after 2 filter pads were formed		

With varied sources of paper materials being recycled, multiple kinds of inks are introduced into the recovery process and due to the increase in digital print media in office and professional use, inkjet printed media are especially becoming very heavily studied [Chwalek, 2010]. Deinking processes are very efficient, for inks from conventional printing. Nonimpact printing technologies use inks that contain significantly smaller pigment particles than traditional processes. This has created a fear that inkjet ink cannot be removed during recycling. Due to the nature of inkjet ink, inkjet printed newspaper and direct mail act like a mop filled with ink [INGEDE, 2009]. As a result, both printed goods do not fit into high-grade paper recycling systems. Inkjet inks are either dyes that stain paper fibers or are very small particle pigments [Chovancova, 2005] that are readily dispersed within the paper slurry. Therefore, only dark shaded recycled paper may be produced [Retner, 2008].

Toner used in liquid electrophotographic printing (Indigo) causes another deinking problem [Firth, 2009]. Liquid toner creates very flexible ink film that comes off the substrate during the deinking process creating flexible specs in the recycled stock. With the current recycling process, it is almost impossible to get rid of these flexible specs. Therefore, recycled papers contain visible specs that are unacceptable by consumers [INGEDE, 2008]. According to laboratory deinking efforts of HP‘s scientists it is possible to deink LEP (Liquid Electrophotographic) prints via neutral deinking chemistry [Ng et al., 2009].

Flexo packaging is a sector of the printing industry, which is constantly growing, despite the economic downturn which occurred in 2010. Ae package not only has to be aesthetic;y pleasing, but also functional, to inform the consumer about its content, and protect its content from mechanical and chemical damage, such as oxidation, or deterioration by moisture. Packages are therefore becoming more and more sophisticated, and may be equipped with sensors or RFID tags or both [Hutchinson, 2002; Kipphan, 2001].

Manufacturers and customers are becoming more and more concerned about the environmental friendliness of the package. Environmental concerns have brought about a change in the packaging industry [Berg, 2007]. It has been found that consumers tend to purchase food products produced in a more sustainable way and about 45% of these consumers continue to buy "green" even with the higher price tag [Bruhn, 2009]. It was estimated that about 62% of U.S. consumers tend to buy from companies that put forth an effort to reduce waste and minimize pollution [Bruhn, 2009]. The food packaging industry is considering bio-based materials, which have become the replacement for products produced from nonrenewable resources.

Printing inks should produce less volatile organic components, thus water based and UV curable inks are employed wherever possible [Bruhn, 2009]. Post consumer wastes are being recycled, thus requiringUV and water based inks to be deinked. For water based flexo inks, acrylic chemistry is the primary binder used. [Kipphan, 2001]. Acrylic resins are also used in inkjet ink formulations [Samuel and Edwards, 2010]. Acrylic resins are soluble in an alkaline environment, but they precipitate at a pH less than 7, where free acrylic resins are formed from sodium and ammonia salts of acrylic polymers. In the process of deinking, an ink has to be detached from the paper to enable it to be collected by flotation. Because of the hydrophilic nature of flexo water based inks, their detachment is relatively easy, but flotation is difficult becausethe acrylic resins in the inksact like dispersants. Not only is the chemical nature of acrylics a problem, but their small particle size is also not suitable for flotation [Chabot, 1999]. Another approach to deinking these inks would be to formulate alternative water based resin chemistries to improve for more efficient deinking [Fischer, 2012].

This work focused on the improvement of flotation methods by means of pH change towards neutral and acidic regions, in combination with selected surfactants. The impact of temperature on deinking was also monitored. Re-pulping and deinking temperatures in the range of 30°C-50°C were studied in order to flocculate the acrylic resins and other binders used in the water-based ink formulations. Furthermore, different soy oils, derived from byproduct of food grade soy materials, were tested to determine if they could replace the oleic acid used in the INGEDE deinking protocol process.

CHAPTER II

LITERATURE REVIEW

Inkjet Technology

Inkjet technology belongs to non-impact-printing methods (NIP), printing without master image carrier such as printing plate, or engraved cylinder. Inkjet ink is very fast growing and versatile printing process [Klass, 2009]. It is very adaptable technique able to print on practically any substrate [Hutchinson, 2002; Hudd, 2008]. In this process, ink is transferred directly onto the substrate, based on computer signal. The intermediate image carrier is not needed as it is needed in the flexography and other conventional printing processes. Inkjet technology uses an extremely simple method of forming an image. Forcing a stream of tiny droplets onto the substrate creates an image. Inkjet printing can produce high quality images that are comparable to quality of conventional printing. However inkjet's speed is still not on the same level as the speed of conventional printing [Kipphan, 2001]. There are multiple inkjet methods. Their difference is in the way they deposit and control the stream of ink droplets. Some of the technologies might differ in ink choices. The basic division of inkjet technologies is visualized in Figure 1. The majority of these technologies use fluid inks while others can use hot melt inks as well.

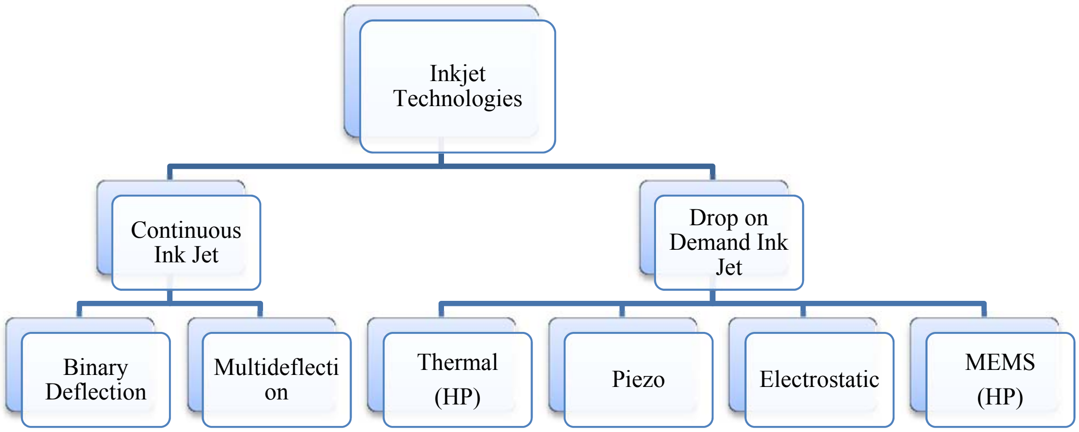

Figure 2.1 Inkjet technologies [Kipphan, 2001; Hudd, 2008]

Inkjet Inks

Inks for NIP technologies have special properties. The most important characteristic of the inkjet ink is fluidity. Ink should not clog the inkjet nozzles. In addition, the ink has to operate at a wide range of temperatures, ranging in between 5-45°C [Hudd, 2008]. With improving inkjet technology, the trend is to create smaller nozzles, which results in higher resolution images. Inks for office printers are primarily made from water-soluble dye. Dye based inks have brilliant colors and excellent contrast. They offer extensive color gamut. However they tend to fade over the time. They are more economical than pigment based inks [Kipphan, 2001]. Pigment based inks for inkjet printers are quick drying. The drying time is roughly 100 times shorter than that needed for dye ink drying. Once dry, the inkjet ink layer will be approximately a half micron thick. Drying mechanism of liquid inkjet inks is evaporation and absorption seen in the Figure 2.2 [Kipphan, 2001].

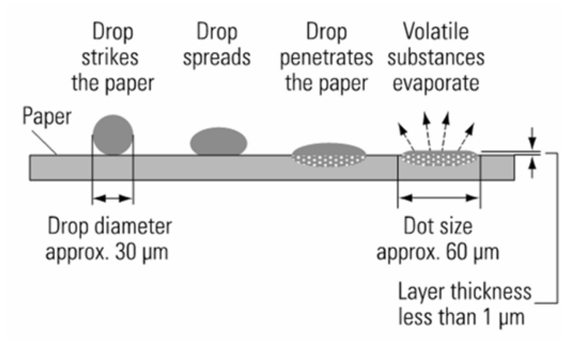

Figure 2.2 Drying mechanism of inkjet ink [Kipphan, 2010]

Pigmented inkjet inks are mostly used in high-end printers. Pigment based inks are stable and have a long shelf life. They are suitable for outside applications, since they are fade resistant [Hudd, 2008].

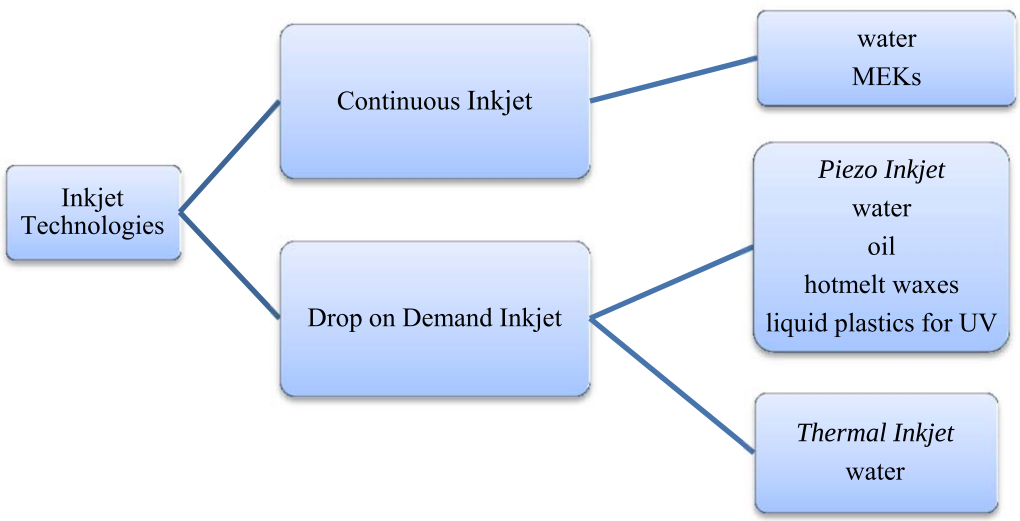

Figure 2.3 Solvents for inkjet technologies [Kipphan, 2001]

The viscosities of inkjet inks are very low. They range between 2-20 cPs. Despite changes in viscosity with shear rate, the majority of inkjet inks can be qualified as Newtonian [Magdassi, 2010]. Their viscosity has to be properly adjusted. Very low viscosity inks tend to spread fast before ink drying. For best printing results, the drop should be as spherical in shape as possible. This requires the adjustment of ink surface tension to 22-45 mN/m [Magdassi, 2010; Hudd, 2008]. The most suitable operating surface tension for solvent based inks range between 25-30 mN/m. The surface tension of water-based formulations is typically higher [Schmid, 2010]. The quality of a printed image is strongly related to the substrate characteristics and ink suitability. According to Kipphan, inkjet inks have a tendency to bleed on an absorbent substrate. Smearing is an issue for non-porous media [Kipphan, 2001]. Another important characteristic of water-based inks is their pH. The resin portion of an ink jet ink is often insoluble if the pH is very low. This is typical when acrylic resins are used [Magdassi, 2010]. For safety reasons, solvent-based inks can be used in continuous and piezo ink jets. Water-based pigmented inks can be utilized in continuous, thermal and piezo ink jets. The pigment particle size cannot be larger than the nozzle opening of the ink jet print head. Superior color strength is due to smaller pigment size. Inks have to be free of pigment agglomerates and should not settle. Solvent-based inks often use a blend of multiple solvents. As many as eight solvents can be used in an ink. Each digital ink is formulated with regards to the print head design. According to Schmid [Schmid, 2010], a typical water-based inkjet ink formula would contain the ingredients presented in Table 2.1.

Table 2.1 Generic inkjet ink formulation [Schmid, 2001, Hudd, 2008]

Constituent	Amounts	Role
Water	50 - 90%	Carrier
Pigment/Dye	1 - 15%	Color
Co-solvent/Humectant	5 – 50%	Keeps nozzles unclogged Ink vehicle Improves ink film development
Surfactants	0.1 – 2%	Enhances ink wetting
Resin	0.2 – 10%	Increases print's stability Boosts print gloss
Biocides/ Fungicides	0.02 -0.4%	Controls microorganisms growth
Buffering Agents	0.05 – 1%	Adjusts pH
Anti-corrosion Aid	0.01 – 1%	Inhibits corrosion
Total	100 %	

The deinking complications with NIP inks and toners have their origin in the physical and chemical composition of the ink because their structure and chemistry is often more complex than that of conventional inks [Carre and Magnin, 2003].

Flexography

Flexography is a printing process using a master image carrier, which is a raised image on a flexible photopolymer plate [Kipphan, 2001]. Ink is deposited from an ink fountain to metering roll, which may or may not be present, to an anilox roller equipped with a doctor bladeto doctor the excess ink from the surface, thus leaving ink only in the recessed cells of the anilox roll. The ink in the recessed cells of the anilox roll is then deposited onto a plate mounted on a plate cylinder. From the plate, the image is deposited onto the substrate (Figure 2.4).

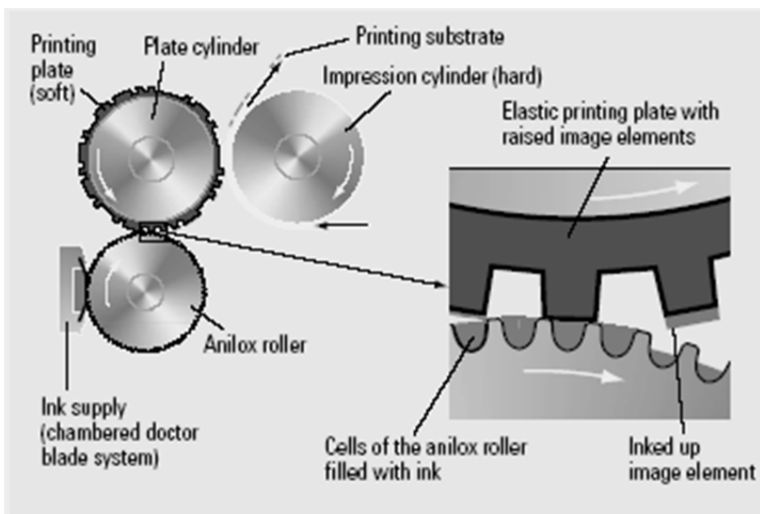

Figure 2.4 Principle of flexo printing [Kipphan, 2001]

Flexo is a process, which is growing even in today's non-favorable economic situation [Foley, 2005]. It is relatively cheap, compared to gravure. Its growth is mainly due to constantly improving print quality, its advantage of being able to print on virtually any substrate, constantly improving ink chemistry, rapid development in printing plate materials, and anilox quality. Flexo presses are equipped with servo motors, ensuring fast press set up and registration, resulting in less set-upwaste [Foley, 2005]. Flexo is especially growing in the packaging sector, where it is competing with offset printing for customers [Cole, 2010], using vivid colors, multiple color stations with the possibility of including specialty spot colors, special effect pigments, or metallic effects. Flexography is able to print on virtually any substrate, which can be paper, board, film or foil, aluminum, among others [Kipphan, 2001]. Paper substrates represent newsprint, uncoated papers, one side coated papers, two side coated, label stock, as well as boards, which can be different quality, from uncoated ones to the best quality SBS boards.

Today, recycled fibers represent about one third of the total fibrous material used as a source for flexo paper substrates [Alesse, 2001]. The rapid growth of Flexo is a reason and justification for improving the performance of deinking and recycling of flexo packaging paper substrates.

Many attempts have been made to use flotation deinking of water-based flexo inks, mostly for flexo newsprint [Upton et al, 1997; Ben et al, 1995; Fernandez, 1996]. Early trials were quite unsuccessful, because of the small particle size of the detached ink particles in the washing filtrates, which are not easy to trap and remove [Upton, 1997]. Flexo newsprint predominantly uses low molecular weight emulsion polymers, which probably create problems during washing and flotation [Chabot et al., 1999]. Water based packaging inks contain emulsion polymers along with smaller molecules of solution polymers in their formulas, thus there is a hope that the deinking process of packaging materials will be more successful in creating larger detached ink particles, than were formed during flexo newsprint deinking [Upton, 1997; Chabot et al., 1999].

Water Based Ink Chemistry

The inkjet and flexo processes use three different ink chemistries, which are solvent based, water based and UV-curable [Kipphan, 2001]. The industry is becoming more and more environmentally concerned, and therefore has reduced the use of solvent-based inks, which release undesirable volatile organic compounds. Water based and energy curable inks are the preferable choices. From a printing point of view, water-based inks are sustainable and cost effective in comparison with their solvent-based alternatives. Inks contain three basic components, colorants, resins or binders, and solvents [Kipphan, 2001; Magdassi, 2010]. To tailor inks for specific purposes, additives are also included in the formulation. Depending on the type of ink end-use, additives like waxes, anti-foaming agents, anti-pinholing additives, anti-slip agents, plasticizers, dispersants, wetting agents, and other additives are put into the ink formula [Kipphan, 2001; Magdassi, 2010]. Water based inks are formulated around acrylic acid and polymers and copolymers made out of it, such as acrylates, methacrylates, polyester acrylates, and polyurethane acrylates (Figure 2.5).

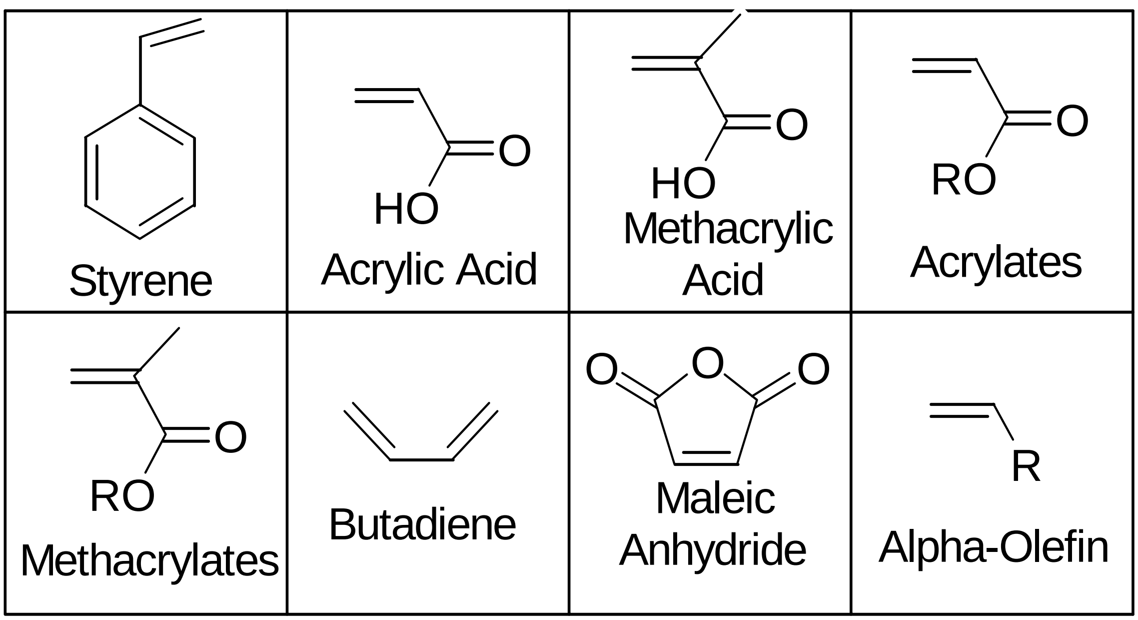

Figure 2.5 Monomers taking part in copolymerization of acylates used in water based inks

Along with acrylic acid, monomers like styrene, maleic acid, methacrylates, butadiene and alpha olefins (Table 2.2) are employed in the formulation of water based inks [Wyatt, 2008]. Each of the monomers is responsible for the development of specific ink properties (Table 3). Methyl methacrylates add water resistance to the final ink formulations, while acrylates impart ink flexibility. Therefore, it is always beneficial to use several different chemistries in ink formulations, because each component imparts different properties to the final ink. Acrylic polymers are acidic in nature, and need to be neutralized in order to keep them in the solution. The ammonium ion is the most common base, along with sodium ion, and amines, which are not as volatile, and give better pH stability on the press.

Table 2.2 Building blocks of acrylic resins for water based inks

Contributing Monomer	Final Property
Methyl methacrylate	Water resistance, block resistance, hardness, gloss retention, fast dry speed
Styrene	Water, block resistance, hardness, initial high gloss, poor gloss retention, fast dry speed
Short chain acrylates and methacrylates (R<8)	Flexibility, stain, rub resistance, adhesion
Acrylic and methacrylic acid	Adhesion, resolubility, hardness, solvent and grease resistance
Long chain acrylates and methacrylates (R>10)	Water resistance, flexibility, adhesion

Water based inks contain two different types of resins, solution and emulsion resins [Wyatt, 2008]. Solution resins may be dissolved in water in an alkaline environment, to create a true solution. Solution polymers are used in ink formulations to grind and disperse pigments. Their degree of polymerization is around 15,000. Because they have short chains, they are suitable for vigorous shaking and mixing, which happens during pigment dispersion. Solution resins enhance the ability of water to wet the pigment particles. They are responsible for ink resolubility on the press, and color stability of the printed ink.

Emulsion polymers are a second class of polymers, necessary for water based ink formulations [Wyatt, 2008] Emulsion polymers have a degree of polymerization around 150,000.They are long chain polymers, necessary for the development of ink film forming properties. They are added at the end of the ink formulation process, as a letdown vehicle. Because of their emulsion state, they are not suitable for vigorous mixing during pigment dispersion. Anyhow, emulsion resins do not wet pigments, but exhibit excellent ink drying properties. Emulsion resins form an emulsion, thus they cannot be dissolved in water. They are responsible for viscosity stability on the press, and are able to maintain a relatively stable viscosity under high shear conditions. Depending on their chemical make-up, emulsion polymers impart ink hardness or flexibility after drying, water resistance, and gloss. Both types of resins, solution and emulsion resins are necessary components of water based ink formulations and must be present in ink formula [Wyatt, 2008]. The example of starting flexo ink formulation is given in the Table 2.3.

Table 2.3 Starting formulation of water based ink [BASF, 2011]

Ingredient	[%]	Purpose
Pigment Dispersion	40-50	Colorant
Joncryl 2640 or 624 emulsion	30-50	Letdown emulsion for adhesion, flexibility and water resistance
Joncryl 60 resin solution	0-10	Resin solution for enhanced transfer, gloss and resolubility
Jonwax 28	5-10	PE wax emulsion for rub and scratch resistance
Surfactant	0-2	Improved film wetting
Silicone emulsion	0-1	Improved slip and adhesion
Alcohols	0-5	Improved dry speed and film wetting
Antifoam	0-1	Reduced foaming
Water	0-5	Diluent
TOTAL	100	

Pressure Sensitive Labels

Recycled pulp carries a multitude of contaminants. Besides ink particles, there are others that influence the recycling process and the quality of the final product. Pressure sensitive adhesives (PSA,) also called stickies, are typical macro contaminants. Therefore, before solving the problem of submicron flexo ink or inkjet ink pigment, macro particles have to be removed from the pulp.

Pressure sensitive labels are designed to adhere virtually to any substrate using very light pressure. The adhesion takes place without creating a chemical reaction [Creton, 2003]. A PSA label has a “sandwich” structure. It consists of the following layers: laminate, facestock, primers and adhesives. Each layer of this compact assembly plays a role in the recycling process. Stickies complicate the paper fiber recovery but also present problems associated with paper machine operations [Galland, 2006]. Often, stickies adhere to wires and other parts of paper machinery. This can further cause paper defects [Abubakr, 2000; Crossley et al., 2000]. Screening is an efficient and well-accepted stickies removal method. According to Cameron and Forester [Cameron and Forester, 2000], larger PSA particles play the most important part in the successful removal. The length of ta PSA particle presents its longest dimension while the width of the particle is its second largest dimension [Venditti et al., 2007]. The other properties responsible for stickies removal are their density and hydrophobicity. A PSA has a high elastic modulus and under specific conditions it tends to form large particles [Houtman et al., 2004]. Multiple studies indicate that the pulping temperature affects the particle size of stickies. An elevated pulping temperature (60°C) will create numerous small sized stickies. On the contrary, a lower pulping temperature (40°C) will result in more compact adhesive particles (Abubakr and Bormett, 1998; Peng, 2000, Galland et al., 2006]. In addition to pulping temperature, the trend is to lower the pulping time as well. The reason for doing so is to preserve the adhesives length while conserving energy [Merza and Haynes, 2006].

The chemistry of PSA can explain the fracture or the compactness behavior of the PSA particles in the given pulping conditions. Similar to water-based ink, adhesives have acrylic or modified acrylic chemistry. In addition to this class, adhesives are often natural rubber or polyester based [Abubakr and Bormett, 1998; Galland, 2006]. These materials are soft and weak, viscoelastic solids [Verhulst et. al., 2006, Creton, 2003]. Beside the base polymer, the adhesive formulation can consists of tackifying resin, plasticizer and stabilizer [Guo et al., 2000].

Acrylic Based PSA

Acrylic based PSAs are very popular due to the formulation flexibility, low cost and good performance [Venditti et al., 2007; Guo et al., 2000]. Acrylic PSA are often copolymers of a long side-chain acrylic having a low glass transition temperature (T_g). An example would be n-butyl acrylate [Creton, 2003]. Quite often, the short-side chain acrylic accompanies the long-side chain acrylic. An example of a short-side chain acrylic is methyl acrylate. Its role is to adjust the $T_{g.}$ Acrylic acid might be found in a PSA formulation if there is a need to improve adhesion s. The role of the acrylic acid is to also optimize the elongation properties of the PSA. An acrylic based PSA can contain a tackifying resin, but will perform well without one [Creton, 2003].

Styrenic Block Copolymers Based PSA

The most modern PSA's are formulated using styrenic block copolymers. The blocks are a combination of styrene-isoprene-styrene (SIS) triblock and styrene-isoprene (SI) diblock. The blocks are fused together with a low molecular weight resin having high T_g. This low-molecular weight resin is based on a five-carbon ring. The unique feature of such a resin is its miscibility with the isoprene phase along with immiscibility with styrene phase. In contrast to acrylic based PSAs, styrenic block based adhesives must contain a tackifying resin [Creton, 2003].

PSA Recycling

The green movement encourages paper recycling. The government supports these efforts. Due to modern pressure sensitive post stamps the issue of stickies removal became important for postal services. Therefore, experts from industry and the USDA's Forest Products Lab worked together to address the issue associated with pressure sensitive labels in posaget stamps [Peng, 2000]. The environmentally benign adhesive (EBA) was classified and testing protocols were prepared. The list of EBA pressure sensitive adhesive was collected in a Qualified Product List in USPS P1238-F [Peng, 2000].

In addition, the U. S. Postal Service along with the Tag and Label Manufacturers Institute, INC developed a series of protocols to set PSA recycling standards.

Deinking Processes

Deinking of old printed-paper is done using multiple steps, involving screening, cleaning, washing and/or flotation. Stock is first shredded, soaked, and deinking chemicals are added. Old print is decomposed into fibers. Paper waste is re-pulped via a disintegrator or pulper [Carre and Galland, 2007]. The main goal is to separate ink film from fibers, which can be done based on differences in their physical properties such as specific gravity difference. Large particles (100 to 300μm) are removed mainly by screening and cleaning, while smaller particles are removed mostly by flotation or by a washing method [Moss, 1997]. Often, the deinking process involves a combination of these techniques. The flotation process introduces the air bubbles into the fiber slurry, diluted to about 1% consistency (Figure 6). The movement of the slurry and the air bubbles force the ink to float in the form of foam. The ink foam is then collected. Increased temperature positively influences results of flotation deinking. The flotation process takes place in a flotation cell (Figure 7). Flotation is designed to eliminate hydrophobic elements. Often, surfactants are used during the flotation process [Carre and Galland, 2007].

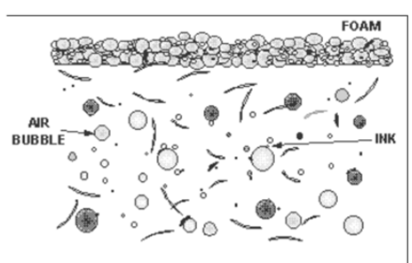

Figure 2.6 Flotation mechanism [Carre and Galland, 2007]

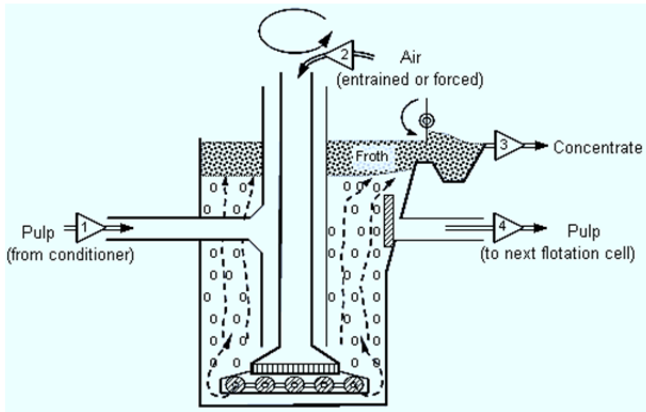

Figure 2.7 Schematic of flotation cell [http://en.wikipedia.org/wiki/File:FlCell.PNG]

During the washing process, the fibers are separated from the removed ink, physically, due to differences in particle size (Figure 2.8). Washing methods can produce whiter fibers, however, it requires large amounts of water. Therefore, the washing method is not viewed as “green”.

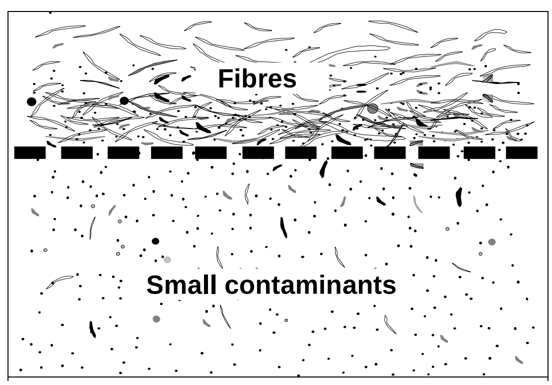

Figure 2.8 Washing mechanism [Carre and Galland, 2007]

Surfactant addition is essential in order to decrease the surface tension of aqueous slurries, which will decrease with increased concentration of surfactant. This action will be observed until the surfactant's critical micelle concentration is acieved (Figure 2.9). After this point, the surface tension of the liquid will continue to be the same despite additional amounts of surfactant [Kosswig, 2000]. An elevated temperature decreases the surface tension, which results in a reduced bubble merging. The reduction in bubble coalescence results in a higher amount of smaller bubbles. This might then increase the number of collisions among ink and air bubbles [Beneventi et al, 2006].

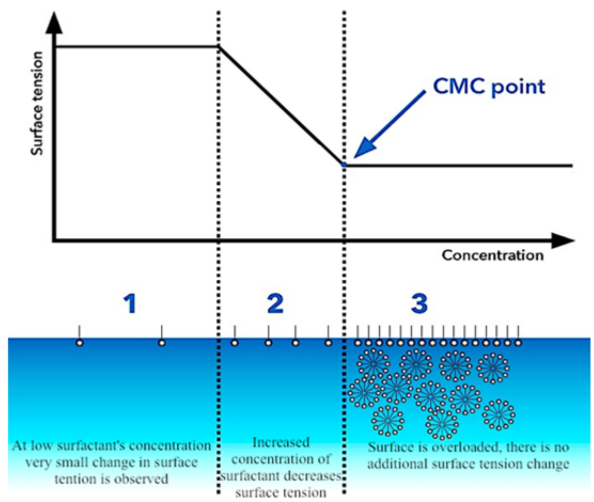

Figure 2.9 Visualization of the arrangement of the critical micelle formation [http://www.attension.com/critical-micelle-concentration.aspx]

Smaller air bubbles improve deinking efficiency [Van de Ven et al, 2001]. Another way of creating small bubbles is through the application of an electric field. The electrolysis of the water generates small bubbles, which then improve the deinking efficiency. This is also done at a slightly elevated temperature [Jagannadh and Hsieh, 1993].

Traditionally, the deinking process involves highly alkaline conditions. The alkaline environment causes the solubilization of the acidic ink binders of water-based inks used in inkjet technology, as well as, in traditional flexography. Further, this causes the dispersion of the pigment particles into the recycling slurry. In some cases, two stage flotation processes were performed, acidic stage followed by alkaline flotation [Galland, 1997; Galland 1993]. The collection of the pigment in the flotation method is strongly dependent on the particle size. Conventionally, the flotation deinking process benefits from the ink particles in the range of 20 micron in size. The challenge of flexo ink flotation is their small sub-micron particle size. In addition, most inks both traditional and NIP technologies have sub-micron primary pigment particles, because of the relationship of particle size to the wavelength of visible light [Frimova, 2005, Chovancova, 2005].

The colloidal stability of water-based inks was studied using different ions such as Na^{+}, Ca^{2+} or Al^{3+} [Zhang, 2007]. It was found that colloidal stability decreases with decreasing pH, and water based ink reach a zero charge below pH 3.1. Especially Al^{3+} was very efficient in coagulating water based ink particles [Zhang, 2007]. Another study, dealing with deinking of water based printed films measuring zeta potential of water based ink, showed that they reach zero charge at pH =3.6 [Gecol, 2004]. Above this value, water based inks are negatively charged in water solution. Some deinking studies state that the combination of flotation processes with implementation of an electric field can make the deinking of these inks more efficient [Shemi, 2008].

Contaminants are removed during the recycling process. This can be done since they have different characteristics than fibers, fines and fillers. Size is one of the differences. Washing can separate those particles that are smaller than fibers. Screening is used to separate those contaminants that are larger and stiffer than fibers. Other dissimilarity is the density. If the size of the particle is large enough and its density is other than 1, it can be removed by centrifugal cleaning. There are cleaners designated to remove high-density particles (density superior to 1). Others are engineered to remove particles that have density inferior to 1. Finally, surface properties can differentiate fibers from contaminants.

Pulping Consistency and Typical Pulping Conditions

Pulping consistency varies between 5% - 18% and it is based on the efficiency of the pulper. The benefit of higher pulping consistency is lower water use and increased concentration of pulping chemicals [Gottsching and Pakarinen, 2000].

Typically, caustic soda is used with the intention is to swell the paper fibers and ease the ink removal. At this stage; pH in the pulper ranges between 9-10. The efficiency of fatty acid soaps,collectors, depends on a highly caustic environment. Caustic soda is changing the color of the fibers, leaving them yellowish. Hydrogen peroxide is a bleaching aid that is used with intentions to reduce the yellowish cast of fiber. The efficiency of the bleaching agent is assured at high pulping consistencies at elevated temperatures [Gottsching and Pakarinen, 2000].

The addition of chemicals makes the recycling process more efficient. Dosing chemicals are applied in small quantities at specified intervals and order. Often sodium silicate is used as a dosing chemical. It is a water-soluble polymer with ion binding power [Gottsching and Pakarinen, 2000]. Sodium silicate is also an effective dispersant with buffering control, keeping the pH in a high range. Typically, 1% of sodium silicate is used in conventional fatty acid soap deinking. It was observed that an increased dose of sodium silicate from 1% to 2% decreases the total flotation loss of the fiber, fines and ash. On the other hand, it was noted that a doubled dose of sodium silicate decreases the ink removal [Beneventi et l., 2007]. Alkaline deinking has been proven to produce the brightest pulp, but true-neutral, non-sulfite deinking can produce similar brightness results [Morrow et al., 2005].

Neutral Deinking

Neutral deinking is challenging and has issues that do not exist in alkaline deinking. Among these are the lower ink detachment, higher ink redeposition and poor ink removal in the flotation step [Roring and Haynes, 1998]. On the other hand, work performed in multiple world location showed that sulphite based neutral deinking can produce similar ERIC values of the final deinked pulp. The benefit of neutral deinking is the decreased stickies formation and better paper machine runnability [Haynes and Merza, 2006].

Scientists from HP presented the prospect of near-neutral deinking without using bleaching aids, while still obtaining "good deinkability". Their focus was the deinking of dye-based inkjet printed substrates and LEP with the possibility of effectively transferring near-neutral deinking approach on other prints as well [Bhattacharyya et al., 2010]. This achievement was completed through the addition of nonionic surfactant during pulping and minute portion of anionic surfactant during flotation. It was found that a nonionic surfactant with an HBL value in the range of 10-12 was crucial for the successful deinking. This near-neutral deinking resulted in high flotation yield and had small fiber loss [Bhattacharyya et al., 2010].

Acidic Deinking

Ethoxylated amines were identified as deinking nonionic surfactants functioning well in acidic conditions [Gecol et al., 2002]. Despite their nonionic categorization, in acidic regions their behavior is of a cationic nature. Titration of specific ethoxylated amine revealed protonation in acidic environment. In general, ethoxylated amines demonstrate excellent wetting properties and emulsification both in acidic and alkaline regions [Gecol et al., 2002]. There is not much information about acidic region deinking using surfactant; therefore this work will focus on surfactant identification and their deinking capabilities in an acidic environment.

Ink Re-deposition

With low colloidal stability of the dispersed and detached ink particles there is often a probability that it will redeposit onto the fiber surfaces [Gottsching and Pakarinen, 2000]. There are three types of ink re-deposition. First type is lumen loading where the tiny ink particles enter the lumen via the pits of the fiber wall. This re-deposition is independent from the ink's surface properties. Both hydrophilic and hydrophobic particles can enter the lumen [Gottsching and Pakarinen, 2000]. Secondly, there is chemical re-deposition on the fiber surface. Last type of re-deposition is mechanical. Large ink particles re-deposit via last two mechanisms. The re-deposition can be omitted if the surface of the ink particles becomes hydrophilic. Caustic soda, peroxide and water glass assure the desired hydrophilic character of the fibers. Even a small presence of hydrophobic ink surfaces can cause re-deposition [Gottsching and Pakarinen, 2000].

Flotation Surfactants

A typical flotation is a three-step process and requires hydrophobic particles. It is a separation process and will not separate hydrophilic particles [Gottsching and Pakarinen, 2000]. First, the ink particles detach from the paper fibers. Secondly, ink particles adhere to the air bubble surface. Lastly, the froth removal takes place. The successful froth removal includes the ink particles removal from the flotation cell [Zhao et al., 2004]. Depending on the dosing and surface properties, surfactants can positively and negatively influence the deinking process. This unwanted effect can cause extreme frothing and weak ink flotability [Beneventi et al., 2010; Zhao et al., 2004]. Typically, the amount of surfactant used is in the range of 0.025 – 0.25% based on oven dry solids [Spence et al., 2009].

Surfactants used in flotation include both hydrophilic and hydrophobic groups. They can vary in their nature. The choice ranges from cationic, anionic, nonionic, and amphoteric. Though, the typical choice would be anionic fatty acid and nonionic surfactants [Zhao et al., 2004].

Dispersants

There are multiple reasons for adding a surfactant into a deinking process. Some surfactants act as dispersants. Their addition facilitates the separation of the fibers and ink particles. Further, it keeps them apart through the flotation process. Also, they have the power to change the particles nature from hydrophilic to hydrophobic. Lastly, their role is to act as frothers. Dispersants should create a stable foam layer for ink removal in floatation deinking [Zhao et al., 2004]. Dispersants also give solubilizing surface chemistry to ink particles. Ink particles with such surface chemistry can negatively influence the desired reaction with fatty acid soap collectors. Therefore, when it comes to flotation deinking, dispersants should be avoided or used with precaution [Zhao et al., 2004].

Nonionic surfactants are used as dispersants. Water hardness has no effect on their function. Some examples include ethoxylated linear alcohols, ethoxylated alkyl phenols, ethoxylated fatty acids, oligoethylene-oxide alkyl ether, and polyethyleneoxide alkyl ether [Zhao et al., 2004].

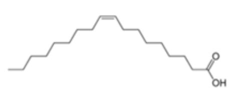

Figure 2.10 Oleic acid (18 carbons, 1 double bond)

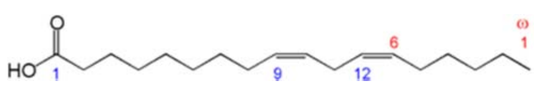

Figure 2.11 Linoleic acid (18 carbons, 2 double bonds)

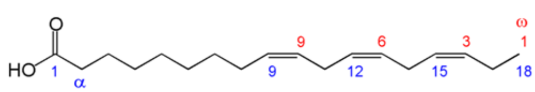

Figure 2.12 Linolenic acid (18 carbon atoms, 3 double bonds)

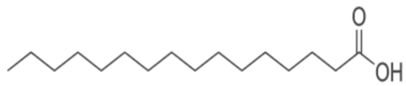

Figure 2.13 Palmitic Acid (16 carbon atoms, no double bonds)

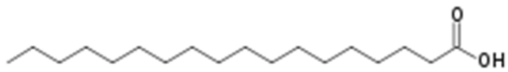

Figure 2.14 Stearic Acid (18 carbon atoms, no double bonds)

Collectors

The addition of collectors into the deinking process causes agglomeration of the tiny ink particles. They improve the hydrophobicity of ink particles. Collectors also provide a hydrophobic surface to agglomerated particles. Besides agglomerating the ink particles, collector also adheres to air bubbles. Collectors are included in the pulping step or before flotation. There is also option to add them in the steps [Gottsching and Pakarinen, 2000; Ruthland and Pugh, 1997]. There are a variety of collectors. They can be as simple as fatty acids (Figures 2.10-2.14), but also more complex semi-synthetic and synthetic grades can be used. Soap collectors are added in higher dosage than semi synthetic and synthetic collectors.

Fatty acids form soaps that adhere to ink through calcium ions [Gottsching and Pakarinen, 2000]. These collectors are made through the saponification of the triglycerides. The richest fatty acids are the ones having 16-18 carbons. Elevated pH during pulping stage is especially critical when fatty acid soaps are used as collectors [Gottsching and Pakarinen, 2000]. Collectors based on fatty acid-calcium soap chemistry produce foam desired for ink removal and result in good final brightness. Often, there can be too much foam generated. Therefore, some collectors will act as defoamers [Zhao et al., 2004]. Fatty acid soap collectors can be carried to a paper machine and negatively influences the paper production by depositing onto the paper machine [Gottsching and Pakarinen, 2000]. One deinking study indicates that better deinkability is obtained with combination of fatty acid-surfactant blend than with fatty acid soap alone [Beneventi et al., 2007].

Water hardness has no impact on synthetic collector's performance. Their dose is significantly lower than that of fatty acid soaps. The final brightness of the pulp is unfortunately lower than pulp retrieved using natural or semi-synthetic collectors.

Synthetic collectors may act as ink dispersants in the pulping stage [Gottsching and Pakarinen, 2000]. Synthetic collectors also have hydrophobic and hydrophilic part. Therefore, they can be anionic, nonionic or cationic. Nonionic surfactants are the most typical ones used in deinking. Among those, ethylene oxide and propylene oxide copolymers, alcoxylated fatty alcohols and alcoxylated fatty acids play the most important role [Gottsching and Pakarinen, 2000]. From am environmental point of view, it is preferable to use ethoxylated fatty alcohols and fatty acids due to their easy biodegradability.

Semi-synthetic collectors are emulsions and combine the benefits of natural soaps and synthetic collectors. They are water-miscible. The dosage is roughly half of soap collectors and function well is soft water. It is possible to obtain similar pulp brightness as with fatty acid soaps. On the other hand semi-synthetic collectors are more susceptible to process changes than fatty acid collectors. Semi-synthetic collectors are added into pulping stage. They require activation time in order to act in the flotation [Gottsching and Pakarinen, 2000].

When comparing conventional fatty acids soaps to a surfactant –fatty acid blend, Beneventi et al noted that the blend has a positive impact on ink removal along with decreased fiber loss as well as other losses [Beneventi et al., 2007]. This effect can be even improved when using a surfactant-fatty acid blend along with 2% by weight of sodium silicate [Beneventi et al., 2007].

Frother

Froth is necessary for successful ink removal. Frother adsorbs on the fiber while reducing the bonds between fibers. The concentration of the frother is critical. The frother adsorbs onto the ink particles. It decreases their surface energy and adversely affects e ink removal. Also, too much foam causes an increase in fiber loss [Göttsching and Pakarinen, 2000].

Hydrophilic Lipophilic Balance (HLB)

HLB depicts interactions between nonionic surfactant and hydrophobic and hydrophilic material. With low HLB value, the impact from the hydrophobic component of the molecule is greater than from its hydrophilic portion, while with the high HLB situation is opposite. HLB value is a helpful tool in predicting water-soluble properties of a nonionic surfactant [Göttsching and Pakarinen, 2000]. An application for surfactant has an HLB requirement. If the HLB value of the surfactant matches the HLB requirement of the application, the surfactant will perform very well. The HLB scale range is between 0.5 – 19.5. For illustration, an HLB value of oleic acid is 1.0 while sodium oleate's HLB is 18.0 [Göttsching and Pakarinen, 2000]. Examples of HLB requirements for different pigments are listed in the Table 2.4 and Table 2.5.

Required HLB for Pigments Used in Water-based Inks

Table 2.4 Organic pigment's HLB requirement [http://www.airproducts.com/~/media/Downloads/Data%20Sheets/surfynolCT-136-datasheet-120-9930.ashx]

Organic Pigment	Required HLB
Azo Yellow	13-15
Phtalocyanine Blue	11-13
Phtalocyanine Green	10-14
Quinacridone Violet	11-13

Table 2.5 Inorganic pigment's HLB requirement [http://www.airproducts.com/~/media/Downloads/Data%20Sheets/surfynolCT-136-datasheet-120-9930.ashx]

Inorganic Pigment	Required HLB
Carbon Black	10-12
Molybdate Orange	16-18
Red Iron Oxide	13-15

Problem Statement

Both printers and papermakers are trying to be more "green", and thus the recycling of post consumer waste is becoming a must. With recycling, all kinds of mixed waste come to recycling facility. Therefore, recycling facilities have to be flexible and be able to remove macro and micro contaminants. Due to environmental concerns, more and more water-based ink is being used in conventional and NIP technologies. The recycling of water-based inks is challenging due to small pigment particle size often submicron in size. Traditional deinking eliminates significantly larger particles. Therefore novel water-based inks for flexography and inkjet pose a huge issue to recycling facilities. This experimental work will focus on recycling of stickies and deinking of water-based prints. In addition, mentioned deinking ideas and approaches will be applied on other NIP printed substrates. Following are the scientific questions that helped to guide experimental work.

1. Is it possible to eliminate stickies while positively impacting tht deinking process of water-based conventional and NIP inks?

   The chemistry of conventional and NIP water-based ink is very comparable. The pigment particle used in NIP is significantly smaller then pigment used in eonventional water-based flexo inks. While pigment sizes are different, resin chemistries are alike. Pressure sensitive adhesives are in general acrylic based. Water-based inks are based on the same chemistry. Therefore the pulping conditions have an impact on adhesive as well as on water-based inks.

2. Which pulping conditions play most important role in elimination of macro-contaminants? Will these conditions also affect deinking of water based conventional and NIP inks?

   High pulping temperatures cause fracture of the pressure sensitive adhesive and it creates numerous small sized stickies in the recycling process. Therefore, pulping temperatures will be changed and their impact on stickies removal and deinking will be monitored.

   In addition to pulping temperatures, the chemicals used during pulping negatively affect the particle size of the adhesive as well. Pulping pH will therefore be shifted into the low pH regions. In the acidic regions, carboxylic acid groups are pronotaned, which is causing the agglomeration of the binder and respectively growth of adhesive particle size. This should be desirable for screening and stickies separation. In theory, similar mechanism will occur within water-based inks.

3. Which of the deinking processes will be most suitable for deinking of water-based conventional and NIP inks?

   Traditionally, deinking is done by washing and/or flotation. Washing and flotation are two main techniques for ink particle removal. Washing often results in whiter pulps. Washing requires large amounts of water, which is not sustainable. In this experimental work deinking will be performed via flotation. For successful washing, the particle size, shape and surface properties predetermine the success of the process. The flotation process is based on the collision of air bubbles and ink particles. The particle size of the ink for successful flotation has to be in the range of 10-250 microns. A model system will be used to monitor and optimize the flotation. In the model system, only inks will be treated under flotation deinking conditions. It is expected that inks will precipitate under acidic conditions and solubilize at alkaline conditions, as it happens with water-based inks. At first, only model inks will be tested in flotation deinking experiments, with variable pH, mixing speed and temperature. the change in particle size due to flotation conditions will be monitored. If n optimum precipitation conditions are found, then these conditions will be further tested in real fibrous system, using printed paper substrates in flotation deinking experiments.

In addition to standardized INGEDE type flotation, proposed flotation process will be carried out also under acidic conditions. This is proposed in the anticipation of leaving acrylics, maleics and copolymer chemistries in free acid stage, in which they are insoluble in water, thus more suitable for flotation. To overcome the small particle size of digital inks and water based flexo inks, agglomeration prior to flotation will be carried out. Agglomeration will employ select surfactants to create particles above 25 micron in size. Alternative methods will be used to polarize acrylic resins and employ direct electric current for their separation in a modified electrophoresis process.

4. What is the effect of pH on water-based conventional and NIP inks?

Traditionally, deinking is performed in an aqueous alkaline environment. Alkaline pH does not favor deinking of water based inks because of their nature- if the acrylic polymers, present in water based inks stay in salt form, they are soluble in the aqueous solutions. The flexo-water based ink fragmentation is significantly reduced when moving away from alkaline deinking towards neutral conditions. This work will therefore examine near neutral and non- traditional, low pH regions for flotation deinking process. Alkaline conditions described in INGEDE method 11p will be followed as well.

5. Which pulper will be used for repulping? Are there any energy benefits related to one or the other pulping device?

   A Hobart type pulper will be used as a reference pulper. This type of pulper is widely used in recycling and it is accepted by laboratory method "INGEDE Method 11p". During the experiments MicroMaelstrom^{TM} Laboratory pulper will be used for waste processing. This instrument was chosen for its similarity to pulpers used in industry. In addition, preliminary studies indicate that similar consistencies can be processed in both pulper types. The MicroMaelstrom^{TM} Laboratory pulper also has the potential to cut down the processing time.

Contributions of this Work to Forward the Science in the Field

The contribution of this experimental work is to improve the recycling of pressure sensitive label stock and water-based ink for conventional printing process and for NIP technology inkjet. The approach is to solve the problem of stickies and inks in one, not in two separate studies. The hope of succeeding is that the chemistry of both contaminants (ink and stickies) has much in common. Therefore, the goal is to target one contaminant first while influencing the removal of the other as well. The ultimate goal is to transfer deinking technology to NIP printed substrates.

Also, the experimental work will follow and combine the recycling protocols for the PSA recycling method and INGEDE recycling method for inkjet/water-based ink removal and deinking assessment.

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CHAPTER III

ELIMINATION OF PRESSURE SENSITIVE LABEL AND DEINKABILITY OF WATER BASED FLEXOGRAPHIC AND NIP INKS IN ONE RECYCLING STEP

Summary

Due to environmental concerns, water-based inks are more progressively being used in conventional and nonimpact printing (NIP) technologies. Water-based flexo inks, as well as, inks used in NIP technologies contain significantly smaller pigment particles than traditional litho inks [Chovancova et al, 2005; Frimova et al, 2005]. Conventional deinking eliminates significantly larger pigments than particles coming from new ink systems. Therefore, novel water-based inks for flexography and inkjet pose a huge issue to recycling facilities. Pressure sensitive label is a significantly larger contaminant of recycled fibers than inks. It was realized that its chemistry and chemistry of novel inks is very similar. Both types of contaminants are based on acrylic chemistry.

This experimental work focuses on the deinking of water-based flexo and NIP inks. Elimination of pressure sensitive adhesives in this experimental work serves as a model for ink elimination procedures due to similar chemistries, thus similar behavior. The impact of pH on stickies and ink agglomeration during deinking was studied. Experiments demonstrated that an acidic pH causes acrylic based inks and stickies to grow in size, which eases their removal.

Introduction

Environmental concerns and a shortage of various raw materials have made consumers aware of the need to recycle. The paper and printing industries are following these eco trends as well [Tischner et al, 2003]. Recycled fiber comes from various sources. The criteria for recycled paper are high. They require the fiber to be clean of impurities, since it is further used for the production of cardboard, packaging and newsprint paper grades, office paper, and hygiene paper. Consumers goods made out of recycled fiber should be light colored, which requires the elimination of the previously used ink [Laroche et al, 2001; Retner, 2008]. A recycled paper stream carries a multitude of contaminants. To simplify their characterization, they can be divided into two major groups. The first group is represented by macro contaminants, such as pressure sensitive adhesive (PSA). As mentioned, recycled pulp has to result in light colored products. But before solving the deinking issue and choosing proper deinking chemistry, macro contaminants have to be eliminated first. Typically, screening techniques are used to separate macro contaminants from the recycled pulp. Removal efficiency of macrostickies is 80% for particles ranging in size from 800 μm to 1000 μm. The successful complete removal of stickies is accomplished if the particle size reaches 2000 μm or more [European Recovered Paper Council, Retrieved 2013]. The second group of contaminants that enters the paper recovery system is called micro contaminants. Typical representative of the second contaminant's group would be the colorant. Inks and dyes are significantly smaller in size than stickies. Elimination of both groups of contaminants is based on their size. The larger the size of the contaminant means easier and more efficient removal. Flotation is the preferred method for deinking. Its principle is to collect ink particles on air bubbles and create froth layer. Froth is later removed by scraping. The particle size for effective flotation process has to be in the range of 10 µm to 250 µm [European Recovered Paper Council, Retrieved 2013]. There is wide pallet of chemistries that assure ink particle agglomeration.

In this experimental work, a simple approach is taken. The goal is to demonstrate that a simple change in pH can positively influence the growth of both pressure sensitive adhesive and ink particles. The chemistry of pressure sensitive label adhesive is based on acrylic polymers [Creton, 2003]. The choice of acrylic resin is abundant and it allows flexibility in a PSA's formulation. Furthermore, acrylic based chemistries are cost efficient and excellent performers [Guo et al, 2000; Venditti et al., 2007]. The chemistry of conventional flexo and NIP water-based ink is very comparable. While pigment sizes are different, resin chemistries are alike, mostly based on acrylic polymers chemistry.

Recycling and pulping conditions impact removal of adhesives as well as water-based inks. Due to the complexity of recycling, the focus of the experiment is to eliminate the macro contaminants first, and to comprehend the behavior of acrylic materials in various environments. High pulping temperatures cause fracture of the pressure sensitive adhesives and create numerous small sized stickies within the recycling process. In addition to unfavorable pulping temperatures, the chemicals used during pulping may negatively affect the particle size of the adhesive as well.

Therefore, the goal of this experiment is to create an ambient environment for the growth of PSA and ink agglomeration. Further, screening and flotation could benefit from this particle enlargement. In addition, it is possible that this would allow lower amounts or the partial omission of deinking additives.

Experimental

The first part of the experimental work was oriented on re-pulping, screening, handsheet preparation and evaluation of stickies formation. The second part of the experiment was focused on the behavior of resin and ink in various pH environments. A MicroMaelstrom™ Laboratory Pulper (see Figure 3.1) was used for substrate pulping. The duration of pulping was set-up to 10 minutes at 650 RPM.

Figure 3.1 MicroMaelstrom™ laboratory pulper

Re-pulping experiments were done with the help of a three factorial statistical design. The weight of variables on re-pulping was monitored. The first set of experiments was performed using unprinted "multipurpose" office paper (20lbs) with varied level of unprinted semi gloss label stock (60lbs). A high pulping temperature cause fracture of the pressure sensitive adhesive and creates numerous small sized stickies in the recycling process [Cameron et al., 2000]. Therefore, pulping temperatures were altered and their impact on stickies removal and deinking was monitored. Nine deinking runs were designed at different pH and temperature (Table 3.1). In three experiments, the pulping pH was adjusted to pH 9, which is commonly used within the paper recycling industry

[Galland, 2006]. In addition, pulping in the neutral region was performed [Galland et al., 1997]. Finally, pulping pH was shifted into the low pH region. The pH level in all experiments was adjusted with 1N sodium hydroxide or 1N hydrochloric acid.

Each of the nine runs from the laboratory pulper was screened. A laboratory vibratory screen with slots of 0.006" was used to screen the recycled pulp. The accepts were collected on a 200 mesh round screen. Handsheets were then prepared from the accepts. The aim was to evaluate the amount and size of stickies that passed through the screens into the accepts, if any. This screening was done using an RCA Specification (2012) for paper labels (Litho, Semi Gloss) that are coated with pressure sensitive adhesive. Protocol RC IAP – evaluates adhesive presence in paper handsheets via image analysis. RCA Specification employs dyeing of the handsheets with the goal of targeting unwanted residue of pressure sensitive adhesive [RCA Specification, Retrieved 2011].

Further, 20 g of "model" acrylic resin (water-based, commercial) was dissolved in 2 liters of deionized water. A total of three solutions were made and their pH adjusted to 5, 7 and 9 respectively. Solutions were stirred for 5 minutes and filtered with a Buchner funnel. Filter pads were stained using modified RCA specifications (RCA protocol deals with stickies identification. Since acrylic resin is the building block of PSA, this specification was used for resin dyeing and resin identification within the system). The next step was to prepare a "model" ink. The ink used was magenta water based packaging flexographic ink. 20 g of ink was diluted in 2 liter of deionized water. Similarly to the "model" resin, three of such ink solutions were prepared with the same pH adjustments. All ink solutions were stirred for 5 minutes using a laboratory air mixer (Model CM-100, Morehouse-Cowles, Inc.) with a propeller blade. Speed was adjusted to 1000 RPM. Ink solutions were filtered through filter pads.

Results and Discussion

Stickies from each run were examined for length and width (Table 3.1). Based on the qualitative evaluation, it was observed that temperature plays an important role on stickies formation, which was confirmed by other laboratories [Guo et al., 2000; Venditti et al., 2007; Cameron et al., 2000; Galland, 2006]. In addition to these findings, it was noted that pH value is significant in stickies formation (Figure 3.2-3.4). The lower pH region produces long and thick stickies, formed by agglomeration of multiple stickies (Figure 3.2). In the neutral pH region stickies become more or less individual (Figure 3.3). Their length is somewhat similar to the length of stickies obtained in the low pH region. Their width is significantly less than that of the width of blended stickies. Stickies that were produced in the alkaline pulping conditions are individual, very fine and their length is somewhat less than the length of stickies from the neutral region (Figure 3.4). According to theory, complete stickies removal can be achieved if the size of the stickies is above 2000 μm [European Recovered Paper Council, Retrieved 2012]. In this experiment, the length and width of stickies was monitored. In all cases, the length corresponds to the criteria for successful removal. On the other hand, the width parameter of 2000 μm was achieved only under acidic re-pulping conditions (see Table 3.1).

Table 3.1 Effect of pH and pulping temperature on stickies formation

Experiment	Stickies (%)	Pulping Temperature (˚C)	pH	Stickies Width (cm)	Stickies Length (cm)
1	10	35	5	0.2 - 0.4	0.5 - 3.0
2	25	40	5	0.2 - 0.3	0.5 - 1.5
3	5	45	5	0.1 - 0.2	0.5 - 1.5
4	5	35	7	0.1	0.3 - 1.0
5	10	40	7	<0.1	0.2 - 1.0
6	25	45	7	<0.1	0.2 - 1.0
7	25	35	9	<0.1	0.3 - 0.8
8	5	40	9	<0.1	0.2 - 0.8
9	10	45	9	<0.1	0.2 - 0.8

Statistical evaluation of nine pulping experiments was performed. Analysis of variance for stickies length and width was done. The results indicate that both of the morphology parameters (width and length) are greatly influenced by pH . The pulping temperature also plays an important role, while the level of stickies in the pulp seems to be unimportant. Due to absence of stickies within the accepts, a smaller experiment was re-run to confirm the effect of pH on stickies formation. This time the pulping conditions and level of stickies were the same. The only condition that was varied was pH. The aim of the additional experiment was to observe the impact of pH on the stickies size and formation. Again, an important effect of pH on size of stickies was confirmed (see Figure 3.2-3.4).

Figure 3.2 Stickies@ pH5, 40°C

Figure 3.3 Stickies @ pH7, 40°C

Figure 3.4 Stickies @ pH9, 40°C

The second part of the experiment was to implement the above findings on water-based resin and water based inks. In all cases, lower pH regions resulted in precipitated matter and thus formation of larger particles (see Figure 3.5-3.8). The lower acidic conditions caused the precipitation of the water-based resin while the alkaline environment had no impact on resin agglomeration (Figure 3.7, 3.8).

Figure 3.5 Acrylic resin @ pH 5

Figure 3.6 Acrylic resin @ pH7

Figure 3.7 Acrylic resin @ pH 9

Filtration and staining of resin filter pads showed that there is no material left behind for the alkaline resin solution. It was also compared to unused but stained filter paper (Figure 3.8, 3.9). On the other hand, the acidic solution and its impact on precipitation is obvious, when examining the filter pads from acidic resin solution (Figure 3.8).

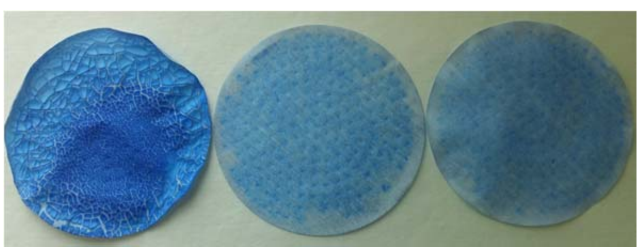

Figure 3.8 Stained filter pads with acrylic resin residue. (Left filter pad comes from acidic resin solution, neutral resin solution pad is in the middle, and filter pad on right is from alkaline resin solution.)

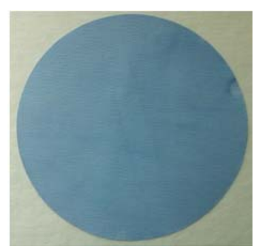

Figure 3.9 Stained plain filter paper

Water-based inks in general have a slightly alkaline pH. Water-based ink used during the experiment had pH of 8.5. It was not a surprise to observe the precipitation of water-based ink in acidic environment. However, for the purpose of this study it was essential to adjust the pH of the water based ink to 5. Within seconds, the ink particles agglomerated and "kicked out" ink could be seen on the sides of the beaker (Figure 3.10). On the other hand, water-based inks in the alkaline region stayed unchanged.

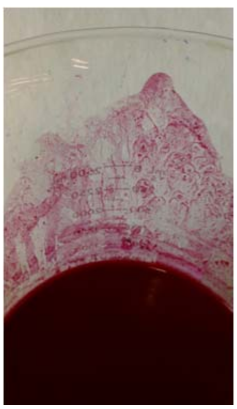

Figure 3.10 Ink @ pH 5

Figure 3.11 Ink @ pH 7

Figure 3.12 Ink @ pH 9

All three inks were filtered with the purpose to collect and quantify the precipitated matter. Ink that was adjusted to pH 5 was filtered for a duration of 20 minutes and the filter cake showed large amounts of agglomerated ink particles. The collected pigment was dark in color. The ink whose [H was adjusted to 7 showed some precipitated particles. This was due to pH adjustments using 1N hydrochloric acid. Ink that had alkaline pH did not leave behind any residue and filtration was accomplished immediately.

Figure 3.13 Filter pads with ink residue, left is the pad from acidic ink, center ink adjusted to pH 7, right ink adjusted to pH 9

The morphology of stickies in various pH environments was correlated to the morphology of ink particle size. In addition to pulping temperatures, the chemicals used during pulping greatly affect the particle length and width of the adhesive as well. In the acidic regions, carboxylic acid groups should be protonated, which most likely causes the agglomeration of the binder and respective growth of adhesive particle size. This particle growth is desirable for screening and stickies separation. In theory, a similar mechanism occurs within water-based inks. While inks present submicron contaminants, PSAs are viewed as macro contaminants. Also, the deinking concept can be better illustrated with the macro contaminants, which was the aim of this experimental work. Flexo water-based ink fragmentation was significantly reduced when moving away from alkaline environments towards neutral. It was found that small particles of water-based flexo inks (respectively digital) can be overcome in acidic regions. This behavior was demonstrated using a water-based acrylic resin in the free acid stage, when it becomes insoluble, resulting in large particles. Traditional recycling is performed under alkaline conditions where the precipitation of acrylic materials does not occur. It is acknowledged that acidic deinking is not standard, but its results are hopeful for further study. It is anticipated to implement the agglomeration concept into ongoing experiments related to true stickies removal and deinking, using flotation.

Conclusion

Current work was focused on deinking of water-based flexo and NIP inks, along with pressure sensitive adhesives all in one step. The experimental study used recycled pulp macro and micro contaminants. Macro contaminants in this study were stickies, while micro-contaminants were ink particles. It was demonstrated that both types of contaminants are formulated around the same chemistry, which would be acrylic. The behavior of visible macro contaminant in various pH region suggested that particle growth occurs in acidic pH. Similar performance was noted using water-based ink in a low pH region, while the alkaline region had no impact on particle growth. Elimination of both types of contaminants benefited from larger particle sizes. Therefore, application of these findings is desirable, despite the fact that traditional recycling is done in alkaline environment. Recycling efforts are ongoing with aim to implement some of the steps shown here.

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CHAPTER IV

ANIONICALLY SURFACE TREATED INKJET AND FLEXOGRAPHIC INKS AND THEIR DEINKABILITY

Summary

Pre-recycling study of water-based flexographic ink and water-based thermal inkjet inks was explored. The charge of water-based pigment particles was determined using Mütek PCD 03 Particle charge detector. Ink's behavior was examined under wide pH scale. Evaluation of the circuit water was done. Optical properties of the membrane filters used for separation of the recycled water from the residual pigment were performed. Density evaluation as well as CIELAB coordinates pointed out the cleanliness of acidic circuit waters.

It was determined that alkaline environment is desired for complete ink detachment from the printed substrate. The benefit of acidic milieu is the agglomeration of the pigment in water-based ink. Flotation deinking of model inkjet inks (no fibers involved) was carried out using laboratory scale flotation cell. Agglomeration and flotation of inkjet inks using various surfactants was used to better understand ink's behavior during true deinking. The ultimate goal was to optimize the inkjet ink detachment during re-pulping and at the same time assure its minimal re-deposition.

Introduction

Paper recycling efforts are put to test when recycling water based inkjet and flexographic water-based inks. On one hand these inks were developed with the aim to print with more eco-friendly materials. On the other hand they create a problem to recycling facilities, because they are very difficult to deink [Fischer; 2011]. A recycling challenge comprises of the compilation of the proprietary pigments, ink's, paper's and paper's treatment formulas. The issue is complex and should be solved by combining multidisciplinary efforts. Following experiment will present the unknowns in very simple way but recycling experts have to solve the recycling challenge utterly.

When preparing the pigments for these novel print processes, the goal is to keep the particle size less than 150nm [Chakvattanatham et al., 2010; Leelajariyakul et al, 2008]. Further, prepared pigment dispersions have to demonstrate colloidal stability and minimal growth of particle size over the course of shelf life. Unwanted agglomeration would demonstrate itself as a problem with clogged inkjet nozzles or imperfect ink transfer from anilox rolls, when using flexo printing process. Therefore, to overcome this issue, pigment's surface is treated to assure its stability. Multitude of polymeric dispersants along with various surface treatment techniques and polymer encapsulation can be used to assure colloidal stability of these sub-micron pigment particles [Shakhnovich et al., 2009; Tauber et al., 2010, Zhang et al., 2009, Yu, 2006]. In general, these treatments result in pigment with anionic nature [Chakvattanatham et al., 2010; Rahman, 2003]. In aqueous inks, polymeric dispersants are often used to assure stable pigment dispersions. Anchor groups allow the polymeric dispersants adsorption onto pigment exterior (Fu et al., 2011). Further, organic pigments are often surface treated.

The pigment surface treatment can be done by polymer adsorption [Wijting et al, 2008], by polymer grafting [Yoshikawa et al., 1997], by polymer encapsulation [Nguyen et al., 2008] and also by inorganic coating [Yuan et al, 2008; Wijting et al., 2008]. The treatment should provide the final ink with the desired colloidal stability and any other needed attributes. It is known that polymer-encapsulated pigments show superior wettability [Wu et al., 2011]. In addition, polymer encapsulation treatment protects pigment's stability against centrifugal force, temperature, pH value and electrolytes [Fu et al., 2011]. The separation forces introduced between the ink particles allow the ink stability. These can be sole steric or electrostatic forces or the combination of the both types. The distance between the ink particles is due to the stabilizing groups adsorbed on their surface. Stabilizing groups can be covalently attached to the pigment.

Further, pigment surface possess functional groups coming from carboxylic or sulphonic acid groups, both are anionic in alkaline region [Johnson and Belmont, 1999; Chakvattanatham et al., 2010]. The presence of last mentioned acid groups equips the pigment particles with electrostatic repulsive forces in aqueous media. This phenomenon is also known as self-dispersing property. It allows the ink to stay in dispersed stage without a need of any other dispersing aid [Chakvattanatham et al., 2010)].

To complicate the issue even more, different pigments might have various surface properties therefore might require surface modifier with different degree of hydrophobicity. Therefore, inkjet ink has to be formulated using well-chosen pigment along with surface modifiers having appropriate hydrophilicity [Chang et al., 2003]. In addition to pigment modification, paper substrates are also engineered to be more suitable for inkjet ink. Due to high amounts of water in inkjet ink formulations, drying and ink setting is an issue and slows down the printing process [Swerin et al., 2008]. To assure the crispness of the inkjet printed image, aqueous part of the inkjet ink is being absorbed into the paper while pigmented portion links to the coating's pigment for optimal performance [Batz-Sohn, 2008; Wedin, 2006]. Similarly to pigment, paper substrate has also anionic characteristics therefore anionic surface treatment is applied to assure the receptivity of the printing medium [Rahman, 2003]. Ink's penetration into the paper substrate increases with low polarity of the substrate. In such environment, the interactions between the water based ink and the surface sizing agents are not favorable [Costar et al., 2010]. Often, fumed silica is used in combination with other pigments to assure good printability and gloss [Batz-Sohn, 2008; Lee et al., 2004]. Polar part of the surface energy of the paper coating was found to be associated to the quantity of cationic polymer in the paper coating [Costar et al., 2010].

According to the researchers within the paper recycling field, [Beneventi et al., 2010; Zhao, 2004] the classification of surfactants falls into three major categories.

First, they play the role of a dispersant. The goal is to detach the ink particles from the paper fiber and avoid any additional re-deposition later, during the course of deinking process. Secondly, the surfactant facilitates the agglomeration of single ink particles. At this stage, surfactant also causes ink particles to become hydrophobic. In addition, it adsorbs to paper fiber. It changes the surface of the hydrophilic fiber to more hydrophobic. As a negative result, hydrophobic fiber will be removed during the flotation stage causing lower yield. Finally, surfactants have tendency to foam. Taking advantage of the froth formation accomplishes the goal of flotation deinking. Additionally, frother adsorbs on the surface of the fibers. Such adsorption can cause lower fiber-fiber bonding thus increased fiber loss.

Materials and Methods

Aqueous Flexographic Ink Sample Preparation

While performing this experimental study, it was assumed that flexographic inks are very similar in nature to water-based inkjet inks, if we do not consider smaller particle size of pigments, and smaller degree of polymerization of acrylic resins in inkjet inks. In some cases only water-based flexographic ink was tested and applied on the substrates due to limited availability of aqueous inkjet inks. Table 4.1. represents the typical composition of the water-based flexographic ink.

Table 4.1 Composition of typical water-based flexographic ink [Argent et al., 1999]

Component	**Porous substrates (wt %)**	**Non porous substrates (wt %)**
35% Water based pigment dispersion	35.0 - 45.0	45.0 - 55.0
Acrylic solution resin	28.0 - 32.0	8.0 - 12.0
Acrylic emulsion resin	10.0 - 15.0	25.0 - 35.0
Water	10.0 - 15.0	5.0 - 10.0
Amine	0.5 - 1.5	0.5 - 1.5
Wax	0.5 - 1.5	0.5 - 1.5
Wetting agent	NA	0.2 - 0.5
Total	100.0	100.0

Table 4.2 Experimental ink formula

Ingredient	Amount (wt %)	Solids (wt%)
39% Magenta flexographic dispersion	50.0	19.5
34% Joncryl 60 solution resin	10.0	3.4
48% Joncryl 624 emulsion resin	22.0	9.7
DI water	18.0	NA
Antifoam agent	0.2-0.5	0.2-0.5
Total	100.0	32.6

Water based flexographic ink was prepared in the laboratory. The composition of the in-house made ink can be seen in the Table 4.2.

DuPont Teijin film Melinex ST 506 gauge 500 (PET) was used for printing. PET film was printed using above mentioned water-based flexo packaging ink (Table 3.2). Wire wound Meyer rod #12 was used to apply the ink film. After printing, PET was dried in the oven at 40 °C for 10 minutes.

Flotation of Model Water-Based Inks

5.6g of wet flexographic ink (1.85g solids) was used in the air flotation. Flotation deinking of model ink (no fibers involved) was carried out using 2L laboratory scale flotation cell. The air flotation was carried in various pH region. Acidic pH of the water and ink mixture was adjusted to 5 using 0.1N hydrochloric acid. In order to slightly elevate alkalinity of naturally alkaline ink (pH=8.7) the solution of 0.1N sodium hydroxide was used.

The air flow into flotation cell was adjusted to 1L/min. Sodium soap created according to INGEDE recipe was used to create the froth. Flat spatula was used for foam removal. Air-flow was stopped after 12 minutes and rest of the solution was filtered.

Residual water in flotation cell was collected. 100 ml of the residual water was filtered through a cellulose nitrate membrane filter with 0.45 µm pores diameter. Membrane filter was dried in a desiccator. Optical properties of membrane filters were evaluated using X-Rite Spectrophotometer 530 series at D_{65}. CIE LAB values of the membrane filters were recorded.

Ink Removal from Plastic Prints

Flexo printed PET substrate was cut into 2"by 7" strips. Alkaline nonionic surfactant (Varonic T-205), acidic nonionic surfactants (Solplus D-540), 0.1N acidic (HCl) and 0.1N alkaline (NaOH) solutions were used for ink removal from plastic prints. The effect of these four deinking agents on ink release from PET was observed. Multiple drops of each of the solutions were deposited on the printed PET strips. The drops of deinking agents were wiped in 20 minutes intervals, one drop at the time. Further, INGEDE chemicals were used to repeat above mentioned experiments (Sodium hydroxide 0.6%, Sodium silicate 1.8%, Hydrogen peroxide 0.7% and Oleic acid 0.8%) [INGEDE, 2009].

Wet Inkjet Ink Testing

Water-based HP ink cartridges, C8752A (Magenta 775 ml) and C8751A (Cyan 775 ml) were obtained from HP. pH of these aqueous inks was measured and was found to be 8.9. Vivera inks are designed specifically for HP Edgeline MFPs and are dye-based. HP Vivera water-based inkjet inks cyan (Figure 4.1.) and magenta were dissolved in DI water in order to measure their electrical potential.

Figure 4.1 HP Cyan and magenta Vivera ink cartridges

The composition of the both inkjet samples is proprietary. However, some of the information about the ink formulations were retrieved and they are presented in the Table 4.3. and Table 4.4.

Table 4.3 Composition of Vivera ink C8752A magenta (http://www.hp.com/hpinfo/globalcitizenship/environment/productdata/pdf/ij_c8752a_us_eng_v1.pdf)

Ingredient	% by weight	CAS #
Water	> 70	7732-18-5
Tripropylene glycol	< 10	24800-44-0
2-Imidazolidinone, 1-(2-hydroxyethyl)-	< 5	3699-54-5
Modified magenta pigment 564	< 5	Proprietary

Table 4.4 Composition of Vivera ink C8751A cyan
http://www.hp.com/hpinfo/globalcitizenship/environment/productdata/Countries/br/ij_c8751a_br_eng_v1.pdf

Ingredient	% by weight	CAS #
Water	< 80	7732-18-5
Tripropylene glycol	< 10	24800-44-0
Tetraethylene glycol	< 5	112-60-7
Cyan pigment	< 2.5	Proprietary
Ethoxylated glycerol	< 2	Proprietary
1-Aza-5-ethyl-3,7-dioxabicyclo(3.3.0)octane	< 1	Proprietary

10mL of 5 diluted inkjet ink was tested in Mütek PCD 03 Particle Charge Detector. Anionic polyelectrolyte PVSK (Polyvinyl Sulfuric Acid Potassium Salt 0.001N) was used as titrant in all of the experiments.

Dried Inkjet Ink Testing

Recycling process is dealing with the printed samples. Once printed, ink is well settled and aged. In order to mimic the real situation, dried ink samples were tested as well. Paper samples were printed by HP using Vivera aqueous inkjet ink (Figure 3.2). Weight difference was made between 120 sheets of printed and 120 sheets of unprinted papers (see Table 4.5). It was calculated that difference between same amount of unprinted and printed sheets is 4.84g. This weight represents printed dry ink. In theory, inkjet ink might have ~ 8% solids, therefore it was estimated that 60.5 g of ink was used to print above mentioned 120 sheets.

Figure 4.2 Inkjet printed paper sample

Inkjet inks were oven dried for 48 hours at 70 °C. The entire liquid portion was evaporated and dried ink and resin system was left behind. Dried ink was collected. When performing actual air flotation deinking, flotation slurry consistency was adjusted to 0.8%. 2L laboratory scale flotation cell takes 16g of oven dried material, therefore it was calculated that approximately 0.2g of dry ink was submitted to flotation deinking. Hence, 0.2g of dried ink was diluted in the DI water and was tested in Mütek PCD 03 Particle Charge Detector to determine pigments particle charge after it went through aging process.

Table 4.5 Weight of printed and unprinted multipurpose paper

HP Multipurpose Paper	**Weight of 120 sheets [g]**	**Weight of ink [g]**
Unprinted	455.67	NA
Printed	460.51	4.84

Results and Discussion

The success of the deinking is linked to many factors. In this particular study, model flexographic ink was prepared in the laboratory according to the formulation represented in the Table 4.2. Ink was printed on PET substrate. The goal of the study was to better understand behavior of ink particles during the deinking and during the flotation phase. Separation of the ink particles from fibers was this way omitted and the center of attention was the ink behavior. Study was focused on the pH and its role in the deinking. Surface charge of the wet packaging ink was measured (see Figure 4.3) while its dry version was not tested. It was not possible to resolubilize the dry form of the experimentally prepared ink formulation in deionized water.

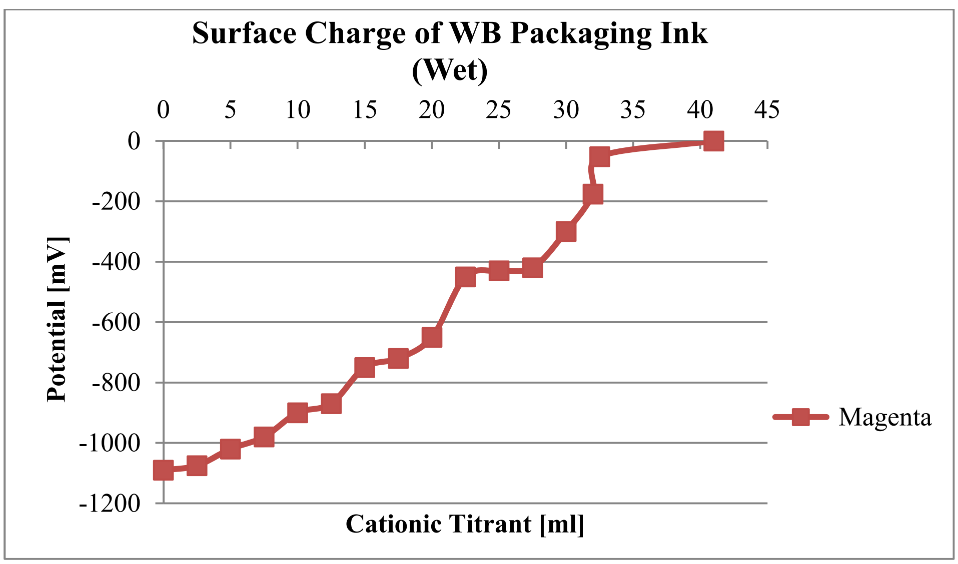


Figure 4.3 Surface charge of wet water based flexo ink

The experiment revealed the anionic character of the pigment that was used for preparation of the water-based flexographic ink.

Table 4.6 Particle charge of water based flexographic ink

Wet ink testing	**Potential [mV]**	**Titrant to neutralized charge [ml]**
Magenta solution	-1090.0	41.0

Based on the surface charge (plot represented on the Figure 4.3), during the charge neutralization, particle charge of flexographic ink went through few plateaus. It is possible that the organic pigment is treated to withstand the quick change in potential charge. One of the plateaus is visible in the -400mV region. This phenomenon is most likely desirable and it assures the ink stability if sudden change in electrical charge occurs. This plateau could demonstrate the protection of the ink from unwanted pigment's agglomeration.

WB Ink	**WB Ink (pH 5)**	**WB Ink (pH 9)**
Foam		
	Foam dark in color	Foam light in color
After Deinking	Clear phase + sedimentation of agglomerated particles	Homogenous ink
		

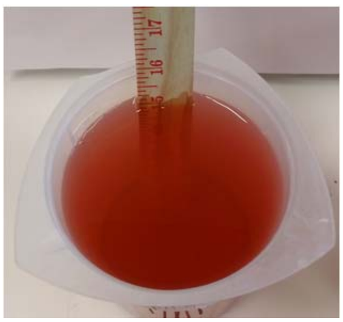
Figure 4.4 Effect of pH on ink and its removal

On the other hand, efficient ink removal of submicron pigment particles benefits from the ink agglomeration. It is easier to remove number of agglomerated ink particles then single ones. It was noted that during flotation, acidic environment had ability to agglomerate ink particles of flexographic ink. The froth that was created in acidic pH was dark in color (Figure 4.4). Froth that was created in the alkaline environment was significantly lighter in color (Figure 4.4). Alkaline environment did not cause the pigment particles to agglomerate. Therefore, it is speculated that the alkaline environment acts as dispersing agent while the acidic environment behaves as a flocculant. Acidic region causes the ink particles agglomerate and settle down (Figure 4.4).

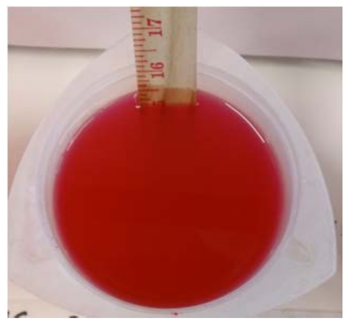
Figure 4.5 Agglomerated pigment particle in acidic region at the froth's surface

Figure 4.6 No visible agglomerates in alkaline deinking at the froth's surface

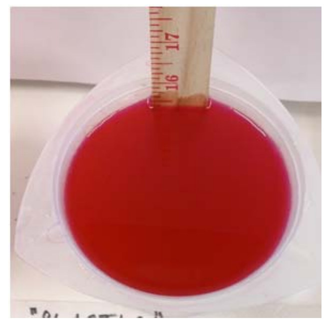
After flotation deinking of printed PET samples, the residual water was studied. The color difference was observed for waters having acidic, neutral and alkaline pH (pH 5, 7, 9, respectively). Color difference of froth can be observed on the Figure 4.5. and 4.6. The residual water for pH 5 was significantly clearer than water for pH 7 or pH 9, see Figure 4.7. It appears that water at pH 9 is significantly stronger in color. It suggests that in alkaline pH region, the ink is in its free form. Residual water with pH 7 is inferior in coloration. It was noted, that plastic PET squares have the highest amount of undetached ink when compared to pH 5 or pH 9. Stronger coloration of the residual water means more of the pigment detached, but due to the small particle size, less ink was removed during the flotation. Therefore, light coloration of the residual water signifies efficient ink removal.



pH 5 residual flotation cell water



pH 7 residual flotation cell water



pH 9 residual flotation cell water

Figure 4.7 Residual waters after flotation of PET in various pH environments

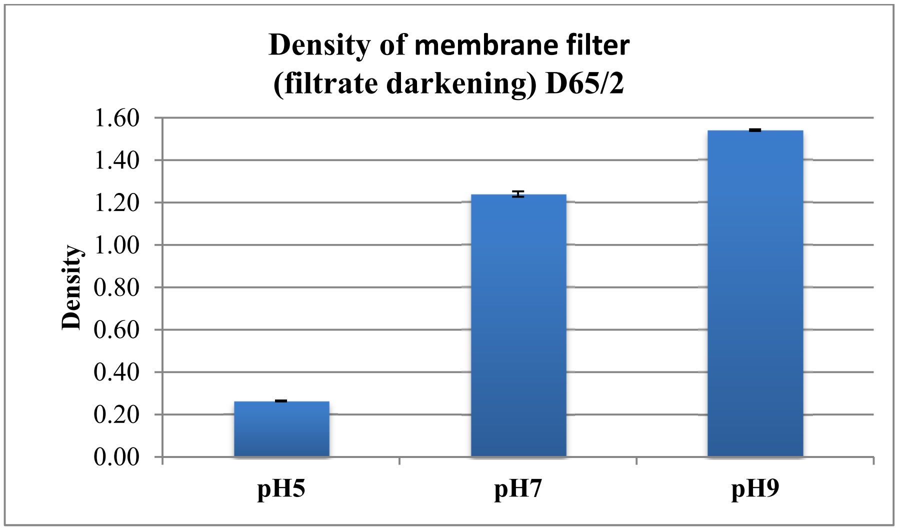


Figure 4.8 Optical density of three membrane filters used to filter residual water after deinking of PET -magenta printed

As per Figure 4.8, optical density of the membrane filters coming from alkaline and acidic regions are significantly different. The membrane filter coming from acidic region has the lowest optical density. The optical density of membrane filters that were used for alkaline waters are significantly higher. Therefore it is assumed that large amount of agglomerated pigment was removed in acidic region. This would have effect on the lower coloration of the membrane filter. On the other hand, alkaline environment is gentle on the pigment surface and did not cause ink agglomeration. Therefore, the ink was not successfully removed during flotation. This would also cause the ink to stay behind and stain the membrane filter.

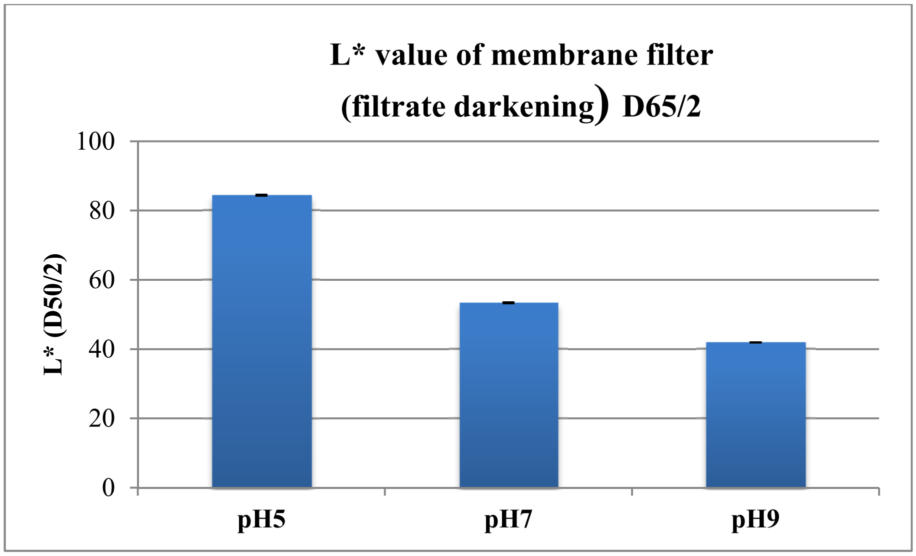


Figure 4.9 CIE L value of three membrane filters used to filter residual water after deinking of PET at different pH-magenta

The CIE L value measured on the three sets of membrane filters support the same theory (Figure 4.9). While alkaline residual waters retained most of the pigment, the acidic water was the most pigment free and resulted in the lightest coloration (see Figure 4.9). Secondly, neutral regions were somewhat superior than the pH 9 environment.

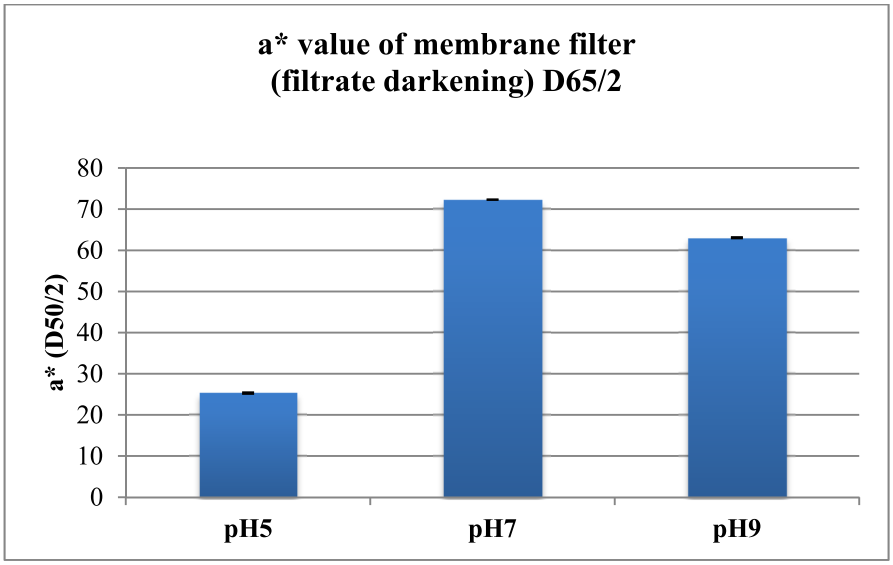


Figure 4.10 CIE A value of three membrane filters used to filter residual water after deinking of PET at different pH-magenta printed

The CIE A value of membrane filters represented on Figure 4.10. indicates that the most beneficial environment for successful ink removal occurs in the acidic region. The A value of alkaline environment is significantly higher than that of acidic. The B values of the neutral and acidic waters are negative (see Figure 4.11). The B value of the alkaline waters was significantly higher. In order to successfully re-use and recycle the paper, it is desirable to yield product with lower B value. The yellow component of the B coordinate is not desired. To an observer, it demonstrates itself as non-clean.

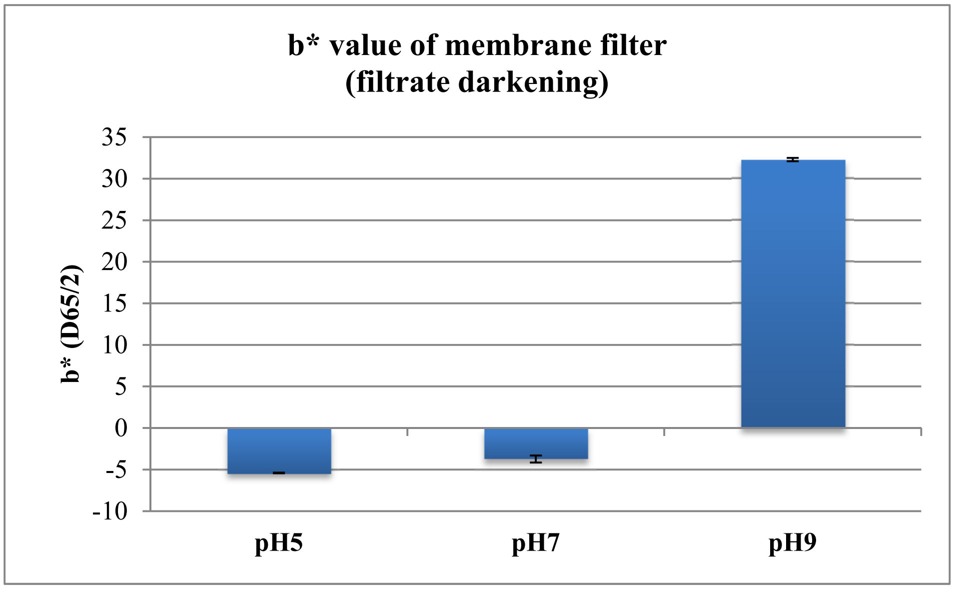


Figure 4.11 CIE B value of three membrane filters used to filter residual water after deinking of PET -magenta printed

Table 4.7. Ink removal results

Deinking solution	Ink Removal					
	20 minutes	40 minutes	60 minutes	80 minutes	100 minutes	>100 minutes
Varonic T-205	90%	100%	100%	100%	100%	100%
Solplus D-540	10%	20%	30%	30%	30%	100%
0.1 N NAOH	100%	100%	100%	100%	100%	100%
0.1 N HCl	0%	0%	0%	0%	10%	10%

Ink removal study demonstrated that solutions that are alkaline in nature will dissolve the water-based ink almost immediately. Results from the ink removal are summarized in the Table 4.7. The areas covered with alkaline deinking agents were wiped clean immediately see Figure 4.12. This is true for specimen treated with 0.1N NaOH as well as with the drop of surfactant Varonic T-205. On the contrary, acidic solutions had minimal or no removal effect on the water-based ink (Figure 4.13). Acidic surfactant Solplus D-540 removed some of the ink, mostly on the outsides of the drop edges. However, it has significantly less removal power if compared with the Varonic T205. This study proved that in order to successfully remove the ink from the substrate during recycling, one has to use the alkaline deinking agents.

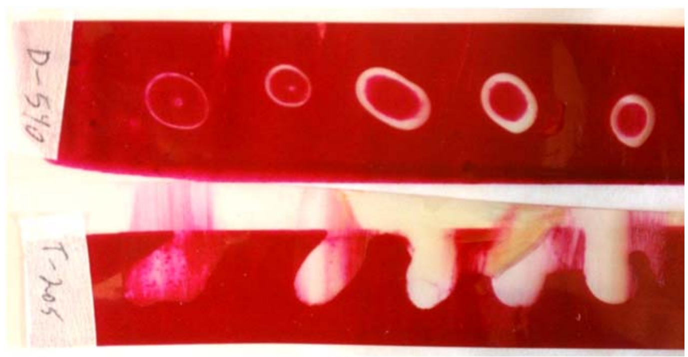


Figure 4.12 Ink removal via dispersant

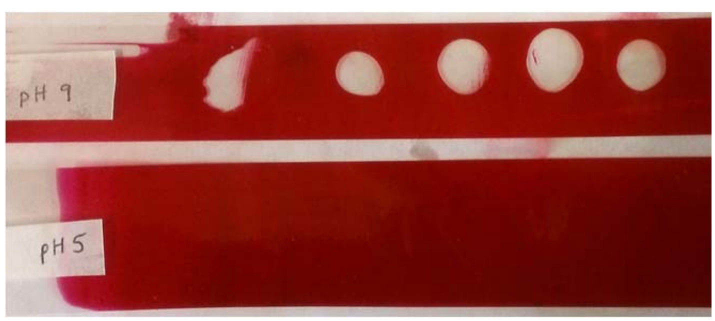


Figure 4.13 Ink removal via acid or base solution

The effect of surfactants on releasing of the ink from PET was observed. Selected surfactants and solutions had pH ranging from 2 – 10. It was found that surfactants and solutions with low pH do not act as dispersants and have no or minimal effect on ink detachment from the substrate. On the other hand, alkaline surfactants had ability to detach the ink from the substrate, but consequently the inks were dispersed in the aqueous environment and were not agglomerated. Results are summarized in the Table 4.8 below.

Table 4.8 Deinking solutions

Deinking Solution	pH	Results
Varonic T-205	10	Good ink detachment/ No agglomeration
Solplus D-540	5	No ink detachment/Good ink agglomeration
INGEDE chemicals	9.5	Good ink detachment/ No agglomeration
0.1 N NaOH	13	Good ink detachment/ No agglomeration
0.1 N HCl	1.1	No ink detachment/Good ink agglomeration

First, potential of both inkjet inks was tested in their liquid form. In order to obtain information about ink's behavior once printed, ink was tested after drying. This allowed mimicking the ink setting and aging on the substrate. The liquid as well as dry ink samples had similar behavior (see Table 4.9 and Table 4.10). Titration curves for wet and dry cyan and magenta ink are illustrated on Figure 4.14 and 4.15. Both of the inkjet inks were found to be anionic in the nature. The cyan inkjet ink was found to be slightly more anionic than the magenta ink. Both inks consumed approximately the same amount of cationic polyelectrolyte Poly-Dadmac to become electrically neutral (Figure 4.14 and 4.15).

Table 4.9 Wet inkjet ink particle charge

Wet ink testing	**Potential [mV]**	**Titrant to neutralized charge [mL]**
Magenta solution	-1147.0	32.2
Cyan solution	-1303.0	27.2

Table 4.10 Dry inkjet ink particle charge

Dry ink testing	**Potential [mV]**	**Titrant to neutralized charge [mL]**
Magenta	-1127.0	25.0
Cyan	-1126.0	31.0

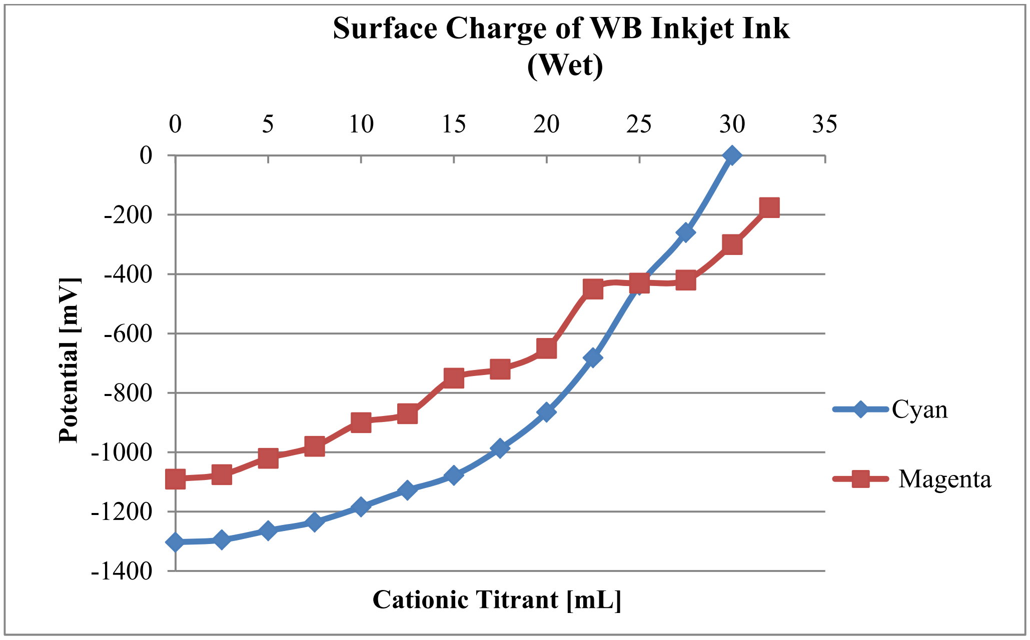


Figure 4.14 Surface charge of wet water based inkjet inks

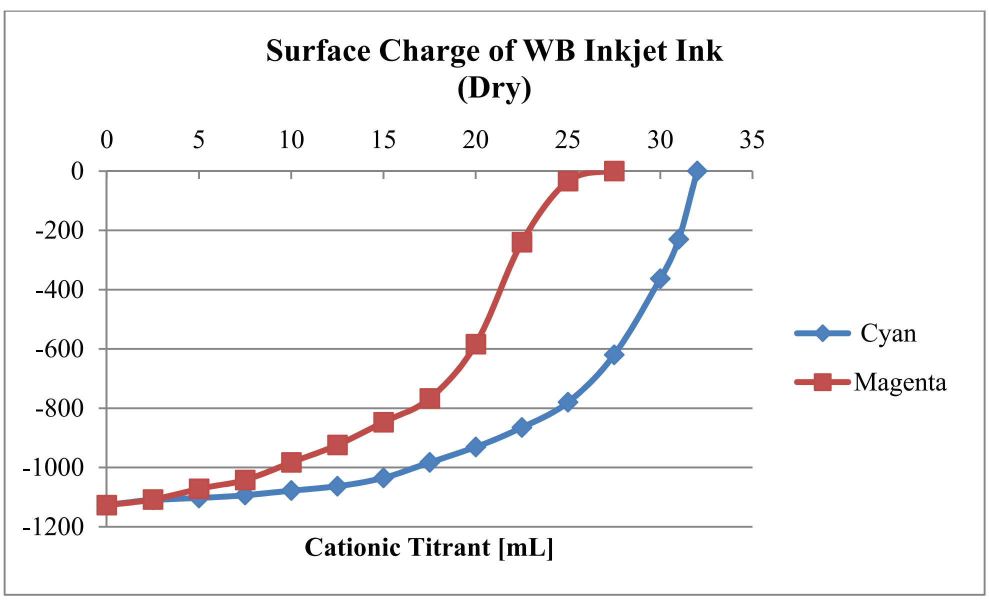


Figure 4.15 Surface charge of dry water based inkjet inks

Conclusion

The importance of the pH and its role in the deinking was examined. Alkaline pH is desirable for ink detachment. Acrylic polymers with abundance of –COOH groups in water based inks stay in salt form, which is water soluble. On the other hand, ink agglomeration is essential for its removal. Acidic pH has the ability to agglomerate the pigment, once it is detached and present in deinking water. Low pH causes the ink particles to collide and settle down. Cationic surfactants and polyelectrolytes also cause agglomeration of anionic pigment particle. Maybe the best effect of deinking could be found in two stage treatment, first alkaline,for achieving ink detachment and second acidic, causing agglomeration. Combination of alkaline pH and addition of agglomerating agent might be desirable option for ink jet ink removal and will be further studied.

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CHAPTER V

SOYBEAN OIL FOR ENHANCED DEINKING OF LITHO PRINTS

Summary

Three types of food grade soybean oils were tested to determine if their byproducts can be utilized in the paper recycling industry. Free fatty acids were extracted from these commercially available soybean-oils “A”, “B” and “C”. Experimental fatty acids were utilized in one loop air flotation deinking of litho-printed paper substrates. It was found that the three experimental fatty acids used in deinking differ in their chemical composition, namely acid number and saponification number. The effect of each of the soy-oil free fatty acids on deinking was studied, quantified and compared to the standard INGEDE 11p procedure. The INGEDE method employs commercially available oleic acid and experimental fatty acids were tested as its replacement. INGEDE method 11p was slightly modified due to unavailability of a Hobart type pulper. Therefore, a MicroMaelstrom™ Laboratory Pulper was used instead. The substrate used for deinkability study was heavily printed from both sides by sheetfed offset lithography. Due to heavy ink coverage, none of the four fatty acids had the power to deink such substrates in a one loop flotation recycling experiment. Besides INGEDE deinking evaluations, further deinking assessments were performed. Deinkability factors DEM_{Lab} and DEM_f factors were used to express the success of ink removal from the pulp, since ERIC instrument measuring equivalent residual ink concentration considered in INGEDE scoring, was not available. Dirt count analysis of deinked handsheets was performed by scanning them using an Epson Perfection V500 Photo scanner followed by processing of scanned images by Verity IA Color Image Analysis software. Overall, it was found that

two of the three experimental fatty acids (fatty acid from oil "C" and free acid from soy oil "B") performed better than the standard, using oleic acid. It was also found that the lower was the acid number of free fatty acid; the better was the deinking performance.

Introduction

In the recycling facilities, the first step of the deinking process focuses on repulping of the printed substrate. Repulping occurs in an aqueous environment, typically in a basic pH range. Mechanical agitation allows the breaking of the fiber network. Breaking of the bonding between the fibers and the ink particles is fundamental for the ink detachment from the fibers. Addition of deinking chemicals in the repulping stage facilitates the ink detachment. In general, repulped stock will be dark with visible contaminants floating on the surface. Such pulp will produce a dark, speckled paper substrate that will be unacceptable for the customer. Therefore, the major goal of the recycling is to eliminate the ink particles and improve the optical properties of the recovered pulp (Renner, 2000). Based on studies performed by multiple researches, the strength of the fiber-ink bonding depends on pigment particle size, ink formulation, printing process, ink film thickness and ink depth penetration [Carre et al., 2000; Pekarovicova et al., 2003]. Further, ink aging and its raw components will also impact the deinking efforts [Angellier et al., 2004; Haynes, 2000].

This experimental study was focused on deinking via INGEDE Method 11p and its modification. The deinking protocol consisted of offset printed stock repulping followed by the air flotation and further handsheet preparation (INGEDE Method 11p, 2009). Free fatty acids extracted from three types of commercially available soy oils were tested as a replacement of oleic acid used in INGEDE Method 11p (INGEDE Method 11p, 2009). The objective of the study was to determine if three fatty acids coming from three types of soybean oil would produce the deinked pulp with comparable optical properties to the deinked pulp prepared using oleic acid. The effect of each of the soy-oil byproducts on deinking was observed and quantified. The main focus was to investigate whether the free acid extracted from food grade soybean oil can replace commercially available oleic acid. This work is applicable in the field of utilization of byproducts from soybean processing and also in improving deinking processes as designed by the INGEDE method.

Materials and Methods

Analysis of Soy Oils

The Michigan Soybean Promotion Committee provided three commercially available soybean oils. Their typical use is found in the food industry. The differences in their internal structure was analyzed via saponification and acid number testing (ASTM Standard D94-07, 2012; ASTM Standard D664-11a, 2011). Sodium soaps were prepared from each of the three soy-oils. In order to replace oleic acid used in INGEDE protocol, it was necessary to extract free fatty acids from the soy oils. The extraction of fatty acids was performed (Standard Methods for the Analysis of Oils, Fats and Derivates, Method IV.A.4; 1982).

Offset Sheetfed Printed Substrate

The offset sheetfed litho printed substrate was obtained from North American Color, Kalamazoo, MI. The substrate was heavily color-printed from both sides, see

Figure 5.1. Physical and optical properties of the unprinted sheet are illustrated in Table 5.1.

Figure 5.1 Sheetfed offset litho printed paper side 1 and side 2

Table 5.1 Properties of unprinted base sheet used for deinking

Physical properties of Unprinted Base Sheet	
Grammage (g/m^2)	115
Thickness (µm)	75.0
Ash content (%) @ 525˚C	45.0
Optical Properties of Unprinted Base Sheet	
Brightness	86.7
Luminosity (Y)	83.1
L*	92.9
a*	1.24
b*	-2.52

Deinking

Prior to the deinking, printed and unprinted substrates were aged for 72 hours at 60°C as per INGEDE Method 11p (INGEDE Method 11p, 2009). After aging, printed and unprinted substrates, respectively, were torn to 2x2 cm pieces and were conditioned in the paper laboratory for 24 hours, 23±1°C at 50±2% relative humidity. Due to the unavailability of a Hobart type pulper used in INGEDE Method 11p, a MicroMaelstrom™ Laboratory Pulper type of slush–maker was used instead. Repulping parameters (RPM and repulping time) versus particle dirt count and diameter size were examined prior this experimental study. The most suitable conditions were selected and they are listed in Table 1. Dilution water hardness was adjusted as per INGEDE requirement. INGEDE protocol lists the homogenization process as optional. During our experimental study, all of the pulps were homogenized using a TAPPI disintegrator. A total of eight repulping and flotation experiments were conducted using the four fatty acids. Repulping, storage and disintegration process parameters are listed in Table 2. The goal of the repulping is to break the bonds between ink and fibers. It was achieved first by applying shear forces, secondly by addition of deinking chemicals. Pulping time was constant for all experiments and its length was 10 minutes. The speed of the MicroMaelstrom™ Laboratory Pulper was set to 500 RPM and the temperature was adjusted to 45°C by using the built in thermostat. After defibration, repulped stock was diluted to 4% consistency using dilution water with fixed hardness value of 128mg Ca^{2+}/L. Next, repulped stock was stored for an hour in the water bath at 45°C. After storage, TAPPI disintegrator was used to disintegrate fiber bundles for 1 minute. Prior to the air flotation, undeinked stock was taken for preparation of 2 filter pads and 10 handsheets. The rest of the undeinked pulp was taken and was subjected to flotation deinking. A small 2L laboratory flotation cell was used for all deinking trials. Due to the volume of the cell, each of the experiments was repeated twice. This way, larger amounts of deinked pulp suitable for handsheets and filter pads formation were obtained. The flotation cell aeration was fixed to flow rate of 1L/min. The duration of flotation deinking was 12 minutes. A paddle scraper was used for froth removal over the course of flotation. The removed froth was collected in a reject tank. The yield of the flotation was calculated once the reject was dried and deducted from the original floated slurry weight. The final consistency of the deinked stock was calculated and was subjected to preparation of the handsheets, filter pads and membrane filters.

Table 5.2 Repulping, storage and disintegration process parameters

Re-pulping recipe	Sodium hydroxide	0.6%
	Sodium silicate	1.8%
	Hydrogen peroxide	0.7%
	Oleic acid/Acid from soy oil #1 or #2 or #3	0.8%
Re-pulping conditions	Water hardness adjusted to:	128mg Ca^{2+}/L
	Temperature	45˚C
	pH	9.5±0.5
	Consistency	6%
	Mixing speed	500 RPM
	Re-pulping time	10 min
Storage	Consistency	5%
	Duration	60 min
	Temperature	45˚C
Disintegration	Consistency	4%
	Duration	1 min
	Temperature	45˚C
Flotation	Consistency	0.8%
	Duration	12 min
	Temperature	45˚C
	Aeration flow rate	1L/min

Note: a/ 2 Filter pads and 10 handsheets were formed from undeinked pulp

b/ 2 Filter pads, 10 handsheets were prepared from

deinked pulp

c/ 2 membrane filters were prepared from water obtained after 2 filter pads

were formed

Results and Discussion

In order to better understand the differences between three soy-based oils, determination of Saponification number of oils and Acid number of free fatty acids was performed (see Table 3.) Saponification number allowed identifying the amounts of free and bound acid groups per gram of tested oils, while the Acid number determines amount of free acid groups per gram of tested oil or fatty acid. The slight differences in amounts of saponification numbers were found for soybean oil “B” (199.40) and soybean oil “C” (197.71). Slightly higher saponification values were determined for soy oil “A" (201.19). Further processing of oils “A”, “B” and “C” resulted in their free fatty acids (FFA). The acids numbers of these FFA were determined and are represented in the Table 5.3.

Table 5.3 Acid numbers of free fatty acid

Free Fatty Acid	**Acid Number**
From oil “A”	202.6
From oil “B”	196.2
From oil "C"	194.8
Oleic Acid	200.3

Deinkability evaluation parameters according to INGEDE Method 11p focus on pulp and process parameters. The objective of pulp parameters are high reflection of deinked pulp represented by luminosity value Y, high cleanliness of deinked pulp characterized by dirt particle area A and no discoloration of deinked pulp depicted by chromaticity value a* . The goal of process parameters is to assure good ink removal represented by ink elimination IE and lastly the cleanliness of circuit water characterized by filtrate darkening ΔY. Due to unavailability of the instrument capable of measuring the effective residual ink concentration (ERIC), deinking evaluation assessment by DEM_{Lab} factor (Rao et al., 1998) was done. The DEM_{Lab} factor uses the color difference between unprinted deinked pulp (US) and deinked pulp (DS) in relation to the color difference between unprinted deinked pulp (US) and printed undeinked pulp (BS). Technidyne Brightness Meter S-5 with C/2°geometry of light source was used. The DEM_{Lab} factor was calculated according to following formula:

$$DEM_{Lab}=\left(1-\frac{\sqrt{(L^*_{US}-L^*_{DS})^2+(a^*_{US}-a^*_{DS})^2+(b^*_{US}-b^*_{DS})^2}}{\sqrt{(L^*_{US}-L^*_{BS})^2+(a^*_{US}-a^*_{BS})^2+(b^*_{US}-b^*_{BS})^2}}\right)100[\%]$$

Where:

(US) - unprinted deinked pulp

(DS) - deinked pulp

(BS) - printed undeinked pulp

In general, the deinkability factor is presented on a scale from 0-100%. A deinking factor closest to the 100% will represent the sample that was flawlessly deinked. The color difference of a sample to a reference sample as a vector in the L*a*b* color system (CIELAB) was used to develop DEM_{Lab} deinkability factor. Three axis (LAB) evaluates the color in three dimensional color space (CIE Proceedings, 1932; Fleming, 2003).

During the evaluation, deinkability factor DEM_f developed by Papiertechnische Stiftung (PTS) in Munich, Germany was used. Deinkability factor DEM_f considers brightness difference between the deinked pulp and pulp before deinking. It is calculated using averaged brightness values of unprinted deinked pulp, deinked pulp and printed undeinked pulp (Renner, 2000).

$$DEMf = \frac{Brightness\ (DS) - Brightness\ (BS)}{Brightness\ (US) - Brightness\ (BS)}\ 100\ [\%]$$

Where:

(US) - unprinted deinked pulp

(DS) - deinked pulp

(BS) - printed undeinked pulp

Based on both deinkability factors (DEM_{Lab} and DEM_f), free fatty acid from oil "C" has the highest deinking efficiency while free fatty acid from oil "A" resulted in the least deinked pulp (see Table 5.4). Free fatty acid from oil "B" was somewhat less efficient than free fatty acid from oil "C". In the present study, the main focus was not necessarily to obtain perfectly deinked pulp, but to determine if the free fatty acid extracted from food grade soybean oil can replace commercially available oleic acid. In addition, the paper substrate was heavily printed. In order to achieve more progressive deinkability results, deinked pulp would have to undergo multi-looped deinking systems, rather than one step deinking flotation.

Table 5.4 Deinkability efficiency of various free fatty acids

Acid type used for Deinking	Deinkability DEM_{Lab} [%]	Deinkability DEM_f [%]
Oleic Acid	40.1	36.8
FFA from oil "A"	31.6	29.1
FFA from oil "B"	50.2	45.9
FFA from "C"	59.2	56.4

Additionally, the deinking evaluation focused on the dirt count. Handsheets were scanned using Epson Perfection V500 Photo scanner. Evaluation of the scanned handsheets was done with the help of Verity IA Color Image Analysis software (VERITY IA Light and Dark Dirt, 3.4.0). Scanning resolution was set to 1200dpi. The inspected area was set to $13000mm^2$. Dirt count is illustrated in the Table 5 and Figure 5.2.

Table 5.5 Handsheets dark objects count (in PPM) of different pulps

Acid type used for Deinking	Unprinted deinked (US)	Printed undeinked (BS)	Printed deinked (DS)
Oleic Acid	34	108774	37188
FFA from oil "A"	15	101993	46005
FFA from oil "B"	60	94165	22690
FFA from oil "C"	27	108721	15362

The lowest dirt count (PPM Holey) was measured on the handsheets prepared from deinked pulp using FFA from oil "C". Free fatty acid extracted from oil "B" resulted in deinked pulp with lower dirt count than that processed with standard oleic acid. The least effective was the FFA coming from soy oil "A".

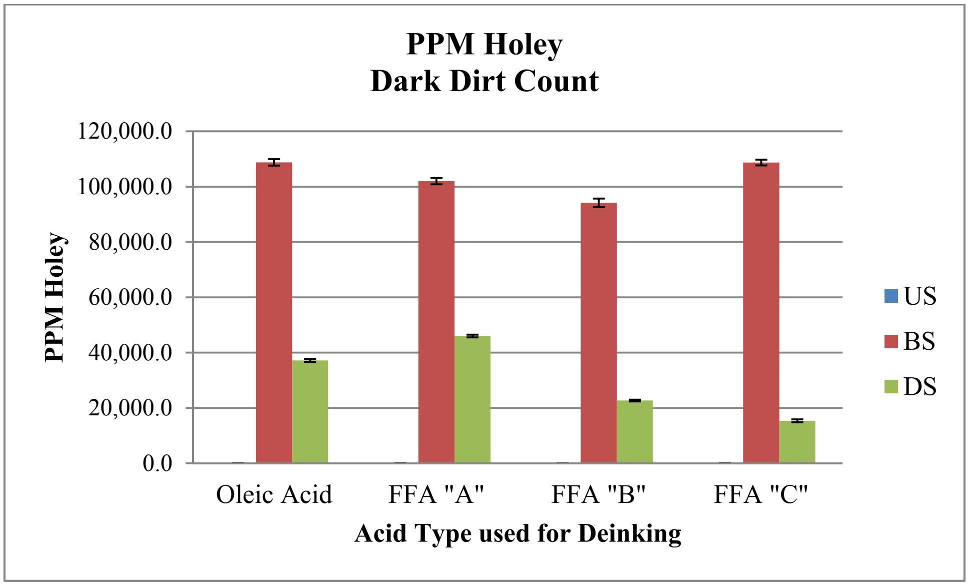

Figure 5.2 Dark dirt count on handsheets before (BS) and after deinking (DS)

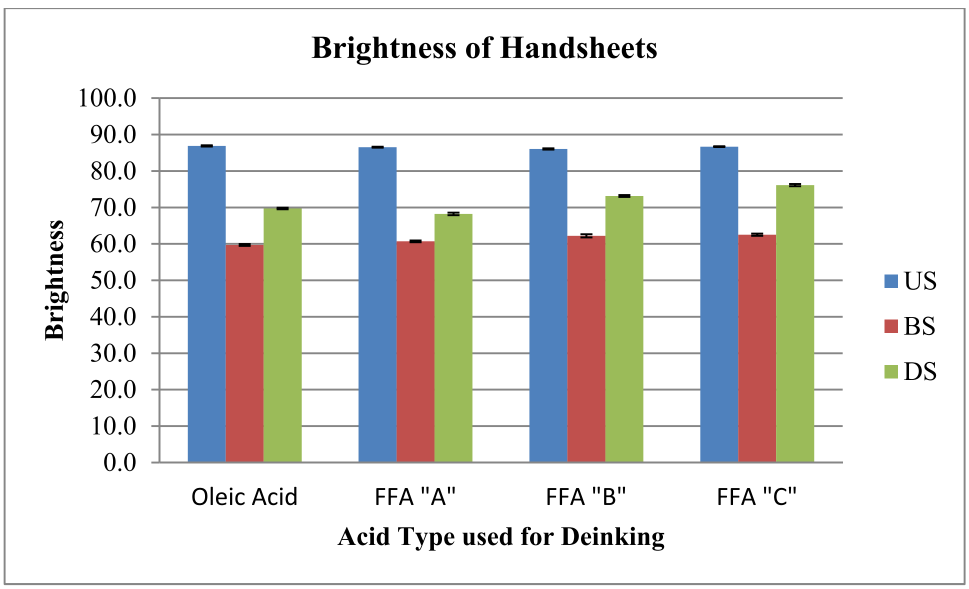

Figure 5.3 Brightness (%ISO) of handsheets before (BS) and after deinking (DS.

Brightness of prepared handsheets was measured at 457nm. Handsheets were prepared from deinked unprinted pulp, printed undeinked pulp and printed deinked pulp. Deinking employed four available fatty acids. As per Figure 5.3 it is evident that the brightest handsheets were prepared from the pulp deinked with free acid obtained from soy oil “C”, followed by the free acid from oil “B”. Both free acids resulted in brighter handsheets than those prepared from pulp deinked with standard oleic acid. Free acid soy oil “A” provided deinked pulp with the lowest brightness.

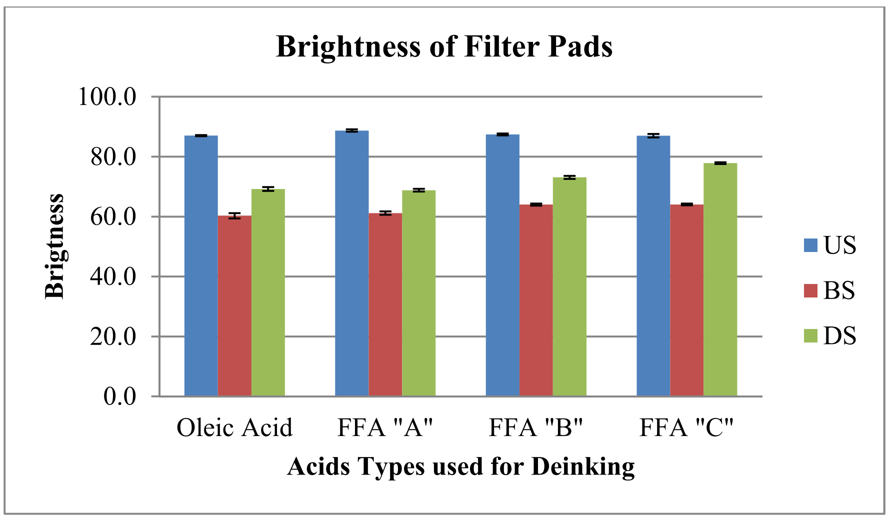

Figure 5.4 Brightness of filterpads before (BS) and after deinking (DS)

Similarly to handsheets, the brightness of filter pads was measured at 457nm (Figure 5.4). Filter pads were prepared from the same deinked unprinted pulp, printed undeinked pulp and printed deinked pulp as handsheets. Again, deinking employed the set of four acids. The brightest filter pads were received from the pulp deinked with free acid obtained from soy oil “C”, followed by the free acid from soy oil “B” (see Figure 5.4). Both free acids resulted in brighter handsheets and filterpads than those prepared from pulp deinked with standard oleic acid. Free acid from soy oil “A” provided deinked pulp with the lowest brightness that was similar to the oleic acid.

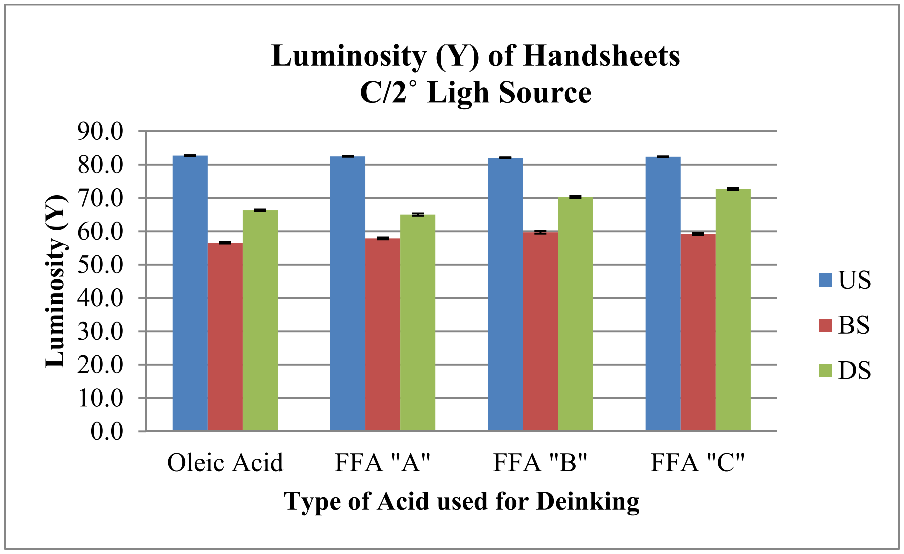

Figure 5.5 Luminosity of handsheets before (BS) and after deinking (DS)

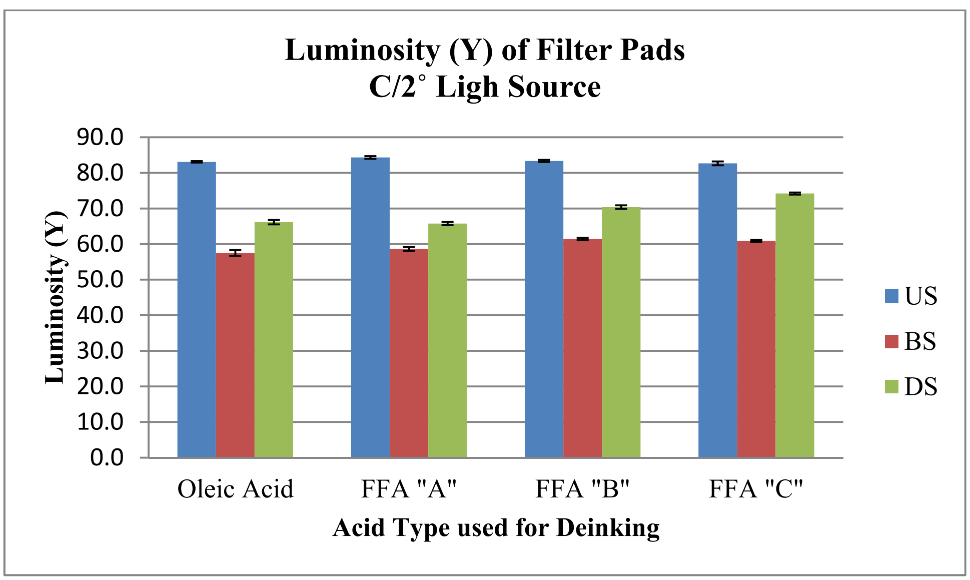

Figure 5.6 Luminosity of filter pads before (BS) and after deinking (DS)

Luminosity Y of handsheets (Figure 5.5) and filter pads (Figure 5.6) provide a similar trend that was observed while measuring brightness. Once again, the free acid that was extracted from soy oil"C" resulted in the deinked pulp with the highest luminosity. The rest of the free acids performed slightly better or similarly to the standard oleic acid. Filtrate darkening represents the variance between the luminosity of the reference membrane filter (tap water) and the test membrane filter (filter pad filtrate).The difference $\Delta Y = Y_{Ref} - Y_{DP}$ represents the filtrate darkening. According to the INGEDE standard, two samples of deinked pulp were submitted to the test. The result is illustrated in the Figure.5. 7, and shows smallest darkening increment when using FFA from oil "C", following by FFA from oil "B", further FFA from oil "A" and the largest darkening was found when using standard oleic acid.

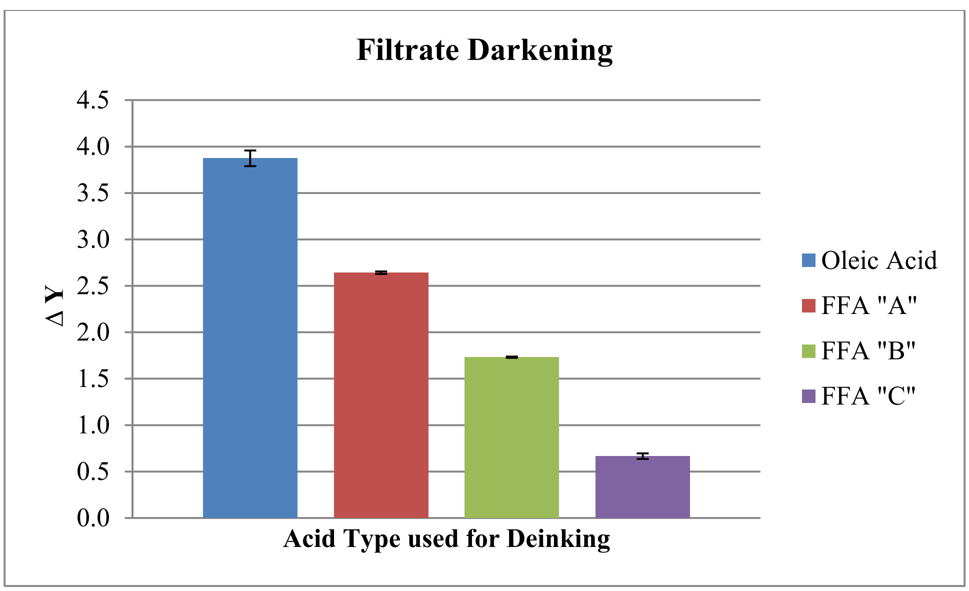

Figure 5.7 Filtrate darkening

Further, lightness (CIE L*) of handsheets and filter pads was monitored (Figure5.8 and Figure 5.9). For both, filter pads and handsheets, it was found that the free acid obtained from soy oil "C" produces lighter deinked pulp and therefore lighter final product.

Optical properties of handsheets from deinked pulps, including the deinking yield, are summarized in Table 5.6. The highest deinking yield was obtained with "free acid from low linoleic soy oil" "A". Standard oleic acid and "free acid from high oleic acid" "B" resulted in similar deinking yields, while "free acid from everyday pure soy oil" "C" gave the lowest yield.

Table 5.6 Optical properties of handsheets from deinked pulp

Free Acid Type	Statistics	Y	ΔY	A	L*	a*	b*	Brightness	Yield %
Oleic Acid	Average	66.3	3.87	37188	85.1	1.26	-2.92	69.7	86.6
	StDev	0.8	-	1633	0.4	0.09	0.18	0.7	0.1
FFA from "A"	Average	65.0	2.64	46005	84.5	1.37	-2.79	68.2	92.9
	StDev	1.1	-	1581	0.6	0.24	0.12	1.1	0.1
FFA from "B"	Average	70.3	1.73	22690	87.2	1.34	-2.30	73.2	86.6
	StDev	0.9	-	1029	0.5	0.24	0.20	0.89	0.2
FFA from "C"	Average	72.7	0.67	15362	88.3	1.33	-2.68	76.1	84.1
	StDev	0.9	-	1653	0.4	0.18	0.32	1.0	0.1

Conclusion

The deinkability efficiency of three experimental fatty acids obtained by extraction from three types of soybean oil “A”, “B” and “C” was studied. The deinkability potential of experimental fatty acids was compared to the deinkability power of oleic acid that is used as a standard fatty acid in INGEDE 11p method. The substrate used for deinkability study was heavily printed from both sides and therefore none of the four fatty acids had power to deink such a substrate in one flotation loop experiment. Overall, it was found that two of the three experimental fatty acids (fatty acid soy oil “C” and free acid from soy oil “B”) performed better than the standard used oleic acid. One of the fatty acids was found to perform slightly poorer than oleic acid. Based on some characterizations performed on the fatty acids, it can be concluded that the lower acid number of fatty acid is more beneficial in ink removal.

Acknowledgement

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CHAPTER VI

DEINKING OF INKJET PRINTED PAPER USING FATTY ACID FROM SOYBEAN OIL AND BENTONITE CLAY

Summary

Food grade soybean oil ”C” and bentonite clay was used in one loop - flotation deinking of inkjet printed-paper. First, the deinkability of substrate using fatty acids extracted from soybean oil was compared against oleic acid alone. Oleic acid is used in INGEDE method, which is deinking protocol, widely used in paper recycling industry. It was found that fatty acids from soybean oil have positive effect on deinkability. Their performance was better than that of oleic acid, typically used in deinking. Second part of the experiment focused on clay and its adsorption ability viewed as very promising if used in removal of sub-micron hydrophilic inkjet ink pigment particles. The surface of the bentonite clay was altered using fatty acids from proprietary soybean oil. Different levels of hydrophobicity of clay were achieved. Overall, it was found that clay has positive effect on the coloration of recycled water coming from deinking stream. On the other hand, the color of the clay that was used in the deinking experiments had negative effect on the final paper color. The unwanted coloration of the paper could be omitted by using the clay with whiter color, or by separating colored clay from paper fibers.

Introduction

Absorbent materials have ability to collect and remove unwanted matter from the aqueous phase. Some of the absorbent material's characteristics are hydrophobicity, oleophilicity, reusability and biodegradability (Reynolds et al, 2001). Clays and clay minerals are widely utilized in many industries, including paper industry. The benefit of clays is their high surface area and porosity (Gitipour et al, 1997). Bentonite clay is considered as an effective flocculant suitable for deinking (Horacek, 1992; Mahony, 1993). Some of the studies proved that treated clay can facilitate collection of fine inkjet pigment particles at near neutral pH region (Basilio and Sheppard, 2011). In order to improve sorption characteristics of the clays, various surface treatments can be considered (Vengris et. al, 2001). Clays can be organically modified to become hydrophobic and therefore useful in water-based flotation deinking. The elimination of the pigment particles is facilitated by the flocculation of the deinking agent (Cody and Magauran, 1992). In order to convert the hydrophilic surface of the natural clay, oils or fatty acid can be used (Basilio and Sheppard, 2011).

The goal of deinking is to successfully remove sub-micron hydrophilic ink particles. This work was oriented on deinking experiment focused to use clay particles that would absorb colored ink particles. It was expected that this would have positive impact on ink removal and the purity of the circuit water. In order to successfully remove the froth with clay-ink particles, clay particles have to be hydrophobic. It was desired to see if the commercially available food grade soy-bean oil can replace industrial oleic acid. The fraction obtained by extraction of fatty acid from soybean oil served as a hydrophobic matter for clay surface coating.

Materials and Methods

Soy Oil

Proprietary soybean oil “C” was one of three soybean oils provided by the Michigan Soybean Promotion Committee. Sodium soap and free fatty acid fraction was prepared from oil “C”. Properties of extracted fatty acid and sodium soy soap were being tested against standard oleic acid.

Inkjet Printed Substrate

Inkjet printed Multipurpose substrate obtained from HP laboratories was submitted for recycling. Substrate was heavily printed on one side, see Figure 6.1.

Figure 6.1 Inkjet printed substrate

Physical and optical properties of unprinted sheet are depicted in the Table 5.1. INGEDE method 11p was followed during deinking. Repulping step was done in MicroMaelstrom laboratory pulper due to unavailability of Hobart type pulper.

Table 6.1 Physical properties of unprinted base sheet used for deinking

Physical properties of unprinted base sheet	
Grammage (g/m^2)	76.0
Thickness (µm)	96.5
Ash content (%) @ 525˚C	27.0
Hercules Size Test [sec]	29.6
Surface Energy [dynes/cm]	38.7
PPS (CP 1000) Porosity [ml/min]	1505.3
PPS (CP 500) Porosity [ml/min]	1526.0
PPS (CP1000) Roughness [µm]	4.7
PPS (CP1000) Roughness [µm]	5.6
Optical properties of unprinted base sheet	
Brightness	96.2
Luminosity (Y)	86.5
L*	94.5
a*	2.6
b*	-5.4
Opacity [%]	89.7

Preparation Sodium Soap from Soy-Oil "C"

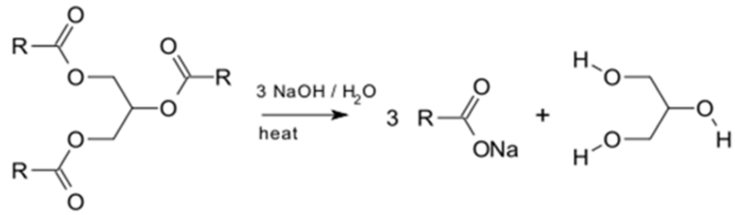

Figure 6.2 General saponification reaction of triglycerides resulting in sodium soap and glycerin

Figure 6.3 Beginning of saponification

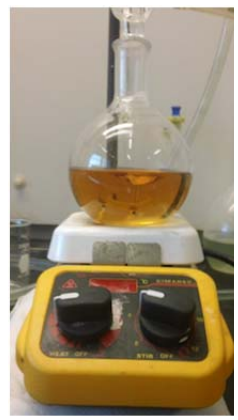

Figure 6.4 End of saponification

Saponification reaction took approximately 20 minutes. At the beginning of saponification reaction, soy oil had milky appearance (Fig. 6.3). As the saponification proceeded, the clearing out of the solution appeared (Fig. 6.4), which signified the end of saponification reaction. Further, solid sodium soap was prepared by "salting-out" reaction (Fig. 6.5).

Figure 6.5 Solid sodium soap made from soy-oil “C”

Preparation of Fatty Acid from Sodium Soap “C”

Next step was to prepare free fatty acid. This reaction was based on “Determination of the total crude fatty acids contents within alkaline soaps”reference needed. First, sodium soap was dissolved in water and further was neutralized with 4N sulphuric acid until precipitated white mass stopped forming on the surface of the water (or until methyl orange, pH indicator, did not change the color).

Figure 6.6 Dissolved sodium soap

Figure 6.7 Neutralized alkaline soap

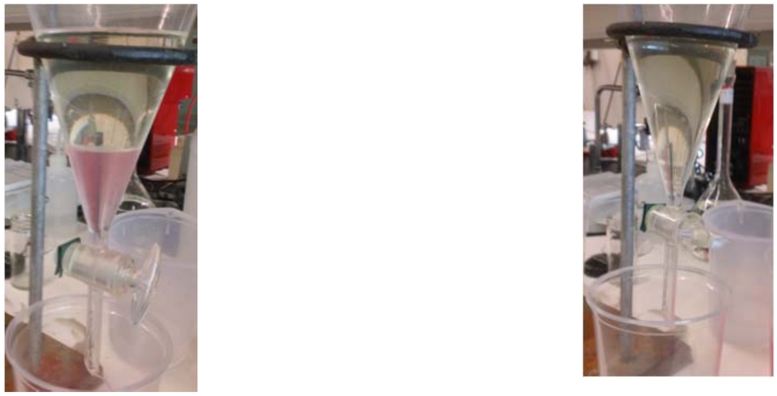

Figure 6.8 Separation of aqueous and oily phase

Deinking

Before deinking trial, unprinted and printed samples were aged for 72 hours at 60˚C according to INGEDE Protocol 11p (INGEDE Method 11p, 2009). After aging, printed and unprinted substrate was torn to pieces 2x2cm in size. Further, prepared paper samples were conditioned in the paper laboratory for 24 hours, 23±1˚C at 50±2% RH. MicroMaelstrom^{TM} Laboratory Pulper was used instead of Holbart type pulper described in INGEDE Method 11p. Repulping parameters (RPM and repulping time) versus particle dirt count and diameter size were examined prior this experimental study (Husovska, 2013). The most suitable conditions were selected and they are listed in Table 6.1. Dilution water hardness was adjusted as per INGEDE requirement. INGEDE protocol lists the homogenization process as an optional one. During our experimental study, all of the pulps were homogenized using a TAPPI disintegrator. Total of eleven experiments were done. One of the experiments served as a standard and was executed by close following of INGEDE method. This deinking procedure involves oleic acid in its deinking recipe. The next experiment involved free fatty acid extracted from proprietary soybean oil “C”. The goal of this study was to see if oleic acid could be replaced by other source of free fatty acid coming from renewable source such as soy. Lastly, set of nine experiments focused on other mechanism, which could improve deinkability of inkjet printed substrate. Experiments that involved treated clay are represented in the Table 6.2.

Re-pulping facilitates the rupture of bonds between ink and the substrate. First, paper slurry, at higher consistency, takes advantage of shear forces and ink particle could be partially detached. Secondly, addition of deinking chemical assists the breakdown of the ink-fiber agglomerate.

Re-pulping time was set to 10 minutes for all experiments. The speed of the MicroMaelstrom™ Laboratory Pulper was set to 500 RPM and the temperature was adjusted to 45˚C by using the built in thermostat. Re-pulped stock was diluted to 4% consistency using dilution water with fixed hardness value of 128mg Ca^{2+}/L. In the next step, repulped stock was stored for an hour in the water bath at 45˚C. After storage, TAPPI disintegrator was used to disintegrate fiber bundles for 1 minute. Prior to the air flotation, undeinked stock was taken for preparation of 2 filter pads and 10 handsheets.
The rest of the undeinked pulp was taken and was subjected to flotation deinking. A small 2L laboratory flotation cell was used for all deinking trials. Due to the volume of the cell, each of the experiments was repeated twice. This way, larger amounts of deinked pulp suitable for handsheets and filter pads formation were obtained.

The flotation cell aeration was fixed to flow rate of 1L/min. The duration of flotation deinking was 12 minutes. A paddle scraper was used for froth removal over the course of flotation. The removed froth was collected in a reject tank. The yield of the flotation was calculated once the reject was dried and deducted from the original floated slurry weight. The final consistency of the deinked stock was calculated and was subjected to preparation of the handsheets, filter pads and membrane filters. Standard deinking according to INGEDE protocol, as well as its modified version that included free fatty acid from soy oil "C" added all of the deinking chemicals during the re-pulping stage. Experiments that involved treated clay omitted fatty acid addition in re-pulping stage but used treated clay in flotation stage.

Table 6.2 Repulping, storage and disintegration process parameters for experimental clay aided deinking study

Re-pulping recipe	Sodium hydroxide	0.6%
	Sodium silicate	1.8%
	Hydrogen peroxide	0.7%
Re-pulping conditions	Water hardness adjusted to	128mg Ca^{2+}/L
	Temperature	45˚C
	pH	9.5±0.5
	Consistency	6%
	Mixing speed	500 RPM
	Re-pulping time	10 min
Storage	Consistency	5%
	Duration	60 min
	Temperature	45˚C
	Mixing speed	100 RPM
Disintegration	Consistency	4%
	Duration	1 min
	Temperature	45˚C

This procedure was adopted to avoid detachment of free fatty acid from the clay's surface. In addition, INGEDE recipe assures the formation of sodium soap once free fatty acid reacts with sodium hydroxide. Due to skipped addition of fatty acid in re-pulping, sodium soap from oil "C" in various levels was added into flotation cell to assure froth formation. Table 6.2 represents the conditions during air flotation.

Table 6.3 Flotation deinking parameters

Flotation	FA "C" treated clay/ Sodium soap "C"	See DOE
	Consistency	0.8%
	Duration	12 min
	Temperature	45˚C
	Aeration flow rate	1L/min

2 Filter pads and 10 handsheets were formed from undeinked pulp. Further, 2 Filter pads, and 10 handsheets were prepared from deinked pulp. According to INGEDE Method 1, cellulose nitrate membrane filters with 0.45μm pore diameter should be used for filtrate darkening test. During the experiments, the pigment particles passed though that membrane filter. Therefore, the clarity of process water was assessed via 1205 UNICO Vis Spectrophotometer. The purity of the recycled water was determined via circuit water's absorbance. The measurement was performed on single 525nm wavelength. The specific wavelength was chosen after determining the peak of the highest absorbance value of recycled water solution. The peak occurred at the same wavelength for all performed experiments. The coloration of the repulped paper slurry can be visualized on Figure 6.9.

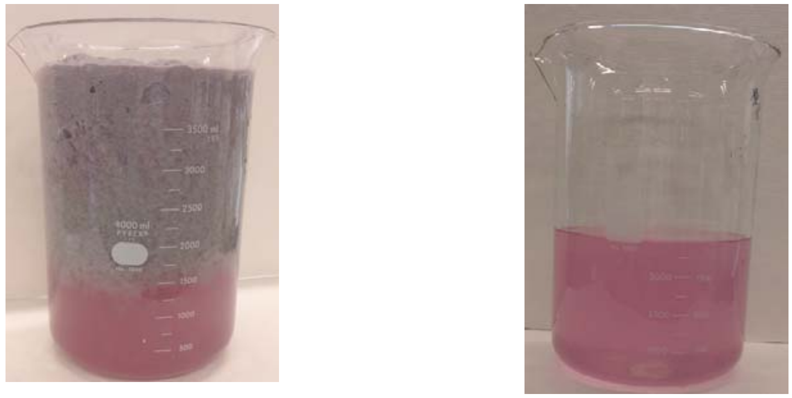

Figure 6.9 Repulped slurry and filtered repulped liquor without fibers

Coating of Clay Particles with Hydrophobic Material

In order to assure the hydrophobicity of the clay's surface, clay was treated using free fatty acid from proprietary soy-oil "C". Isopropyl alcohol was used as liquid medium. Fatty acid from soy-oil" C" was slowly introduced into the liquid phase while vigorously mixing on the stir plate. Clay was introduced as a last ingredient. Three types of clays were screened. Clay #1 (Bentonite clay with low pH in water environment~ pH=5), West Bentonite Ca^{2+} clay (pH = 10.52) and Southern Bentonite Na^{+} clay (pH=9.59), clays can be seen on Figure 6.10.

Figure 6.10 Three types of clays in undeinked filtrate (no fibers)

For deinking trial it was decided to use acidic Bentonite clay. Description of clays and their characteristics are depicted in the Table 6.4.

Table 6.4 Properties of treated clays

Experiment	**FA dosage [%] on clay**	**Clay type**	**Result**
#1	1.1	Bentonite	Partially clear water/partially hydrophobic/sedimentation
	1.1	WB Ca^+	Colored water/not hydrophobic/sedimetation
	1.1	SB Na^+	Colored water/not hydrophobic/sedimentation
#2	2.2	Bentonite	Clear water/partially hydrophobic/sedimentation
#3	4.4	Bentonite	Clear water/ hydrophobic/sedimentation

Clay Charge Determination

0.5g of acidic Bentonite clay sample was diluted in 40 g of DI water. The charge of the clay was detected using Mütek PCD 03 Particle charge detector and results can be found in the Table 6.5.

Table 6.5. Cationic clay

Sample	Potential [mV]	pH
Untreated Bentonite Clay	+280	3.6
Treatment #1 on Bentonite	+300	3.7
Treatment #2 on Bentonite Clay	+380	3.7
Treatment #3 on Bentonite Clay	+380	3.8

Design of Experiment

Design of experiment was set up to see if either amount of clay, treatment of the clay or the amount of sodium soap in flotation cell impacted the efficiency of the deinking. Amount of clay used in flotation deinking (Table 5.6.) varied between 6.25% to 18.75% (calculated on weight of oven dried fibers). Three levels of sodium soap were used during flotation step. Dosage of sodium soap was 1.56%, 3.12% and 4.7% calculated on OD fibers.

Table 6.6. Flotation experiment

Experiment	**Level of FA [%]**	**Amount of Clay [%]**	**Amount of Soap [%]**
1	1.1	6.2	0.75
2	1.1	12.5	0.25
3	1.1	18.7	0.50
4	2.2	6.2	0.25
5	2.2	12.5	0.50
6	2.2	18.7	0.75
7	4.4	6.2	0.50
8	4.4	12.5	0.75
9	4.4	18.7	0.25

Results and Discussion

In the model study where fibers were not involved, clay proved to be suitable adsorbent of dispersed water-based inkjet ink particles. Acidic bentonite clay underwent hydrophobic treatment where various levels of oleic acid were introduced on the clay's surface. The treatment of clay using fatty acid influenced degree of the clay's hydrophobicity and therefore deinking efficacy as well. Naturally, the surface of the clay is hydrophilic, but with the fatty acid treatment can be modified and become partially hydrophobic. The benefit of the both hydrophilic and hydrophobic groups on the clay can play important role in the flotation deinking of the aqueous inks. Such modification of the clay can result in absorbent characteristics of the clay and ink particles while assuring good affinity to the air bubbles. The affinity of clay particles to the air bubbles is crucial as they bring the unwanted ink particles onto the surface where they can be removed. For evaluation clays performance, we used INGEDE Method 11p, which is a standard deinkability method widely accepted within paper industry. Deinking evaluation was assessed by DEM_{Lab} factor (Rao et al., 1998). The DEM_{Lab} factor considers the color variance between unprinted deinked pulp (US) and deinked pulp (DS) in relation to the color difference between unprinted deinked pulp (US) and printed undeinked pulp (BS). Technidyne Brightness Meter S-5 with C/2˚geometry of light source was used.

The DEM_{Lab} factor was calculated according to following formula:

$$DEM_{Lab}=\left(1-\frac{\sqrt{(L*_{US}-L*_{DS})^2+(a*_{US}-a*_{DS})^2+(b*_{US}-b*_{DS})^2}}{\sqrt{(L*_{US}-L*_{BS})^2+(a*_{US}-a*_{BS})^2+(b*_{US}-b*_{BS})^2}}\right)100[\%]$$

Where:

(US) - unprinted deinked pulp

(DS) - deinked pulp

(BS) - printed undeinked pulp

Typically, the deinkability factor DEM_{Lab} is represented on a scale from 0-100%. Material with the deinking factor closest to the 100% will be perfectly deinkable. The color difference of a sample to a reference sample as a vector in the L*a*b* color system (CIELAB) , and it was used to develop DEM_{Lab} deinkability factor. Three axis (CIE LAB) evaluate the color in three dimensional color space (CIE Proceedings, 1932; Fleming, 2003).

Table 6.7 Deinkability efficiency of various chemistries (Experimental conditions of experimets 1-9 are given in the Table 6.6)

Experiment	**Deinkability DEM_{Lab} [%]**	**Deinkability DEM_{f} [%]**
INGEDE	21.9	20.4
INGEDE /FA from oil "C"	34.8	31.6
1	22.3	19.3
2	1.6	0.8
3	1.7	2.2
4	20.2	16.9
5	1.6	0.8
6	7.4	5.3
7	16.2	12.8
8	6.5	4.6
9	6.3	5.3

Based on both deinkability factors (DEMLab and DEMf), deinkability efficiency of "modified" INGEDE chemistry was better than standard INGEDE that uses oleic acid (Table 6.7). Experiments that involved treated clays were evaluated apart from INGEDE and "modified" INGEDE chemistries. Both deinkability factors suggested that lower amounts of clay and higher amount of soap positively influence the deinkability of inkjet inks. The reason of negative effect of large amounts of clay is its unwanted coloration, which negatively affects color of handsheets. Conversely, the benefits of the clay in flotation deinking cannot be omitted. It was demonstrated that the cationic clay absorbs anionically treated pigment of the water based inkjet ink. INGEDE method 11p takes into consideration the cleanliness of the processing water. The purity of circuit water represented by the filtrate darkening ΔY was difficult to perform. In this experiment, the particles of the inkjet ink were passing through the membrane filter and therefore objective judgment of the filtrate's coloration was not possible. Evaluation of recycled water via spectrophotometry was done instead. The absorbance values of all recycled waters were detected. In general, clay had positive effect on recycled water cleanliness. The cleanliness of the circuit water was improved in experiments that involved clay. The purity of recycled water was superior for modified INGEDE method using free fatty acids from soybean oil that that using regular oleic acid. In addition, larger amount of sodium soap positively influenced froth formation and resulted in cleaner pulp and cleaner recycled water. On the other hand, larger amount of soap removed more fibers and that resulted in lower yield. Optical properties of handsheets made from deinked pulp, including the deinking yield, are summarized in Table 6.8. The lower Y and brightness of handsheets may be cause by retention of clay in the handsheets, which may be also supported by higher yield obtained in all experiments including clays (Table 6.8). Clay adsorbed the pigment, but it was trapped in final handsheets. It would be beneficial if the clay could be separated from fibers in last stage so that colored clay could not become part of the handsheet. Then we could observe full benefit of clay ability to absorb pigment and purify waters in deinking process.

Table 6.8 Optical properties of handsheets from deinked pulp

Experiment	Statistics	Y	L*	a*	b*	Brightness	Yield %	Absorbance at 525 nm %
INGEDE	Average	70.3	87.1	0.7	-1.3	71.6	52.8	0.100
	StDev	0.9	0.4	0.1	0.4	1.3	0.6	-
Modified INGEDE	Average	72.4	88.2	0.7	-1.3	73.7	53.6	0.053
	StDev	0.9	0.4	0.2	0.4	1.3	0.7	-
1	Average	63.5	83.7	0.9	-0.7	64.0	78	0.009
	StDev	1.3	0.7	0.4	0.6	1.8	1.2	-
2	Average	55.1	79.1	0.8	0.6	54.5	80.1	0.000
	StDev	1.0	0.6	0.2	0.6	1.6	1.9	-
3	Average	52.0	77.3	1.5	0.2	51.7	95.3	0.000
	StDev	0.6	0.4	0.1	0.4	1.0	0.4	-
4	Average	61.2	80.8	0.6	0.6	63.2	84.9	0.006
	StDev	1.5	0.8	0.3	0.8	2.1	1.1	-
5	Average	53.2	78.0	0.9	0.3	52.8	91.0	0.005
	StDev	1.2	0.7	0.1	0.6	1.6	1.0	-
6	Average	54.9	78.8	1.2	0.5	54.0	77.4	0.000
	StDev	0.5	0.3	0.1	0.4	0.9	1.6	-
7	Average	62.1	83.0	0.4	0.2	61.8	81.0	0.011
	StDev	1.9	1.0	0.2	0.9	2.8	1.5	-
8	Average	54.7	78.9	0.6	0.3	54.3	89.4	0.000
	StDev	1.1	0.6	0.2	0.7	1.7	1.6	-
9	Average	54.1	78.5	0.8	0.0	54.0	92.3	0.004
	StDev	0.8	0.5	0.2	0.4	1.1	1.4	

Conclusion

It was found that fatty acid from soy-bean oil has positive effect on deinkability of the inkjet printed substrate. Deinkability results were slightly better than deinkability results obtained with the standardly used oleic acid. Clay was found to have positive effect on the recycled water purity and it was proven that has exceptional adsorbent capability of pigments within short period of time. Overall, it this study, clay did not improve deinkability if compared to INGEDE 11p method. Bentonite clay had dark shade and negatively influenced the brightness of the final handsheeets. According to some of the authors the brightness of the recycled pulp improved due to the clay addition (Basilio and Sheppard, 2011). Therefore, clay with brighter color should be selected and considered for further study, or separation of clay from fibers would clearly improve brightness of handdsheets.

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CHAPTER VII

CONCLUSION

The presence of novel water based inks in paper recycling stream complicates the deinking process and severely reduces optical quality of final product. Pigment particle size of these water based inks is significantly smaller than that required for efficient removal during flotation deinking.

Current work was focused on deinking of water-based flexo and NIP inks, along with pressure sensitive adhesives. Both types of material are formulated around acrylic chemistry. Experimental study revealed the behavior of visible contaminant, pressure sensitive label, in various pH regions. It was observed that the particle growth occurs in acidic pH. Water-based ink behaves similarly in a low pH region. The alkaline region had no influence on particle growth. Removal of macro and micro contaminants benefited from larger particle sizes. Therefore, application of these findings is desirable, however it is acknowledged that traditional recycling is done in alkaline environment.

The significance of the pH and its role in the deinking was further examined. Alkaline pH is necessary for ink detachment from the substrate. Acrylic polymers with abundance of –COOH groups in water based inks stay in salt form, which is water soluble. On the other hand, ink agglomeration is essential for its removal. Acidic pH has the capability to agglomerate the pigment, once it is detached and present in deinking water. Low pH causes the ink particles to collide and settle down. Cationic surfactants and polyelectrolytes also cause agglomeration of anionic pigment particle. It is predicted that the best effect of deinking could be reached in two stage deinking treatment.

First step being alkaline for achieving ink detachment. Second loop would be acidic, causing the pigment agglomeration. Combination of alkaline pH and addition of agglomerating agent might be desirable option for novel, water based ink removal.

Further, the deinkability efficiency of three experimental fatty acids obtained by extraction from three types of soybean oil “A”, “B” and “C” was considered. The deinkability potential of experimental fatty acids was compared to the deinkability power of oleic acid. Oleic acid is used as a standard fatty acid in deinking INGEDE 11p method. The substrate used for deinkability study was heavily printed from both sides and therefore none of the four fatty acids had power to deink such a substrate in one flotation loop experiment. Overall, it was found that two of the three experimental fatty acids (fatty acid soy oil “C” and free acid from soy oil “B”) performed better than the standard used oleic acid. One of the fatty acids was found to perform slightly poorer than oleic acid. Based on some characterizations performed on the fatty acids, it can be concluded that the lower acid number of fatty acid is more beneficial in ink removal.

Further, this founding was applied and deinkability of inkjet printed medium along with experimental fatty acid from soybean oil “C” was studied. It was found that fatty acid from soy-bean oil has beneficial effect on deinkability of the inkjet printed substrate. Deinkability results were slightly better than deinkability results obtained with the standardly used oleic acid.

In addition, previous findings suggested that acidic regions can help with agglomeration of submicron ink particles. Therefore bentonite clay with acidic character was chosen. In addition to its acidic surface, it acted as a adsorption medium. Clay’s surface was partially coated with experimental fatty acid from soybean oil “C” to assure its floatability during air flotation and thus successful removal. Clay was found to have positive effect on the recycled water purity and it was proven that has exceptional adsorbent capability of pigments within short period of time.

APPENDIX

Before caring out the deinking experiment, pulping conditions were established. As the testing material sheet-fed offset oil based printed paper substrate was chosen. First, the pulping experiments were performed using MicroMaelstrom™ laboratory pulper. Further, experiments were expanded and pulps were processed not only in laboratory pulper, but in addition they were disintegrated in TAPPI disintegrator. The consistency was set to 4% for all of the experiments. Temperature of the repulping water was set to 35°C for all of the experiments.

Experiment #	**MicroMaelstrom™ laboratory pulper**	
	Time [min]	**RPM**
1	5	400
2	10	400
3	15	400
4	5	500
5	10	500
6	15	500
7	5	600
8	10	600
9	15	600

Handsheets were prepared from all of 18 experiments using TAPPI handsheet making standard (T-205). Handsheets were further scanned using EPSON PERFECTION V500 Photo scanner and evaluated using Verity IA Color Image Analysis (VERITY IA Light and Dark Dirt, v 3.4.0) software.

Three handsheets from each experiment were evaluated (54 handsheets) from both sides (108 scans total). Light and dark contaminants of the handsheets surface were the focus of the evaluation. Light contaminants represented the unrefined paper chunks while the dark areas corresponded to ink particles or printed lumps of unrefined paper.

Experiment #	MicroMaelstrom™ laboratory pulper		TAPPI Disintegrator
	Time [min]	RPM	Time [min]
10	5	400	1
11	10	400	1
12	15	400	1
13	5	500	1
14	10	500	1
15	15	500	1
16	5	600	1
17	10	600	1
18	15	600	1

Experiment #	MicroMaelstrom™ laboratory pulper		Dirt diameter [microns]				
			112>≤ 160	160>≤ 195	195>≤ 225	225>≤ 252	252>≤ 276
	RPM	Time [min]	Dirt count (No./100 cm^2)				
1	400	5	1476	665	382	198	138
2	400	10	1738	700	357	200	129
3	400	15	1611	612	312	165	95
4	500	5	1578	660	338	183	124
5	500	10	2100	819	404	206	124
6	500	15	2208	875	349	188	103
7	600	5	1653	693	370	184	116
8	600	10	2153	873	446	429	138
9	600	15	2431	846	382	170	98

Below on the left is the picture of the handsheet formed from the pulp processed in MicroMaelstrom ™ laboratory pulper only (500RPM/ 15 minutes). Picture on the right represents the handsheet made from the pulp coming from experiment #15. During experiment #15 pulp was first processed in MicroMaelstrom ™ laboratory pulper under same conditions (500RPM/ 15 minutes) and in addition it was disintegrated for 1 minute in TAPPI disintegrator. Visually as well as quantitatively it is evident that disintegration has positive effect on the “dirt” size, count and uniformity. For successful deinking, it is desirable for the ink particle to have diameter between 50 – 200 microns.

	
Handsheet from experiment #6	Handsheet from experiment #15

Figure 1 Effect of additional disintegration on handsheet formation

Experiment #	**MicroMaelstrom™ laboratory pulper**		**TAPPI Disintegrator**	**Dirt diameter [microns]**				
				112> ≤160	**160> ≤195**	**195> ≤225**	**225> ≤252**	**252> ≤276**
	RPM	**Time [min]**	**Time [min]**	**Dirt count (No./100 cm^2)**				
10	400	5	1	2507	1231	691	318	269
11	400	10	1	2740	1263	687	361	221
12	400	15	1	2440	1094	568	294	169
13	500	5	1	2215	1060	579	334	209
14	500	10	1	2503	1001	796	419	270
15	500	15	1	2629	1032	586	319	185
16	600	5	1	2021	981	531	278	174
17	600	10	1	2459	1128	595	308	185
18	600	15	1	2498	988	477	236	137

Statistically there was not significant difference between 500 RPM and 600 RPM under 10 or 15 minutes and their direct effect on dirt count and size formation. Energy consumption was considered as well. It was decided that further repulping experiments will be conducted at 500 RPM for duration of 10 minutes and the pulp will be further processed in disintegrator for 1 minute.

As discussed previously, soluble sodium and insoluble calcium soaps were prepared from isolated fatty acids mixtures from every single soy oil sample. Deinking protocol INGEDE method 11p is being followed and the oleic acid serves as a standard.