Water Based Soy Inks for Packaging

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Keywords: water based, flexo, formulation, soy polymer, acrylic vehicle, optical properties, ΔE, end use properties

Abstract

Many printing inks use volatile solvents in the formulation, which are hazardous to the environment from emission of VOC's and at the same time, synthetic resins in these inks are not biodegradable. These problems and particularly the volatile price of petroleum are main reasons to look for new resources for making more environmentally friendly printing inks. The majority of the commercially available water-based inks are formulated based on using acrylic resins, synthetic colorants, solvents/water and additives, which are the common main components for formulating printing inks. Soybean protein is a potential renewable raw material for replacement of acrylic resins. In this research, soy proteins were tested for their suitability to partially or fully replace acrylic emulsion resins in water based packaging inks. The focus was on formulating inks for linerboards, because linerboard is a substrate printed with 100% water-based ink formulations, and the linerboard packaging sector is growing rapidly. The first step was formulating water-based ink based on fully acrylic solution and emulsion polymers as resins. Next, the letdown portion of the ink was formulated with soy polymers, adding them in increments 10-20-30 up to 100% replacement of acrylic emulsion portion of fluid packaging ink. A blue ink was formulated, and its printability, rheology, and end use properties such as rub resistance, gloss, and adhesion were tested and compared to fully acrylic formulations. It was found that the soy polymer did not affect the final color of packaging ink, measured as delta E. ΔE for all soy formulations was less than 1.0, when fully acrylic formulation was used as a standard. Selected end use properties of soy inks were similar to fully acrylic formulations. This research will help to achieve the formulation of a truly environmentally friendly water-based ink, while eliminating emission of VOCs.

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Introduction

Printing ink is a colloidal system that is typically comprised of colorant, resin or polymer, solvent and additives. Some of the resins, solvents or colorants contaminate the environment, soil and water. Several inks use solvents which emit volatile organic components (VOCs) into the environment, and it is significantly hazardous to environment and public health. The U.S. Environmental Protection Agency has a mission to reduce the emission of VOCs to minimize the short or long-term adverse environmental and public health effects. Some of the resins which are used in ink also contain VOCs and non-degradable components. Acrylic resins are widely used in water-based ink chemistry. They are based upon petroleum chemistry availability of which is greatly fluctuating. The ink industry is facing continuous cost pressure due to raw material availability. Prices are rising up as the demand is increasing. The printers are being affected by the continuously rising prices of fuel and transportation cost. All the products are dependent on natural gas and petrochemicals. Sustainability is the answer to control the scarcity of raw materials by replacing them with renewable and biodegradable sources.

Nowadays, water based inks contain 90% - 95% less VOCs than solvent based inks. Even the EPA suggests using water-based inks over solvent based inks when and where possible and applicable. Everybody is talking about sustainability, customers, and sellers are all talking about being sustainable. The demand by print customers for printed products that have minimal environmental impact is growing at an extremely rapid pace. A Company's environmental friendliness is very important these days, because of the growing number of inquiries from customers. Sustainability – is a common sense systems concept of meeting the needs of the present without compromising the ability of future generations to meet their own needs.

Water based inks are used in rotogravure, flexography, screen and digital printing processes. Printers are using water-based inks as a replacement for solvent-based inks. These water-based inks are based on acrylic resin chemistry, which is not biodegradable. However, acrylic resin-based inks are popular for their stability, color reproduction and gloss. Soy is one of the sustainable alternatives, which can be used to replace the acrylic resins in water-based inks. Soy oil is already been successfully being used in lithography and letterpress inks.

Soy oil was already successfully implemented in lithographic printing processes, including litho inks for printing newspapers, books, magazines and newborn babies' footprints (Swiatek,1992; Browner,1992; Erhan, 1995). Newsprint soy inks can be successfully deinked and newsprint can be recycled and reused. Soybeans include about 40% protein and 20% oil. They contain three natural surfactants: soy protein, soy lecithin, and soy saponin. Soy proteins are obtained through the extraction of soybean oil. They form the byproduct that remains after the removal of the hulls and oil from the flake (Xu,2011; Kinsella,1972). Soy protein concentrate is made by removing the aqueous liquid part of the soybeans and it contains approximately 65-72% protein. Soy protein isolate is made from defatted soy flour by removing the carbohydrates of the bean. It is the most refined form of soy proteins and it contains 90% protein (Xu,2011; Kinsella,1972). Soy protein is used in a variety of foods, such as salad dressings, frozen desserts, breads, and breakfast cereals; also, it can be used as a natural polymeric emulsifier, foaming agent, and texture-enhancer. The other industrial products that use soy protein include adhesives, asphalt additives, resins, cleaning materials, cosmetics, inks, paints, plastics, polyesters and textile fibers (Smith,1996). The basic application of industrial-grade protein is as a binder in paper coatings.

Proteins are built by condensation reaction of amino acid monomers, which create peptide bonds. Water molecules are released as a result of condensation reaction between amino acids (Graham,1983). Soy protein has a complex 3-D shape and contains 19 different amino acids, which are held together in a coiled structure by peptide bonds. Proteins contain positive and negative functional groups. The functional groups found in soy protein consist of: amino, carboxyl, hydroxyl, phenyl and sulfhydryl (Graham,1983).

Acrylic solution and emulsion polymers and their various copolymers are widely used in water based ink formulations. Water-based flexo inks are formulated with various acrylic polymers and copolymers serving as solution and emulsion resins to grind and disperse pigments and create ink films, and impart necessary properties such as rheology, adhesion, or rub resistance. The printing industry sometimes feels shortages of these acrylic polymers, with associated higher prices. The aim of this project is to determine if a particular soy protein (ProSoy 7475) can be used to partially replace acrylic resins in water-based flexo inks, mainly in the letdown portion of the ink, thus replacing primarily emulsion resins, responsible for film forming, to create more environmentally friendly inks, with the goal not only to reduce environmental pollution, but also to create an ink with better sustainability and printability.

Experimental procedure

Soy Protein (ProSoy 7475) was provided by ARRO Corporation. A blue pigment dispersion was obtained from American Inks & Technology Ltd. Company under the commercial name “PB15-44”. Other materials that were used in this research were also provided by the same company. Table 1 gives the physical and chemical properties of ProSoy 7475. Table 2 gives the physical and chemical properties of the pigment dispersion. Other materials such as Isopropyl alcohol, defoamer (FC-613), acrylic Varnish (AC0073), wax, ammonia (NH_4OH) were also used in ink formulations.

Preparation of a ProSoy 7475 water based vehicle was done in an air mixer. There are four key variables affecting the rate of ProSoy solubility. Increased rate of solubilization is observed with increasing levels of the following variables: temperature, pH, shear rate and time. Solids level were adjusted as desired. Solids limitation is reached due to increased viscosity of soy vehicle containing higher amount of solids. A solids level of ~20% for ProSoy 7475 was found to be a good starting point. Formulation of soy vehicle is given in the Table 3. The water was heated to desired cooking temperature, which was on average 60° to 76°C. Then, ammonia water at 5% concentration was added under agitation (typical pH range of final solution should be 9.0 to 10.5). ProSoy was added under good agitation, such that the powder was immediately pulled below the surface and got wetted. Agitation with a vortex mixer was maintained for 40 minutes at the desired cooking temperature (60oC-76oC). Other formulation ingredients were later added under agitation to the protein solution

Dry Appearance:	Off White to Tan Granular Powder
Solution Color:	Opaque Light Brown
Bulk Density	672 kg/m^3
Moisture	15% Maximum
Solution Solids	20%
Particle size	325 Mesh

Table 1. *Physical & Chemical Properties of ProSoy 7475 powder*

Appearance	Blue Liquid
pH	8-10
Solubility in Water	Miscible
Specific Gravity (g/cm^3)	1.11
Viscosity (cP) - Centipoise)	15-25

Table 2. *Physical and chemical properties of pigment dispersion (PB15-44)*

Material	[Wt. %]
Water	80
ProSoy	15
Ammonia or Amine	0.4 to 1.0
Isopropyl Alcohol	4
Biocides	As Needed
Antifoam	As Needed

Table 3. *Soy vehicle formulation*

Acrylic water based ink formulation proceeds as per the guideline shown in the Table 4. A commercial water based acrylic ink was prepared as per the formula weight used in commercial ink formulation by using acrylic vehicle AC0073 (Table 4). pH was adjusted with 5% ammonia water to pH - 9.1. Viscosity was measured as efflux time - on Zahn cup 2 at controlled temperature 250 C, efflux time was 25 seconds.

Acrylic Ink Formulation using AC 0073 Vehicle		
Material	Weight in gm	Purpose
Pigment Dispersion PB-15-44	43.50	Provides Color
H2O (DI water)	07.00	Carries Pigment to the Substrate
Acrylic Varnish (AC 0073)	48.10	Holds pigment on substrate
Wax (AIT-PE-35)	01.00	Provides elasticity
Defoamer (FC-613)	00.40	Controls foaming issues
Total weight	100.00	

Table 4. *Standard water based flexo ink formulation with acrylic polymers*

Material	Ink 1	Ink 2	Ink 3	Ink 4	Ink 5	Ink 6
PB-15-44	43.5	43.5	43.5	43.5	43.5	43.5
H2O (DI water)	7	7	7	7	7	7
Varnish (AC 0073): (ProSoy 7475)	**100:0**	**20:80**	**40:60**	**60:40**	**80:20**	**0:100**
WAX (AIT-PE-35)	1	1	1	1	1	1
Defoamer (FC-613)	0.4	0.4	0.4	0.4	0.4	0.4
Total weight	100	100	100	100	100	100

Table 5. *Acrylic/soy water based ink formulation (Formula Weight in gm)*

Inks were printed by a flexo hand proofer on recycled coated board. Anilox screen was 220 LPI. Optical and end use properties were tested on ink drawdowns with an x-Rite eXact spectrodensitometer.

Results and discussion

Various soy inks were formulated (Table 6), but the solution resin in pigment dispersion was always acrylic. Properties of these inks were compared to 100% acrylic water based flexo ink (Standard, Table 6). Inks were tested for their shelf life as pH and viscosity variation over 6 months. As shown in Figure 1, pH value of acrylic ink value ranges from 8.9 to 9.1 and the viscosity ranges from 25 to 26 s measured as efflux time on Zahn #2 cup (Figure 2). For 20% soy vehicle addition, pH changed from 9.1 to 9.2, at 40% soy vehicle addition pH varied from 8.9 to

9.1, at 60% soy vehicle pH changed from 8.8 to 9.0, at 80% soy addition pH was found in range from 8.7 to 9.0 and at 100% soy vehicle measured pH varied from 8.9 to 9.1. When compared, the pH difference between acrylic ink vehicle and soy vehicle, ink pH is almost negligible and within the expected range.

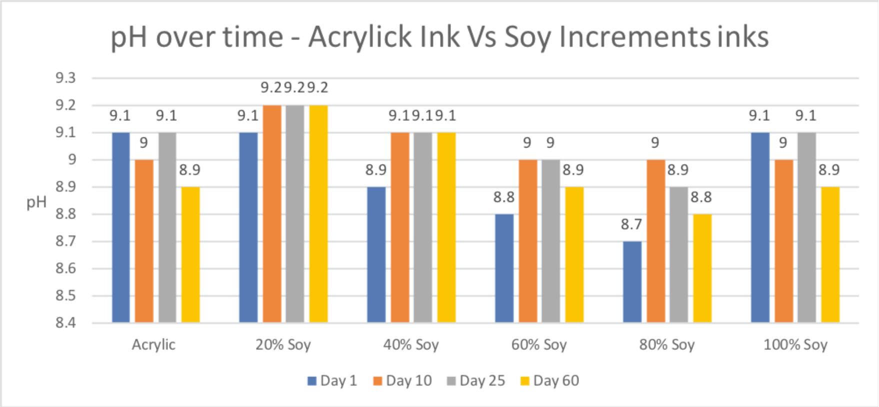

Figure 1. *pH of acrylic vs. soy ink over time period of 60 days*

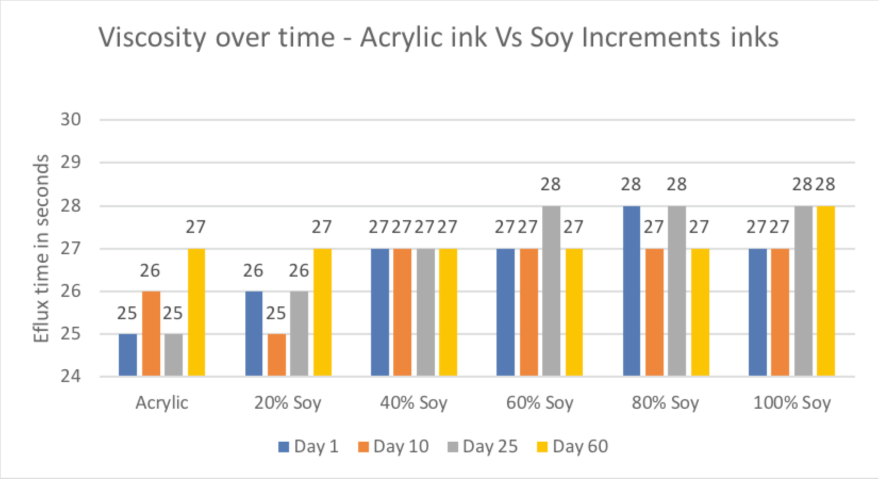

Figure 2. *Viscosity of acrylic and soy ink over time period of 60 days*

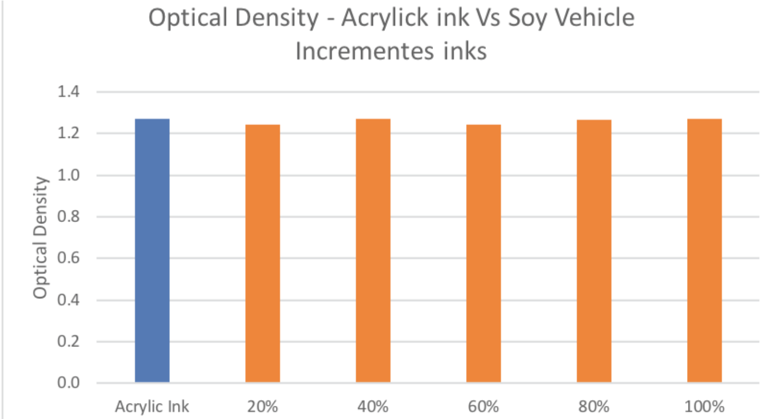

Figure 3. *Optical Density (Acrylic ink Vs Increments of ProSoy 7475) at 100% tone step*

The viscosity of acrylic ink ranges from 25mPa to 27mPa, whereas viscosity of soy vehicle ink depends on soy vehicle percentages, and ranged from 26mPa to 28mPa. It was noticed that the viscosity of acrylic ink was almost constant over time, whereas viscosity of soy vehicle ink showed a slight increase with soy vehicle addition and time. The optical density of acrylic ink at 100% tone ranged from 1.26 to 1.29, whereas optical density of soy vehicle increments ranged from 1.24 to 1.27 at the same tone step (Figure 3). Thus, there was no significant difference in optical density between acrylic resin based ink and soy vehicle based ink at 100% tone step (Figure 3). Acrylic ink CIE LAB and soy vehicle CIE LAB were compared on 100% cyan tone step, and there was almost no difference noticed (Figure 4). ΔE_{cmc} was calculated with acrylic ink as a standard. The largest ΔE difference 0.98 was between acrylic and 100% soy varnish ink, which cannot be noticed by human eye and it is an acceptable E tolerance.

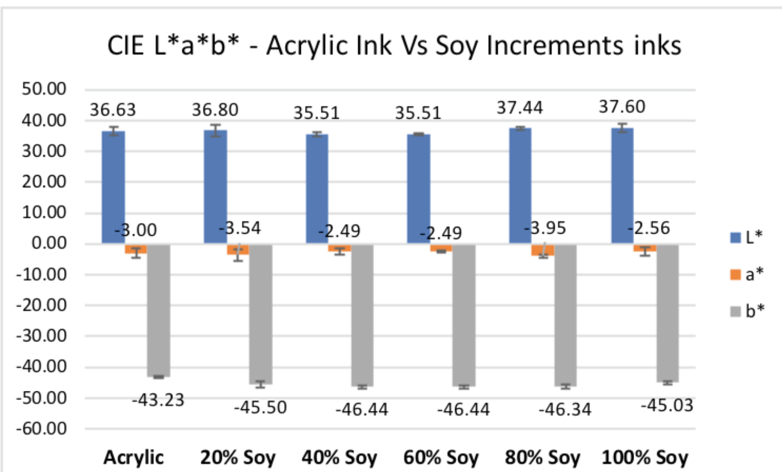

Figure 4. *CIE LAB(Acrylic ink Vs Increments of ProSoy 7475 on 100% tone step)*

The tape adhesion test according to the ASTM F2252-03 standard only requires 0.75-1.0″ wide 3M #610 tape for tape adhesion testing for water-based inks. To perform the test, the 3M #610 tape was used. The tape was applied over the printed surface and removed by pulling it away from the ink film surface. If the ink sticks onto the tape and gets peeled off, the tape adhesion test failed. Acrylic ink showed excellent result for 3M tape test. Inks with 20% and 40% soy vehicle increments showed also excellent tape adhesion performance. Inks with 60-100% soy vehicle had slightly poorer adhesion. They exhibited lower adhesion than acrylic ink, and their performance dropped down to level 4 (Figure 5).

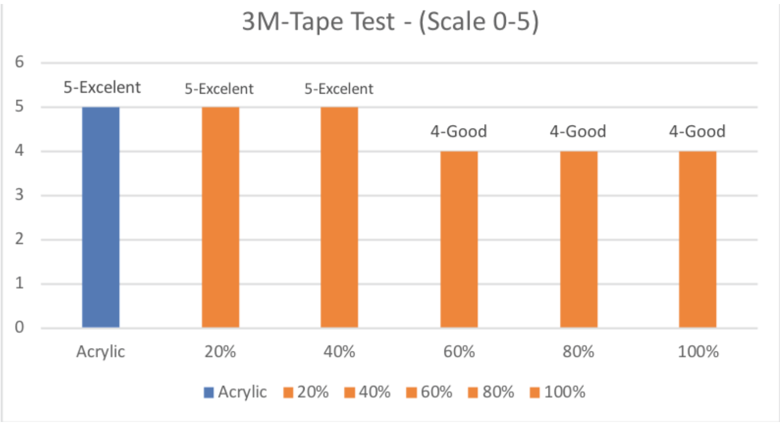

Figure 5. *Tape Test (Acrylic ink Vs Increments of ProSoy7475)*

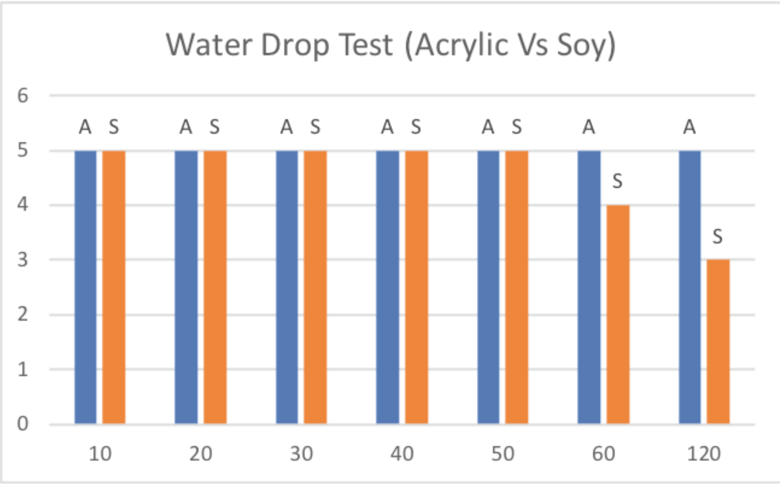

Figure 6. *Water Drop Test (Acrylic ink Vs Increments of ProSoy7475)*

A water drop test was carried out to check the ink interaction with the water on substrate over time both on 100% acrylic ink and 100% increment soy vehicle ink. Time duration for test was ranged from 10 seconds to 120 seconds with the time gap of 10 seconds till 60 seconds and after that tested for 120 seconds. The results were graded on scale from 0 to 5, 5 being the excellent adhesion (Figure 6). Acrylic ink showed excellent water resistance at water drop test for all time durations tested. Ink containing 100% soy vehicle showed at 60 seconds and 120 seconds worse results as compared to acrylic ink (Figure 6).

Conclusions

Soy proteins were tested for their suitability to partially or fully replace acrylic emulsion resins in water based packaging inks. The focus was on formulating inks for linerboards, because linerboard is a substrate printed with 100% water based ink formulations, and the linerboard packaging sector is growing rapidly. It was found that viscosity and pH stability over time was comparable between 100% acrylic and soy/acrylic inks. The color comparison between the target acrylic ink and the increments of soy ink in terms of color difference was found below ΔE_{cmc} less than 1, which was in accord with the E standards used in the graphic and printing industry. Tape adhesion test was slightly worse at soy/acrylic mixed vehicle inks than 100% acrylic ink. Many other end-use properties were comparable between acrylic and soy/acrylic inks.

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Acknowledgement

Authors would like to thank American Ink and Technology for providing various raw materials for ink formulations.