

# **Inkjet Ink with Soy Protein**

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## **Abstract**

Resins, colorants, solvents and additives are the main components that are used to formulate printing inks. Some of these chemicals contaminate the soil, water and environment when released into landfills, water streams and atmosphere. These ingredients even create potential health hazards upon contact with the human body. These problems and particularly the volatile price of petroleum are main reasons to look for new resources for making more environmentally friendly printing inks. Soybean protein and soybean oil are potential renewable raw materials for this replacement. Soy oil is already successfully implemented in lithographic printing processes, including litho inks for printing newspapers, books and magazines. There is a lack of information about soy protein use in inks. In this research, soy protein was used as a resin for water-based inkjet ink formulations. Also, an acrylic water-based inkjet ink was formulated in order to compare with soy ink. Both of them were printed onto plain paper with a Dimatix inkjet printer. Properties of these inks were compared before and after printing. The soy-based inkjet ink showed better results in some of the tests.

## **Introduction**

The soybean is a legume low in saturated fat, with no cholesterol. It is comprised of eight vital amino acids and is known to be a good source of fiber, iron, calcium, zinc, and vitamins. Soybeans include about 40% protein and 20% oil. <sup>[1]</sup> The functional groups found in soy protein consist of: amino, carboxyl, hydroxyl, phenyl and sulfhydryl. <sup>[2]</sup> Soy proteins exist in three major forms: soy flours, soy protein concentrates and soy protein isolates. <sup>[1, 3]</sup>

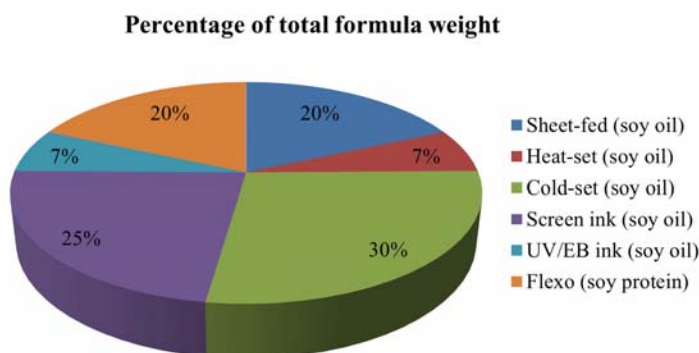
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Soy flour is made by grinding the soybean and contains about 50-59% protein. Soy protein concentrate is made by removing the aqueous liquid part of the soybean and it contains approximately 65-72% protein. <sup>[1, 3]</sup> Soy protein isolate is made from defatted soy flour by removing the carbohydrates (water-soluble) of the bean. It is the most refined form of soy proteins and contains 90% protein. <sup>[1, 3]</sup> Soy proteins are used in a variety of foods, such as salad dressings, frozen desserts, breads, and breakfast cereals; also, they can be used as natural polymeric emulsifiers, foaming agents, adhesives, resins, cleaning materials, cosmetics, inks, paints, plastics, polyesters and textile fibers. <sup>[4]</sup> The basic application of industrial-grade protein is as a binder in paper coating. <sup>[5]</sup>

So far, soy oil is predominantly employed in printing ink, particularly lithographic ink. <sup>[6]</sup> In fact, soy oil has replaced petroleum-based organic resins, which brings certain benefits such as: sustainability and renewability, more vivid, easy to de-ink <sup>[7]</sup> and a reasonable price. <sup>[8]</sup>

Various amounts of soybean material (oil or protein) are used in different printing processes. <sup>[9, 10]</sup> About 40 percent soybean oil is used in black ink and 30 percent soybean oil is used in colored news ink. Sheet-fed litho inks employ around 20 percent of soybean oil, while cold-set offset inks contain roughly 30 percent of soy oil. Business forms are printed with inks containing about 20 percent soybean oil. Screen inks contain 25 percent soy oil, and UV/EB curable inks include only 7 percent soy oil. <sup>[9, 10]</sup> In the flexographic process, inks contain about 20 percent soy protein in the vehicle. <sup>[10, 11]</sup> These percentages are illustrated in Figure 1.



*Figure 1: Soybean consumption in printing processes <sup>[10]</sup>*

Water-based inkjet inks are usually formulated with acrylic resins as binders. The aim of this research is to investigate if the soy protein can be used as a main resin in water-based inkjet inks, or if it is possible to replace acrylic resins in inkjet inks with soy protein to create an environmentally friendly ink, with the ultimate goal not only to reduce environmental pollution, but also to create an ink with better printability.

Inkjet printing technology is divided into two main categories: continuous ink jet (CIJ) and drop-on-demand (DOD), which each of them has several subdivisions. [12, 13] There are three main subdivision with drop-on-demand (DOD) that are: thermal, piezo, and electrostatic. The piezo method is used in a Dimatix printer that was applied in this research. Piezo inkjet processes use a piezoelectric material in its chamber construction. By using a voltage from an electric field, the piezoelectric material undergoes distortion, and then its shape changes and imports pressure to the ink, thus a drop of ink is ejected from the nozzle. [13, 14] The ink jet process employs four main types of inks: water-based, solvent-based, phase-change and UV curable. [13] The most important advantage of water-based inkjet ink is that it is environmentally friendly. Water based ink is not expensive and it is preferably used on the porous surfaces such as paper and paperboard. Water based inkjet inks may cause corrosion of the print heads, thus the heads need to be made to withstand the alkaline environment, which makes them more expensive. Evaporation and absorption are two drying mechanisms that are involved in drying of liquid inks, and absorption is more prevalent in the water-based inkjet process [13]. The finished ink should be able to keep its properties for a prolonged time (shelf-life). These main ink properties consist of: ink color stability, stable viscosity, surface tension, pH, pigment content, and particle size. [13, 15]

Drop formation is one of the important printing steps. If an ink drop is divided into several small drops (or satellites), they cannot be deposited accurately and consequently an unclear image will be created. The behavior of fluids during printing is controlled by the Reynolds, Weber and Ohnesorge numbers. These numbers show the relationship between surface tension, viscosity, ink specific gravity and nozzle diameter (Re, We, Oh). [16]

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\eta}{(\rho\gamma\alpha)^{1/2}}$$

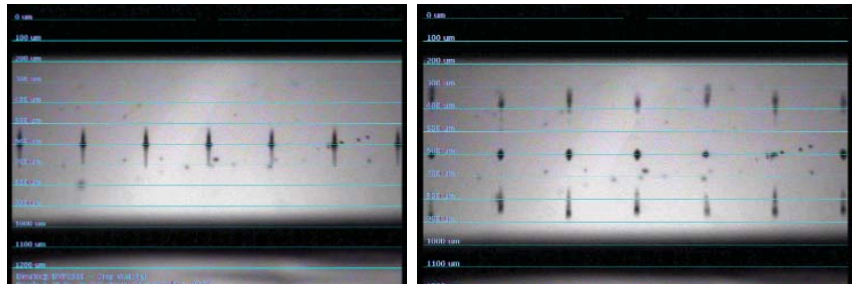
Where,  $\rho$  is the density (kg/m<sup>3</sup>),  $\eta$  is the dynamic viscosity (Pa.s),  $\gamma$  is the surface tension (N/m) and  $\alpha$  is a characteristic length (nozzle diameter (m)). [16, 17] The Z number is a dimensionless number that is the inverse of the Ohnesorge number (Oh). It is a ratio between the Reynolds number and square root of the Weber number, and is independent of fluid velocity ( $v$ ): [18]

$$Oh = \frac{\sqrt{We}}{Re} = \frac{\eta}{(\rho\gamma\alpha)^{1/2}}$$

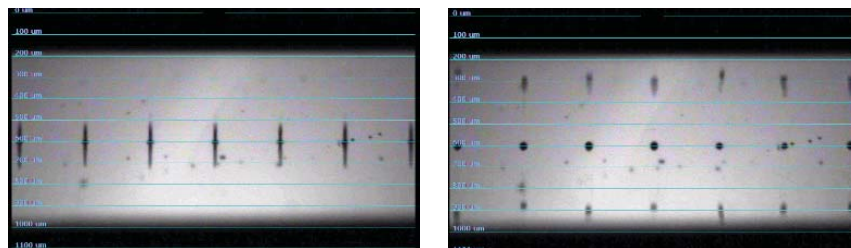
Recent research indicated that the best value for the Z number are between 4 and 14. It was found that a drop with the Z number above 14 often breaks into two ink drops, while a drop with the Z number below 4 sometimes sticks to the inkjet nozzle. [19] However, a more recent paper reported successful jetting below Z=4, along with theoretical confirmation using computational fluid dynamics. [20]

## Experimental

The experimental was divided into two parts; the first was formulation of a water-based inkjet ink based on soy protein (Pro-Cote 4610E) and the second was based on acrylic polymer (Joncryl 678). Soy powder was in acid form, so it needed alkali to be dissolved. This was tried with three alkalis; sodium hydroxide, sodium carbonate, and ammonium hydroxide. Ammonium hydroxide gave the best result. Soy powder was dissolved in DI water by use of ammonium hydroxide. Also, biocide was applied to prevent of growth of bacteria. The same method was done with an acrylic resin. After preparation of polymer, inkjet inks were formulated. Similar methods with the same amounts was applied for both kinds of formulas; soy-based and acrylic-based. It used a pigment dispersion (Cyan Clariant), which was mixed with the polymer binders. Ethylene glycol and Carbowet 300 (Air Product) were added as humectant and surfactant, respectively. Design of Experiments was used to optimize the ink formulations. According to the DOE, eight different formulations were made by use of three factors: polymer (soy and acrylic), pigment dispersion (two levels), and surfactant (two levels). Inks were tested on plain paper with a Dimatix Material Printer DMP-2800. The print head permits users to fill cartridges with any jettable fluid and print directly with the DMP. Also, a commercial Epson inkjet ink was used as a standard to compare ink properties. Figures 2 and 3 shows jettability of two kinds of inkjet inks (acrylic and soy).



*Figure 2: Acrylic-based inkjet ink*



*Figure 3: Soy-based inkjet ink*

The prints of these two kinds of inkjet inks on plain paper are illustrated in Figures 4 and 5.

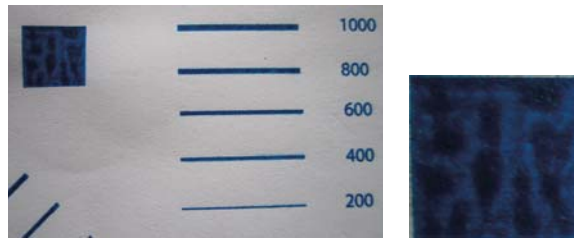


Figure 4: Acrylic-based inkjet ink with Z number 14.68

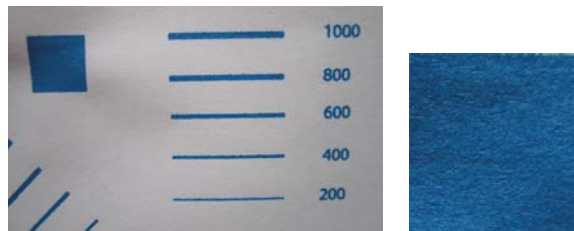


Figure 5: Soy-based inkjet ink with Z number 8.69

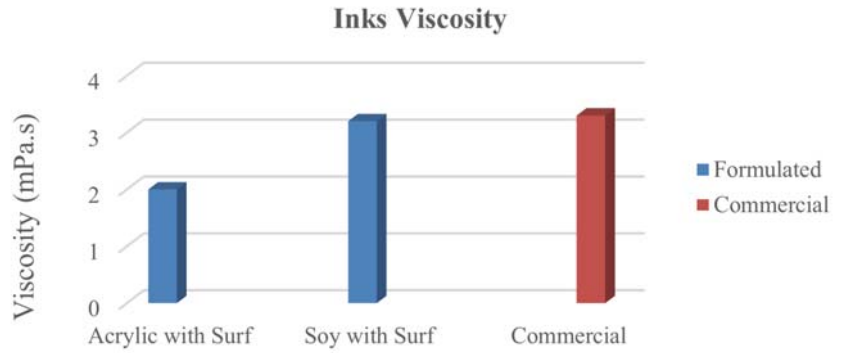
### Results and Discussion

The most important properties of formulated inkjet inks (Acrylic and Soy) with 10 g pigment dispersions were measured, including viscosity, surface tension, specific gravity, particle size, and pH. Finally, the Z numbers of all inks were calculated. These properties are listed in Table 1.

	Acrylic without Surf.	Acrylic with Surf.	Soy without Surf.	Soy with Surf.	Commercial Epson Ink
Formulas No.	1	2	3	4	5
pH	8.54	8.51	9.21	9.19	8.47
Particle size (nm)	160	167	197	188	125
Viscosity (mPa.s)	2.0	2.0	3.2	3.2	3.3
Surface tension (mN/m)	39.34	38.76	34.82	34.76	34.01
Specific Gravity (g/cm <sup>3</sup> )	1.03	1.03	1.03	1.03	1.08
Z number	14.79	14.68	8.69	8.69	8.54

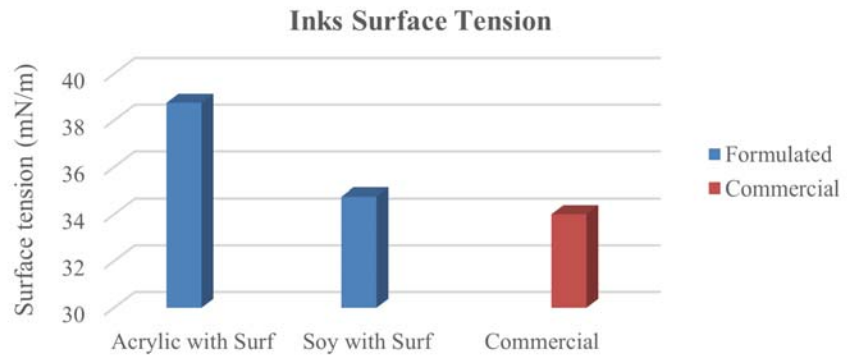
Table 1: Ink properties results

Figures 6, 7 and 8 shows comparison of viscosity, surface tension, and Z number of formulated inkjet inks with commercial Epson Ink, respectively. A TA instrument “AR2000 Rheometer” was employed to measure the viscosity. Figure 6 illustrates that the viscosity of soy-based inkjet ink is more than the viscosity of acrylic-based inkjet ink and also, soy-based ink viscosity is closer to the commercial Epson ink viscosity than acrylic-based ink. Both soy and acrylic inks behaved as Newtonian fluids.



**Figure 6:** Viscosity of formulated inkjet inks (acrylic and soy) and commercial

Figure 7 shows that the soy-based inkjet ink has surface tension less than the acrylic-based inkjet ink, but again soy-based ink surface tension is very close to the commercial Epson inkjet ink. The surface tension of inks was determined with an FTA 200 dynamic contact angle.



**Figure 7:** Surface tension of formulated inkjet inks (acrylic and soy) and commercial

Again, the Z number of soy-based ink is almost the same as the commercial Epson inkjet ink. This is shown in Figure 8.

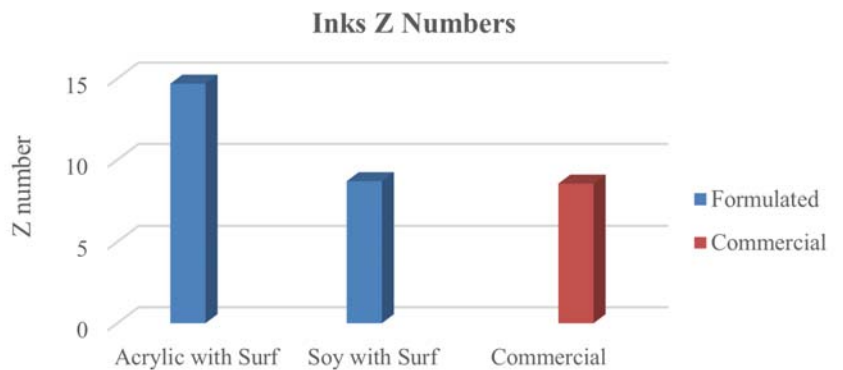


Figure 8: Z number of formulated inkjet inks (acrylic and soy) and commercial

All three Figures show that the soy-based inkjet ink is much closer to the commercial Epson inkjet ink than the acrylic-based inkjet ink.

The printability tests of optical density in cyan mode and CIE L\*a\*b\* value were measured with a SpectroDensitometer X-Rite 530. Figure 9 illustrates that the acrylic-based inkjet ink gives higher optical density than the soy-based inkjet ink, thus the acrylic polymer has a better ability to develop color. Also, as expected from Figures 4 and 5, the soy-based inkjet ink has lower standard deviation than the acrylic-based inkjet ink, which means it has higher print uniformity and lower mottle.

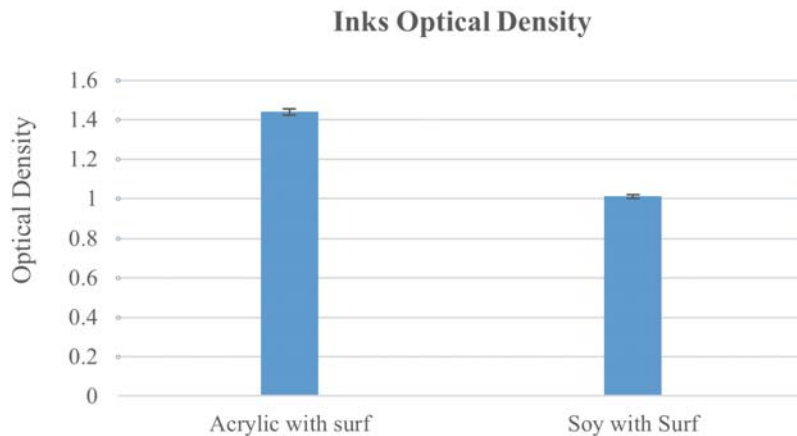


Figure 9: Optical density of soy-based and acrylic-based inkjet inks

To determine the color of each formulated inkjet ink, the CIE L\* a\* b\* of inks (acrylic and soy) were measured. Both formulated inkjet inks were made from the same cyan pigment dispersion, and thus their color should be quite similar. They were good in b\* or bluish, but the acrylic-based inkjet ink had higher a\* value than soy-based inkjet ink, which means the soy-based inkjet ink is closer to the cyan area. Also, the soy-based ink had higher illumination than the acrylic-based ink (Figure 10).

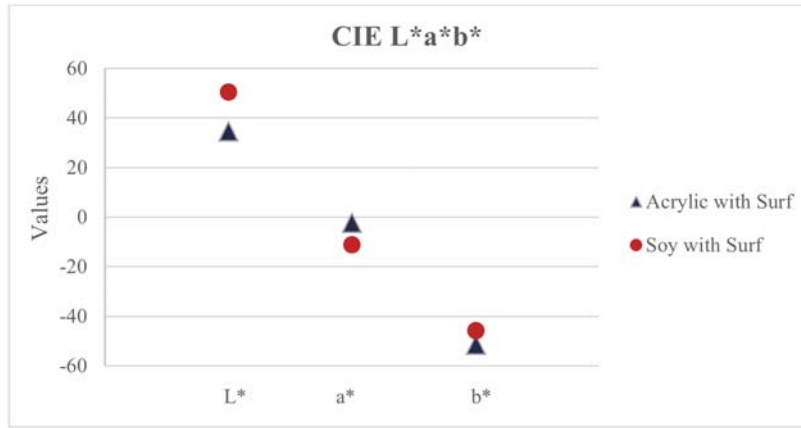


Figure 10: CIE L\* a\* b\* Values of all inkjet inks

As is apparent from Figure 11, that the color of the soy-based ink is more in the blue-green area, and because it used the same cyan pigment dispersion for both of polymers (acrylic and soy), it can be seen that the pigment dispersion is more compatible with the soy polymer than the acrylic polymer in generating cyan color.

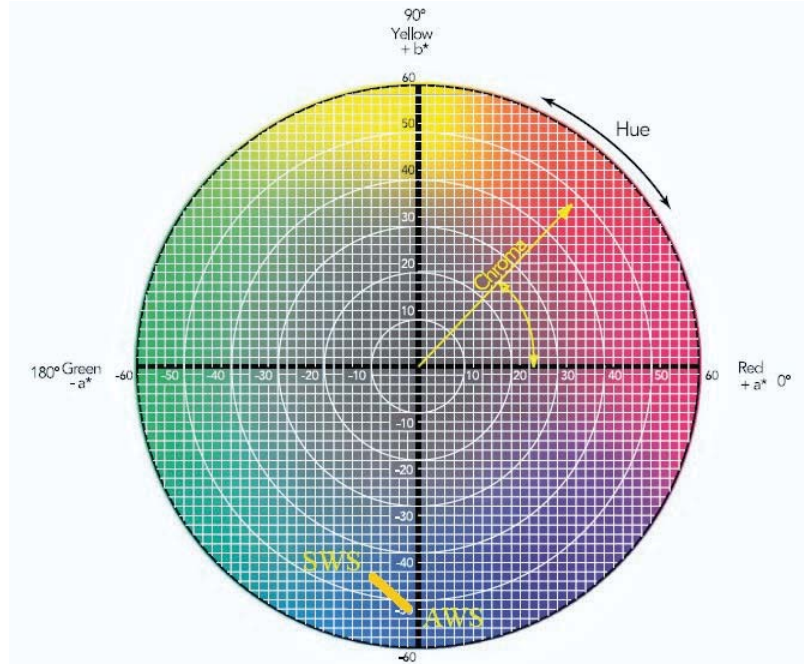


Figure 11: Illustration of CIE a\*b\* values of acrylic and soy inks



## Conclusion

This work was dedicated to formulation of a soy-based inkjet ink. The ink was made with Pro-Cote 4610 soy polymer in various bases. It was found that the best alkali for soy polymer was NH<sub>4</sub>OH. After combining the soy varnish with the pigment dispersion, the soy polymer deagglomerated and the finished ink exhibited particle size in a jettable range for inkjet printing. Design of Experiments was applied for optimization of inkjet ink. Soy-based inks were formulated along with acrylic ones. It was found the soy-based inkjet ink with surfactant and 10 g pigment dispersion had viscosity, surface tension and Z number almost equal to the commercial Epson inkjet ink. Also, it revealed the most uniform color image with the least mottle on the surface of plain paper was obtained with the soy inks.

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