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**Effects of Oligomer-to-Monomer Ratio on Ink Film Properties of White UV-Curable Gravure Ink for Printing on Biaxially Oriented Polypropylene (BOPP)**

by Eubert C. Go

A thesis submitted in partial fulfillment of the requirement  
for the degree of Master of Science  
in the School of Print Media  
in the College of Imaging Arts and Sciences  
of the Rochester Institute of Technology

May 2009

Primary Thesis Advisor: Dr. Scott A. Williams  
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School of Print Media  
Rochester Institute of Technology  
Rochester, New York

Certificate of Approval

Effects of Oligomer-to-Monomer Ratio on Ink Film Properties of White UV-Curable Gravure Ink for Printing on Biaxially Oriented Polypropylene (BOPP)

This is to certify that the Master's Thesis of

Eubert C. Go

has been approved by the Thesis Committee as satisfactory  
for the thesis requirement for the Master of Science degree  
at the convocation of

May 2009

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## **Abstract**

The high shear rate environment of gravure requires very low viscosity, fluid inks. The problems associated with low viscosity such as spilling, crawling, scumming and crazing, have hindered the development of UV-curable gravure inks. This led the researcher to study UV-curable gravure ink formulation. The effects of oligomer-to-monomer ratio and pigment dispersion loading on white ultraviolet (UV)-curable gravure ink film properties (surface cure efficiency, abrasion resistance, substrate adhesion, and ink film flexibility) were investigated. In this study, molecules normally used as monomers, in UV-curable systems, were selected as oligomers relative to the selected monomer, Glycerol Propoxylate Triacrylate (GPTA). The selected oligomers were, Trimethylolpropane Triacrylate (TMPTA), Trimethylolpropane Ethoxylate Triacrylate (ETMPTA), and a commercially available oligomer, Commercial Product A, used in flexographic ink applications. The outcome of this research created a starting point for white UV-curable gravure ink formulation, which will be used in the researcher's family printing business.

The results of the experiment showed that oligomer-to-monomer ratio did not have significant effects on surface cure efficiency, substrate adhesion, and ink film flexibility in the range from 70 to 90% oligomer concentration. Abrasion resistance was dependent on the type of oligomer. Using oligomer Commercial

Product A, a soft oligomer, in combination with monomer Glycerol Propoxylate Triacrylate (GPTA), exhibited a decrease in abrasion resistance from 70:30 to 90:10 ratio. However, when using oligomers Trimethylolpropane Triacrylate (TMPTA) and Trimethylolpropane Ethoxylate Triacrylate (ETMPTA), oligomer-to-monomer ratio had no effect on abrasion resistance within the same range. Titanium dioxide pigment dispersion loading on 70:30 ratio (TMPTA:GPTA) did not have significant effects on substrate adhesion and ink film flexibility. Surface curing efficiency increased to 100% (from 99.5% with no pigment present) with pigment loadings equal to about 20%, but would begin to slightly decrease from complete curing at concentrations exceeding 40%. A significant decrease in abrasion resistance, caused by increased friction, was observed at 20 percent loading. There was, however, an increase in ink film strength from 30 to 50 percent pigment loading.

Developments in UV ink components and persistent research will most likely solve the issues of UV-curable gravure inks. This research opened up a wide array of research opportunities in UV-curable gravure ink formulation and taken a step towards creating an effective white UV-curable gravure ink.

## **Chapter 1**

### **Introduction**

#### **Introduction**

Ultraviolet curable inks have the advantage of being environmentally friendly, rheologically stable, and cost effective in terms of the energy consumption. A big advantage of UV-curable inks is the absence of evaporation in gravure cells, which solves the problem with clogging present in solvent-based inks. However, UV-curable ink has yet to prove itself in the gravure process. There are a few problems that UV-curable inks need to overcome before it can be feasible in the gravure market. Rheology has been the biggest issue for UV-curable inks in gravure. In this research, a starting point for white UV-curable gravure ink formulation was developed by studying the effects of oligomer-to-monomer ratio and pigment loading on ink film properties of UV-curable ink. Print samples were subjected to a set of ink testing procedures that were performed to determine the effects. The results in this research provide valuable information in the development of UV-curable gravure inks used in package printing applications.

## **Statement of the Problem**

Currently, there has not been any breakthrough in UV gravure inks (Mathes, 2008). Developments in UV-curable gravure inks have been slow because of the low viscosity requirement of the gravure printing process. Viscosity is one major factor that makes it difficult to formulate UV-curable gravure inks. Spilling, crawling, scumming and crazing are among the UV-curable gravure ink problems (Wermuth, Oberholzer, & Sakar, 2008). The high shear rate of the gravure printing process requires very low viscosity inks with a Newtonian flow. This research attempted to formulate a white UV-curable ink that met gravure printing viscosity and had a Newtonian flow. This was achieved by studying the effects of oligomer-to-monomer ratio and pigment loading on UV-curable ink film properties.

## **Personal Interest of Study**

The researcher comes from a family that owns a flexible packaging printing business, which utilizes the gravure printing process. The aim of this research was to develop a white UV-curable gravure ink to be used in the family business.

## **Chapter 2**

### **Theoretical Basis**

This chapter covers the basic concepts related to the research. Information about gravure printing, substrate, ultraviolet curing, wet ink properties, and dry/cured ink properties are covered. This section will help printing and non-printing professionals understand the information created in this research.

### **Printing Principles**

#### Gravure Printing

A gravure printing unit has four basic components: the doctor blade, image carrier or cylinder, impression roller and the ink pan. The image area is either cut or etched into the cylinder in the form of cells. During printing, ink fills up these cells by immersing and rotating the cylinder. The excess ink is wiped off the cylinder by a reciprocating doctor blade, leaving ink in the etched cells. The substrate is passed in between the cylinder and the impression roller. Pressure is applied between the cylinder and the impression roller, which causes the ink to transfer onto the substrate.

## **Substrate Principles**

“Nonpaper substrates” refer to substrates printed using the gravure process that are not made of paper. Examples of nonpaper substrates are cellophane, metalized paper and plastics. These materials have one thing in common; they are nonporous, which is a critical factor in drying gravure inks. All types of plastic films can be printed using the gravure printing process provided that the surface energy level of the film is higher than that of the ink or coating. These films are: Polyethylene and copolymers –LDPE, LLDPE, HDPE, EVA, Polypropylene – non-oriented and oriented (BOPP), Polyvinyl Chloride (PVC or vinyl), Polyethylene Terephthalate (PET or Polyester), Nylon- non-oriented and oriented (BON), Polystyrene, and Cellophane (GAA, 2003).

### **Biaxially Oriented Polypropylene**

Polypropylene (PP) is the ideal polymer for packaging film because of its resistance to grease and oil, moisture permeation, and abrasion. It also provides high tensile strength at high temperatures, has good impact and flexibility at very low temperatures, and its stiffness makes it easy to process on any converting line. The term biaxially oriented came out when it was discovered that PP could be extruded into sheet and film (sheet is  $> 0.25$  mm, film is  $< 0.25$  mm). Oriented means stretched and biaxial means in two directions. Therefore, the film is stretched in both directions, machine direction (MD) and cross-machine direction (CD). When PP is biaxially oriented, it becomes very strong with a very high level

of clarity. Biaxially Orientated Polypropylene (BOPP) replaced Cellophane, the most widely used clear packaging film in the world. There are two ways to process BOPP: tubular (bubble) and tenter frame (Pasquini, N., 2005).

Biaxially Oriented Polypropylene films suffer from corona discharge treatment losses over time. Corona discharge treatment is a surface-treatment process that improves the bonding treatment of a substrate. Most plastic substrates, such as BOPP, have chemically inert and nonporous surfaces with low surface tensions, which cause them to be non-receptive to bonding with printing inks. To address the problem of surface treatment loss, solvent based gravure inks based on nitrocellulose are modified with Titanium Acetyl-Acetone (TAA), which acts as an adhesion promoter (Leach, R.H., 2007).

#### Physical Properties of Biaxially Oriented Polypropylene

Table 1 lists some of the physical properties of ExxonMobil Chemical Bicolor™ 20MB666.

**Table 1: ExxonMobil Chemical Bicor™ 20MB666 - Biaxially Oriented Polypropylene Physical Properties (ExxonMobil Chemical, 2009)**

Property	Nominal Value	Unit	Test Method
Coefficient of Friction (Both sides)	0.25		ASTM D1894
Elastic Modulus (MD)	319000	Psi	ASTM D882
Elastic Modulus (TD)	508000	Psi	ASTM D882
Tensile Strength			ASTM D882
MD: Break, 4.9 in Jaw Separation	19600	Psi	
TD: Break, 4.9 in Jaw Separation	39900	Psi	
Tensile Elongation			ASTM D882
MD: Break, 4.9 in Jaw Separation	200%		
TD: Break, 4.9 in Jaw Separation	65%		
Gloss (45 degrees)	85		ASTM D2457

*Coefficient of Friction (COF).* Coefficient of friction is an important film property. It refers to the ratio between the force required to move one surface over another to the total force applied normal to both surfaces (Selke, Culter, & Hernandez, 2004).

*Tensile Strength.* Tensile strength is the stress required to permanently deform or break a material. It is affected by temperature and the test environment (Selke, Culter, & Hernandez, 2004).

*Elastic Modulus.* Elastic modulus is the ratio of stress to elastic strain in tension. A material that has a high elastic modulus would be rigid and requires more stress to produce a certain amount of strain on the material (Selke, Culter, & Hernandez, 2004).

*Tensile Elongation.* Tensile elongation is the maximum length increase (in percent) of a material before it breaks under tension (Selke, Culter, & Hernandez, 2004).

*Gloss.* Gloss is a measure of how reflective a material is at a specified illumination angle. (Selke, Culter, & Hernandez, 2004).

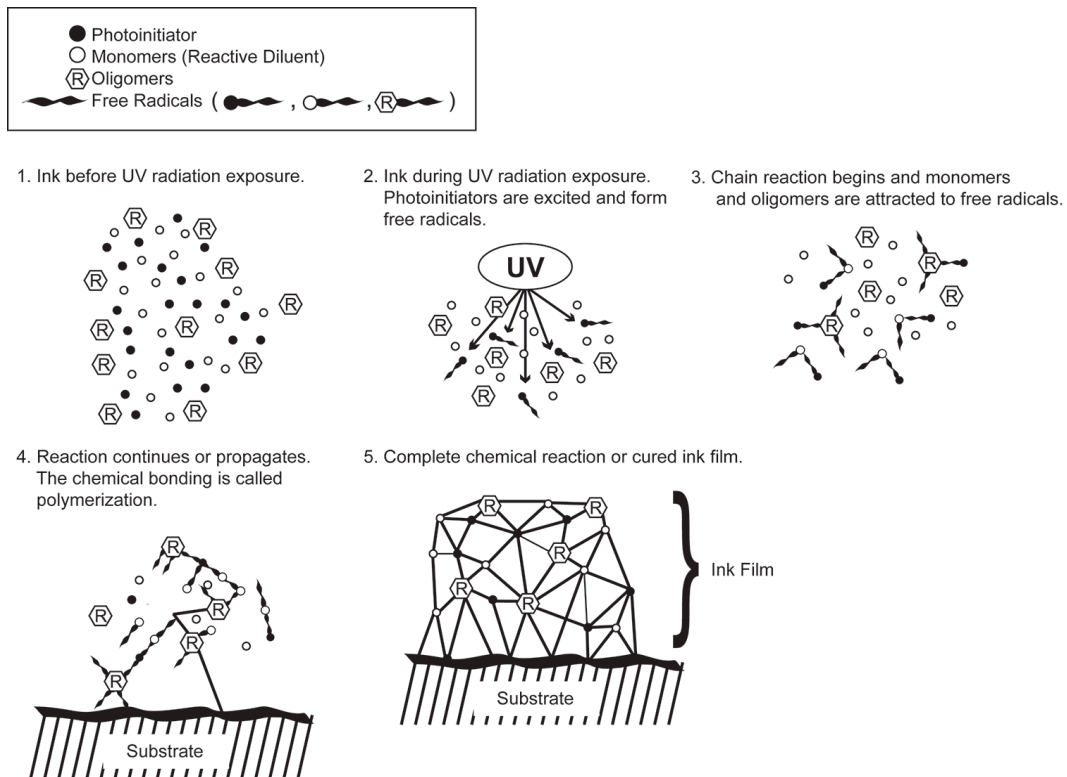
## **Ultraviolet Curing Principles**

A typical ultraviolet curable ink formulation is composed of the following: pigment, monomer, oligomer, photoinitiator, and other additives. Pigment gives color to the printing ink. A monomer is a single molecule that can bond with other monomers to create a three-dimensional network or polymer. An oligomer is a polymer containing a few monomers. Photoinitiators are photosensitive molecules which when exposed to light or radiation, get into an excited state or react with other molecules, creating free radicals.

When a sufficient amount of energy is supplied to a covalent bond, the bond breaks to create free radicals. In the case of ultraviolet curable inks, when UV radiation of a suitable wavelength and intensity penetrates the ink film, this

causes the photoinitiators to create free radicals. Free radicals are molecules with unpaired electrons, which are highly reactive. These free radicals then react with monomers and oligomers in the formulation creating a three-dimensional network or polymer. This process is called free radical polymerization (Holman R. and Oldring P., 1988).

The key steps in the UV curing process are initiation, propagation, and termination. Figure 1 shows these steps.



**Figure 1: UV Ink System (Balmer & Flint Ink Corporation, 2002)**

## **Wet Ink Properties**

### Surface Energy

In the gravure printing process, the image carrier has the printing area etched into it in the form of cells. Ink fills these cells and is transferred to the substrate by various forces, depending on the type of substrate used for printing. There are two types of substrates: porous and non-porous. Porous substrates, like paper, have interstices (gaps) that allow the passage of gases and fluids. Ink is transferred to a porous substrate by capillary action. However, for non-porous substrates, like plastic, capillary action is not present. This case is dependent on the surface tension and surface energy relationship between the ink and the substrate. In order to wet a non-porous substrate, the ink surface energy must be at least 10 dynes/cm lower than that of the non-porous substrate (Thomson, B., 2004). If the ink surface energy were less than 10 dynes/cm, the ink would not adhere to the substrate. In this case, the substrate would require corona discharge treatment to raise the surface tension allowing the ink to adhere to the substrate (Podhajny, 2004).

Surface tension is defined as the force per unit length that acts across any line in a surface, tending to pull the surface closed. It is expressed in either dynes per centimeter (dynes/cm) or millinewtons per meter (mN/m). Surface tension may be measured using a surface tensiometer. This device is based on force measurements of the interaction of a probe with the surface of the sample fluid.

This probe is hung on a balance and brought into contact with the liquid interface. Surface tension is calculated using the forces experienced by the balance as the probe interacts with the surface of the liquid.

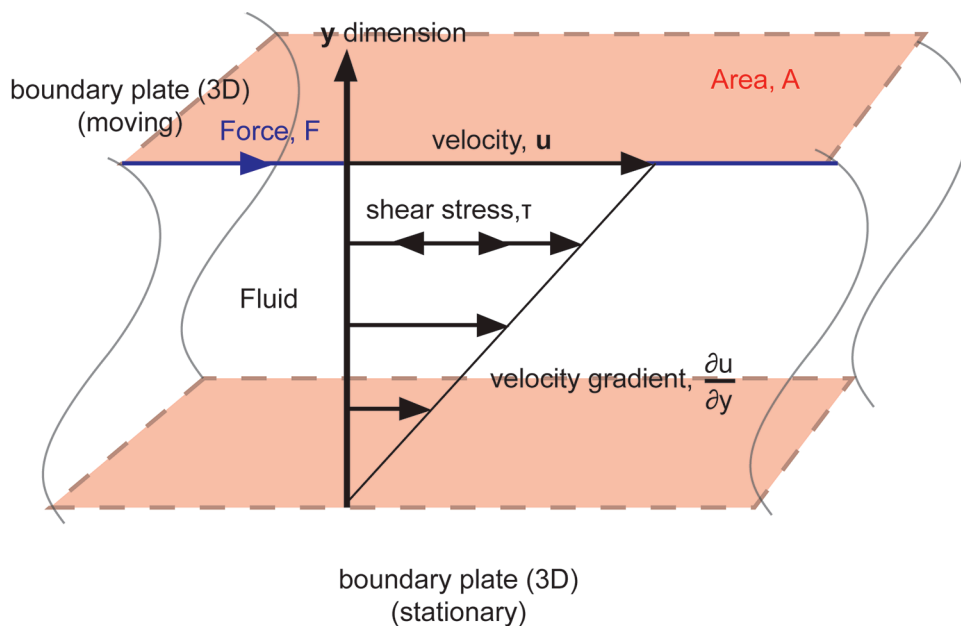
The Du Nouy ring method involves using a platinum ring that is submerged below the liquid interface and then raised upward. Surface tension is calculated using the force required to detach the ring from the liquid interface. The detachment force is measured by hanging the ring on a balance or a torsion wire arrangement. Surface tension is calculated by the amount of force (in dynes) required to detach the ring with a specific diameter (in cm).

### Viscosity

Viscosity is the quantity describing the internal friction or resistance of a fluid to flow. In the gravure printing process, ink viscosity is a very important factor that needs to be maintained and monitored. It affects print uniformity, color consistency, printability, drying speed, trapping, gloss, adhesion, and penetration. The range of viscosity for typical solvent-based gravure inks is between 15 and 25 seconds on a Zahn Cup No. 2 at 25°C. Ink viscosity is dependent on the press conditions such as: the speed of printing, shape and depth of the engraved cells, wiping characteristics of the doctor blade, print design parameters, and the nature of the substrate. Printing at high speeds requires faster drying inks, which means lower ink viscosity. Absorbent substrates like paper require lower viscosities compared to non-porous

substrates like plastic films (GAA, 2003).

*Newtonian Fluids.* Considering two parallel planes of Area A shown in Figure 2, the plane at the top is moving and the other at the bottom is stationary. In between these two planes is the fluid. Consider the fluid to be several planes on top of each other. Applying a force F on the top plane will move the top plane, which results in a velocity (v) and a velocity gradient in between those two planes.



**Figure 2: Laminar Shear of Fluid between Two Plates (Wikipedia, 2008)**

$$\text{velocity gradient} = \frac{du}{dy} = D \text{ (rate of shear) (s}^{-1}\text{)} \quad (1)$$

The shearing stress ( $\tau$ ) is the force per unit area and it is proportional to shear rate ( $D$ ) for a Newtonian fluid as presented in Equation 2 and 3.

$$\tau = \frac{F}{A} \quad (2)$$

$$\tau = \eta D \quad (3)$$

Whereby  $\eta$  represents the coefficient of viscosity of the fluid, equivalent to the shear stress over the shear rate. Hence, using all the equations previously stated, the unit of viscosity can be derived as follows:

$$\text{shearing stress } \tau = \frac{F \text{ (newtons)}}{A \text{ (square meter)}} = \text{pascal (Pa)} \quad (4)$$

$$\text{shear rate } D = \text{velocity gradient} = \frac{du}{dy} = \frac{\text{ms}^{-1}}{\text{m}} = \text{s}^{-1} \quad (5)$$

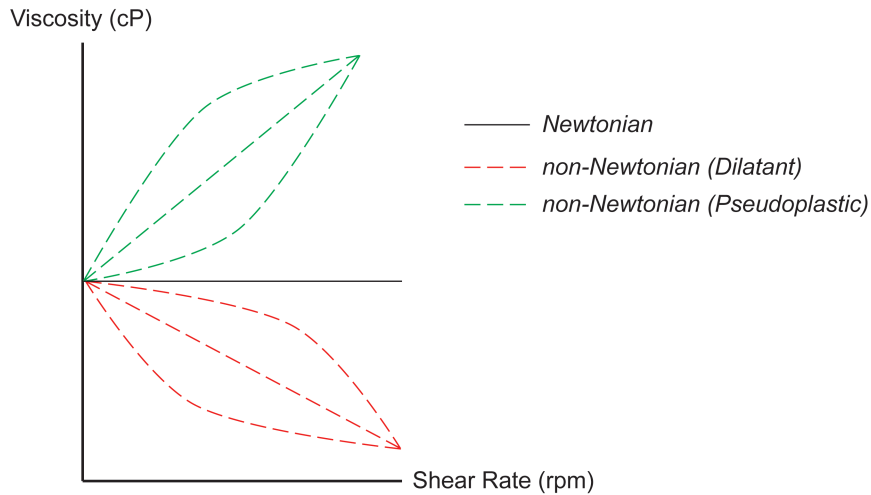
$$\text{coefficient of viscosity } \eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{D} \text{ (Pascal second) or (Pa s)} \quad (6)$$

where 1 Pa s = 10 poise; 1 m Pa s = 1 centipoise

Centipoise is the most commonly used unit of viscosity in the ink industry and will be used for this research.

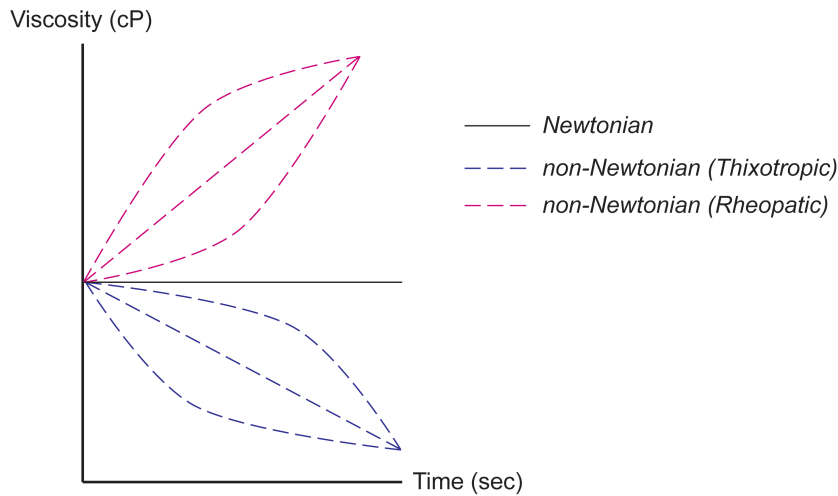
Newtonian fluids are fluids whose stress versus rate of strain curve passes through the origin. It can also be described as fluids whose viscosity

remains the same for varying shear rates. Examples of Newtonian liquids include water, solvents used in inks, light mineral oils, and UV-curable inks. A Newtonian fluid is presented graphically in Figure 3 wherein the relationship between viscosity and shear rate is a straight line.



**Figure 3: Viscosity vs. Shear Rate**

Non-Newtonian fluids are fluids whose viscosities change depending on either the duration of stress or the amount of stress applied to it. There are several types of non-Newtonian fluids. Non-newtonian fluids whose viscosities change on the amount of stress applied to it are either dilatant or pseudoplastic (shown in Figure 3). Non-newtonian fluids whose viscosities change on the duration of stress are either rheopectic or thixotropic (shown in Figure 4). Printing inks used in other printing processes (lithography and flexography) are thixotropic non-Newtonian fluids.



**Figure 4: Viscosity vs. Time**

*Viscosity Measurement.* There are several ways to measure viscosity, two of which are by flow cup and by the rotating cylinder principle. The flow cup is the simplest manual method to measure viscosity. This involves recording the amount of time required for a specific amount of ink to flow through a small orifice. Viscosity is expressed in flow time (seconds), which is the time required from the start ink flow through the orifice until the stream of ink first breaks into droplets. Flexographic and gravure printing commonly use the Zahn flow cups for monitoring and maintaining press viscosity. For gravure package printing, viscosity ranges from 20-30 seconds on a Zahn #2 flow cup (GAA, 2003). Running viscosity for gravure printing is 15 cP at printing temperature (Pekarovicova, Bhide, Fleming, & Pekarovic, 2003). The rotating cylinder principle involves a cylinder or disc submerged in the ink at a specific speed or torque. Viscosity is expressed in either centipoise (cP) or milliPascal-seconds

(mPa.s) at different speeds (rate per minute or rpm). This is the force necessary to rotate the cylinder. This type of viscosity measurement method is useful for studying the flow behavior of non-Newtonian fluids.

Both the flow cup and rotating cylinder method of measuring ink viscosity have advantages and disadvantages. The type of method is dependent on the application. Flow cups are commonly used for proofing and press runs for routine control. Rotating cylinders, on the other hand, are used in ink laboratories since this method is more accurate compared to the flow cup method. A summary of the advantages and disadvantages of both methods is presented in Table 2.

**Table 2: Comparison of the Flow Cup and Rotating Cylinder Viscosity Measurement Methods (Herbert, 2008)**

Flow Cup Method	Rotating Cylinder Method
<p><i>Advantages</i></p> <ul style="list-style-type: none"> <li>• Inexpensive</li> <li>• No special skills required</li> <li>• Portable</li> </ul> <p><i>Disadvantages</i></p> <ul style="list-style-type: none"> <li>• Inaccurate measurement</li> <li>• Prone to operator error</li> <li>• Maintenance issues (unclean hole, uncalibrated)</li> <li>• Every cup can only read a limited range of viscosity</li> </ul>	<p><i>Advantages</i></p> <ul style="list-style-type: none"> <li>• Accurate measurements</li> <li>• Measures more than viscosity (shear rate, sag, thixotropic behavior)</li> <li>• Can measure a wider range of viscosity compared to flow cup method</li> </ul> <p><i>Disadvantages</i></p> <ul style="list-style-type: none"> <li>• Expensive</li> <li>• Requires special skills to operate</li> <li>• Bulky</li> </ul>

## **Dry/Cured Ink Properties**

In this section, the various dry/cured ink testing methods are reviewed to understand its importance to printing production and this research as well. These are: abrasion resistance, substrate adhesion, ink film flexibility, and specular gloss.

### Abrasion Resistance

Abrasion resistance refers to the ability of the ink film to wear. It is an important property of printed products, especially in package printing. As speeds of printing and packaging machines rise, there is a need for improved abrasion resistance because of the greater risk of scuffing from surfaces such as other printed materials or parts of the machine. There are several instruments that are available in the market to perform abrasion resistance on prints, two of which are used in this research. These are the Sutherland Rub Tester and the Ugra Abrasion Tester. The Sutherland Rub Tester uses a 3-inch by 6-inch printed sample (printed side facing upward) that is attached to the base of the device. A counter-test paper with a standard roughness is cut down to 2-inches by 7-inches and attached to the test weight. The weight is then placed in position on top of the base such that the receptor and the printed sample are in contact with each other. The number of strokes is set on the device and the test is started. The printed sample is then visually examined for abrasion (Paul N. Gardner Company, Inc., n.d.).

The Ugra Abrasion Tester is placed on top of the test sample with counter-test paper exactly covered by a friction stamp. The test is then executed by moving the abrasion sled from one end to the other. This device is equipped with a stroke counter. The result of the test is judged visually for signs of abrasion. It can either be the color transfer to the counter-test sample or the abrasion on the printed sample (Ugra, n.d.).

### Adhesion

Set-off refers to the transfer of ink from one substrate to another. This problem occurs when the ink does not adhere to the substrate on impression. Hence, all printed ink films should be tested for adhesion. Adhesion test is performed according to the ASTM F 2552-03 Standard Practice for Evaluating Ink or Coating Adhesion to Flexible Packaging Materials Using Tape. This test involves laying the printed sample on a flat surface and using adhesive tape to hold its position. Next, a 1-inch by 6-inch pressure-sensitive tape (Scotch™ #600 or #610) is applied to the cross direction width of the substrate, leaving a short tab free for grasping. A rubber roller is used to remove all the air bubbles on the tape. The tape is pulled in such a way that the angle between the tape and the substrate is at about a 150° angle. Each sample is evaluated based on how much ink residue is covering the tape (ASTM F 2552-03).

### Flexibility

Flexibility test involves holding the printed sample between the thumb and forefingers for each hand with about half an inch in between the hands and flexing the sample. Then the sample is examined visually for any ink removal (Leach, R.H., 2007).

### Specular Gloss

Specular gloss refers to the mirror-like reflectance of light from the surface of an ink film. The amount of specular reflection is dependent on the surface gloss of the substrate and ink. A gloss meter is used to measure the amount of specular gloss on an ink film. This device is comprised of a light source placed to one side of the normal and a photoelectric measuring cell on the other. The light source illuminates the ink surface and is reflected to the photoelectric cell. Illumination angle can be varied from 10-70 degrees, depending on the brand and model of gloss meter. Sixty degrees gloss is commonly used in the printing industry (Justice, 1995).

## **Chapter 3**

### **Review of the Literature**

In this chapter, literature studies about ultraviolet (UV)-curable ink components, composition, and curing equipment will be reviewed for the purpose of understanding the topic of this research. In addition, previous studies in UV-curing technology will be reviewed, including but not limited to oligomer-to-monomer ratio and pigment loading effects on the characteristics of UV-curable inks and coatings. Recent developments and trends of UV-curable ink are also included.

#### **Ultraviolet (UV)-Curable Inks**

Radiation is the term used to describe the passage of energy from a transmitting source to an absorbing body without interaction with any intervening matter (Leach, R.H., 2007). At present, there are three types of radiation-curing technology that are used in printing inks: ultra-violet (UV) curing, infrared (IR) curing, and electron-beam (EB) curing. Both UV and EB curing technologies use the same mechanism to dry ink film, which is free radical polymerization. Unlike other ink systems, these inks have a common characteristic described as the ability to change instantly from a fluid/liquid phase to a cross-linked solid phase by means of chemical reaction caused by UV or EB radiation. The only difference

between UV and EB curing is that EB ink formulation does not contain photoinitiators (Holman, R. and Oldring, P., 1988).

### Ink Components

Ultraviolet curable inks function the same way as conventional inks. Formulation is very similar to other inks, which have a pigment, vehicle, solvent, and additives. Pigments for UV-curable inks are chosen according to end-use requirements. Solvents are low-viscosity monomers. The vehicle is composed of oligomers, and the additives contain an amount of photoinitiators that respond to UV radiation and start the reaction (Leach, R.H., 2007). The general formulation for UV-curable inks is as follows: Pigment 15-20%, Oligomers 20-35%, Monomers 10-25%, Photoinitiators 5-10%, and other additives 1-5%.

*Pigments.* Pigments are used to impart color to the printing ink, either by themselves, or in combination with other components such as metallic, various micas, or other raw materials (GAA, 2003). Table 3 shows a list of pigments used in the gravure printing process.

**Table 3: Pigments Used in the Gravure Printing Process (Leach, R.H., 2007)**

<b>Color</b>	<b>Pigment (class, generic name)</b>
Yellow	Monoarylide (PY 3, PY 74, PY 98) Diarylide (PY 12, PY 13, PY 14, PY 17, PY 83)
Orange	Same as yellows (PO 5, PO 13, PO 16, PO 34)
Red	Lake Red C (PR 53:1) Permanent Red 2B (PR 48) Lithol Red 4B (PR 57) Permanent Scarlet (PR 166)
Violet	PMTA (PV 2, PV 3) Indanthrene (PV 23, PV 37)
Green	Phthalocyanine (PG 7) PMTA (PG 2)
White	Titanium Dioxide (PW 6)
Extender	Alumina (PW 24) Calcium Carbonate (PW 18) China Clay (PW 19)
Black	Carbon Black (PB 7)
Metallics	Monoazo Yellow (PY 3, PY 74, PY 98) Diaryl Yellow (PY 12, PY 13, PY 14, PY 17, PY 83) Pyrazolone Orange (PO 13, PO 34) Monoazo Orange (PO 5) Monoazo Red (PR 2, PR 3, PR 166, PR 184, PR 185) Monoazo Red – Laked (PR 48, PR 53, PR 57) Phthalocyanine Blue (beta form) (PB 15, PB 16) Zinc Sulphide (PW 7) Metallics (PM 1, PM 2)

\*PY = Pigment Yellow ; PO = Pigment Orange; PR = Pigment Red; PV = Pigment Violet; PG = Pigment Green; PW = Pigment White; PB = Pigment Black; PB = Pigment Blue

*Oligomers.* Oligomers are substances that provide the vehicle for the UV ink. They are similar to monomers, except that they have already been partially polymerized, which makes them more viscous or thicker (Todd, R.E., 1994). During curing, the monomers react with the oligomers to create chains in three dimensions (Wentink, S.G. and Koch, S.D., 1981). In the printing industry, mainly resins/oligomers with acrylate functionality are used to provide the necessary reactivity to enable adequate cure for modern, high-speed presses. Table 4 shows the three main resin types used in UV ink formulation (Leach, R.H., 2007).

**Table 4: Some Acrylated Oligomers (Leach, R.H., 2007)**

<b>Resin Type</b>	<b>Typical Properties</b>
Epoxy Acrylate	Inexpensive, fast curing
Polyurethane Acrylate	Toughness, chemical resistance
Polyester Acrylate	Low viscosity, good pigment wetting

*Monomers.* Monomers, just like solvents used in conventional inks, are diluents used to adjust or control the viscosity of the ink. They are lost during curing (Todd, R.E., 1994). There are only a few monomers that are acceptable for use in the printing industry. Many good viscosity-reducing acrylates are not used because they are toxic and volatile (Leach, R.H., 2007). Table 5 lists the types of monomers and Table 6 lists some acrylated monomers with different functionality.

**Table 5: Types of Diluents Used in UV Curable Inks (Holman, R. and Oldring, P., 1988)**

<b>Diluent</b>	<b>Characteristic</b>
Monofunctional monomers	Lacks the ability to cross-link, good viscosity reduction, good ink flexibility
Difunctional Acrylates	Good pigment-wetting and ink-making properties
Trifunctional Acrylates	Good viscosity reduction, fast curing, capable of extensive cross-linking
High functionality monomers	Good reactivity, low viscosity, good cutting power, fast curing
Non-reactive plasticizing diluents	Good viscosity reduction, aids pigment wetting, powerful solvent

**Table 6: Some Acrylated Monomers (Holman, R. and Oldring, P., 1988)**

<b>Product</b>	<b>Common Abbreviation</b>	<b>Functionality</b>	<b>Irritancy Rating</b>
Ethyl Hexyl Acrylate	EHA	1	Severe
Hydroxy Ethyl Acrylate	HEA	1	Severe
Phenoxyethoxy Ethyl Acrylate	PEEA	1	Moderate
Butanediol Diacrylate	BDDA	2	Severe
Hexanediol Diacrylate	HDDA	2	Moderate
Dianol 22 Diacrylate	DDA	2	Mild
Neopentyl Glycol Diacrylate	NPGDA	2	Severe
Triethylene Glycol Diacrylate	TEGDA	2	Severe
Glycerol Propoxylate Triacrylate	GPTA	3	Mild
Propoxylated TMPTA	PTMPTA	3	Moderate
Ethoxylated TMPTA	ETMPTA	3	Moderate
Trimethylolpropane	TMPTA	3	Moderate
Pentaerythritoltriacylate	PETA	3	Severe

*Photoinitiators.* Photoinitiators, as its name suggests, start the chemical process of polymerization after it is exposed to UV radiation. It initiates the curing process after absorbing UV energy by forming free radicals or cations, depending on its class (Wentink, S.G. and Koch, S.D., 1981). There are three general classes of photoinitiators that have different curing characteristics. These are: Alpha-Hydroxy-Ketones (AHKs), Alpha-Amino-Ketones (AAKs) and Mono & Bis-Acyl-Phosphine-Oxides (MAPO/BAPO). The AHK family of photoinitiators absorbs light below 300 nm and is best for curing overprint varnishes and clear coatings. The AAK family of photoinitiators, on the other hand, absorbs light above 300 nm and is suitable for colored or pigmented inks since they do not compete with pigments in short UV wavelengths. They are generally combined with AHK to increase curing efficiency by widening the spectrum of absorbance. The MAPO/BAPO family of photoinitiators is commonly used for curing opaque white inks since the pigment (Titanium Dioxide) used in these inks has a very high absorbance in UV range (10 to 400 nm) of the spectrum. These photoinitiators absorb within the 420 to 440 nm range (Ciba Specialty Chemicals, 2005).

## **UV Curing Printing Ink Formulation**

The formulation of UV curable printing ink is very extensive. Every formula is dependent on the application or end-user requirements. Table 7 shows the

general formula used for UV curable ink (Holman R. and Oldring P., 1988).

**Table 7: A Generalized UV Curable Printing Ink (Holman R. and Oldring P., 1988)**

Component	Percentage
Acrylate resin, or blend of resin (oligomers)	40-60%
Difunctional Acrylate diluent (monomers)	10-20%
Pigment	15-23%
Photoinitiator	3-8%
Photosynergist	2-5%
Wetting agent/surfactant	1%
Wax	2%

#### Advantage and Disadvantages of UV-Curable Inks

Ultraviolet-curable inks offer a number of advantages. Among them are: good adhesion to a wide variety of substrates, rapid curing, application to most printing processes, viscosity stability, reduced dot gain, capability to be left on the press overnight, unaffected by the pH of the paper, no Volatile Organic Compounds (VOC) in formulation, energy efficient drying, ability to print on thermally sensitive substrates, space saving (UV lamps take much less space than thermal ovens), immediate stackability for finished products, and excellent ink film properties (Holman, R. and Oldring, P., 1988).

However, just like conventional inks, UV-curable inks also have disadvantages. They are: vehicle system causes irritation, may require slightly

toxic washing solutions, require a totally shielded UV radiation source, require air extraction due to ozone production, difficulty in recycling printed paper, very low viscosity is often difficult to formulate without resorting to hazardous monomers, expensive cost, and difficulty curing heavy film weights (Holman, R. and Oldring, P., 1988).

### Curing Equipment

Ultra-violet curing equipment is comprised of three main components: the UV source, reflectors, and ancillary equipment.

*UV Source.* The most widely used source of UV radiation in the printing industry is the mercury vapor lamp. Depending on the curing application, commercially available lamps are divided into three categories: low pressure ( $10^{-3} - 10^{-2}$  Torr), medium pressure ( $10^2$  Torr), and high pressure ( $10^3$  Torr).

*Reflectors.* Reflectors' direct energy is produced by UV lamps and comes in three basic configurations: semi elliptical, planar (non-focused), and parabolic. Aluminum is used in the construction of reflectors, either chemically brightened or using an electro brightening process to maximize reflectivity (Holman, R. and Oldring P., 1988).

### Ancillary Equipment

*Shuttering.* In the event of a line stoppage, it is very important that

flammable or heat-sensitive substrates are not exposed to UV radiation for a long period as it could be ignited or melted. Also, mercury vapour lamps cannot be switched off and on at will since they require a long start-up time. Therefore, shutters are installed to the UV lamp assembly, which closes automatically when the line or press is stopped. Then, the UV lamp is switched to half its power (Holman, R. and Oldring, P., 1988).

*Cooling.* All medium pressure mercury vapor lamps are cooled by means of drawing air over the lamp's surface, which serves many functions. One function is to maintain the temperature of the lamps. Overheating significantly reduces the lifetime of the lamp, and varying temperature causes varying spectral output, which consequently reduces curing efficiency. Another function of the cooling system is to draw ozone away from the workplace. As stated earlier, as one of the disadvantages of using UV curing, UV radiation produces ozone, which is harmful to human beings. Extraction fans are also placed near the substrate for the purpose of drawing out fumes and preventing rise in substrate temperature. Ultraviolet beams also emit an infra red (IR) element, which is one source of heat. It is extremely important that this does not reach the substrate, especially heat-sensitive substrates. Filtering the IR using either water filtration or dichroic reflectors does this. Water filtration involves providing a water sink in the UV beams pathway before it reaches the substrate. This is a very effective method of controlling substrate temperature, but it also affects curing efficiency. Dichroic reflectors are specially designed reflectors; wherein, longer

wavelengths like IR pass through and UV radiation and are reflected. This also causes significant loss in curing efficiency. Water jacket involves installing a water jacket underneath the substrate. Intimate contact between the substrate and the water jacket control the substrate's temperature. Cool air jets may also be used together with this system. Unlike the water filtration and dichroic reflectors, this technique does not affect the lamp's spectral output and curing efficiency (Holman, R. and Oldring P., 1988).

*Shielding.* Ultraviolet radiation is extremely hazardous. Prolonged exposure to UV radiation can cause skin cancer and temporary or even permanent blindness. This is an integral part that UV curing system manufacturers should consider. It is also important that the curing area does not have any reflective material to prevent stray radiation from contacting the work force (Holman, R. and Oldring P., 1988).

## **Current Issues & Trends**

### UV/EB Market

Despite difficult times in the economy, the UV market still fared well in 2007. Marcel Gatti, Rahn Group vice president of energy curing, stated:

The downturn in the U.S. economy and the weakening dollar has created a highly competitive market, especially in the second half of 2007, where even smaller volumes were battled for with high intensity. Nevertheless, going into 2008 we remain optimistic for UV/EB market as a whole, as it continues to benefit from above

average growth rates over other technologies due to ever increasing penetration into new applications. We are also benefiting from an increased awareness for total converting costs and productivity gains versus a simple kg by kg cost comparison between conventional and UV/EB materials (Pianoforte, 2008).

The ultraviolet (UV) and electron beam market (EB) has been growing at a rate of 7% each year (Spaulding, 2009). Recent developments in UV/EB ink and coating formulations and curing equipment have given printers new opportunities. Growth has been mainly in UV flexo and UV inkjet in the packaging area particularly in flexible packaging, food packaging, and folding carton (Pianoforte, 2008). The strongest growth for UV/EB technology will be in the food package printing industry after the Food and Drug Administration (FDA) approved of the use UV/EB inks and coatings for food packaging and even when it comes in contact with food (Anon, 2008).

#### Light Emitting Diode (LED) Ink

New curing technologies have also given printers more opportunities. Light-emitting diode (LED) curing technologies was in the spotlight during Drupa 2008. Two market drivers for LED curing technology would its capability to consume less energy and produce lower wavelengths compared to the typical mercury-containing UV curing lamps. Toyo Ink Manufacturing Corporation Ltd, Sun Chemical, Triangle Digital INX, and Hexion Specialty Chemicals are among the companies that introduced LED-curable products. This technology has

successfully been implemented in sheetfed offset and wide format inkjet (Savastano, 2008). With UV-LED equipment prices declining and more printers becoming confident about implementing this technology, it will soon be implemented in other printing processes; i.e., gravure, flexography, and screen (Spaulding, 2009).

### UV Gravure Ink

Recent advancements in press technology have given printers the capability to mix different printing processes according to their customers' requirements. This is widely applied in the packaging industry. Offset presses, like the Drent Goebel VSOP equipped with UV/EB curing, allow the integration of various printing (screen, gravure, flexo, and digital) and finishing (hot-foil stamping, laminating, and die cutting) modules. The flexibility of these machines allows printers to harness the benefits of every printing process to produce high-quality print products. In narrow web label printing on clear film, UV process inks are typically printed using flexography, while UV white is printed using screen. This is because flexography does not have the capacity to print thicker ink films. Using screen printing slows down the press. Gravure printing, on the other hand, can achieve faster press speeds and the same ink film thickness. Currently, there has not been any breakthrough in UV gravure inks (Mathes, 2008). One of the major problems with UV gravure inks is scumming (Wermuth, Oberholzer, & Sakar, 2008). However, there are commercially available UV gravure coatings.

## **Previous Research**

### Oligomer-to-Monomer Ratio

In 2005, Sartomer Company, Inc., based in Exton, PA, did a similar study on the influence of monomers on the physical performance properties of oligomers. This study involved using monofunctional, difunctional, and multifunctional monomers on various oligomers. Formulations contained a 50:50 oligomer:monomer ratio and 4% photoinitiator. Properties studied were surface cure, resistance to acetone, pendulum hardness, flexibility, stain resistance, and viscosity (Sartomer Corporation, Inc., 2005).

It was revealed that the monomer functionality had a significant effect on the oligomer dilution. The most effective diluents are the monofunctional monomers, followed by difunctional, trifunctional, and tetrafunctional monomers (Sartomer Corporation, Inc., 2005).

The surface cure test revealed that higher functionality monomers produced better cure rates compared to lower functionality monomers, regardless of the oligomer used. Also, ethoxylated monomers, having the capability of overcoming surface oxygen inhibition, produced fast cure speeds. However, their performance varies with the oligomer (Sartomer Corporation, Inc., 2005).

The chemical resistance test using Acetone swab had similar results to the surface cure test. Higher functionality monomers exhibited better chemical resistance compared to lower functionality monomers. For monomers with the same functionality, the monomer that had a higher molecular weight exhibited better chemical resistance as a result of higher cross-linking density. Ethoxylation also contributed to chemical resistance. Chemical resistance was dependent on the oligomer used as well. It was revealed that oligomers with faster curing speed and higher functionality exhibited the best chemical resistance (Sartomer Corporation, Inc., 2005).

Pendulum hardness test revealed that higher functionality monomers and oligomers produced better pendulum hardness results. The flexibility test revealed that monomer functionality is inversely proportional to film flexibility. Also, ethoxylated monomers produce more flexible films compared to unethoxylated monomers of the same functionality. Finally, the stain resistance test revealed that higher functionality oligomers and monomers had better stain resistance (Sartomer Corporation, Inc., 2005).

A separate study performed by Sartomer revealed that abrasion resistance was dependent on the type of oligomer. In that study, the oligomers were categorized as either hard or soft. Soft oligomers provide high flexibility, good impact resistance, and high elongation at break. However, these types of oligomers have poor pencil or pendulum hardness. Contrary to soft oligomers,

hard oligomers provide good pencil or pendulum hardness but poor flexibility, impact, and elongation. The goal of the study was to determine the optimum soft and hard oligomer ratio to provide good balance of abrasion resistance, impact resistance, and pendulum hardness (Sartomer Corporation, Inc., 2002).

### Pigment Loading

A study conducted by Bo Yang (2005) involved using Real Time FTIR (Fourier Transform Infrared) spectroscopy to monitor acrylate double bond conversion and induction period of pigmented ultraviolet (UV)-curable systems. It was seen from the results of the study that the introduction of pigment to oligomer decreases the final acrylate double bond conversion or the maximum cure efficiency but increases the induction period. Besides pigment loading, factors that affect cure efficiency such as pigment type, photoinitiator type and concentration, spectrum output of UV lamps; inhibitor levels, and pulsed UV exposure were also studied. Each type of photoinitiator has its own distinct absorption regions and extinction efficiency of absorption peaks. It is essential that spectral output of the UV lamp match the absorption region of the photoinitiator. Also, certain pigment types absorb certain UV energy wavelengths, which decrease UV availability for the photoinitiator. Therefore, an appropriate photoinitiator and lamp pair was to be used to achieve maximum cure efficiency. It was also seen that high concentrations of inhibitors used to extend UV ink shelf life and pulse UV exposure reduced cure efficiency. Real

time FTIR is one of several ways to determine cure efficiency of ultraviolet-curable inks and coatings. However, this technique has some limitations. One is its incapability to determine surface cure, which is very valuable information for properties such as adhesion, hardness, gloss, and hiding power. Finally, certain pigment types like black and white possess strong interference to the IR laser beam used in this device, and thus, cannot be studied using this technique (Yang, 2005).

Optical properties of pigments also affect UV curing efficiency. Pigments absorb, scatter and even reflect UV light. A study conducted by Ciba Specialty Chemicals, Inc. (2001) involved utilizing integrated transmission spectrum to determine the scattering and reflection in certain wavelength regions where photoinitiators absorb UV radiation to form free radicals. Pigment particle size and shape affects the amount scattering and reflection of UV light (Jahn and Jung, 2001). An increase in pigment particle size causes an increase in cure efficiency (Macarie & Ilia, 2007).

#### Inert Gas Atmosphere Curing

Most UV curing applications are performed in the presence of air where oxygen inhibition has been a major issue. The free radicals formed by the degradation of photoinitiators are scavenged by oxygen molecules, which yield peroxy radicals. These species cannot react with acrylate double bonds, which consequently decreases cure efficiency. To solve this problem, UV curing is

performed in an inert gas atmosphere. Nitrogen is the typical gas used in UV curing, but there are also other alternatives. In 2003, a study to eliminate oxygen inhibition in UV-curing of acrylate coatings by carbon dioxide was conducted. Carbon dioxide has two advantages over nitrogen. One is that it is well available and inexpensive. The other is that it is heavier than air, which makes it easy to contain and avoid loss. The results of the study showed significant improvements in curing efficiency especially with thin films, poorly reactive monomers, resin containing inefficient photoinitiators, filtered light, and low intensity light. In addition, the study showed several factors that pronounce oxygen inhibition, which aided in explaining the results of this research. These factors are: increase of oxygen concentration in the atmosphere, increase of sample temperature, decrease in resin viscosity, decrease in ink film thickness, low photoinitiator concentration, less efficient photoinitiator, poorly reactive monomer and functional oligomer, low UV light intensity, and filtered UV light (Studer, Decker, Beck, & Schwalm, 2003).

## **Summary**

The low viscosity requirement of the gravure printing process remains a problem in the formulation of UV-curable gravure ink. To meet this requirement, low viscosity resins must be formulated which produces a thin ink film prone to oxygen inhibition. However, performing UV-curing in an inert gas atmosphere can solve this. Oligomer-to-monomer ratio plays a critical role in final ink

properties such as cure efficiency, abrasion resistance, adhesion, and flexibility.

Pigment loading, physical and optical properties affect these properties as well.

## **Chapter 4**

### **Research Statement**

Ultraviolet curable gravure inks have the advantage of being environmentally friendly, rheologically stable, and cost effective in terms of the energy consumption. However, crawling and crazing remains a problem with UV curable inks for the gravure printing process because of its low viscosity requirement. Viscosity of UV-curable inks is controlled by oligomer and monomer components in the formulation. In this research, the researcher seeks to understand how the oligomer-to-monomer ratio and pigment dispersion loading of a UV-curable gravure ink formulation affects ink film printability, flexibility, resistance to abrasion, and viscosity.

## **Chapter 5**

### **Methodology**

#### **Raw Materials**

##### Substrate

The substrate used for this research was a clear Biaxially Oriented Polypropylene (BOPP). A clear film was needed because white ink is commonly printed on clear film. This type of film was chosen for this research because it is the primary material used for printing in the researcher's company. The ExxonMobil Bior™ 20MB666 Biaxially Oriented Polypropylene was used to create the print samples. This film has a thickness of 0.002 inches (50.8 microns) and was cut down to 5-inch by 8.5 inch sheets.

Before producing the printed samples, the surface tension on the substrate was checked using a set of dyne solutions ranging from 30 to 50 dynes/cm. In order to achieve effective ink adhesion, the substrate surface tension has to be at least 10 dynes/cm higher than that of the ink. The test was performed by dipping a swab into the dyne solution (starting with 30 dyne/cm solution) and dragging it across the surface of the substrate. If the solution beaded up before two seconds, this was an indication that the dyne solution was at a higher level than the surface tension of the substrate. If this was the case, a

higher level of dyne solution was selected and the same procedure was performed. This was repeated until the dyne solution that would not bead up in two seconds was found. The test was performed on both sides of the substrate because only one side was treated. The side that had the higher surface tension was used for printing. The results of this test showed the ExxonMobil Bicolor™ 20MB666 has a dyne level of about 50 dynes/cm. The surface tension of the benchmark ink (Pharmaflex Supreme White) was about 39 dynes/cm. Hence, corona treatment was no longer necessary since the ink's surface tension was 10 dynes/cm lower than that of the substrate. This difference in surface energy was enough for the ink to wet the substrate.

#### Benchmark Ink

The ink used as a benchmark was the Pharmaflex Supreme White (RPL900634) made by Water Ink Technologies. This is an ultraviolet-curable flexographic ink that is used for printing on various substrates including Biaxially Oriented Polypropylene. Some of the properties of Pharmaflex Supreme White are listed in Table 8.

**Table 8: Some Properties of Pharmaflex Supreme White**

<b>Ink Properties</b>	<b>Measurement</b>
Surface Tension	39 dynes/cm
Viscosity	1134 – 1296 centipoise (Brookfield Digital Viscometer)  40 - 41 seconds (Zahn Cup #3)

### Ink Components

A list of raw materials is found in Table 9. The white pigment used is the TI-PURE<sup>®</sup> made by DuPont, which is a rutile grade of Titanium Dioxide. Rutile grade titanium dioxide, or CI Pigment White 6, was chosen because it is preferred in most printing applications for its higher refractive index, superior hiding power, ability to scatter to light in ink films, and least wear on gravure cylinders. Trimethylolpropane Triacrylate (TMPTA), Trimethylolpropane ethoxylate (14/3 EO/OH) Triacrylate (ETMPTA) and Commercial Product A were used in the study to determine the effect of oligomer viscosity on ink film properties and rheology. TMPTA and ETMPTA are trifunctional monomers that help increase curing rate in energy curable systems, but they can also be used as low viscosity oligomers because of their high functionality (Braddock, 2003). Among the three oligomers, TMPTA has the lowest viscosity. Commercial Product A, on the other hand, has the highest viscosity and ETMPTA has a viscosity value in between the other two oligomers. Glycerol Propoxylate (1 PO/OH) Triacrylate (GPTA) is one of the commonly used monomers in the

graphic arts industry. It was used in this study to achieve the gravure printing viscosity requirement (15 to 20 cPs). The molecular structures for the oligomers and monomer used in this research are shown in Table 10. IRGACURE 814 belongs to the Bis-Acyl-Phosphine-Oxides (BAPO) class of photoinitiators, which is suitable for white inks since its absorbance region is within 420 to 440 nm range. Flexcure D-30 LV and Sartomer SR614 (Alkoxylated Nonylphenol Acrylate) was used to create the white dispersion.

**Table 9: List of Raw Materials for Creating White UV-curable Gravure Ink**

<b>Component Type</b>	<b>Propriety Name</b>
Oligomer	Trimethylolpropane Triacrylate (TMPTA), Trimethylolpropane Ethoxylate (14/3 EO/OH) Triacrylate (ETMPTA), Commercial Product A
Monomer	Glycerol Propoxylate (1 PO/OH) Triacrylate (GPTA)
Photoinitiator	IRGACURE 814 (Bis-Acyl-Phosphine- Oxides)
Pigment	Dupont TI-PURE (Rutile grade Titanium Dioxide, Pigment White 6)
Self-initiating Resin	Flexcure D-30 LV (Trade Secret)
Pigment Dispersing Aid	Sartomer SR614 (Alkoxylated Nonylphenol Acrylate)

**Table 10: Molecular Structures of Oligomers and Monomer Used**

Chemical Name	Molecular Structure
Trimethylolpropane Triacrylate (TMPTA)	
Trimethylolpropane Ethoxylate (14/3 EO/OH) Triacrylate (ETMPTA)	
Glycerol Propoxylate (1 PO/OH) Triacrylate (GPTA)	<p style="text-align: center;"><math>l + m + n \sim 3</math></p>

## Ink Formulation

### Resin

Using the oligomers, monomer and photoinitiator in Table 9, the researcher produced 15 clear formulations with three different oligomers. Each set was comprised of five subsets with each subset having a different oligomer-to-monomer ratio (Table 11). A total of fifteen resins were formulated.

**Table 11: Resin Systems**

Component	Chemical Name	Composition (%)														
		Set 1					Set 2					Set 3				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Oligomer	TMPTA	90	80	70	60	50										
	ETMPTA						90	80	70	60	50					
	Commercial Product A											90	80	70	60	50
Monomer	GPTA	10	20	30	40	50	10	20	30	40	50	10	20	30	40	50

Since the photoinitiator used was in powder form, it needed to be dissolved in the oligomer and monomer mixture. To assist in dissolving, Methyl Ethyl Ketone (MEK) was used. MEK, also known as Butanone, is an organic compound with the formula  $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{CH}_3$ . It is used as a solvent in various processes involving gums, resins, cellulose acetate and nitrocellulose coatings and in vinyl films. The researcher conducted an experiment to determine the best solvent for IRGACURE 819. The amount of 0.9 grams of IRGACURE 819

was dissolved using two solvents, MEK and Acetone. The researcher determined that it required a lesser volume of MEK to dissolve IRGACURE 819. Therefore, MEK was the solvent chosen. The sample volume for each formulated resin was 40 ml.

A detailed breakdown of the actual quantity of each resin system is presented in Table 12. The oligomer, monomer, and solvent for each formulation were placed inside a 100-ml beaker. A VWR® Spinbar® Polygon Magnetic Stir Bar with a length of two inches and a diameter of 5/16 inches was then placed inside the beaker and covered with a 4-inch by 5-inch Parafilm “M” Laboratory Film by Pechiney Plastic Packaging. The beaker was placed on top of a 7-inch by 7-inch Fisher Scientific Stirring Hotplate and was allowed to stir for five minutes at maximum stirring level of ten. The Parafilm was removed, set aside and 0.9 grams of IRGACURE 819 was added to the solution while it was mixing. The beaker was then covered with the same Parafilm and left to stir for 30 minutes.

**Table 12: Actual Quantity of Formulated Resins**

Component	Chemical Name	Composition (ml)														
		Set 1					Set 2					Set 3				
		1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Oligomer	TMPTA	27	24	21	18	15										
	ETMPTA						27	24	21	18	15					
	Commercial Product A											27	24	21	18	15
Monomer	GPTA	3	6	9	12	15	3	6	9	12	15	3	6	9	12	15
Photoinitiator	IRGACURE 819	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.9
Solvent	MEK	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9

The surface tension of each formulation was measured using the Fisher Scientific Surface Tensiomat<sup>®</sup> 21 (shown in Figure 5). This tensiometer utilizes the du Noüy ring method. The instrument has a platinum-iridium ring. Surface tension was obtained from the force required for the ring to break the surface of the liquid. To make surface tension measurements, several steps were performed. The first step was to zero the torsion balance. To do this, the arm was held using the torsion arm arrest mechanism. The platinum-iridium ring was hung on the hook at the left end of the lever. Then, the torsion arm was released, and the tension adjustment control knob was adjusted until the index and its image were exactly in line with the reference line of the mirror. The zero adjustment knob was turned until the vernier read zero on the outer scale of the dial and the torsion arm was held with the torsion arm arrest mechanism again. This was the end of calibration.



**Figure 5: Scientific Surface Tensiomat<sup>®</sup> 21**

The next step was the actual surface tension measurement. A 40-ml glass beaker was filled with 30-ml of the test liquid and placed on the sample table. The sample table was moved around until it was directly beneath the platinum-iridium ring. The sample table was raised until the ring was immersed in the test liquid. The torsion arm was then released, and the instrument was adjusted to zero reading. The tension adjustment control knob was adjusted until the index and its image were exactly in line with the reference mark on the mirror. The zero adjustment knob was turned until the vernier reads zero on the outer

scale of the dial. The sample table was lowered until the ring was in the surface of the liquid, and at the same time, the tension adjustment control knob was adjusted to keep the index lined up with the reference mark on the mirror. This caused the surface of the liquid to be distended, but the index was kept on the reference. Next, the tension adjustment control knob was continuously turned until the distended film at the surface broke. The scale reading at the break point of the distended film was considered the surface tension of the liquid. The surface tension of all the resins was lower than 40 dynes/cm. Hence, these resins possessed sufficient wetting capabilities.

#### Final Ink

White pigment dispersion for UV ink was formulated to add to one of the resin formulation to determine the effect of pigment addition on ink film properties (adhesion, abrasion, surface cure efficiency, and flexibility). The Covington Engineering® ball mill was used to create the pigment dispersion. This involved placing 260 grams of the components (see Table 13) in a 125ml low-density polyethylene (LDPE) bottle and filling it with chrome-coated beads. The LDPE bottle was then placed on the ball mill and left for eight hours at a speed of 100 revolutions per minute (rpm).

**Table 13: Titanium Dioxide Pigment Dispersion**

Component	Chemical Name	Composition (%)
Pigment	Tronox 800	53
Self-initiating Resin	Flexcure D-30 LV	46
Pigment Dispersing Aid	Sartomer SR614	1

The pigment dispersion was added to the #3 resin formulation and mixed by ultrasonic mixing using the Fisher Scientific Sonic Dismembrator. This resin formulation was chosen because it has the lowest viscosity (15 cPa) out of all the other formulations, which is the ideal viscosity for the gravure printing process. A total of ten 30-ml formulations (Table 14) were created for this research. Surface tension measurements were employed on the ten formulations using the Fisher Scientific Surface Tensiomat<sup>®</sup> 21 and the same procedures stated in the previous section. The surface tension of all the inks formulated was measured at 39 dynes/cm. Hence, these resins possessed sufficient wetting capabilities.

**Table 14: Final Ink Formulation**

Component	Composition (%)									
	1	2	3	4	5	6	7	8	9	10
TiO <sub>2</sub> Pigment Dispersion	0	2	4	6	8	10	20	30	40	50
Resin	100	98	96	94	92	90	80	70	60	50

## **Printing**

Print samples for the formulated resins were made on the Diversified Drawdown Platform in the Print Science Laboratory using a flexo hand proofer. The flexo hand proofer used was of an unknown origin; therefore, specifications of the device could not be determined. There were no imprints on the device that stated the model, manufacturer, or specifications of its components. Print samples for the formulated white inks were made using a Diversified Enterprises' #08 drawdown rod on the same drawdown platform. The #08 drawdown rod is one-half inch in diameter, sixteen inches in length, and produces a wet ink film thickness of approximately 0.0008 inches (20.32 microns). Print samples for the benchmark ink (Pharmaflex Supreme White) were printed using both the flexo handproofer and the #08 drawdown rod to achieve an accurate comparison of results in the testing of ink film properties.

### Printed Samples

Each of the 15 clear formulations was printed five times. The same number of prints was made for each of the 10 white UV gravure ink formulations. The benchmark ink (Pharmaflex Supreme White) was printed five times using the flexo handproofer and five times using Diversified Enterprises' #08 drawdown rod. All five samples were tested for surface cure efficiency. Three print samples were used for the abrasion test, and each of the remaining two samples was used for the adhesion test and the flexibility test. There were 15 clear

formulations with five prints each, 10 white UV gravure ink formulations with five prints each, and a benchmark ink (Pharmaflex Supreme White) with 10 prints, which made a total of 135 prints. Table 15 lists the labels of the prints.

**Table 15: Print Sample Labels**

		15 Resins (flexo handproofer)	10 White UV Gravure Inks (#08 drawdown rod)	Pharmaflex White (flexo handproofer)	Pharmaflex White (#08 drawdown rod)
Cure Efficiency Test A	Abrasion Test B	Print 1	Print 1	Print 1	Print 1
		Print 2	Print 2	Print 2	Print 2
		Print 3	Print 3	Print 3	Print 3
	Adhesion Test C	Print 4	Print 4	Print 4	Print 4
	Ink Flexibility Test D	Print 5	Print 5	Print 5	Print 5

Each of the prints made using the flexographic handproofer were exposed to ultraviolet radiation for a period of ten seconds using the Teaneck Graphics Series “S” Instant FastDraw® Vacuum Frame System exposing unit located in the Print Science Laboratory. The distance from the lamp to the print sample was approximately five inches. This exposing unit has an OLEC Lamphead model LT1 with a spectral output range of 325 – 400 nanometers and an RF53 standard reflector. Ten-second exposure time was not possible for prints made using the #08 drawdown rod because of substrate distortion. Hence, the exposure time was adjusted to three seconds.

## **Ink Testing Procedures**

Several ink testing procedures were performed in this research to determine the effects of monomer-to-oligomer ratio on ink film properties and rheology. The five tests selected were viscosity, surface cure efficiency, abrasion, adhesion, and ink film flexibility.

### Rheology

Viscosity of all formulated inks and resins were also measured using the Brookfield Digital Viscometer model DV-I+ in the Print Science Laboratory. This was performed to determine which resin formulation would meet the viscosity requirements of the gravure printing process and the effect of pigment quantity on the rheological characteristics of the formulated white ultraviolet (UV)-curable gravure ink. A sample quantity of 40-ml of each formulation was used to measure viscosity. The #1 spindle of the Brookfield Digital Viscometer was chosen because it is ideal for liquid inks; for example, gravure and flexographic inks. The spindle speeds used were 4, 5, 6, 10, 12, 20, 30, 50, 60, and 100 revolutions per minute (rpm). The results were recorded in centipoise (cPa). Each measurement was recorded 5 minutes after changing spindle speed.

### Surface Cure Efficiency

Surface cure efficiency is an important property of UV inks. As mentioned

in Chapter 3 (Literature Review), curing of UV inks occurs when the ink is exposed to UV-radiation. This causes the photoinitiators to degrade and generate free radicals, which initiate polymerization/cross linkage between the monomers and oligomers. Insufficiently cured or cross-linked UV ink has residue monomers. Residue monomers are non-cross linked monomers, which may cause skin irritation and can migrate from the UV-ink film to the surface or contaminate foods, thus presenting a potential risk to human beings.

Surface cure efficiency was determined by weighing each cured print sample using the Mettler Toledo AB54 Analytical Balance. This was the “Initial Weight.” After which, the surface of the ink film was wiped with a Fiberweb™ Photex® scanner wipe sprayed with 1:2 Ammonia in water cleaner. This was done to remove any residual monomers present in the ink film’s surface. The ink film surface was then wiped dry with a dry Photex® scanner wipe and re-weighed. This was the “Final Weight.” Surface cure efficiency is calculated using Equation 7.

$$\text{Surface Cure Efficiency (\%)} = \frac{(\text{Initial Weight} - \text{Final Weight})}{\text{Initial Weight}} \times 100\% \quad (7)$$

### Abrasion

The abrasion test was performed using the Ugra Abrasion Tester. The abrasion tester was placed on top of the print sample with counter-test paper exactly covered by a 520-gram friction stamp. The test paper used for this

research was the Gavarti Associates Ltd. Comprehensive Abrasion Test A-3 Standard Receptor. The test was executed by moving the abrasion sled from one end to the other. This device is equipped with a stroke counter. A standard of 33 strokes per minute was used in this research.

Three gloss measurements were performed before and also after the abrasion test on different locations on the print sample using the BYK-Gardner micro-gloss 45°/75°. The illumination angle chosen for this research was 45 degrees because it is ideal for gloss measurement of plastic materials (Ugra, n.d.). The result of each test was evaluated by the percent difference in gloss. Difference in gloss was calculated using Equation 8.

$$\text{Change in Gloss (\%)} = \frac{\left( \frac{A1 + A2 + A3}{3} + \frac{B1 + B2 + B3}{3} \right)}{\frac{A1 + A2 + A3}{3}} \times 100\% \quad (8)$$

where : A1, A2, A3 = gloss before abrasion test  
 B1, B2, B3 = gloss after abrasion test

A high percentage change in gloss would mean that the ink film or resin film has low abrasion resistance and vice versa. Abrasion tests were performed on three out of five print samples for every formulation. The final result was calculated by averaging the three results.

### Adhesion

Adhesion test was performed on print samples of all fifteen ultraviolet-curable resin, ten formulated white ultraviolet-curable gravure inks, and Pharmaflex White. The test was performed according to the ASTM F 2552-03 Standard Practice for Evaluating Ink or Coating Adhesion to Flexible Packaging Materials Using Tape. Each printed sample was laid on a flat surface and taped down to hold its position. Then, a one-inch by six-inch pressure-sensitive tape (Scotch™ #610) was applied to the cross direction width of the substrate, with a short tab free for grasping. A rubber roller was rolled back-and-forth five times on top of the tape to remove all the air bubbles on the tape. The tape was pulled in such a way that the angle between the tape and the substrate was at about a 150° angle. Each sample was evaluated based on the amount of ink residue left on the tape (ASTM F 2552-03). If there was ink residue left on the tape, the print sample was marked “FAIL” under adhesion test. If there was no ink residue left on the tape, the print sample was marked “PASS” under adhesion test.

### Ink Film Flexibility

For the ink film flexibility test, the print sample was folded once, and a weight of 2.7 kilograms (Handbook of Print Media was used as a weight to perform the test) was placed on top of the print sample for a period of 15 minutes. After the test, the sample was evaluated under the Fisher Scientific

Stereomaster microscope located in the Print Science Laboratory. Any visual signs of cracking on the print sample were marked as “FAIL” under the ink film flexibility test. If there were no signs of cracking, the print sample was marked “PASS.”

## **Data Analysis**

Simple statistical models were used in the evaluation of the data sets from the surface cure efficiency test, abrasion test, and viscosity measurements. Averages of the results for the abrasion and the surface cure efficiency test were calculated. Averages of the results for viscosity measurements were calculated only if the sample possessed the characteristic of a Newtonian fluid. The results of the abrasion test and the surface cure efficiency test for all 15 clear formulations were compared to that of the benchmark ink to analyze the results. The same procedure was applied to the abrasion test and surface cure efficiency test for 10 white ultraviolet-curable gravure inks formulations.

## **Limitations**

One of the limitations in this research was that only a limited number of samples were tested. For the results to be statistically significant, a minimum of 1,560 prints should be tested. This is comprised of 780 prints (30 for each of the 15 resin formulation, 30 for each of the 10 white UV ink formulation, 30 for benchmark ink) per two quantified ink tests (abrasion and surface cure efficiency)

(780 prints \* 2 quantified ink tests = 1,560 prints). Testing of this size was not possible due to the limitations of the scope of this research. Another limitation was that the print samples were not cured using an industry standard curing unit, which is capable of applying inert gas to reduce present in the samples, which inhibit curing.

## **Chapter 6**

### **Results**

This chapter presents the results for the five ink film tests (surface cure efficiency, abrasion resistance, substrate adhesion, and flexibility). Tests were performed on both resin and pigmented formulations. The results were divided into two sets. The first set contains the results of the clear formulations and the second set contains the results of the pigmented formulations.

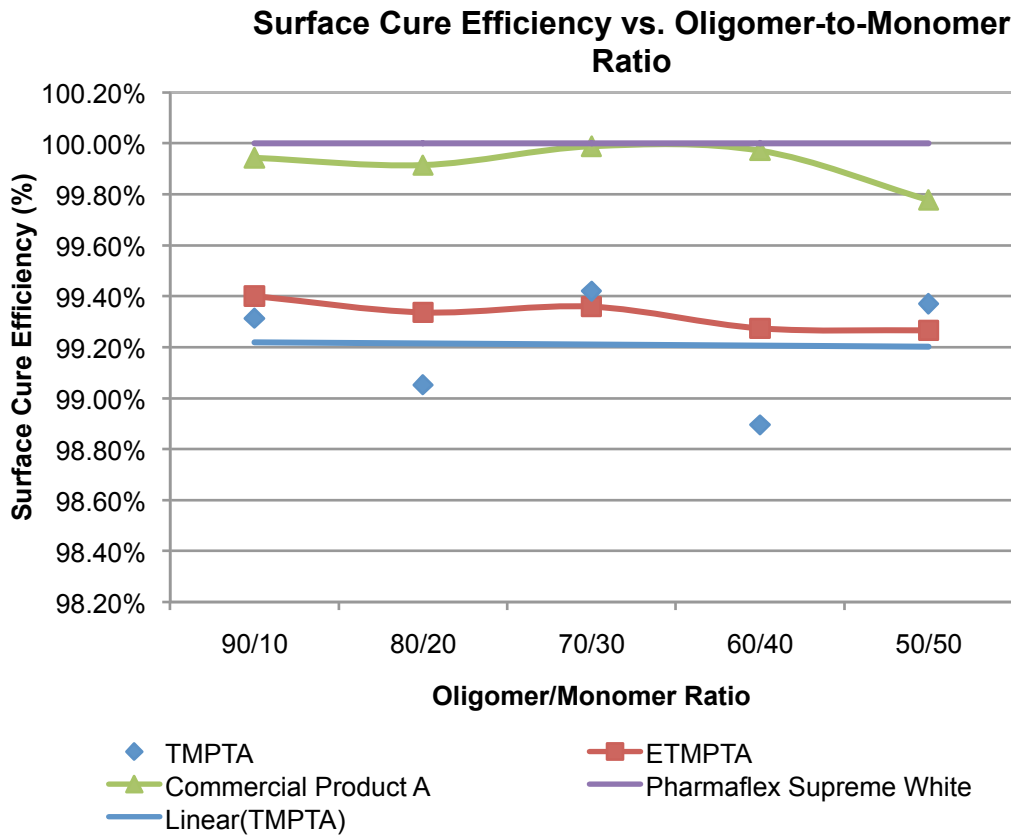
#### **Clear Formulations**

Three different oligomers (TMPTA, ETMPTA, Commercial Product A) were used in creating the 15 clear formulations. Five different oligomer-to-monomer ratios were used (50/50, 60/40, 70/30, 80/20, and 90/10).

#### **Surface Cure Efficiency**

In Figure 6, the surface cure efficiency in percent was compared between the 15 resins formulated and Pharmaflex Supreme White. These comparisons provided several indications. Pharmaflex Supreme White produced 100 percent surface cure efficiency. Out of all the three oligomers used in this research, Commercial Product A produced the highest surface cure efficiency. TMPTA

and ETMPTA had a difference in curing efficiency of less than 0.20 percent, and had lower surface cure efficiency compared to Commercial Product A. Finally, less than one percent of the ink film weight was uncured for all the clear formulations.

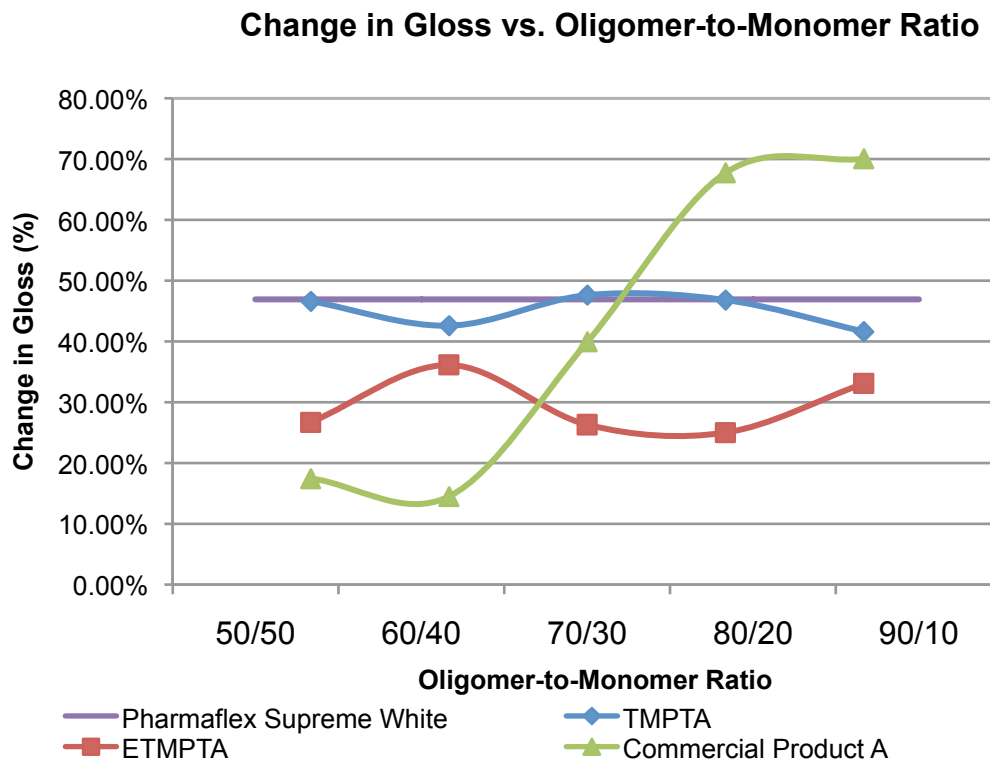


**Figure 6: Surface Cure Efficiency Comparison of the 15 Clear Formulations and Pharmaflex Supreme White**

### Print Performance

*Abrasion.* In Figure 7, abrasion resistance was compared between the 15 clear formulations and Pharmaflex Supreme White. These comparisons

provided several indications. Commercial Product A showed the least change in gloss (most abrasion resistance) at 50:50 and 60:40 oligomer-to-monomer ratio. However at 70:30 ratio, it can be seen that there was about 20 percent increase in change in gloss (decrease in abrasion resistance). Change in gloss continued to increase at 80:20 and 90:10 oligomer-to-monomer ratio. ETMPTA followed Commercial Product A (at 50:50 and 60:40 oligomer-to-monomer ratio) with all (50:50 to 90:10) ratios ranging from between 20 to 40 percent change in gloss. All TMPTA ratios (50:50 to 90:10) were within 40 to 50 percent change in gloss. Pharmaflex Supreme White was at 47% change in gloss.



**Figure 7: Abrasion Resistance Comparison of the 15 Clear Formulations and Pharmaflex Supreme White**

*Adhesion.* Table 16 presents the adhesion test results of the 15 clear formulations and the Pharmaflex Supreme White. It can be seen that all the resins and Pharmaflex Supreme White passed the substrate adhesion test.

**Table 16: Adhesion Test Results for the 15 Clear Formulations**

Oligomer / Benchmark Ink	Ratio (Oligomer/Monomer)	Adhesion Test Result
TMPTA	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
ETMPTA	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
Commercial Product A	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
Pharmaflex Supreme White	NA	PASS

*Ink Flexibility.* Table 17 the ink flexibility presents test results of the 15 clear formulations. It can be seen that all print samples for the 15 clear formulations and Pharmaflex Supreme White print samples did not crack after the test was performed.

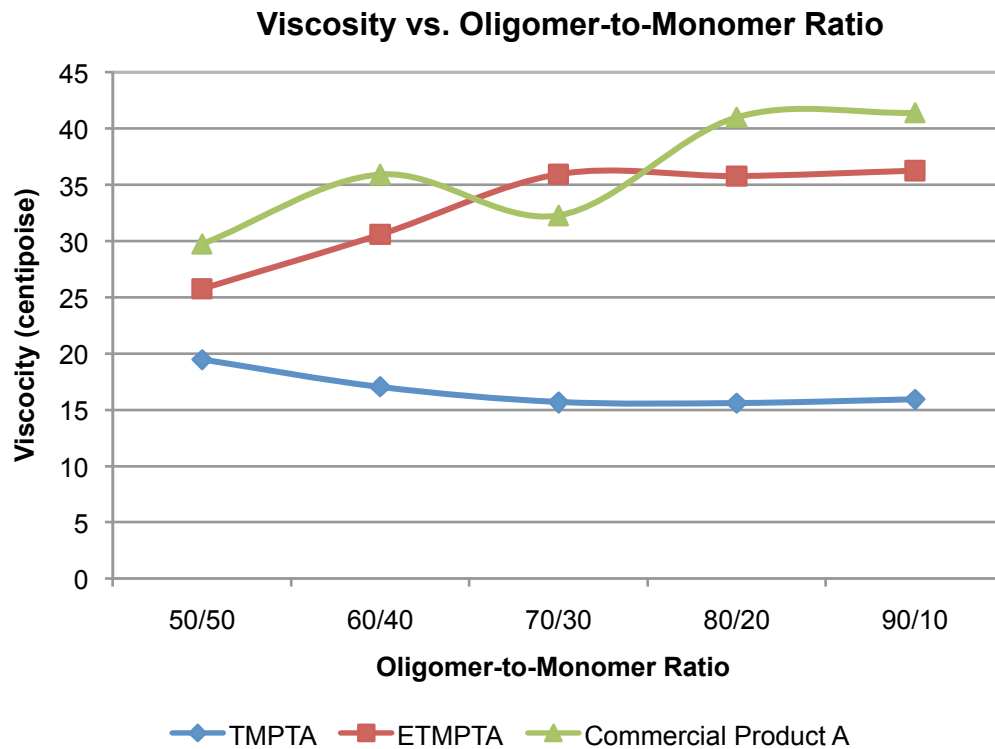
**Table 17: Ink Flexibility Test Results of the 15 Clear Formulations**

Oligomer / Benchmark Ink	Ratio (Oligomer/Monomer)	Ink Flexibility Test
TMPTA	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
ETMPTA	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
Commercial Product A	50/50	PASS
	60/40	PASS
	70/30	PASS
	80/20	PASS
	90/10	PASS
Pharmaflex Supreme White	NA	PASS

### Viscosity Effects

In Figure 8, the viscosities of all the 15 clear formulations were compared. It can be seen that out of all the oligomers that were used in this research, TMPTA produced clear formulations with the lowest viscosity (15 to 20 centipoise). It can also be seen that as the loading of TMPTA was increased, the viscosity of the formulation decreased. Commercial Product A produced clear formulations with the highest viscosity (30 to 41 centipoise). As the quantity of Commercial Product A was increased, the viscosity of the formulation increased. ETMPTA produced the same results when quantity was increased. It produced

clear formulations with viscosity between Commercial Product A and TMPTA (26 to 36 centipoise).



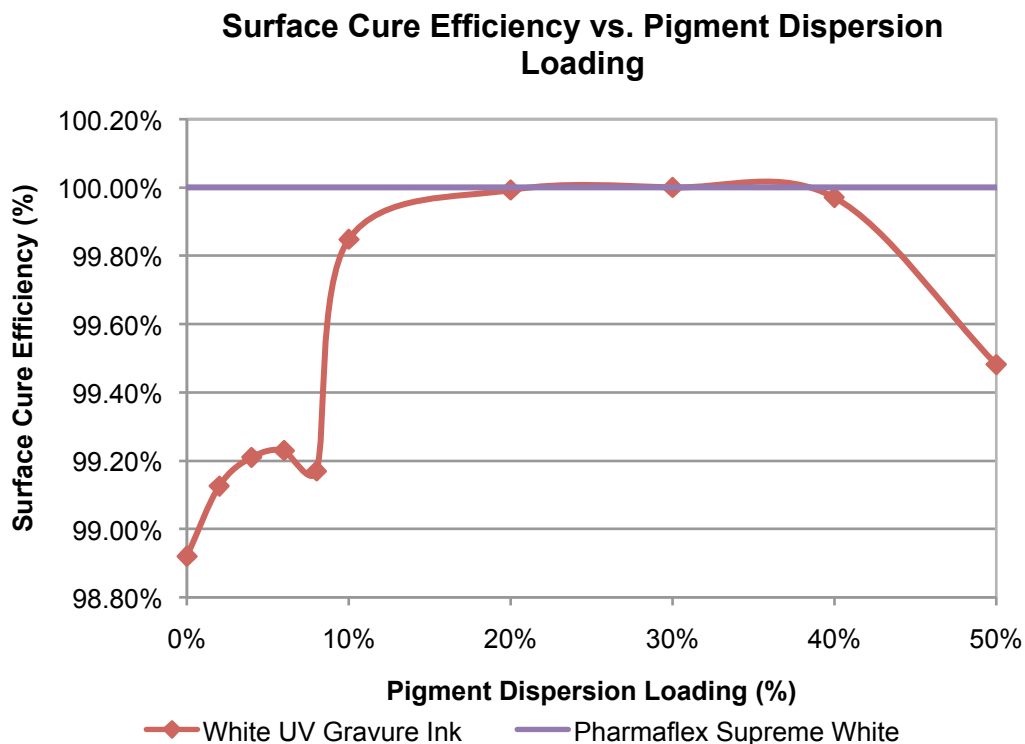
**Figure 8: Viscosity Comparison for the 15 Clear Formulations**

### **Pigmented Formulations**

Ten (10) pigmented formulations were created with each having different pigment dispersion loading (0%, 2%, 4%, 6%, 8%, 10%, 20%, 30%, 40%, and 50%).

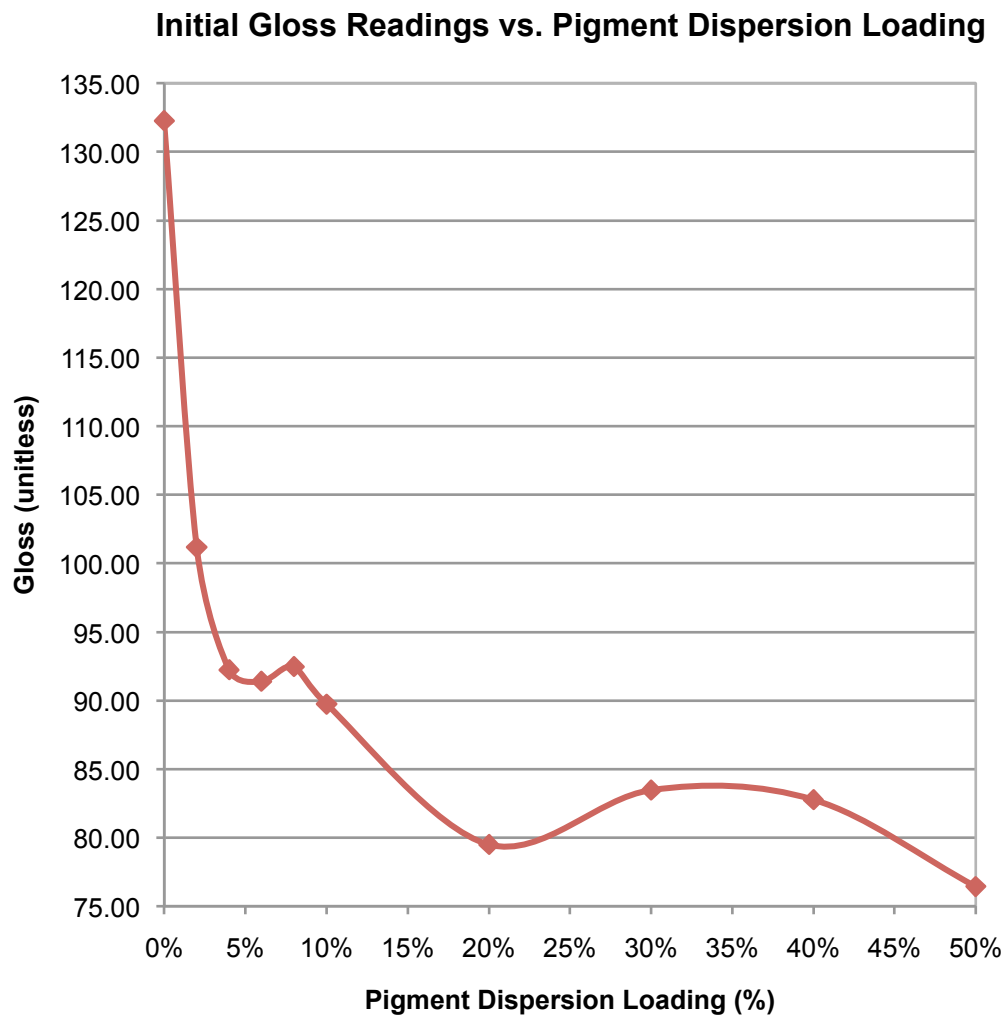
### Surface Cure Efficiency

In Figure 9, the surface cure efficiency in percent was compared between the different pigment dispersion loadings in percent for the #3 resin formulation, composed of 70 percent Oligomer (TMPTA) and 30 percent Monomer (GPTA). Curing efficiency for Pharmaflex Supreme White was at 100 percent. 100 percent surface cure efficiency was found for 20 and 30 percent pigment dispersion loading. Surface cure efficiency gradually increased about 0.3 percent from 0 to 10 percent pigment dispersion loading and decreased about 0.5 percent from 40 to 50 percent pigment loading.



**Figure 9: Surface Cure Efficiency Comparison of Different Pigment Dispersion Loadings and Pharmaflex Supreme White (5 trials/data point)**

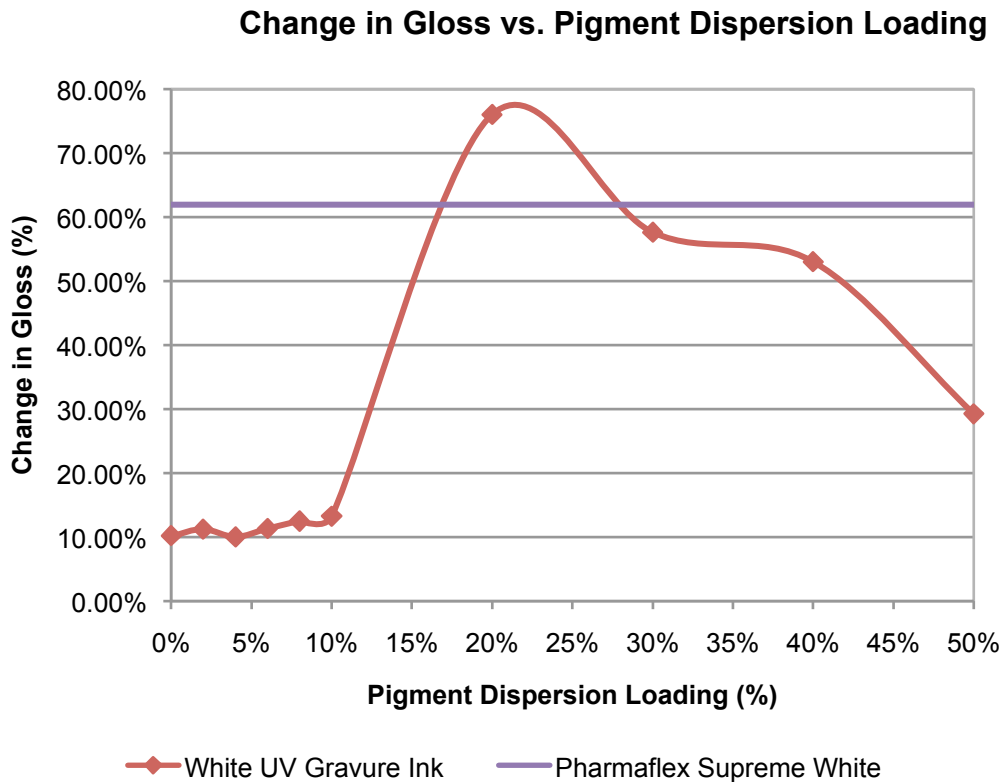
In Figure 10, the effect of pigment dispersion loading in percent to initial gloss reading (unitless) is shown. It was observed that as pigment dispersion loading was increased, the initial gloss readings decreased. There was a logarithmic decrease from zero until 20 percent pigment dispersion loading, where it flattened out.



**Figure 10: Effect of Pigment Dispersion Loading on Initial Gloss Readings of the White Ultraviolet-curable Gravure Ink Printed Samples**

## Print Performance

*Abrasion.* In Figure 11, change in gloss was compared between different pigment dispersion loadings. Zero to 10 percent pigment dispersion loading showed the least change in gloss (most abrasion resistance). The most change in gloss (least abrasion resistance) was at 20 percent pigment dispersion loading. From 20 to 50 percent pigment dispersion loading, there was a gradual decrease in gloss of approximately 45 percent. Pharmaflex Supreme White had a change in gloss of 62 percent.



**Figure 11: Abrasion Resistance Comparison of Different Pigment Dispersion Loadings**

*Adhesion.* Table 18 presents the adhesion test results of 10 different pigment loadings and for Pharmaflex Supreme White. It can be seen that for all pigment dispersion loadings (zero to 50 percent) there was 100 percent adhesion to the substrate. For Pharmaflex Supreme White, there was ink residue left on the tape.

**Table 18: Adhesion Test Results for Different Pigment Loadings**

Pigment Dispersion Loading / Benchmark Ink	Adhesion Test Result
0%	PASS
2%	PASS
4%	PASS
6%	PASS
8%	PASS
10%	PASS
20%	PASS
30%	PASS
40%	PASS
50%	PASS
Pharmaflex Supreme White	FAIL

*Ink Flexibility.* Table 19 presents the ink flexibility test results for 10 different pigment loadings and Pharmaflex Supreme White. It can be seen that for all pigment dispersion loadings (zero to 50 percent), there were no signs of cracking in the print samples after the test. The Pharmaflex Supreme White print sample cracked.

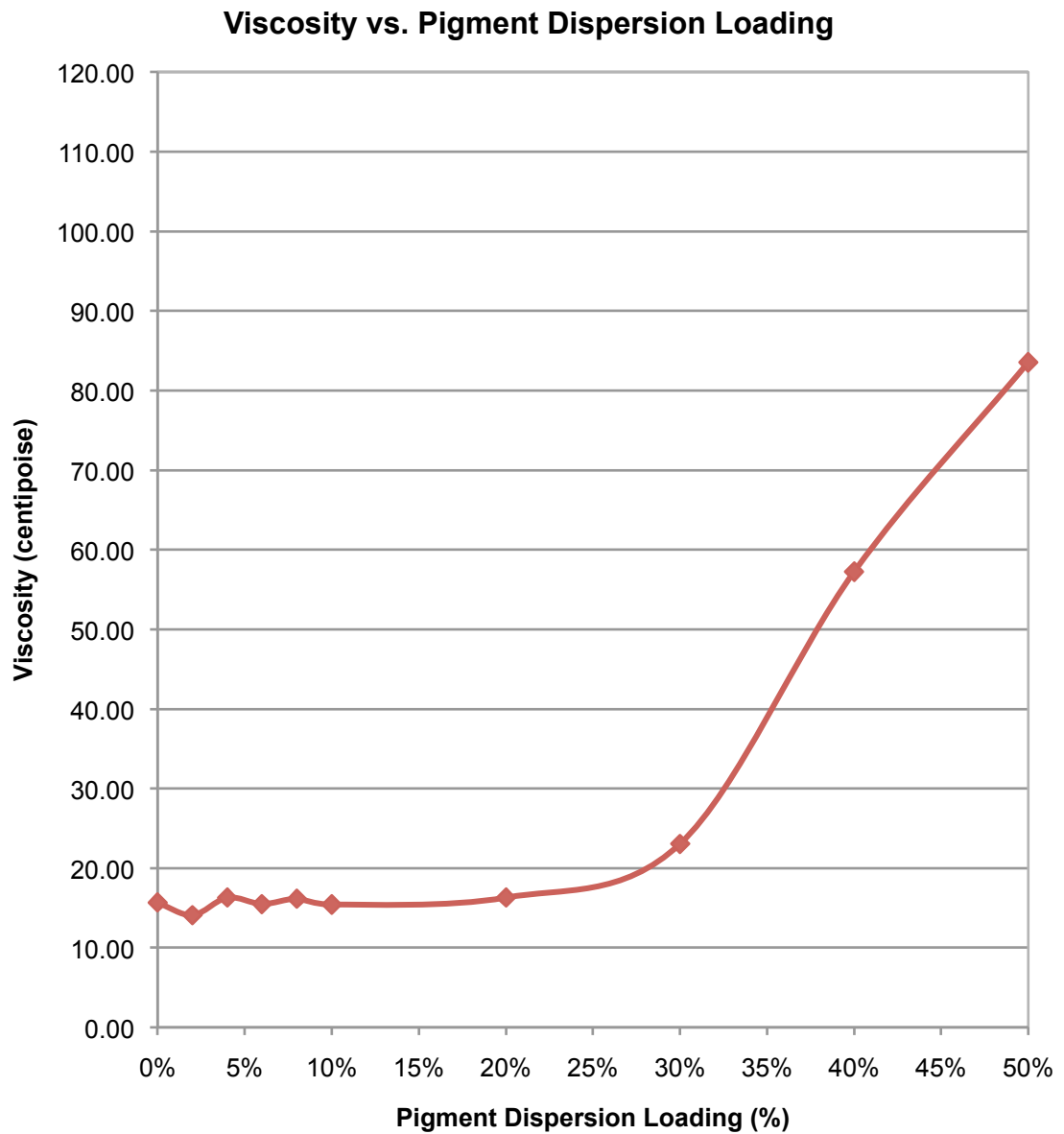
**Table 19: Ink Film Flexibility Test Results for Different Pigment Loadings**

Pigment Dispersion Loading / Benchmark Ink	Ink Film Flexibility Test
0%	PASS
2%	PASS
4%	PASS
6%	PASS
8%	PASS
10%	PASS
20%	PASS
30%	PASS
40%	PASS
50%	PASS
Pharmaflex Supreme White	FAIL

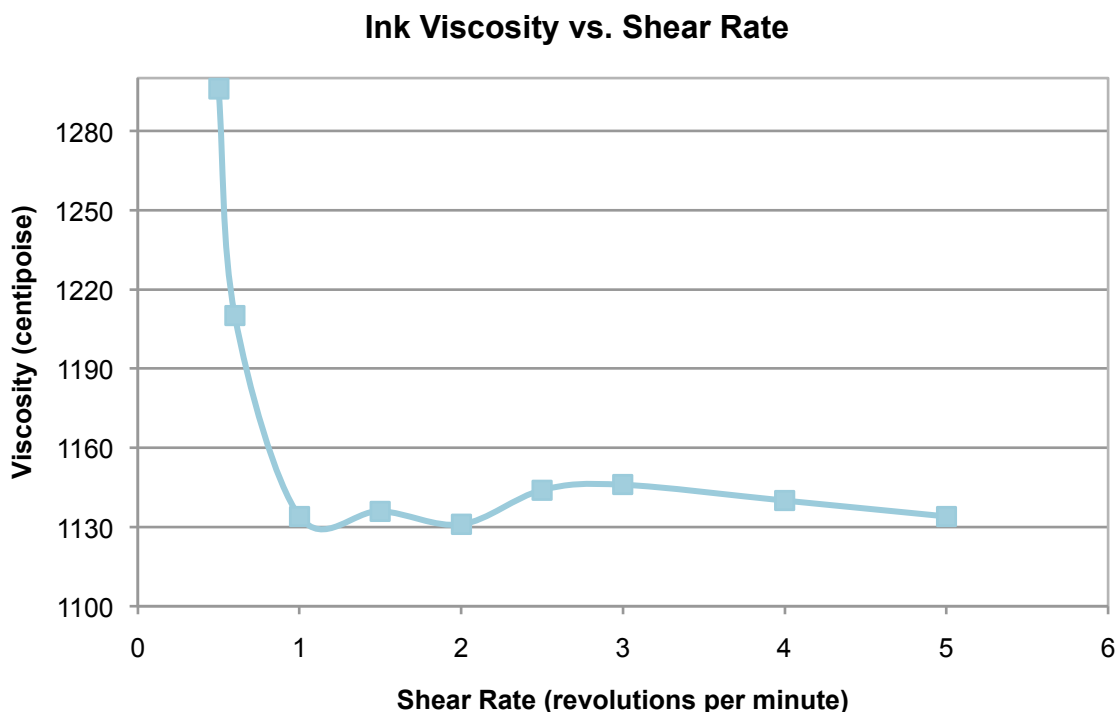
### Viscosity Effects

The averages of the viscosities at different spindle speeds were calculated for every sample to create Figure 12. In Figure 12, the viscosities of the 10 formulations with different pigment loadings were compared. It can be seen that as pigment dispersion loading was increased, viscosity increased. There was approximately a seven centipoise increase in viscosity from 20 to 30 percent pigment dispersion loading, an increase of approximately 35 centipoise from 30 to 40 percent pigment dispersion loading, and approximately 26 centipoise from 40 to 50 percent pigment dispersion loading. Figure 13 presents the viscosity of Pharmaflex White. It can be seen that Pharmaflex Supreme White was non-Newtonian in nature. There was approximately a 900 centipoise difference in

viscosity between the white UV-curable gravure ink formulation with 50 percent pigment loading and Pharmaflex Supreme White. Figure 12 presents the comparison between the viscosities of all the 10 final ink formulations.



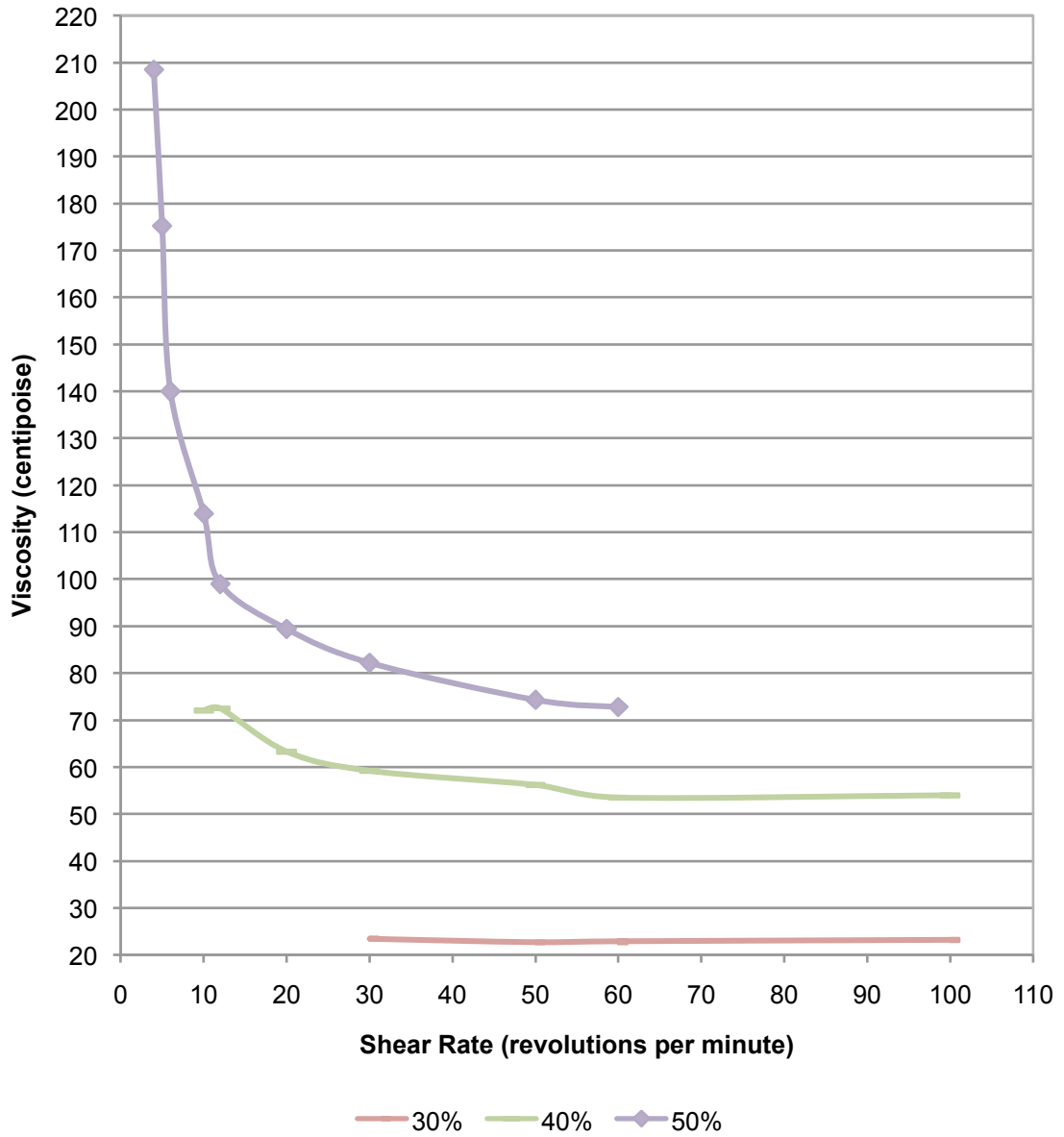
**Figure 12: Viscosity Comparison for Different Pigment Loadings**



**Figure 13: Viscosity of Pharmaflex Supreme White**

Figure 14 presents the viscosities for the ten final ink formulations with different pigment loadings. It can be seen that from 40 to 50 percent pigment dispersion loading, the ink viscosity curve became non-linear (non-Newtonian flow). There were no readings from zero to 50 rpm shear rate for 30 percent pigment loading because the digital viscometer indicated error readings at these range. Error readings were also found at 60 to 100 rpm shear rate for 50 percent pigment loading. From zero to 20 percent loading, the ink viscosity was linear (Newtonian flow).

**Ink Viscosity vs. Shear Rate**



**Figure 14: Viscosity Comparison of the 10 White Ultraviolet-curable Gravure Ink Formulations**

## **Chapter 7**

### **Conclusions**

#### Effect of Oligomer-to-Monomer Ratio on Surface Cure Efficiency

Oligomer-to-monomer ratio did not have a significant impact on the curing efficiency of the 15 clear formulations. There was less than a 0.25 percent difference in curing efficiency between the different oligomer-to-monomer ratios for the three oligomers: Trimethylolpropane Triacrylate (TMPTA), ETMPTA Trimethylolpropane Ethoxylate Triacrylate (ETMPTA), and Commercial Product A. The results for every oligomer-to-monomer ratio were nearly identical. The fluctuations in the readings could most likely be caused by several factors during weighing, e.g., vibrations, dust particles attaching to the substrate, and temperature.

There was, however, a difference in curing efficiency between the three different oligomers. Commercial Product A had the highest curing efficiency amongst the three oligomers. This may be due to two reasons. The first reason was that Commercial Product A has the highest viscosity amongst the three oligomers, which produces a thicker coating during printing. In ultraviolet (UV)-curing applications, oxygen is considered a cure inhibitor. Thicker coating film causes oxygen to be less mobile and have difficulty penetrating the film layer

thus promoting surface cure efficiency. The second reason was that Commercial Product A is listed as a radiation-curable resin. This means that it can cure by itself when exposed to UV radiation thus improving in surface cure efficiency. The difference in surface cure efficiency for TMPTA and ETMPTA was less than 0.2 percent, which was considered insignificant and lead to the conclusion that there was no difference in surface cure efficiency between TMPTA and ETMPTA.

#### Effect of Pigment Dispersion Loading on Surface Cure Efficiency

There was 100 percent surface cure efficiency at 20 to 30 percent pigment loading. The cured ink film exhibited a significant loss in gloss, which means that the ink film was more textured. This increased the surface energy of the cured ink film caused better wetting capability. The increase in texture could have also increased the porosity of the film layer making it act like a “sponge” that absorbs the residual monomers. At 50 percent pigment loading, there was a decline in surface cure efficiency. There are two reasons to explain this result. One was due to pigment overloading. This caused ultraviolet light to scatter back out of the film. The other was the decrease in photoinitiator concentration. Since the photoinitiator was dissolved in the resin formulation, adding more pigment dispersion diluted the photoinitiator in the formulation.

### Effect of Oligomer-to-Monomer Ratio on Abrasion Resistance

For Trimethylolpropane Triacrylate (TMPTA) and Trimethylolpropane Ethoxylate Triacrylate (ETMPTA), oligomer-to-monomer ratio had no significant impact on abrasion resistance. The coating film has better abrasion resistance with ETMPTA compared to TMPTA. As Commercial Product A quantity was increased, there was a decrease in abrasion resistance. This may be because of two reasons. The first reason is physical properties of Commercial Product A. It may be a soft oligomer and increasing oligomer quantity caused the coating film to be softer and less wear resistant. The other reason is the high molecular weight of Commercial Product A. Commercial Product A has the largest molecules out of the three oligomers. Reduced mobility of large molecules slows down the cross-linking process, creating a weak coating film. Although Commercial Product A has the greatest surface cure efficiency among the three oligomers, the surface cure efficiency test did not determine the amount of unconverted acrylate double bonds. A different technique known as Fourier Transform Infrared (FTIR) monitoring is used to determine surface cure efficiency by the amount of converted acrylate double bonds. However, this type of test requires spot UV curing equipment that was unavailable during the course of this research. Performing this type of test might indicate a decrease in conversion of acrylate double bonds as the quantity of Commercial Product A is increased in the formulation.

### Effect of Pigment Dispersion Loading on Abrasion Resistance

Increasing pigment dispersion loading caused a decrease in abrasion resistance. The decrease of initial gloss of the ink film (from glossy to matte) as a result of the increase in pigment loading created a rough ink film surface. This event can be illustrated by dropping rocks on a pool of water. The rocks in this example are the pigments, the pool of water is the resin, and the abrasion resistance test paper is another rock. As more rocks are dropped in the pool of water, there will come a point that the rocks will go over the surface of the water. During the abrasion resistance test, two rocks, the test paper and the pigment, rub against each other. This caused a high amount of friction produced between the two surfaces, which resulted to poor abrasion resistance. More wear results from two rough surfaces rubbing against each other as compared to a rough surface and a smooth surface rubbing against each other.

### Effect of Oligomer-to-Monomer Ratio on Adhesion

Oligomer-to-monomer ratio did not have a significant impact on adhesion. The printed samples for the 15 clear formulations and Pharmaflex Supreme White passed the adhesion test. The oligomers and monomer in the formulation belong to the same chemical class known as acrylates. This was due to the favorable attraction between the substrate and resin molecules. Similar results were found when using the three oligomers because they are of the same chemical class.

### Effect of Pigment Dispersion Loading on Adhesion

Pigment loading did not have a significant impact on adhesion. However, the print sample for Pharmaflex Supreme White failed the adhesion test. Samples were printed using the #08 drawdown rod. It is known that Pharmaflex Supreme White's viscosity was approximately five times greater than the ten white ultraviolet(UV)-curable inks formulated in this research. This caused a thicker ink film to be printed when using the #08 drawdown rod, which was significantly greater than the normal applications of Pharmaflex Supreme White. Consequently, this makes it harder for UV radiation to penetrate the ink film because of the reflection of UV light caused by the increase in pigment quantity. Additionally, this inhibits curing at the bottom portion of the ink film, which may explain the poor bonding between the ink and substrate.

### Effect of Oligomer-to-Monomer Ratio on Ink Flexibility

Oligomer-to-monomer ratio did not have significant impact on ink flexibility. The printed samples for the 15 clear formulations and Pharmaflex Supreme White passed the ink flexibility test. It was observed that ink film thickness had an effect on ink film flexibility. The 15 clear formulations and Pharmaflex Supreme White were printed using the flexo hand proofer, which yielded an ink film thickness of about one to three microns. The coating film and ink film thickness may be too thin to cause an impact on the flexibility of the resins. The stress applied to the coating film was not enough to cause cracking.

### Effect of Pigment Dispersion Loading on Ink Flexibility

Pigment loading did not have a significant impact on ink flexibility. However, the print sample for Pharmaflex Supreme White failed the ink flexibility test. This may be because of the same reason why Pharmaflex Supreme White failed the adhesion test. The viscosity of Pharmaflex Supreme White caused a thicker ink film to be printed when using the #08 drawdown rod, which was significantly thicker than its normal applications. The incomplete curing at the bottom portion of the film left the top ink film free standing without the support from the substrate. This caused the ink film to break during the test.

### Effect of Oligomer-to-Monomer Ratio on Viscosity

Oligomer-to-monomer ratio had a significant effect on viscosity. This was because of the difference in molecular weight and branches between the oligomers and monomer used. Table 20 lists the molecular weights of the oligomers and monomer used in the research. As described in the previous section (Chapter 2: Theoretical Basis), viscosity is the resistance of the fluid to flow. The greater the molecular weight of the fluid, the greater is its resistance to flow. Oligomers have larger molecules compared to monomers. The interaction between those larger molecules created more internal resistance thus increasing viscosity.

**Table 20: A List of Molecular Weights of the Oligomers used in the Research**

Component	Molecular Weight
Trimethylolpropane Triacrylate (TMPTA)	400
Trimethylolpropane Ethoxylate Triacrylate (ETMPTA)	600
Glycerol Propoxylate (1 PO/OH) Triacrylate (GPTA)	428
Commercial Product A	700

#### Effect of Pigment Dispersion Loading on Viscosity

Pigment dispersion loading had a significant impact on viscosity. As pigment dispersion loading was increased, ink that was non-Newtonian in nature was produced. The pigment dispersion was a non-Newtonian fluid while the resin formulation was a Newtonian fluid. The increase in pigment loading caused more pigment particle interaction and caused an increase internal resistance, which turned the ink into a non-Newtonian fluid.

#### **Summary**

Table 21 presents a starting point for formulating white ultraviolet (UV)-curable gravure ink. The researcher chose the TMPTA as the oligomer and GPTA as the monomer for formulation because it yielded a resin formulation that meets the gravure printing viscosity requirement (15 to 20 centipoise). Twenty percent pigment loading was chosen because it was the maximum amount that could be loaded into the resin formulation to make ink within gravure printing viscosity range. Running this ink on an actual commercial gravure press would

determine its performance in the real world environment. It is expected that using a UV lamp with inert gas flow capability would reduce oxygen inhibition and solve cure issues.

**Table 21: Starting point for White Ultraviolet(UV)-curable Gravure Ink for printing on Biaxially Oriented Polypropylene**

Component	Name	Composition (%)
Oligomer	Trimethylolpropane Triacrylate (TMPTA)	55
Monomer	Glycerol Propoxylate (1 PO/OH) Triacrylate (GPTA)	23
Pigment Dispersion	Rutile TiO <sub>2</sub> Dispersion	20
Photoinitiator	IRGACURE 819 (Bis-Acyl-Phosphine-Oxides)	2

The information taken from this research will prove to be valuable in the research and development of UV-curable gravure inks. Ink formulators can benefit from the information in this research. Further experimentation and modification of the starting point formulation could create white UV-curable gravure ink that can be used in gravure printing, enabling gravure printers to utilize the benefits of UV-curable inks.

### **Agenda for Further Research**

The researcher has proposed some modifications in the methods to determine surface cure efficiency and ink flexibility. It would be interesting to see

the results of the surface cure efficiency test for the clear formulations using real time Fourier Transform Infrared (FTIR) monitoring. Infrared (IR) spectroscopy is an analytical chemistry technique that detects vibration characteristics of chemical function groups. To determine the amount of cure in UV inks, the acrylate double bonds are monitored while curing the ink film using spot ultraviolet curing. Another way to determine the degree of ink film flexibility is to print UV ink at different ink film thickness (IFT) using different drawdown rods (starting with the rod that produces the lowest IFT). Every sample is folded and a standard weight is placed on top of it for a specific period of time. The degree of flexibility is determined by the highest IFT the ink can be printed before it cracks.

As stated previously, pigment dispersion loading caused the dilution of photoinitiator in the ink formulation. Maintaining the amount photoinitiator at different pigment loadings may change the results. Also, the pigment used in this research was a rutile grade of titanium dioxide. A valuable study would be to use an anatase grade of titanium dioxide which when compared to the rutile grade has less UV light absorption and result to better curing efficiency.

Finally, only one resin formulation was loaded with pigment dispersion. It would be interesting to see how all the other clear formulations would perform when loaded with pigment dispersion.

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