8-2014

Replacement of Solvent Based Ink by Water Based Inks for Gravure Presses with Low Efficiency Ink Driers

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REPLACEMENT OF SOLVENT BASED INK BY WATER BASED INKS FOR GRAVURE PRESSES WITH LOW EFFICIENCY INK DRIERS

by

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A thesis submitted to the Graduate College
in partial fulfillment of the requirements
for the degree of Master of Science
Chemical and Paper Engineering
Western Michigan University
August 2014

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Western Michigan University, 2014

Rotogravure printing of decorative laminates, wall coverings, or vinyl floorings process often uses solvent based inks. The main constraining factor with solvent based ink is presence of volatile organic compounds (VOC's). Due to the environmental norms on Volatile Organic Compounds (VOCs), and restrictions on using solvent based inks, the ink industry came up with water based ink as more environmentally friendly alternative. Organizations which print decorative laminates, wall coverings, or vinyl floorings with solvent based inks have gravure printing infrastructure, which is often equipped with low efficiency driers capable of drying solvent based inks. In order to comply with environmental norms, it is necessary to switch to water based ink, preferably employing existing drier configuration. One feasible approach to use existing equipment will be to deposit less ink on substrate so that current driers can dry water based ink efficiently. Less ink deposition can be achieved by using engraving with higher resolution, thus employing cells with lesser volume. The aim of this work was to formulate water based inks with higher pigmentation and higher solids content to match solvent based gravure ink. Color strength in terms of CIELAB values was evaluated for each ink and engraving. These color values were compared with reference solvent based ink by calculating ΔE_{ab} color difference.

ACKNOWLEDGEMENTS

It is my pleasure to thank all those who made this thesis possible. I want to thank the Department of Paper Engineering, Chemical Engineering and Imaging for providing all necessary facilities to complete this work. I owe my deepest gratitude and thank to my advisor, Dr. Alexandra Pekarovicova whose guidance; support and encouragement enabled me to develop an understanding of this subject. Her valuable advice during my MS program helped me in maintaining my focus and reaching my potential. I am also thankful to her for providing me with all the resources necessary for this research. I would like to thank my advisory committee members Dr. Paul D. Fleming and Dr. Margaret Joyce for their support and insightful suggestions. Their kind support and guidance have been of great value in this study.

I also want to thank Dr. Veronika Husovska for her suggestions and help during my work. We are really glad to have a person like you at the PCI department, helping all the students and my special thanks go to BASF for providing me with the materials needed to conduct the research.

I want to thank all my friends for their constant support and encouragement, which has helped me a lot in achieving my goals especially Kaustubh, Pritam and Pradnyesh. My deepest gratitude also goes to all those who directly and indirectly helped me in making this work possible.

Acknowledgements- Continued

I really fall short of words, while expressing my gratitude towards Lord Ganesh and my beloved parents Mr. Suresh Dalvi and Mrs. Manorama Dalvi, whose blessings have helped me achieve my goals till date. I would like to thank my younger brother, Mr. Nagesh Dalvi for always being there for Mom and Dad.

Last but not the least I would like to thank my grandparents, my uncles, aunties and my beloved cousins for their love and affection and constant encouragement and support.

Viraj Suresh Dalvi

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CHAPTER 1

INTRODUCTION

The rotogravure printing process is one of oldest and most established printing processes. It is widely used in the packaging and publication industries. The process uses solvent based inks as it best suites the working principals of the gravure press. But lately, environmental concerns have been raised regarding the use of solvent based ink. The main constraining factor with solvent based ink is the presence of volatile organic compounds (VOCs), which evaporate during ink drying and may react in the atmosphere with nitrogen oxide to form ozone. Familiar VOCs found in inks are alcohols, ketones, acetates and glycols. (1) Water based inks offer an alternative for solvent based inks. Water, itself, acts as the solvent in water based ink. The presence of water in ink eventually eliminates the VOC factor. In addition to that, water reduces the risk of toxic substance discharge, hazardous waste, improves working conditions and brings every gravure printing plant under environmental compliance. The introduction of water based inks to the gravure printing industry took time to be accepted, due to differences in the polymer chemistries involved in the making of a water based ink in comparison to a solvent based ink. Due to the presence of water as the main component (solvent) in a water based ink, and alkaline pH of the inks (around 9.0), it was challenging for the ink industry to develop an ink that met the operational standards of the gravure printing process while not corroding the image carrier. (2)

As mentioned earlier, the gravure printing process is used mostly by the packaging and publication gravure industries. Due to the gravure printing process's ability to reproduce high print quality and to be economical during long print runs, it is also extensively used in the printing decorative laminates, vinyl products, outdoor furniture, pool liners and wall coverings. It is a very established printing process and one of widest format (14ft wide machines) (3) employed by the printing industry. (4) (5)

1.1 Rotogravure Printing Process:

The rotogravure printing process is termed as Intaglio Printing. It is a direct printing process, where ink is released from engraved cells. (6) It is used in the printing of porous substrates such as paper and paperboards, as well as on non porous substrates such as aluminum foil, polyester, PE, nylon films, cellulose films, etc. (7) Common applications for this process are publication printing, such as the printing of magazines and catalogues or in packaging, such as gravure printed labels, boxes, shrink sleeves, or currency. Gravure printing is done on various substrates such as newsprint, lightweight coated or supercalendered papers, coated one side paper or different paperboards such as solid bleached sulfate or coated recycled board. Yet another gravure application is product printing, such as wall coverings, decorative laminates, outdoor furniture, currency, or floor covering. Printed electronics is an emerging sector, where rotogravure printing can be employed to offer many advantages over other printing processes, such as a high resolution image carrier and image carrier that is resistant to strong solvents.

Modern day gravure printing press consists of the following components:

Printing Cylinder: Also referred to as the gravure cylinder or image carrier. Gravure cylinders are engraved using electromechanical engraving, direct laser engraving or indirect laser processes. The direct layer process employs a laser to ablate a masking coating on the gravure cylinder, with subsequent chemical etching of the copper layer.

Recessed engraved cells are capable of carrying liquid inks as required by the image design. Size and pattern of engraved cells depend upon the image to be printed. The gravure cylinder can be an integral shaft cylinder, which is heavy in weight or a seamless tube sleeve mounted on a plastic core (8).

Doctor Blade: It's a device whose basic purpose is to wipe the ink from the non imaged areas. ***Inking System***: It consists of an ink pan where ink is continuously pumped through an ink pump. The gravure cylinder rotates in this ink pan where the ink is transferred into the engraved cells on the cylinder.

Impression Cylinder: It's a rubber covered cylinder mounted above the gravure cylinder. Its purpose is to press the substrate against the gravure cylinder to provide support for proper ink transfer, but also aids in driving the substrate through the press.

Rotogravure Printing Process Description:-

- Gravure printing cylinder rotates in ink pan from where engraved cylinder picks up ink.
- Excess ink is wiped from gravure cylinder by doctor blade.
- Substrate passes between nip of gravure cylinder and impression cylinder, where the substrate ogresses against the gravure cylinder.
- As the impression roller presses the substrate against the cylinder, capillary action draws ink from cells on to the substrate. The printed substrate then goes through the driers before proceeding to the next printing unit. (9) (10)

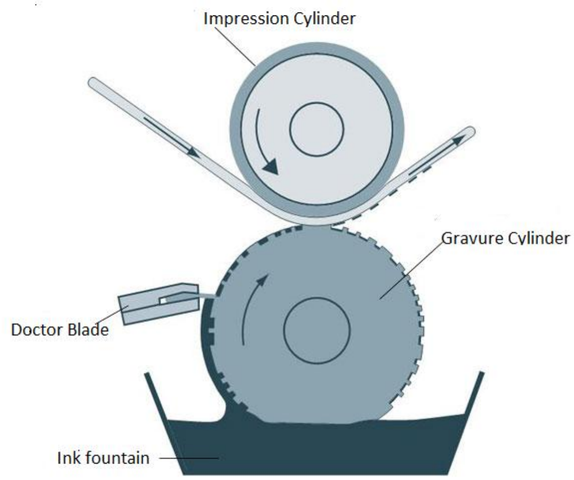


Figure 1: Schematic of Gravure Print Unit (11)

The gravure printing process has advantages over other commercial printing processes as it can print an image with varying ink film thickness, which aids in high quality 3D sensation of the image. This unique feature helps in producing printed images of high quality. Also, it has very few parameters to control which aids in the ease of operation of the press. Its ability to print and operate for long runs makes this process economical.

1.2 Gravure Cell Engraving

Electromechanical Engraving Process: It is currently the most widely used engraving process. In this process a diamond stylus, mounted on an electromechanical head, is vibrated against a rotating gravure cylinder. (12) This vibration mechanism on the cylinder produces miniature recessed cells. The dimensions of the engraved cells depend upon the details of the digital image. Most of the gravure image carriers used today are produced on a steel based cylinder with a layer of engraving copper on it. Copper metal is used because it is workable and soft enough for the diamond stylus (13). Figure 2 gives the workflow of the electromechanical engraving process of a Ballard shell used in the gravure printing industry.

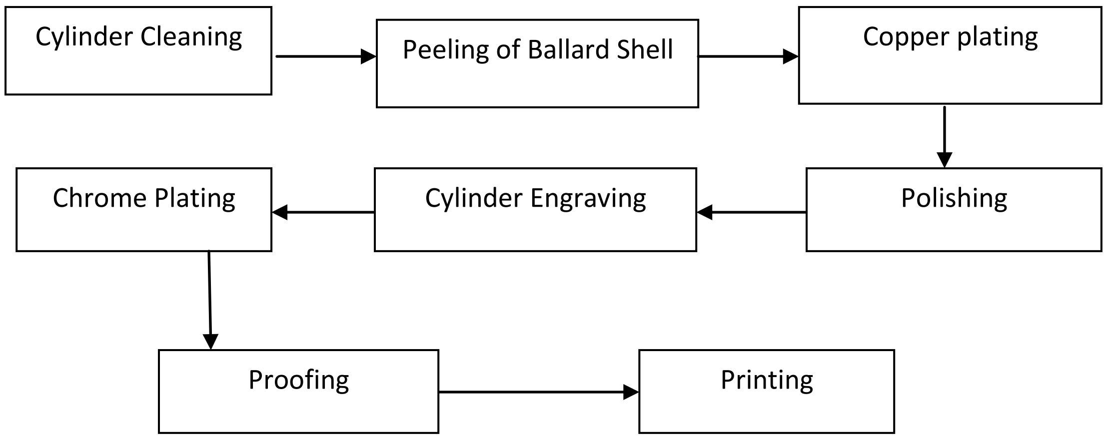


Figure 2: Electromechanical Engraving Workflow (13)

The first step of the workflow process is cleaning, where cylinders are cleaned from ink residuals. After cleaning, the Ballard shell is removed from the cylinder. The Ballard shell is nothing but a non-adhesively plated and engraved top layer of copper and chrome. Then for about 80 microns, the shell, or a new shell, is wrapped around the supporting cylinder and again non-adhesively electroplated with a layer of copper. (13). The copper plated shell then goes for polishing. In this step, the copper layer is polished to give smooth texture to the surface. It also adds roughness to the surface so that ink can be retained on the surface, which will acts as lubricant for cylinder. Then digital data are fed to the engraving heads that engrave (images) the copper cylinder. Cells are engraved in rows, where individual cells may be separated by a channel. To get nested pattern between two adjacent rows of cells, the engraving head is advanced by half a cell. The number of cells per linear inch is called resolution given in Lines/Inch i.e. LPI. (12). After engraving, the cylinder goes in to the degreasing and chrome plating process. The degreasing process makes sure that the engraved cylinder is cleaned from oil and grease. The chrome plating layer prevents the engraved cylinder from being worn out by the doctor blade. In the final stages, the cylinder is proofed for quality. Once verified that it complies with the proofing standards, it is ready for printing operations. (13)

Cell geometry plays an important role in determining the volume of ink transferred to the substrate. Stylus, engraving cell compression angle and resolution (LPI) shapes the cell geometry and in turn the volume of the cell. Stylus angle affects depth of cell. The steeper is the stylus angle, the greater is the depth of the cell. Engraving angle controls the ratio of cell opening to its depth. Table 1 explains the engraving cell compression angles, which are dependent upon oscillation of the diamond stylus. Lines screen is number of cells in a linear inch. If resolution increases, then the number of cell increases, which in turn decreases the depth and width of each cell. (14)

Table 1: Engraving Cell Compression Angle and Nomenclature (14)

Angle	**Length comparison**	**Common Name**
30^o	Vertical length < Horizontal width	Compressed
45^o	Vertical length = Horizontal width	Normal
60^o	Vertical length > Horizontal width	Elongated

Table 2: Cell Volume Conditions ((14)

Factor	Value	Cell Volume
Stylus angle	Increases	Decreases
Lines /Inch (LPI)	Increases	Decreases
Engraving angle	Increases	Decreases

Cell volume differs for solvent and water based inks. Cylinders used for water based inks are engraved with shallower cells than the cylinders to be printed with solvent based inks. The main reason for the difference in depth is due to the difference in the solids content of the inks. Water based inks are formulated at higher solids than solvent based inks, which is why they require shallower cells and deposit less ink to a substrate. Table 3 gives several examples of different cell volumes.

Table 3: Example Of Cell Geometry for Water Based & Solvent Based Ink (15)

Ink-Cyan	LPI	Compression Angle	Stylus Angle	Cell width (microns)	Cell Depth (microns)	Cell Volume in Billion Cubic Microns/Square Inch (BCM)
Water Based	175	30	135	208	43.5	9.63
Solvent Based	175	30	120	208	60.6	13.42

1.3 GRAVURE INKS

Gravure inks are classified as liquid or fluid inks. They are very low in viscosity as the ink needs to be transferred from miniature engraved cells to the substrate within a fraction of seconds. The gravure print process demands ink to be fast drying, so in order to support this characteristic, high volatile solvents are often used. These solvents evaporate after passing through a drier, which result in the film forming of the resin with the pigments. Volatile organic solvents used in rotogravure, such as toluene, are considered to be a source of air pollution. Now a day's water based inks are used to eliminate these harmful solvents, where water itself act as solvent in water based inks. (4) (7) (16)

Components of Gravure Ink and Their Function

Gravure ink has the same basic ingredients as inks for other printing processes. Those are pigments, resins, solvents and additives. Each component has it own effect on properties and printability of gravure ink.

a) **Pigments:** The main purpose of pigments is to impart color or visual identity to the ink. (16) They also provide functional and decorative properties such as lightfastness, opacity/transparency and resistance. Pigments are fine particles and are insoluble in the medium they are dispersed. These fine particles impart color by absorption and scattering of incident light. It is selective light absorption that gives color to pigments. Pigments used for graphic printing are organic and inorganic. There are also decorative pigments with special effects, such as metallic pigments, frequently used in gravure, especially in packaging sector. If molecular level is considered, then chromophores are responsible for color in organic molecules. The example of chromophores can be carbon-carbon double bonds, carbon and oxygen, nitrogen and nitrogen, or nitrogen and oxygen:

-C=C, -C=O, -C=N, -N=N-, -N=O

Some atomic configurations do not support selective light absorption, but help chromophores in increasing their absorption, and these are known as auxochromes. Some auxochromes are as given below:

$-NH_2$, -OH. $–NO_2$, $-CH_3$, -Cl, -Br

Color of pigments is nothing but ability of pigments to scatter light that they do not absorb. It depends upon the refractive indices of the pigments, medium in which pigments is dispersed, size of fine pigment particles and distribution of pigment particle size. (17) Choosing pigments for the gravure printing process can be a complex process. As most quality printing takes place in the gravure process, pigment used in the ink should support all parameters involved. Pigments used should be insoluble in medium dispersed, resistant to solvents and should be unaffected by acids and alkalies. A compatible gravure pigment should display good printability characteristics in a dispersed resin system. If the pigment is not compatible with the resin, then it results in an ink that has poor flow and printability characteristics. (7)

b) **Resins:** Resins acts as binders for pigments. The may be composed of several organic acids and their derivatives, or they can be polymers with high molecular weight. They can be either natural or synthetic. As the resin is a critical component in an ink, when there is need for improvement in ink performance, the resin is the first component ink manufacturers try to modify in order to enhance the ink's properties. Resin properties may affect ink viscosity, ink transfer, resolubility, barrier properties, adhesion, heat resistance, environmental issues or press speeds. Some of the characteristics of resins desired are mentioned below:

- It should give adhesion to substrate.
- Should give a dry, tack free, ink film after its solvent is released from the ink. That means it should also support solvent release.
- Solubility in the dispersed solvent system
- Should enhance printability characteristics, such as gloss and toughness to ink film to give rub resistance. It should also impart flexibility to the ink film so that it won't crack after drying.
- Pigment wetting is needed to provide excellent printability characteristics.
- It should also support any other properties required for end product requirements use, such as heat resistance, low odor and product resistance.

Depending upon the ink requirements, resins can be manufactured from, natural resins or synthetic resins. Natural resins are shellac, manila copal, asphalts, starch & dextrin, gum arabic, rosin from wood, and modified cellulose resins, among others. Polyamides, acrylics, styrene acrylic, vinyl, or urethanes are examples of synthetic resins. (18)

c) **Solvents:** Solvents can be termed as temporary ingredients. They are used in inks to apply a dispersed ink in a vehicle onto a substrate. After application onto the substrate, solvent is eliminated mainly by evaporation or absorption. The most commonly used solvents in the rotogravure process are toluene, ethyl, isopropyl and n-propyl alcohols, acetone, ethyl, isopropyl and n-propyl acetates, methoxy and ethoxy propanols, aliphatic hydrocarbons and water. Selection of solvents is done by considering the following factors:

- Resin system used
- Press speed
- Type of design being printed
- Substrate used for printing
- End use application of product
- Environmental consideration. (7)

d) **Additives:**

Different chemical compounds can be added to gravure inks for various reasons, mainly to enhance overall performance of the ink. This performance can be termed with respect to ink printability characteristics and its success in runnability. Some of the function of additives is as follows:

- Stabilizers and pigment wetting additives prevent agglomeration of pigment particles, modify surface tension of inks and also improve shelf life.
- Defoamers eliminate foam formation during ink manufacturing of ink or while running on press.
- Surfactants decrease the surface tension of the ink and improve substrate wetting by ink.
- Rheology modifiers improve rheological behavior, hold out properties and settling properties (19)

Gravure inks can be classified as solvent based, water based inks, hot melt and UV curable, which are used in some packaging applications.

1.3.1 Solvent Based Inks

Solvent based inks are inks in which pigments and resins are dispersed in an individual solvent or solvent mix. Solvent mixes are chosen for various reasons, such as making the ink more economical with expensive solvent and cheaper diluent, or to tailor the evaporation speed of the ink. Slower solvents will keep the ink open on the press, which may be desirable for offset gravure applications. Faster evaporating solvents are used in direct gravure printing. Solvent based inks are formulated depending upon substrate to be used, necessary end use properties of the ink and press parameters. Generally, solvent based inks have lower solids content than water based inks. Solvent based inks main components are pigments, resin, solvent, or solvent mixture and additives.

The pigment content in a solvent based ink is usually 4-12% by weight. The amount and selection of pigment(s) depend upon its dispersion factor in solvents. The ink should exhibit non-Newtonian flow properties, which will give acceptable printability characteristics. Resin content is 10-30 % by weight. Apart from providing adhesion of the pigments to the substrate, resin should promote ink film formation, impart low odor, bring transparency, and provide pigment wetting. Synthetic resins, such as polyamides, offer more flexibility in ink formation, as they can be fine tuned to suit the end use application of the ink. On the other hand, nitrocellulose brings film forming properties, but is brittle. Because these two are compatible in any ratio, ink formulators use these two resins in many rotogravure packaging applications to achieve different flexible printing inks. Additives are typically added at 2-5% by weight. Additives provide adhesion promotion and are used as slip agents, anti-scuff agents and stabilizers. Solvents are balanced in ink, and they are present in amounts around 40-60% by weight. The solvent used can be of more than one as it depends upon the various press and printability parameters. Packaging ink formulations incorporate solvents, such as ethyl, isopropyl and n-propyl alcohols, acetone, ethyl, isopropyl and n-propyl acetates, methoxy and ethoxy propanols, and aliphatic hydrocarbons. Publication gravure ink uses toluene and aliphatic hydrocarbon solvents. Solvent based inks dry by evaporation leaving the resins and pigments on the substrate. Solvents used in an ink formulation are highly volatile and are easily removed from the substrate by high velocity driers. (7).

Vinyl based inks are used in the printing of vinyl coated paper. Vinyl resins in conjunction with Methyl Ethyl Ketone (MEK) and toluene are used in inks based on vinyl resins. As vinyl based inks are used in vinyl wall coverings, they should be resistant to heat during embossing.

1.3.2 Water Based Inks

In water based inks, pigments are dispersed in an acrylic solution resin with a wetting agent, with the solvent being water. Emulsion resins in water based inks give film forming properties to the ink, high gloss and high rub resistance. By their nature, acrylic resins for water based inks have many carboxyl groups on the acrylic backbone, and as such, are not soluble in water. For their water solubility, an alkaline pH is required. An alkaline environment in water based inks is imparted through the addition of ammonia or amines. Moreover, water based inks have higher solids content than their solvent based counterparts. Ingredients for water based inks are as follows:-

- Pigments
- Resin System
- Water
- Ammonia
- Amines
- Additives
- Co-solvent

The basic principle of water based ink is using an acrylic resin, which is then solubilized in water by the formation of alkaline salts with volatile amine. On drying, ammonia is liberated to reform a water insoluble acrylic resin. Water based ink behavior depends upon its viscosity, surface tension, size and shape of the particles, stability of the pigments in the vehicle system, water resistance, temperature and pH. (2) Water based inks have thixotropic flow behavior. Viscosity decreases with increasing shear and increases with a decrease in shear force. Another important property to be considered is surface tension, as it affects wettability and foaming properties. Surface tension for water is 72 mN/m, as compared to solvent based inks, which have surface tension of around 35mN/m. As water based inks have higher surface tension than most substrates, especially non-porous ones, such as films, surfactants are used to reduce water based ink surface tension. Adding surfactants may increase foaming, which gives need to add anti-foaming agents (20). Pigments stability is achieved through the addition of wetting agents. When considering pigments used in water based inks, their size and shape does matter. The smaller the size of the pigments used, the better the colloidal stability, better the viscosity control and better the color strength of the ink (21). The addition of pigments is 5-20% by weight. (22) Pigment loading is selected by considering various print process parameters.

The temperature and pH of water based inks are important, as slight change in any one can result in a change in viscosity, surface tension, and pigment stability. This affects the printability of the ink in a serious way. Control of ammonia in ink also becomes important as pre-release of ammonia before impression can reduce pH, which in turn can result in the precipitation of the resin in the gravure cells. As water based inks are marginally resolubilized, precipitated resins in cells may not resolubilize during the next revolution of cylinder in the ink duct. (23) For this reason, ammonia and amines are added to water based ink formulations. Ammonia evaporates upon drying, but amines stay in the ink formulation and facilitate ink resolubilization.

Resins systems in water based inks are predominantly acrylic polymers and copolymers with styrene, butadiene, or methacrylates, having various degree of polymerization. Resin systems in water based ink are mixtures of solution and emulsion resin in order to achieve optimum ink performance. Solution resins are soluble acrylic resins with degree of polymerization around 15,000. Their function in an ink formulation is mainly to aid in grinding of the pigment. They also provide pigment stability. Emulsion resins are acrylic resins with large molecules. Their degree of polymerization is around 200,000. They do not dissolve in alkaline water solution, but create emulsions. They support film forming, heat resistance, adhesion and fast drying. Resins are added 10-20% by weight. Ink additives are 2-5% by weight. Here, additives have functions of wetting agents, slip agent, anti scuff agent, and antifoaming agent. The balance in ink is solvent, which is nothing but ammonia water. It is present in 40-60% by weight (22). Small amounts of alcohol is added as a co-solvent in water based ink in order to lower surface tension of ink, which helps to improve the wetting capacity of the ink with respect to the substrate (22) (24) (1).

1.4 Pigment Dispersion

The primary aim of dispersing pigments in a grinding vehicle is to de-agglomerate (particle size reduction) the pigment agglomerates. These pigment agglomerates are formed during the drying of the pigment during manufacture (25). The color strength of the pigment depends upon its exposed surface area. Smaller particle size increases surface area, which in turn increases color strength (4). Chemically, dispersions can be defined as a state of homogeneous suspension of one phase with another phase (26). In ink dispersion scenario, pigment (solid) is dispersed in liquid having grinding resin or solution resin, ammonia water and additives. Pigment grinding is an important step while formulating the ink. Here grinding means crushing of pigment into smaller particles (around 200-300 micrometers). It is also a process of incorporation of pigment particles in to liquid vehicle in certain way protected with wetting agent to combat agglomeration, thus to produce stable suspensions. In order to achieve optimum color strength, pigments have to go through grinding processes, where pigments go through stages of wetting, particle size reduction and stabilization. (27)

Wetting: Pigment wetting refers to displacement of air and pockets from surface of pigment and replacing it by resin solution. Premixing of pigments with vehicle takes place with the aid of mechanical shear force. The pigment/air interface is transformed in to pigment/resin interface. In later stages this wetting phase further aids in the breakdown of agglomerates in clusters of small pigments. (28) (29)

Grinding: After initial wetting stage, it becomes necessary to break down agglomerates into fine particles. This process may be called the grinding stage, which provides breakdown of agglomerates through mechanical action. During breakdown, more small clusters of particles are formed, which require additional wetting, and this in turn causes smaller cluster formation. Such mechanism goes on until small group of clusters remains. This stage of dispersion is very important, as without proper wetting and proper reduction of agglomerates, any unwetted pigment clusters will flocculate.

Stabilization: This stage serves the purpose of keeping separation between reduced agglomerates. Separation or stabilization prevents finely dispersed particles from flocculation or reagglomeration. Surfactant molecules get adsorbed on pigment surface creating repulsive forces, working against attraction i.e. Van Der Waals forces from other pigment particles reagglomeration. (30)

CHAPTER 2

PROBLEM STATEMENT

Due to the environmental norms on Volatile Organic Compounds (VOCs), and restrictions on using solvent based inks, the printing industry has sought more environmentally friendly inks. Water based inks offered that alternative, as they are free of any VOCs. Established organizations printing decorative laminates, wall coverings, or vinyl floorings with solvent based inks have gravure printing infrastructure, which is often equipped with dryers capable of drying solvent based inks. In order to comply with environmental norms, it is necessary to switch to water based ink, preferably employing existing drier configuration. So, one feasible approach would be to deposit less ink on the substrate so that current dryers can dry ink efficiently. Less ink deposition can be achieved by using engraving with higher resolution, thus employing cells with lesser volume. In order to achieve necessary visual appearance and color strength, decorative laminates are printed with solvent based ink with a cylinder engraved between 120-150 LPI resolution (3). Pigment solids used in solvent based for this specific application can be found in the range of 13-15% (31). So if the same percentage of pigment solids is used in water based ink then certainly printing with higher resolution will result in loss of color strength. Considering this factor, it was challenging to maintain the same color strength at higher resolution. The aim of this work is to use water based inks with higher pigmentation and higher solids content. A water based ink will be printed employing higher resolution engraving in order not to evaporate unnecessary water. Water based ink should match necessary CIELAB values of solvent based ink as close as possible. Thus, main focus of this project is to formulate and evaluate water based ink with high pigment content. An ideal way to change pigment solids in a water based ink are by formulating a stable pigment dispersion using various pigment concentrates.

CHAPTER 3

MATERIAL & EXPERIMENTAL

The main focus of this project was to formulate a high pigment solids water based ink for use as a replacement on gravure printing presses, which run solvent based ink. The approach implemented in formulating high pigment concentrate water based ink was by developing pigment dispersion with increasing pigment concentrate and later using it in final ink formulation. In addition to above, pigment dispersion was also subjected to increasing grinding time in order to reduce the particle size of the pigment and later it was analyzed how it affects color strength of final ink formulation. Overall, the whole project was carried in several stages which included developing a solvent based ink, water based pigment dispersion, and water based inks, printing of inks on a laboratory K-proofer with plates engraved at different resolution, print analysis and rheological analysis of inks. Workflow of experimental steps is illustrated in Figure 3.

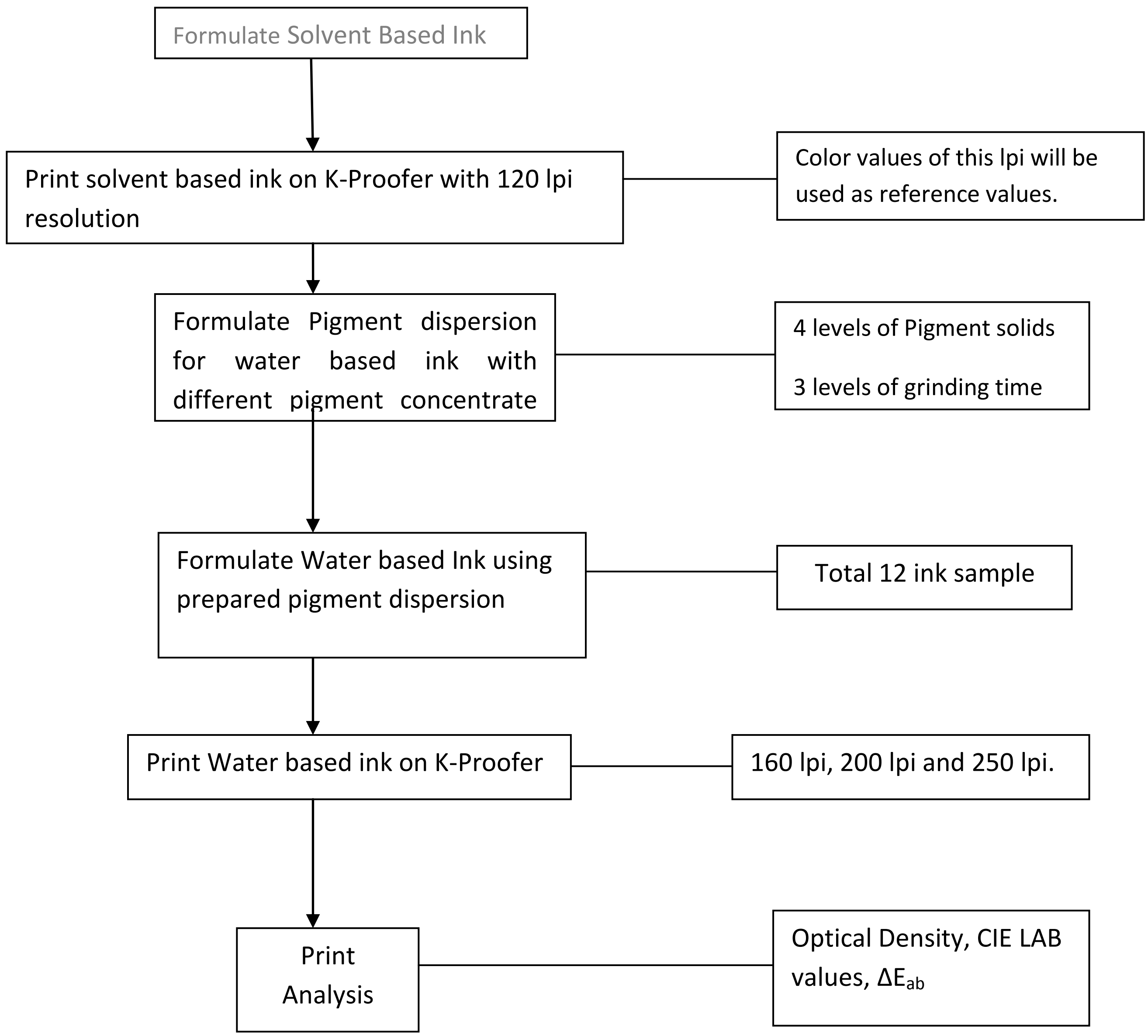


Figure 3: Project Workflow

For formulation of the solvent and water based inks, Heuco Blue 15:3 (Heubach) Phthalocynine blue color pigment was used. Its specification and main details are mentioned in Table 4.

Table 4: Details of Cyan Pigment (32)

Specification	**Heuco Blue Pigment 15:3**
Color Index	515306
Specific surface(m^2/g)	68
Lightfastness (1/25 S_D)	8

3.1 Solvent Based Ink

Chemicals Xylene, Iso-butanol and n-Butylacetate were used for preparation of the resin vehicle mixture. The resin, Laroflex-15, was supplied in powder form by BASF. Details of the resin is given in Table 5:

Table 5: Specifications for BASF Laroflex15 (33)

Specification	**BASF Laroflex15**
Appearance	Fine white powder
Viscosity (20 %solution in toluene)	12-18 cps
Shear rate D	500 s^{-1}
Density at 20^{o}C	1.25 g/cm^3
Vicat softening Temperature	46-48^o C
K value	30
Chlorine mass fraction	40%

3.2 Water Based Ink

Joncryl HPD-96 and Joncryl HPD-196 were used for formulating the pigment dispersions. Joncryl FLX-5000, Joncryl 60 and Joncryl Wax28 were used in the final ink formulation. Tego Defoamer was used as antifoaming agent and Surfynol-104 PA as an additive to decrease the ink's surface tension. A detail of each component's physical and chemical properties is shown in Table 6.

Table 6: Physical and Chemical Properties of Water Based Resins (34) (35)

Specifications	**HPD-96**	**HPD-196**	**FLX-5000**	**Joncryl60**	**Joncryl Wax 28**
Product type	Solution	Solution	Emulsion	Solution	Solution
Appearance	Clear	Clear	Semi-translucent emulsion	Clear	Tan
Viscosity	5000 @25^{o} C (cps)	3800 @25^{o} C (cps)	1000 mPa.s @25^{o}C	55000	25 mPa.s
pH	8.5	8.6	8.9	8.4	9.8
Molecular Weight	16000	9200	>200000	8500	-
Acid Number	220	200	100	215	-
Tg (^{o}C)	88	85	<5^{o}C	85	-

3.3 Experimental

Solvent Based Ink Formulation

The solvent based ink was formulated as follows: 1) Develop solvent mixture. 2) Develop vehicle mixture. 3) Blend solvent mixture, vehicle mixture and Phthalocyanine Blue Pigment in a high speed lab dissolver. The solvent mixture was prepared by mixing xylene, Iso-butanol and n-butylacetate. The amount of each solvent used in final mixture is shown in Table 7. The solvent mixture compatibility with the resin powder and cyan pigments was of utmost importance in finalizing the ink formulation. The vehicle system was formulated by using BASF Laroflex-15 and prepared solvent mixture, as shown in Table 8. The final components listed in Table 9 were mixed in a high speed Lab mixer.

The viscosity of the ink was measured as efflux time and adjusted to 23-25 sec through a #2 Zahn Cup.

Table 7: Solvent Mixture Formulation

Solvent Mixture	**Quantity (%wt)**
Xylene	50
Iso-Butanol	15
n-Butylacetate	35
Total	**100**

Table 8: Vehicle Mixture Formulation

Vehicle Mixture	**Quantity (%wt)**
Solvent Mixture	70
BASF Laroflex-15	30
Total	**100**

Table 9 : Solvent Based Ink Formulation

Components	**Quantity (%wt)**
Pigment	14
Vehicle Mixture	36
Solvent	50
Total	**100**

Water Based Pigment Dispersion

The components used and their purposes for use within the pigment dispersion are listed in Table 10:

Table 10: Pigment Dispersion Components

Component	Purpose
Phthalocynine Blue 15:3	Colorant
JONCRYL HPD96/ HPD 196	Dispersing Resin
Tego Defoamer	Antifoaming Agent
Water	Diluent

Two vehicle mixtures were prepared to create different pigment dispersions. Vehicle 1 was made by dispersing resin HPD-96 and Vehicle 2 was prepared by dispersing resin HPD-196. A composition of vehicle mixtures is shown in Table 11:

Table 11: Vehicle Mixture Formulation

Component	**Vehicle 1 (%wt)**	**Vehicle 2 (%wt)**
Joncryl HPD-96	25.5	-
Joncryl HPD-196	-	30
Antifoam	0.5	0.5
Water	34	24.5

For making the pigment dispersion, a mixture of pigment and vehicle was pre-blended in a high speed Lab dissolver (CM-100) at 2000 rpm. This mixture was then transferred in to a media mill with Zirconium spheres (Company: Zircoa Mill Mates) as a grinding medium. The mixture was agitated at 3000 rpm, for various periods of time, at which point pigment grinding was performed. Pigment dispersions were separated from Zirconium spheres through filtration.

Figure 4: Media Mill (left) and grinding medium Zirconium Spheres (right)

Table 12 gives the conditions used to prepare the pigment dispersion. Formulation can be interpreted with the following example. PD 38AA has 38 %wt pigment dispersed in vehicle 1 and it is grinded for 60 min. With the dispersing resin HPD-96 it was impossible to make a pigment dispersion from the pigment concentrate at 45 %wt and higher due to its high viscosity, which made it impossible to separate the pigment dispersion from the Zirconium spheres.

Table 12: Composition of Water Based Pigment Dispersion (Vehicle 1 contains Joncryl HDP 96 resin, vehicle 2 Joncryl HDP 196 resin as seen in the Table 11)

Pigment Dispersion ID	**Cyan Pigment (% wt)**	**Vehicle 1 (%wt)**	**Vehicle 2 (%wt)**	**Grinding Time(min)**
PD 38	38	62	-	**0**
PD 38A	38	62	-	**30**
PD 38AA	38	62	-	**60**
PD 42	42	58	-	**0**
PD 42A	42	58	-	**30**
PD 42AA	42	58	-	**60**
PD 45	45	-	55	**0**
PD 45A	45	-	55	**30**
PD 45AA	45	-	55	**60**
PD 48	48	-	52	**0**
PD 48A	48	-	52	**30**
PD 48AA	48	-	52	**60**

Water Based Ink Formulation

In this stage, water based inks were prepared according to a starting formulation supplied by BASF. Table 13 provides the details of this ink composition.

Table 13: Water Based Ink Component

Component	Quantity(%wt)	Purpose
Pigment	40	Colorant
JONCRYL FLX-	43	Emulsion Polymer for adhesion
JONCRYL 60	5	Acrylic Resin Solution for gloss and ink release
FOAMEX 1488	0.1	Defoamer
IPA	2.6	Solvent for speed drying
SURFYNOL 104-PA	0.2	Wetting Additive
JONCRYL WAX 28	2.1	PE wax emulsion for scuff resistance
Water	7	Solvent

After the water based dispersion were prepared, they were used in preparation of the Water based Ink. Table 14 gives an example of how ink was prepared. 40% by weight of Pigment dispersion 42 with grinding time of 30 min was mixed with other ink components (mentioned in Table 14) in a high speed Lab Dissolver.

Table 14: Example of Ink Formulation

Component	Quantity(%wt)
PD 42A	***40***
JONCRYL FLX-5000	43
JONCRYL 60	5
FOAMEX 1488	0.1
IPA	2.6
SURFYNOL 104-PA	0.2
JONCRYL WAX 28	2.1
Water	7

Table 15 details the steps of preparation used to create the water based inks. The % pigment solid of each ink is also given. All ink samples were prepared on a weight basis. The pH of each ink was maintained within the range of 8.5 to 9.5. If the pH was found out of range, it was adjusted with 5% wt ammonia in water.

Table 15: Description of Formulated Water Based Ink

Ink Id	**Ink 38**	**Ink 38A**	**Ink 38AA**	**Ink 42**	**Ink 42A**	**Ink 42AA**	**Ink 45**	**Ink 45A**	**Ink 45AA**	**Ink 48**	**Ink 48A**	**Ink 48AA**
Pigment Dispersion Used [%]	PD 38	PD 38A	PD 38AA	PD 42	PD 42A	PD 42AA	PD 45	PD 45A	PD 45AA	PD 48	PD 48A	PD 48AA
Pigment Solids (%)	15.20	15.20	15.20	16.80	16.80	16.80	18	18	18	19.20	19.20	19.20
Final solids	38.44	38.87	38.95	40.07	40.45	40.61	41.98	42.19	42.25	42.56	43.03	43.12

Particle Size Analyzer

After the ink was formulated, a NICOMP 370 DLS was used to determine the particle size of the pigment. The NICOMP uses light scattering principle (photo correlation spectroscopy [19] to measure particle size. Samples were diluted in solvent or water until the light intensity measured between 200-300 kHz. For this project, each ink samples particle size was measured.

Printing

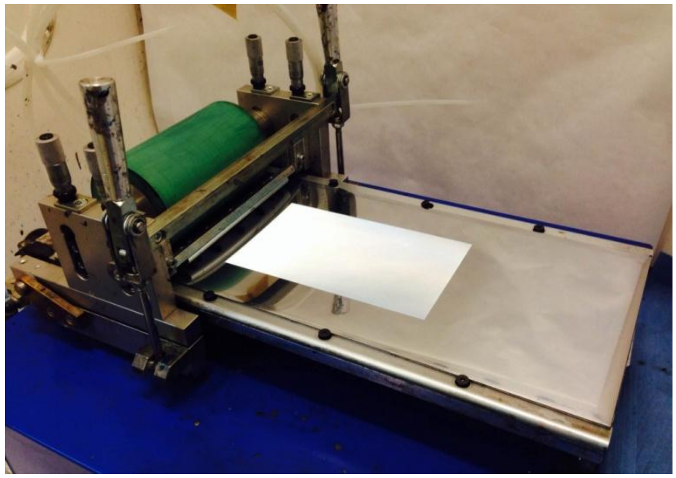


Figure 5: K-Proofer Printing Unit

Center of Ink & Printability- Western Michigan University

A laboratory K-Proofer (RK Print Coat Instrument, as shown in Figure 5), was used to evaluate the printing properties of the inks. An engraved flat plate was fixed to the proofer and substrate attached to the impression rubber roller. The doctor blade pressure and angle was adjusted through a micrometer and knob respectively. In addition, the pressure setting of the impression roller and print speed of proofer could be adjusted by the micrometer controller. Before the start of printing, a calibration of the impression roller pressure and doctor angle pressure was performed. Also, in order to eliminate variables, impression roller pressure, doctor blade angle and pressure, printing speed were kept constant. Table 16 gives resolution of engraving plates used.

Table 16: Printing Resolution

Ink	Resolution [LPI]
Solvent Based	120 (Reference)
Water Based	160
Water Based	200
Water Based	250

Print Analysis

All printed samples were analyzed for color values and optical density. An X-Rite 530 SpectroDensitometer was used to measure color coordinates CIE LAB and optical density values. Color coordinates CIE 'B' and CIE 'L' are very important for color strength assessment of printed sample for a cyan pigment.

Rheological Study

The rheology of the inks was analyzed with a TA Advanced Rheometer AR200 dynamic stress rheometer with Rheology Advantage software. Due to the low viscosity of the inks, a concentric cylinder geometry was used. Each ink sample was pre-sheared at 1000 sec^{-1} for 30 sec in order to eliminate any shear history. The samples were then equilibrated for 2 minutes prior to measurement. To maintain constant temperature of 25^{o}C, a water bath was used.

Steady State Flow: In the steady state flow experiments, the ink was subjected to a controlled increasing shear stress and the resultant shear rate and viscosity measured. During the rotogravure printing process, ink is subjected to a range of shear rates. These shear rates affect the rheology of inks and thus the flow of ink from engraved cells to substrate. In order to assist the free flow of ink, it should have a shear thinning behavior.

Ink Film Coat Weight

The amount of wet ink transferred to the substrate was calculated by using a Varian Atomic Absorption (AA) Spectrometer Model AA240. The working principle of this method is to trace the metal in the printed ink film. Phthalocyanine 15:3 pigment contains copper metal. So to trace the copper metal concentration in the printed sample, a known amount of ink sample or printed sample was digested in Hydrochloric and Nitric Acid in a 1:1 ratio. Then a known amount of ink sample and printed sample was digested in the same chemicals with the same ratio. Digested samples were then injected into the Varian spectrometer. The difference in values of copper concentration gives the value of wet ink transferred onto substrate. (36)

CHAPTER 4

RESULTS AND DICUSSION

Solvent Based Ink

The reference solvent based ink was formulated at pigment solids of 14%. It was printed using a 120 LPI resolution engraved plate. Table 17 gives the CIELAB and optical density values of the solvent based ink print. CIELAB values as mentioned in Table 17 were used as reference values for calculating the ΔE_{ab} of the water based inks.

Table 17: Solvent Based Ink Print Results

Result	Value		
CIELAB	L*	a*	b*
	47.0	-33.2	-56.5
Optical Density	1.8		

Instrument Characterization for Pigment Grinding

Formulating a water based pigment dispersion is the core and most important step in developing a water based inks. The most critical property for a water based pigment dispersion is to have pigment stability. Dispersed pigments should not settle or agglomerate. If the dispersion is compromised, then it highly affects the color reproducibility of the water based ink.

Initially, a three-roll mill instrument was used for preparing the pigment dispersions. But, with the three-roll mill, the pigment was not being well enough dispersed. There was heavy pigment settling and pigment flocculation. Pigment particle size reduction was not found. Regardless of this finding, this prepared pigment dispersion was used to prepare the final water based ink. With this ink, prints were not uniform as ink lay down was uneven. Different resolution prints resulted into almost the same results leading to mottled print and poor color readings. Later, the pigment dispersion making process was switched to media mill process. Table 18 compares observations made between the pigment dispersion prepared with the three-roll and media mill.

Table 18: Comparison between Three-roll Mill and Media Mill

Observation Parameter	**Three-Roll Mill**	**Media Mill**
Pigment Settling	Heavy	None
Flocculation	Present	None
Particle Size Reduction	None	Yes

Grinding effect on Water Based Pigment Dispersions

Viscosity

The developed water based pigment dispersions varied with amount of pigment concentrate in each. They were prepared at different grinding times and with different grinding resins. All of these factors affected the viscosity of the pigment dispersions.

Figure 6 shows how the amount of pigment concentrate, type of grinding resin and grinding time affected viscosity of the pigment dispersion. Viscosity was measured with a Brookfield viscometer@100 rpm with Spindle No 5. From the graph, it can be seen that there is a trend of an increase in viscosity with increasing pigment concentrate level from 38 to 42% wt., It is also observed that as grinding time increased, the viscosity of the pigment dispersion increased, too. A possible explanation can be as grinding time increased, the size of the pigment particles size decreased resulting in the creation of more surface area. Moreover, the differences in viscosity between the pigment concentrate between 38%-42% and 45%-48% were also found. Most likely, the main reason for this difference, besides higher solids, is the type of dispersing resin used in preparing pigment dispersions. Joncryl HPD-96 with viscosity of 5000 cP was used for pigment concentrate 38%-42%, while Joncryl HPD-196 with viscosity of 3800cP was employed for pigment concentrate 45-48%. It was impossible to prepare the pigment dispersion with Joncryl HPD-96 above pigment concentrate 42%. In order to maximize the pigment solids with the ink, the Joncryl HPD-196 was used and a pigment solids up to 48% was accomplished.

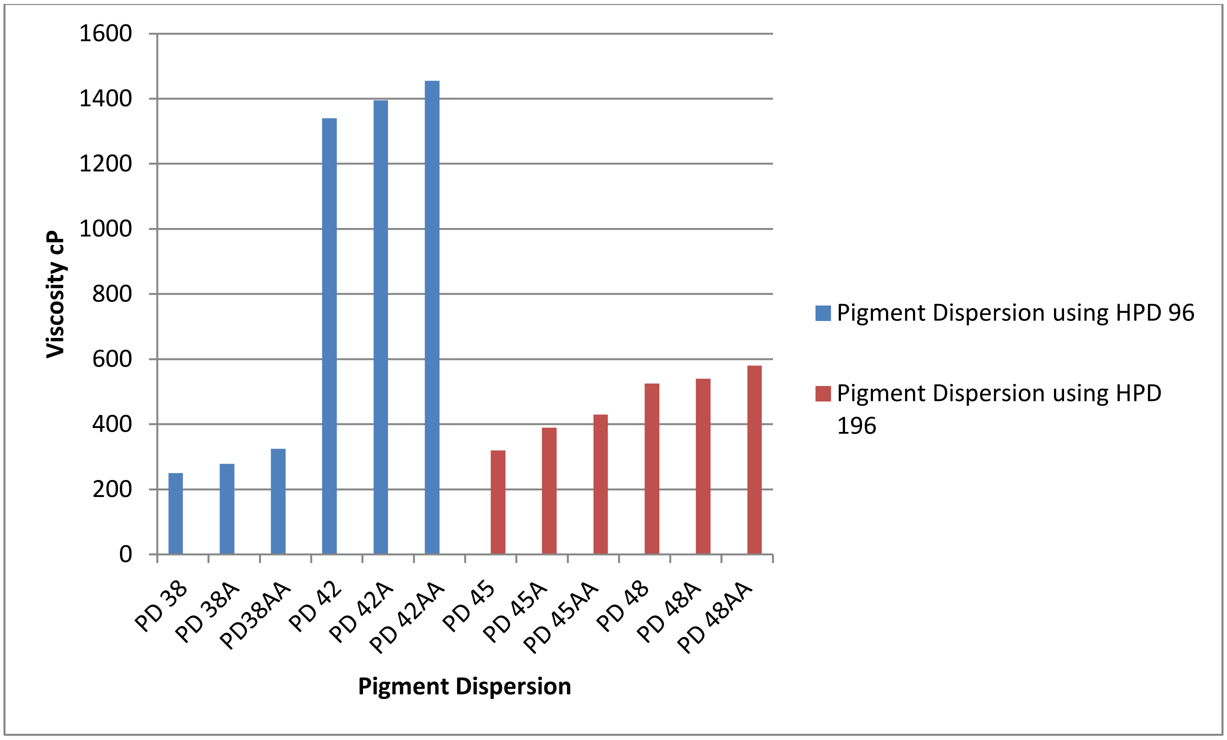


Figure 6: Viscosity of Different Pigment Dispersions

Particle Size of Pigment

Figure 7 gives values for effect of pigment grinding on particle size for each ink with different pigment dispersion. Particle size was measured with a NICOMP 370 particle size analyzer. From the values, it can be seen that the pigment grinding had an effect on pigment particle size. The lowest particle size for each pigment concentrate was achieved after 60 min of pigment grinding.

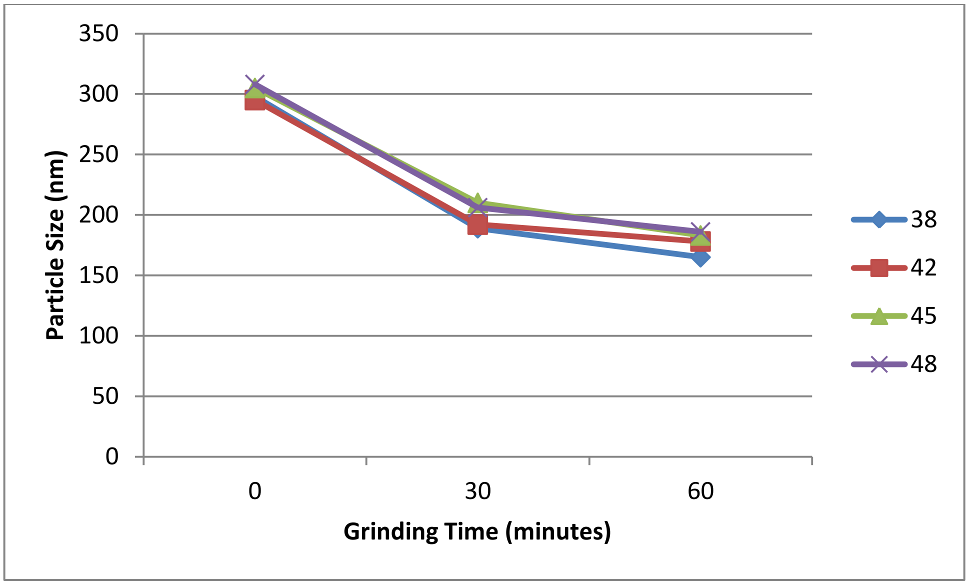


Figure 7: Pigment Particle Size for Different Grinding Time. 38, 42, 45 and 48 denote pigment dispersions at various pigment loads and resin type (as seen in the Table 12)

Rheological Behavior of Inks

Steady Sate Flow

All inks exhibited shear thinning characteristics (Figure 8). From the curves, it can be seen that the solids content of the ink affected the shear thinning behavior of the inks. Inks with higher solids content of the ink were of high viscosity at lower shear rate. Ink 48AA of higher solids, was high in viscosity in comparison to Ink 38 due to its lower solids content.

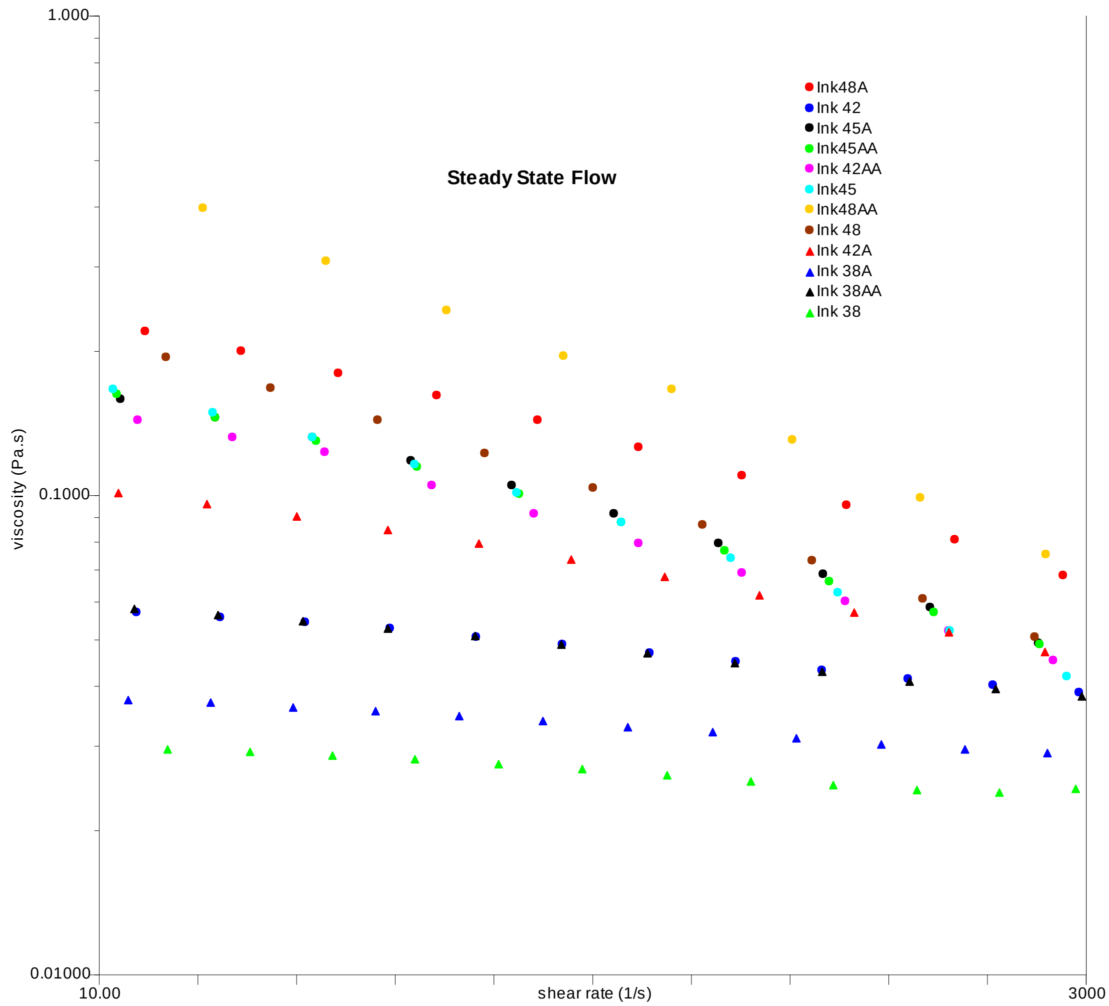
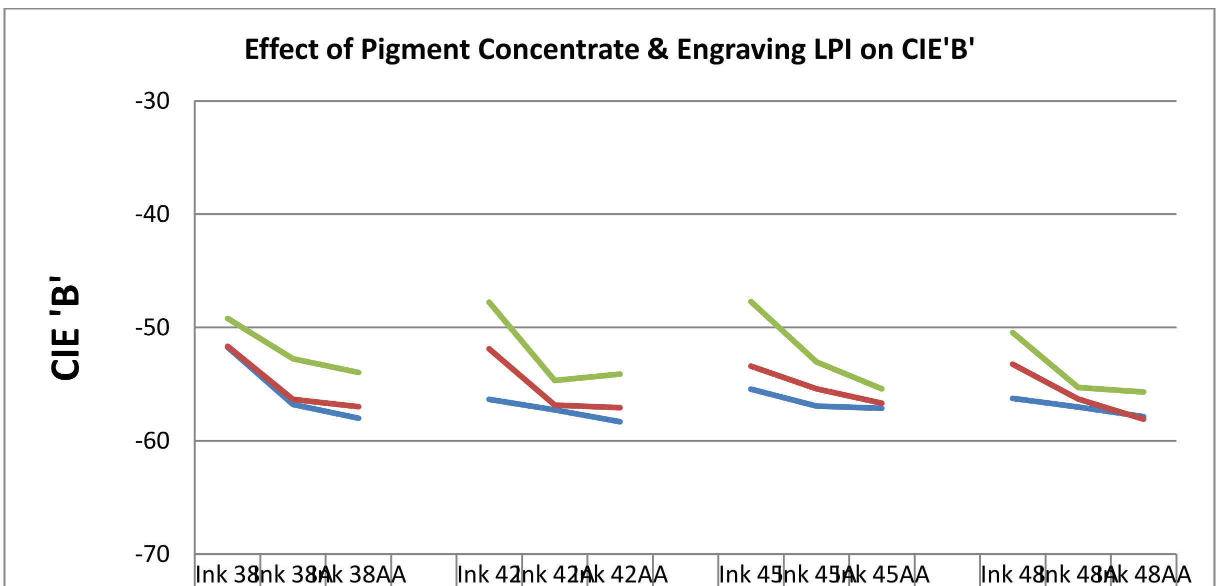


Figure 8: Steady State Flow Results for Water Based Inks

Color Strength

Each formulated ink with different pigment dispersion parameters was printed with 160, 200 and 250 lpi resolution gravure engraved plate. Figure 9 summarizes the effect of pigment concentrate solids, resolution and pigment grinding time on CIE 'B' value of the printed samples.

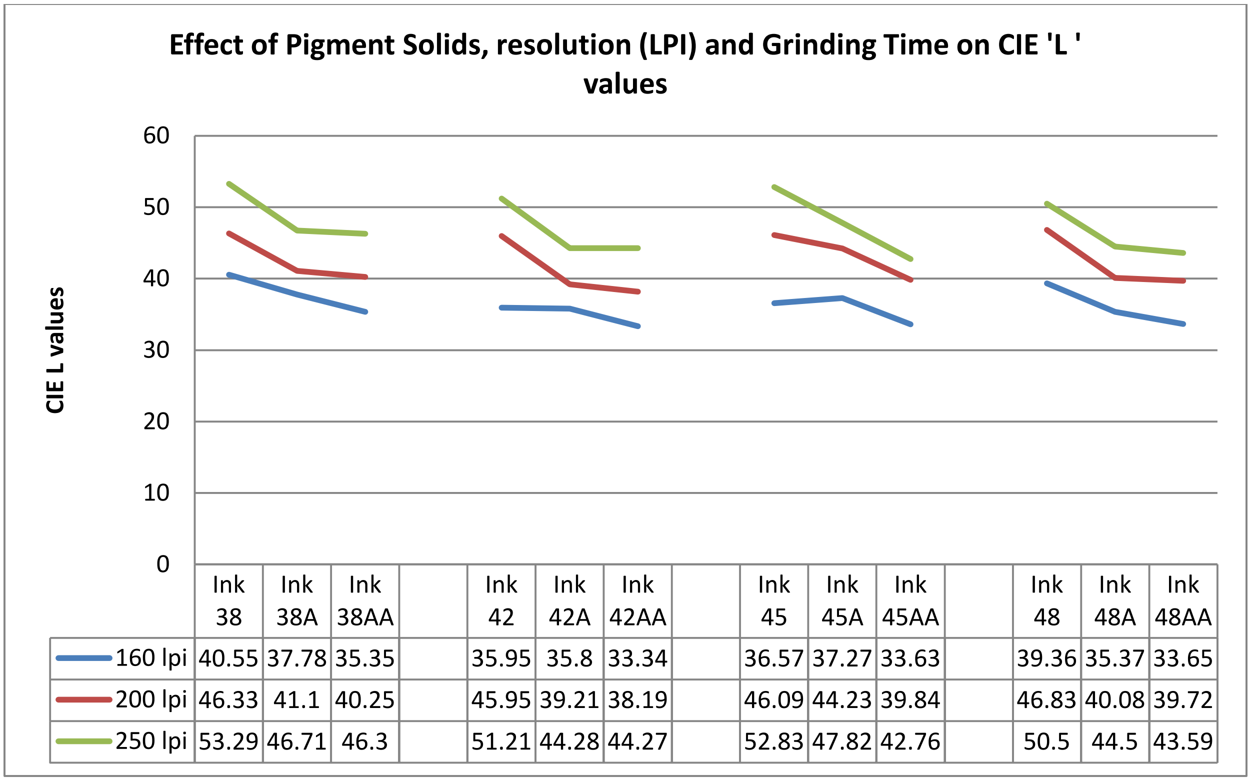
The ‘B’ value for each printed sample indicates that an increase in pigment concentrate in pigment dispersion resulted in an increase of color strength of an ink. Increase in pigment grinding time also resulted in an increase in color strength of final ink formulation. There is significant increase in color values with increase in grinding time.



	Ink 38	Ink 38A	Ink 38AA		Ink 42	Ink 42A	Ink 42AA		Ink 45	Ink 45A	Ink 45AA		Ink 48	Ink 48A	Ink 48AA
160 lpi	-51.7	-56.8	-58		-56.3	-57.3	-58.3		-55.4	-56.9	-57.1		-56.3	-57	-57.9
200 lpi	-51.7	-56.4	-57		-51.9	-56.9	-57.1		-53.4	-55.4	-56.7		-53.2	-56.3	-58.1
250 lpi	-49.2	-52.8	-54		-47.8	-54.7	-54.1		-47.7	-53	-55.4		-50.4	-55.3	-55.7

Figure 9: CIE ‘B’ Values

Figure 10 summarizes the effect of pigment concentrate, resolution and pigment grinding time on CIE ‘L’ value of printed samples. Each ‘L’ value represent pigment concentration in ink, resolution (LPI) and grinding time of pigment dispersion used in final ink formulation.



	Ink 38	Ink 38A	Ink 38AA		Ink 42	Ink 42A	Ink 42AA		Ink 45	Ink 45A	Ink 45AA		Ink 48	Ink 48A	Ink 48AA
160 lpi	40.55	37.78	35.35		35.95	35.8	33.34		36.57	37.27	33.63		39.36	35.37	33.65
200 lpi	46.33	41.1	40.25		45.95	39.21	38.19		46.09	44.23	39.84		46.83	40.08	39.72
250 lpi	53.29	46.71	46.3		51.21	44.28	44.27		52.83	47.82	42.76		50.5	44.5	43.59

Figure 10: CIE ‘L’ Values

Figure 11 shows interaction plot between resin used for making pigment dispersion and pigment concentrate Vs. color values reproduced. It can be clearly seen that inks with higher pigment content and HPD-196 resin clearly affect color strength.

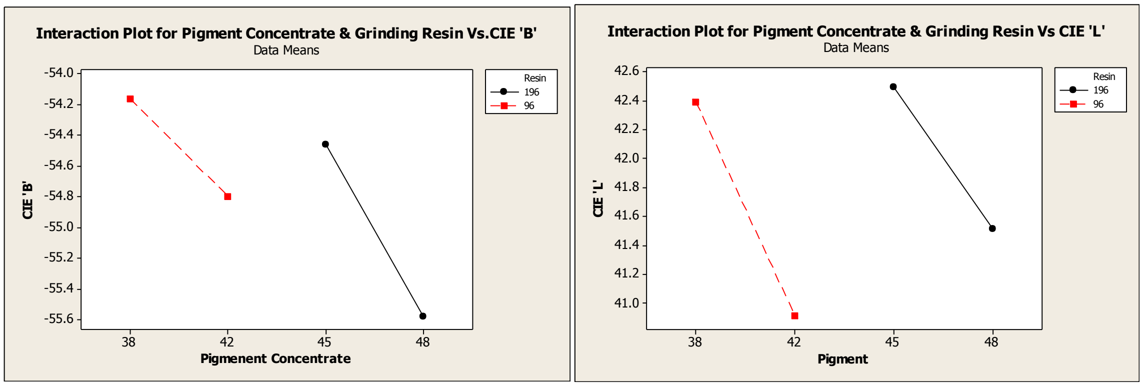


Figure 11: Interaction Plot for Pigment Concentrate & Grinding Resin vs. CIE L Color Values

Figure 12 shows the main effects plot for pigment grinding time and color strength. There is steep increase in color strength for pigment grinding time from 0 min to 30 min. This duration has a maximum effect on pigment particle size, which results in a steep gain in color strength. For pigment grinding time from 30 min to 60 min the change is gradual. This is also an indication that even after increasing the grinding time beyond 60 min, there is little change in color strength as the pigment has reached its saturation level.

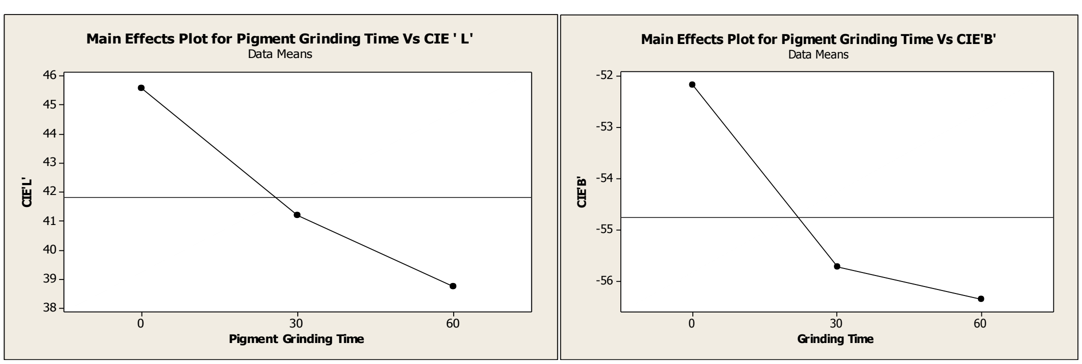


Figure 12: Main Effects Plot for Pigment Grinding Time CIE ‘L’ and CIE ‘B’ Vs

Following Figure 13 shows the main effects plot for different engraving resolution and color strength. It is well known that increase in engraving resolution decrease volume of the engraved cells. Figure 13 shows how an increase in resolution causes a decrease in color CIE 'L' and CIE 'B' values.

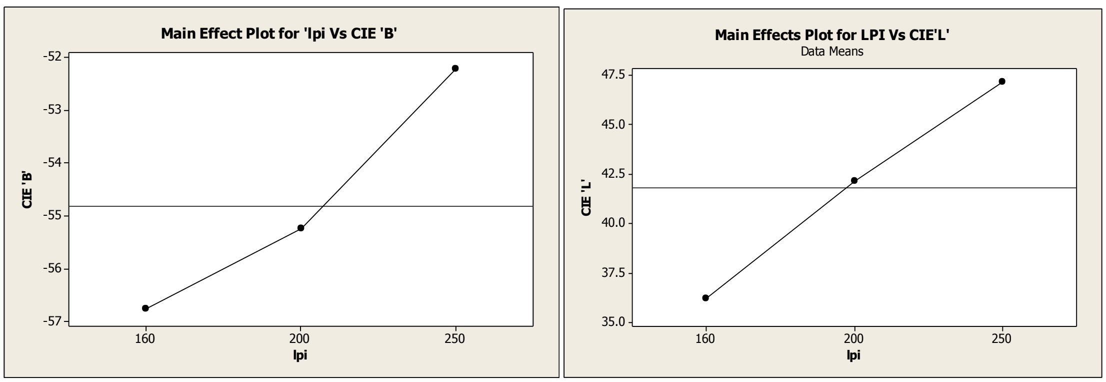


Figure 13: Main Effect Plot for Engraving Resolution (LPI) CIE 'B' & CIE 'L' Vs

Optical Density

Figure 14 shows the optical density for each ink and at different print resolutions. Resolution of engraving has an effect on print density. Higher resolution results in lower optical density, due to less ink being deposited. The grinding process reduces and breaks particle size, causing increase in ink optical density and color strength. (37) Optical density increased with grinding time for each pigment dispersion.

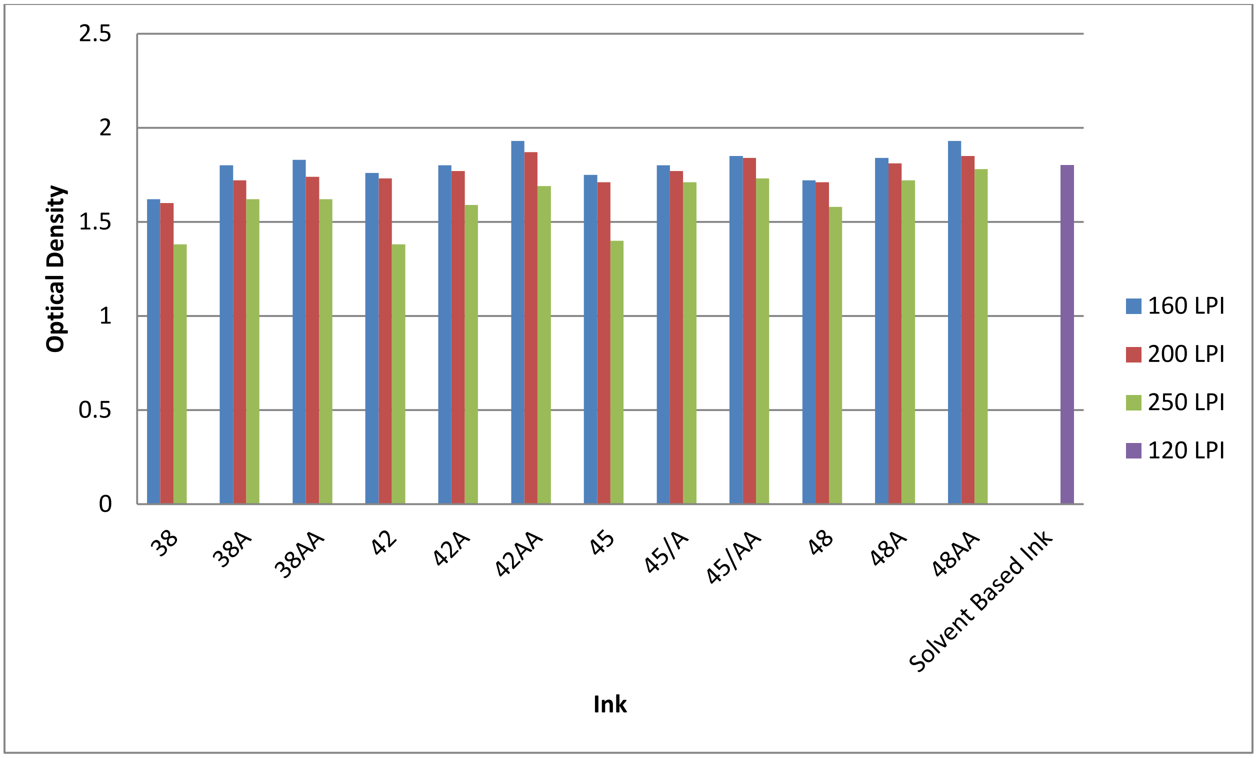


Figure 14: Optical Print Density for Water Based Ink & Solvent Based Ink

ΔE_{ab}

ΔE_{ab} represents a color difference in CIE LAB color space between two samples. Color difference was measured by using X-Rite 530 SpectroDensitometer. Color difference calculations are based on the mathematical formula $\Delta E_{ab} = \sqrt{(L_2\text{-}L_1)^2 + (A_2\text{-}A_1)^2 + (B_2\text{-}B_1)^2}$ .Difference in color values determines the deviation of measured color with respect to the reference color sample. For this project, ΔE_{ab} values were measured with SpectroDensitometer X-Rite 530. Figure 15 shows the value of color (ΔE_{ab}) difference between each water based ink and reference solvent based ink. The results indicate that ΔE_{ab} values differ for each ink sample and for each resolution. The ink sample with 45A printed at a resolution of 200 lpi had the lowest ΔE_{ab} value.

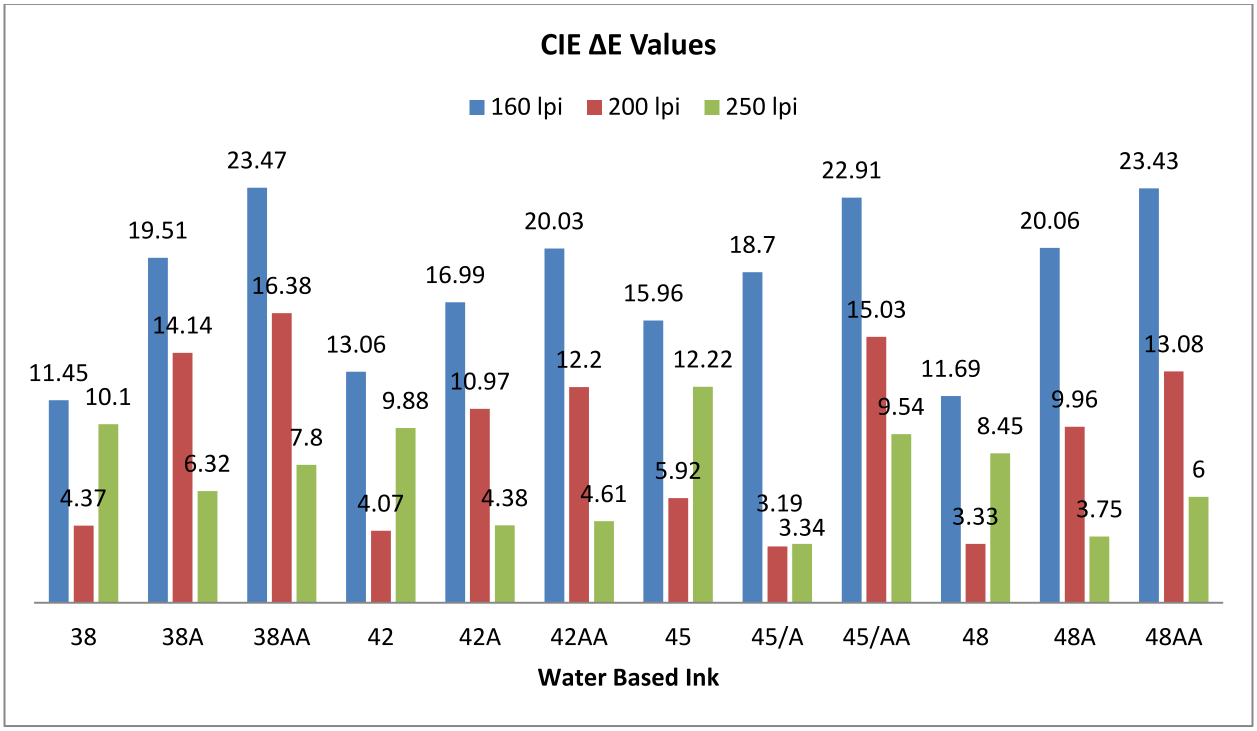


Figure 15: ΔE_{ab} with Solvent Based Ink as Reference

The color difference ΔE_{ab} was analyzed further. From Table 19 it can be seen that for Ink 45A, printed at 200 LPI resolution, the largest color difference came from L values difference, followed by B value. Table 20 gives details of ΔL, ΔA, ΔB for each water based ink formulated.

Table 19: ΔE_{ab} between Solvent Based Ink and Water Based Ink45A-200 LPI

Ink Id	L	A	B
Solvent Based Ink	47.0	-33.2	-56.5
Water Based Ink 45A-200 LPI	44.0	-32.2	-55.4
Delta Difference	ΔL =2.95	ΔA=-0.98	ΔB=-1.08

Table 20: ΔL, ΔA, ΔB between Solvent Based Ink and Water Based Inks.

	160 LPI			**200 LPI**			**250 LPI**		
Ink Id	**ΔL**	**ΔA**	**ΔB**	**ΔL**	**ΔA**	**ΔB**	**ΔL**	**ΔA**	**ΔB**
38	6.4	-6.03	-4.77	0.62	-1.94	-4.84	-6.34	2.14	-7.29
38A	9.17	-18.43	0.28	5.85	-13.45	-0.15	0.24	-6.29	-3.74
38AA	11.6	-19	1.51	6.7	-13.77	0.48	0.65	-6.36	-2.54
42	11	-7.02	-0.16	1	0.04	-4.63	-4.26	2.74	-8.74
42A	11.15	-14.66	0.76	5.7	-13.81	5.11	2.67	-2.95	-1.83
42AA	13.61	-16.55	1.82	8.76	-9.48	0.52	2.68	-2.8	-2.38
45	10.38	-8.89	-1.06	0.86	1.35	-3.1	-5.88	2.99	-8.79
45A	9.68	-15.93	0.43	2.95	-0.99	-1.08	-0.87	0.37	-3.46
45AA	13.32	-19.69	0.62	-2.09	2.34	-2.02	4.19	-8.09	-1.09
48	7.59	-9	-0.23	0.12	-0.68	-3.26	-3.55	1.82	-6.07
48A	11.58	-17.68	0.52	6.87	-10.17	-0.2	2.45	-3.98	-1.21
48AA	13.3	-20.82	1.37	7.23	-11.21	1.6	3.36	-5.09	-0.8

Table 20 shows differences in CIE LAB values between solvent based control ink and water based formulated inks with higher pigment loading. With decreasing cell volume content the stronger inks match better the control solvent based ink (Table 20), and L and B color differences are decreasing. With deeper cells (160 and 200 LPI) the L value is the largest contributor to color difference, followed by B value.

Chroma Difference (ΔC)

ΔC represents a Chroma difference in between solvent based ink and water based inks. Chroma difference was calculated by using mathematical equation $\Delta C = C_2 - C_1 = \sqrt{A_2^2+B_2^2} - \sqrt{A_1^2+B_1^2}$. The chroma difference decreases with increasing resolution (Figure 16), meaning that better match is received when higher pigmentation inks are printed using less cell volume.

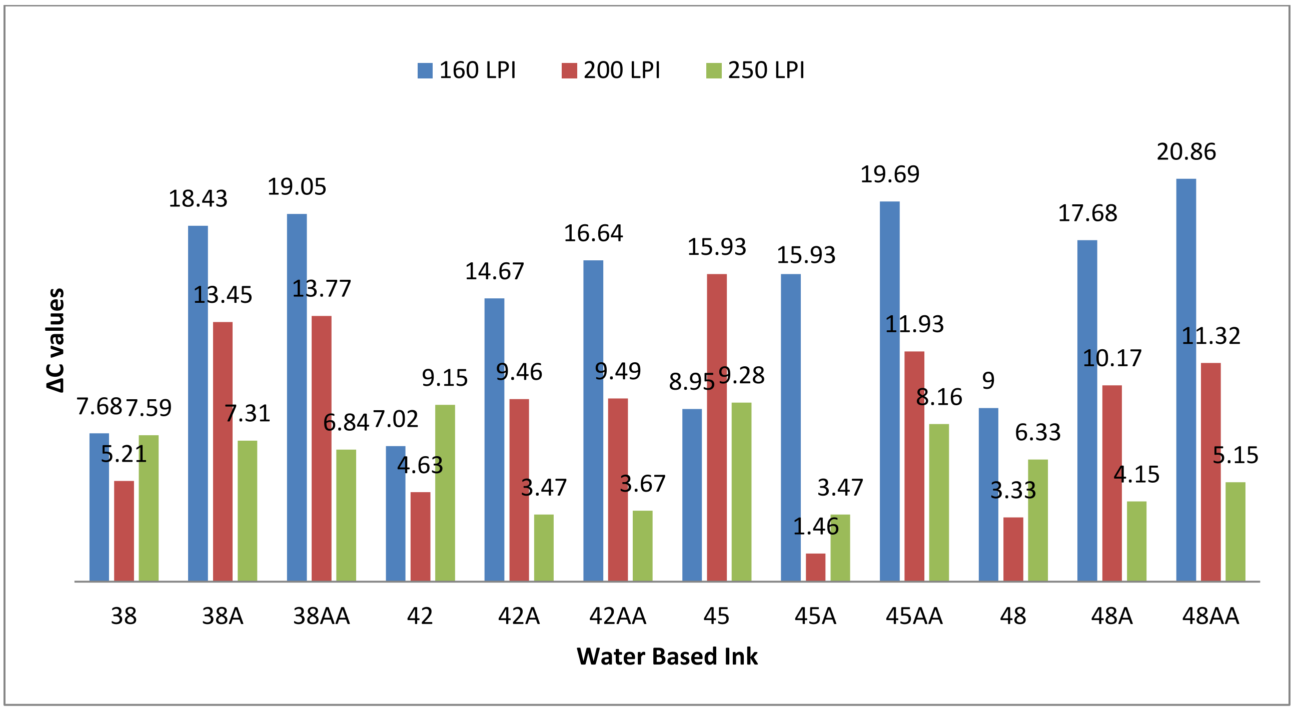


Figure 16: Chroma Difference Values between Solvent Based Ink & Water Based Inks

Table 21: Average ΔC and ΔL Values

Delta Attribute	160 LPI	200 LPI	250 LPI
ΔC	14.6	9.2	6.2
ΔL	10.37	3.71	-24.77

Table 21 shows average values of ΔC and ΔL for each LPI. ΔL at 200 LPI shows lowest value, which shows that CIE 'L' is largest contributor in matching color.

Engraving Cell Volume Vs Percentage of Ink Deposition

Table 22 gives the data of ink deposition with respect to approximate values of cell volumes for different engraving resolution. Wet Ink transfer rate was calculated by using Varian Atomic Absorption (AA) Spectrometer Model AA240. The wet ink deposition percentage decreased with increasing engraving resolution, thus decreasing nominal cell volume (Table 20), which was expected. It was found that decreased cell volume decreased the percentage of transferred ink.

Table 22: Cell Volume vs. Ink Transfer (15)

Engraving Resolution LPI	Approximate Cell Volume (BCM/Sq Inch)	Wet Ink Deposition (g/m^2)	Wet Ink Deposition (BCM/Sq. Inch)	Ink Transferred [%]
120	14.70	6.34	4.1	27.89
160	11.15	3.43	2.21	19.90
200	9.1	2.96	1.78	18.68

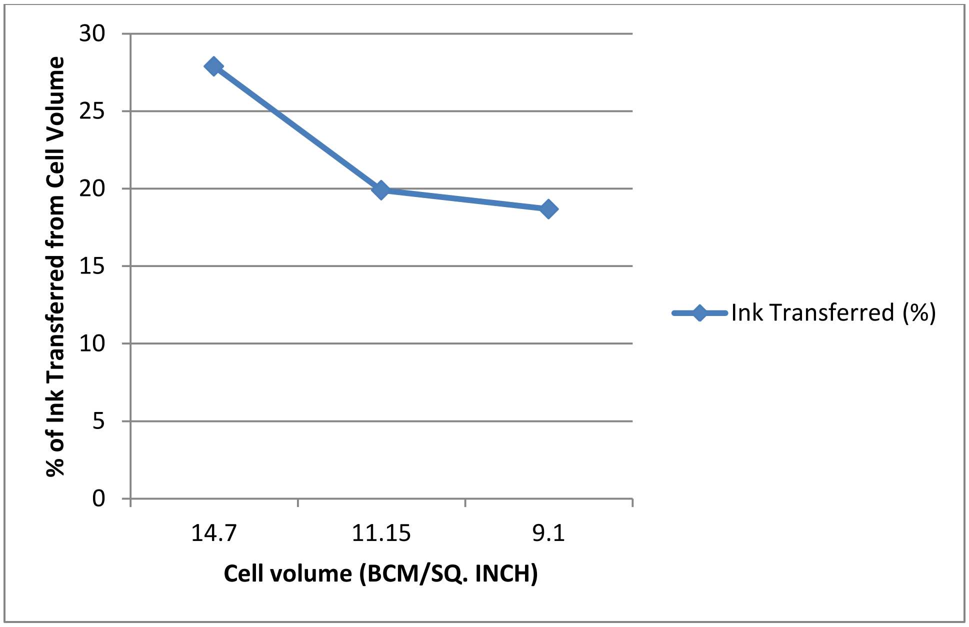


Figure 17: Cell Volume Vs % Ink Transfer

CHAPTER 5

CONCLUSION

The aim of this work was to match CIE LAB values of solvent based ink printed at a lower solid content to water based ink formulated with overall higher solids content and pigmentation. The aim was to deposit lesser water content. This was also aided using different engraving resolution. Reference solvent based ink was printed at a resolution 120 LPI, and water based inks was printed on 160, 200 and 250 LPI resolution. In order to increase the color strength of water based inks, pigment dispersions with varying pigment content were prepared at different grinding times. The inks were analyzed for CIE LAB values, optical density, rheological values and ink transfer from cells. The color strength of the inks was significantly dependent upon level of pigment solids. Pigment particle size also had an effect on color strength of ink. Reduction in particle size increased color strength, which was expected. A significant relationship between resolution and color strength was also found. With higher resolution there was reduction in color strength. Ink 45 A achieved the best match with control solvent based ink. A **Δ**E 3.19 was obtained when printed with the 200 LPI resolution plate and **Δ** E 3.34 for 250 LPI resolution plate. ΔE_{ab} of ink 45A printed at 200 LPI resolution plate showed highest dependence on L value, followed by 'B' value. Ink transfer was measured based on copper analysis in copper Phthalocyanine pigment in the print. It was found that ink transfer decreased with drop of nominal engraved cell volume.

CHAPTER 6

FUTURE RECOMMENDATION

The ink Industry is very interested in increasing color strength of water based ink. The most preferred way to increase water based ink color strength is by developing stable pigment dispersions. By increasing pigment content in pigment dispersions, color strength can be increased. But, there are limitations to this method due to rheological and stability issues that arise while increasing pigment concentration. It is a challenge to develop a high pigment loading dispersion of near Newtonian behavior. This work can be carried further by using mid range molecular weight grinding resins and by introducing hyperdipersants (25) for developing stable pigment dispersions.

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APPENDIX

Table A1: Particle Size of Water Based Inks

Ink ID	Particle Size(nm)
38	298
38A	189
38AA	165
42	295
42A	192
42AA	178
45	305
45A	210
45AA	183
48	308
48A	206
48AA	186

Table A2: Pigment Dispersion Viscosity:

Pigment dispersion ID	Pigment Dispersion using HPD 96	Pigment Dispersion using HPD 196
PD 38	250	-
PD 38A	278	-
PD38AA	325	-
PD 42	1340	-
PD 42A	1395	-
PD 42AA	1455	-
PD 45	-	320
PD 45A	-	389
PD 45AA	-	430
PD 48	-	525
PD 48A	-	540
PD 48AA	-	580

Table A3: Optical Density of Water Based Inks

Ink Id	**160**	**200**	**250**		**Ink Id**	160	200	250
38	1.62	1.6	1.38		**42**	1.76	1.62	1.62
	1.61	1.58	1.38			1.73	1.69	1.61
	1.62	1.56	1.39			1.76	1.62	1.62
AVG	1.62	1.58	1.39		**AVG**	1.75	1.643333	1.616667
SD	0.006	0.02	0.0057		**SD**	0.017321	0.040415	0.005774
38A	1.8	1.72	1.62		**42A**	1.82	1.77	1.38
	1.83	1.69	1.62			1.8	1.73	1.38
	1.8	1.69	1.61			1.82	1.78	1.38
AVG	1.81	1.7	1.616667		**AVG**	1.813333	1.76	1.38
STD	0.017321	0.017321	0.005774		**SD**	0.011547	0.026458	0
38AA	1.83	1.74	1.62		**42AA**	1.93	1.87	1.69
	1.81	1.73	1.61			1.94	1.85	1.68
	1.8	1.74	1.62			1.88	1.84	1.69
AVG	1.813333	1.736667	1.616667		**AVG**	1.916667	1.853333	1.686667
SD	0.015275	0.005774	0.005774		**SD**	0.032146	0.015275	0.005774
45	1.75	1.71	1.4		**48**	1.72	1.71	1.58
	1.61	1.69	1.39			1.61	1.69	1.61
	1.62	1.7	1.39			1.62	1.62	1.62
AVG	1.66	1.7	1.393333		**AVG**	1.65	1.673333	1.603333
SD	0.078102	0.01	0.005774		**SD**	0.060828	0.047258	0.020817
45A	1.8	1.77	1.71		**48A**	1.84	1.81	1.72
	1.61	1.69	1.61			1.61	1.69	1.68
	1.62	1.62	1.62			1.62	1.62	1.69
AVG	1.676667	1.693333	1.646667		**AVG**	1.69	1.706667	1.696667
SD	0.106927	0.075056	0.055076		**SD**	0.13	0.09609	0.020817
45AA	1.85	1.84	1.73		**48AA**	1.93	1.85	1.78
	1.84	1.85	1.71			1.85	1.86	1.73
	1.87	1.84	1.71			1.89	1.87	1.7
AVG	1.853333	1.843333	1.716667		**AVG**	1.89	1.86	1.736667
SD	0.015275	0.005774	0.011547		**SD**	0.04	0.01	0.040415

Table A4: CIELAB values of Water Based Inks

Ink ID	**38**			**38A**			**38AA**		
	L	a	b	L	a	b	L	a	b
160	40.55	-27.2	-51.73	37.78	-14.8	-56.78	35.35	-14.23	-58.01
200	46.33	-31.29	-51.66	41.1	-19.78	-56.35	40.25	-19.46	-56.98
250	53.29	-35.37	-49.21	46.71	-26.94	-52.76	46.3	-26.87	-53.96
Ink ID	**42**			**42A**			**42AA**		
	L	a	b	L	a	b	L	a	b
160	35.95	-26.21	-56.34	35.8	-18.57	-57.26	33.34	-16.68	-58.32
200	45.95	-33.27	-51.87	39.21	-23.77	-56.86	38.19	-23.75	-57.02
250	51.21	-35.97	-47.76	44.28	-30.28	-54.67	44.27	-30.43	-54.12
Ink ID	**45/196**			**45A/196**			**45AA/196**		
	L	a	b	L	a	b	L	a	b
160	36.57	-24.34	-55.44	37.27	-17.3	-56.93	33.63	-13.54	-57.12
200	46.09	-34.58	-53.4	44.23	-32.24	-55.42	39.84	-21.3	-56.68
250	52.83	-36.22	-47.71	47.82	-33.6	-53.04	42.76	-25.14	-55.41
Ink ID	**48/196**			**48A/196**			**48AA/196**		
	L	**a**	**b**	**L**	**a**	**b**	**L**	**a**	b
160	39.36	-24.23	-56.27	35.37	-15.55	-57.02	33.65	-12.41	-57.87
200	46.83	-32.55	-53.24	40.08	-23.06	-56.3	39.72	-22.02	-58.1
250	50.5	-35.05	-50.43	44.5	-29.25	-55.29	43.59	-28.14	-55.7

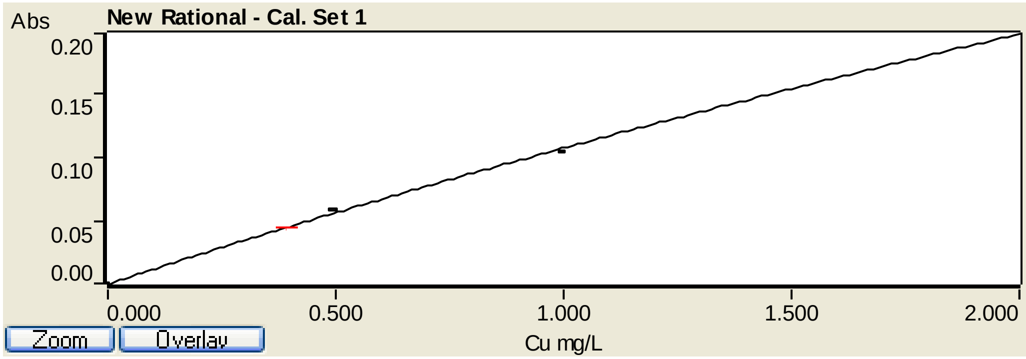

FIGURE A1: Varian Spectrometer Copper Calibration Curve

Table A5: Copper Calibration Readings

STANDARD	ABS.	CONC.
ZERO	0.004	0000
STD1	0.0580	0.5
STD2	0.1026	1
STD3	0.1963	2

Table No A6: Copper Concentration In Ink 45

Copper Concentration in Ink	Ink in %
0.886	0.001473
0.884	0.001471
0.885	0.001475
0.882	0.001479
0.889	0.001475
Average	**0.001475**

Table No A7: Ink Transfer for different LPI

LPI resolution	Copper Concentration in Print	mg/m^2	Ink in %	Ink transfer in gsm
120	0.898	9.36	0.001475	6.34
160	0.459	4.78	0.001475	3.23
200	0.390	4.07	0.001475	2.76

Figure A2: Screenshot of Varian Spectrometer Readings