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Gloss Development of Spray-coated Systems

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GLOSS DEVELOPMENT OF SPRAY-COATED SYSTEMS

By

Aaron W. Clark

B.S. University of Maine, 2002

B.A. University of Maine, 2002

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

August, 2004

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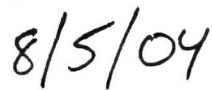
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GLOSS DEVELOPMENT OF SPRAY-COATED SYSTEMS

By Aaron W. Clark

Thesis Advisor: Dr. Douglas W. Bousfield

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
Degree of Master of Science
(in Chemical Engineering)
August, 2004

A spray-coated system involves any substrate on which a liquid coating is applied in a drop-wise fashion. Inkjet printing is the controlled application of drops to print a surface and is the focus of this work. The gloss of the printed substrate is an important attribute of print quality. Print gloss depends on a number of factors, such as ink and media properties. Non-uniform gloss in different regions of a printed image can cause a decrease in quality of a printed sample. However, a good understanding of the gloss development of spray-coated systems is not available in the literature.

Several combinations of inkjet inks and media were characterized in terms of physical properties. Both pigmented and dye-based inks were used with absorbing microporous coated media. These ink/media combinations were printed with an inkjet printer and the final gloss measured. A laser system was used to measure the gloss every millisecond right after printing, around 20 ms after drop impact. Some media were modified with chemicals or other treatments to modify physical and chemical properties.

Fiber swelling in paper-based media was found to lower gloss in those media which contain fibers that can contact water. This reduction in gloss occurred one second

after printing. Media with protected paper fibers do not exhibit this gloss reduction. Plastic-based media with porous coatings obtained the final gloss at 0.1 seconds. Inks can be destabilized by ions on the media surface that leads to low gloss. Some inks were not sensitive to ions on the media. Light color inks were found to have high gloss values at 50% fill compared to 100% fill while most other inks have the opposite behavior. This phenomenon is likely due to the secondary reflection at the ink/media interface; light is able to transmit through the ink layer and reflect at the media surface.

ACKNOWLEDGMENTS

My list of thanks must begin with my advisor, Prof. Douglas W. Bousfield, whose unending patience, encouragement, generosity, and support have made this experience such a pleasurable one. I enjoyed working for him on this project very much; not all graduate students are that lucky.

Of course, many thanks to my thesis committee, which includes Prof. Adriaan van Heiningen and Yubai Bi, for their invaluable time and advice. Also to the inkjet research team at Hewlett-Packard—which Yubai is a part of—who have provided indispensable help throughout this project, Anne Kelley-Rowley and Peter Morris in particular. This research project was funded by Hewlett-Packard.

I would also like to extend my thanks to all the faculty, staff, and graduate students of the Chemical Engineering department here at the University of Maine; most of which have contributed either directly or indirectly to this project.

I must say thank you to my wife, Lori, whose love and support never waiver as she waits patiently for me to finish school (or at least semi-patiently).

Finally, more thanks than words can express to two amazing parents, Wayne and Judy Clark, to whom this thesis is dedicated. From the very beginning, any success in my life has been a result of their perpetual love and encouragement. I am forever indebted to them for that.

TABLE OF CONTENTS

ACKNOWLEDGMENTS.....ii

LIST OF TABLES.....vi

LIST OF FIGURES.....vii

Chapter

1. INTRODUCTION.....1

 1.1 Inkjet Printing.....1

 1.2 Inkjet Media.....4

 1.3 Inkjet Ink.....8

 1.4 Print Quality.....12

 1.5 Ink-Media Interactions.....14

 1.6 Gloss.....17

2. EXPERIMENTAL PROCEDURE.....22

 2.1 Static Gloss.....22

 2.2 Dynamic Gloss.....24

 2.3 Absorption Rate.....26

 2.4 Stylus Profilometer.....29

 2.5 Confocal Microscope.....29

 2.6 Porosimeter.....30

 2.7 Draw-Down Coater.....32

3. INFLUENCE OF SUBSTRATE TYPE ON GLOSS.....34

3.1 Media Description.....34

3.2 Ink Description.....39

3.3 Static Gloss Results.....40

3.4 Dynamic Gloss Results.....43

3.5 Summary.....45

4. INFLUENCE OF SURFACE CHEMISTRY ON GLOSS.....47

4.1 Ink Description.....47

4.2 Influence of Calcium Chloride.....48

4.3 Influence of Other Ions.....52

4.4 Summary.....56

5. INFLUENCE OF INK PIGMENT LOAD AND
IMAGE FILL PERCENTAGE ON GLOSS.....58

5.1 Ink D Group.....58

5.2 Gloss Spike Mystery.....60

5.3 Optical Phenomena.....62

5.4 Surface Features.....66

5.5 Other Surface Treatments.....67

5.6 Roughened Media Surface.....70

5.7 Summary.....71

6. CONCLUSIONS AND RECOMMENDATIONS.....74

REFERENCES.....77

APPENDIX. Visual Basic Acquisition Code.....80

BIOGRAPHY OF THE AUTHOR.....90

LIST OF TABLES

Table 3.1. Media data.....35

Table 4.1. Average coat weight of calcium chloride-treated solutions.....48

Table 4.2. Average coat weight of treated samples, 1.0 M solutions.....52

Table 5.1. Roughness results for inks D1 and D2.....60

LIST OF FIGURES

Figure 1.1.	Idealized contact angle on a smooth solid surface.....	15
Figure 1.2.	Specular (mirror-like) and diffuse (scattering) reflection.....	18
Figure 2.1.	Schematic of dynamic gloss device.....	25
Figure 2.2.	Bristow apparatus with close-up of testing process.....	27
Figure 2.3.	Typical Bristow results.....	28
Figure 2.4.	Mercury porosimetry result for a coated substrate.....	31
Figure 3.1.	Pore size distribution of media A.....	36
Figure 3.2.	Pore size distribution of media B.....	36
Figure 3.3.	Pore size distribution of media C.....	37
Figure 3.4.	Pore size distribution of media D.....	37
Figure 3.5.	Pore size distribution of media E.....	38
Figure 3.6.	Static gloss results for ink A1.....	40
Figure 3.7.	Static gloss results for media C.....	41
Figure 3.8.	Final gloss results for ink B1 for the range of fill percentages.....	42
Figure 3.9.	Dynamic gloss results for ink A1.....	44
Figure 3.10.	Paper-based media and fiber swelling.....	45
Figure 4.1.	20-degree static gloss results for ink B2 on CaCl_2 -treated media.....	49
Figure 4.2.	20-degree static gloss results for ink E1 on CaCl_2 -treated media.....	49
Figure 4.3.	Typical responses of ink B2 on CaCl_2 -treated media C.....	51
Figure 4.4.	Typical responses of ink F1 on CaCl_2 -treated media C.....	51
Figure 4.5.	20-degree static gloss results for ink A1 on ion-treated media.....	53

Figure 4.6. 20-degree static gloss results for ink B2 on ion-treated media.....54

Figure 4.7. 20-degree static gloss results for ink D1 on ion-treated media.....54

Figure 4.8. 20-degree static gloss results for ink D2 on ion-treated media.....55

Figure 4.9. Bristow results for ion-treated samples.....56

Figure 5.1. 20-degree static gloss results for ink D1.....59

Figure 5.2. 20-degree static gloss results for ink D2.....59

Figure 5.3. Magnified image of ink D2, 100% fill, on media C.....61

Figure 5.4. Magnified image of ink D2, 50% fill, on media C.....61

Figure 5.5. Theoretical light interaction with a print for various cases.....63

Figure 5.6. 50% ink D2 on dyed media C.....65

Figure 5.7. 20-degree gloss results for ink D2 printed
on untreated and dyed media C.....65

Figure 5.8. SEM image of ink D2, 100% fill, 80000x magnification.....66

Figure 5.9. SEM image of ink D2, 50% fill, 80000x magnification.....67

Figure 5.10. 20-degree gloss results for ink D2 printed
on untreated and binder-treated media C.....68

Figure 5.11. 20-degree gloss results for ink D2 printed
on untreated and pigment-treated media C.....69

Figure 5.12. 20-degree final gloss values of ink D2,
100% and 50% fill, vs. sheet gloss.....70

Chapter 1

INTRODUCTION

The term “spray-coated system” refers to a rather broad description involving any media on which a liquid coating is applied in a drop-wise fashion. A great number of applications use the method of spray-coating such as automotive painting, coating of ceiling tiles, and other painting applications. Recent studies have explored the potential of paper coating with sprays. Inkjet printing is the controlled application of drops to print a surface and is the focus of this work. The mechanisms that control the development of gloss with inkjet printing are the first concern.

There are many factors which determine the gloss of a printed sample. Gloss is regarded as one of the most fundamentally important properties of an aesthetically pleasing image, and therein lies the motivation for this work. The goal of this investigation is to better understand the mechanisms that control print gloss and the problems encountered in producing a high level of print gloss with an inkjet printer.

Although this thesis is focused on inkjet printing, the same mechanisms should apply to other spray-coated systems. Drops that impact a surface must level and set in a uniform manner to generate high gloss.

1.1. Inkjet Printing

An inkjet printer is any printer that places small droplets of ink onto paper to create an image. These droplets fall onto the paper to form dots which are generally in the range of 40 to 60 microns in diameter; for comparison, the diameter of a human hair

is about 70 microns. Droplet size is matched to the resolution of the printer, for instance a higher resolution photo-quality printer typically uses a smaller drop than what is used in a letter-quality printer. The optimal dot size can be calculated for a given resolution by the equation

$$D = \frac{\sqrt{2}}{dpi} \times 2.54 \times 10^4 \quad (1.1)$$

where D is dot diameter, in microns, and dpi is dots per inch. The dots are positioned precisely, and with steadily progressing technology resolutions of up to 1440x720 dpi can be presently achieved. The dots can have different colors, which are combined together to create photo-quality images. (Tyson, 2001)

Since the invention of the inkjet printer, color printing has become popular. This ability to produce color images was the one major advantage that inkjets traditionally had over expensive laser printers. In the late 1990's, the price of color laser printers reached a level which made them more practical for home use than before. and thus the inkjet's

The basic principle of inkjet printing simply involves propelling a drop of ink from the print-head onto the paper below. This is achieved via non-impact inkjet technology that is classified as either drop on demand (DOD) or continuous, also called electrostatic. Most printers on the market are the DOD type. “Drop on demand” literally implies just what it says—upon receiving a specific electrical pulse, the print head forms the “demanded” ink drop and delivers it to the paper. The DOD technology can be classified further as either thermal inkjet or piezo-electric inkjet.

Most inkjet printers use thermal technology, whereby heat is used to propel ink from the print head onto the paper. In a thermal inkjet printer tiny resistors create heat which vaporizes ink to form a small bubble. As this bubble expands, a small amount of ink is forced out of its reservoir through a nozzle and onto the paper below. When the bubble collapses a vacuum is created which pulls more ink from the cartridge into the reservoir to begin the process anew. Each nozzle delivers extremely tiny drop volumes of around 5 to 10 picoliters for dye-based inks. A typical thermal inkjet printer has upwards of several hundred nozzles, each about the diameter of a human hair. (Tyson, 2001)

The ink used with thermal inkjet technology must be resistant to heat. Also, the heat-based process requires a certain cooling time in each cycle as well. Piezo-electric technology avoids the need for heat and cooling time by utilizing a piezo-electric crystal. With an electric signal the piezo crystal is made to vibrate—much like a common loudspeaker—thereby propelling a drop of ink. When the crystal vibrates inward toward the reservoir, it forces a tiny amount of ink out of the nozzle. When the crystal vibrates

outward away from the reservoir, it pulls in more ink from the cartridge to replace the lost droplet. (Anderson, 2004)

1.2. Inkjet Media

There is an impressive selection today of different paper that is available for inkjet printers, each with its own purpose and capability. A whole range of paper exists, from low cost copy paper to expensive premium high gloss photo paper. Most of the current generation inkjet printers require a high-quality, coated glossy paper to achieve realistic photo-quality output. With advancing technology, future generations of inkjet printers may have the capability to produce high print-quality images on plain copier paper; however much more work is required to make that a reality.

As in any printing technique, paper is the printing ‘medium’ and hence all paper will simply be referred to as ‘media’ or ‘substrate’ throughout the remainder of this work, except where specific names are used, or when referring to actual pulp-wood derived paper. This is done not only to simplify things but also to help avoid confusion. It will soon become apparent that the term “paper” is a poor choice of words in some cases since some media contain no paper at all.

The primary component of any printing medium is its base layer. The base layer provides the structure which supports the printed image. The base layer must be strong enough to avoid mechanical damage yet malleable enough to allow runnability through the printer. Media used in inkjet printing are generally either paper-, plastic-, or photo-based. Most media commercially available today is paper-based. The term paper refers to that which is derived from pulpwood and this is what people commonly associate with

the term “paper”. Paper-based media encompass the entire the range of media quality, from plain copier paper to high quality inkjet photo-paper. The most significant disadvantage of paper-based media is the paper fibers’ susceptibility to swelling and damage when exposed to water. Much less common than paper-based media are media which contain not a single fiber of cellulose. The base layer of these plastic-based media can be composed of bi-axially orientated polyethylene terephthalate, PET. While similar in appearance to paper-based media, media with a plastic base averts the problems associated with fiber swelling and distortion. Plastic-based media also have the unique characteristic of unrivaled strength. Any media which have a paper base layer and also a highly protective plastic coating are termed photo-based media. In stark contrast to paper-based media, the base layer fibers in photo-based media are effectively shielded from any absorbed moisture during an ink application.

Today, about half of paper-based media used in the printing industry are coated. Printing media are often coated for aesthetic reasons since coated paper is smoother with a finer pore structure. Media coatings generally consist of pigment particles, a binder, and a number of other additives in water which act to improve the coating in a desirable way. The proper coating can improve the print quality, smoothness, opacity, gloss, and other attributes of the media to which it is applied. (LePoutre, 1989) Coatings are generally applied as an aqueous suspension to the surface of the media. Once applied, the aqueous phase of the coating is removed simultaneously via evaporation and absorption into the media. After this process, only a dry coating layer remains consisting of pigments, binders, additives, and voids. The pore structure basically governs the fluid absorption properties of the coating and it is the air-filled voids which provide opacity.

LePoutre (1989) emphasized the importance of the pore structure and voids by saying: to describe a paper coating as a mixture of a pigment and a binder is to neglect a third, and perhaps most important component, air. The coating layer may be transparent if the base-layer provides the required opacity.

Pigments provide the structure of the paper coating. The most common clay pigment is Kaolin, of which a great number of variations exist: natural, delaminated (milled natural clay), structured (calcined, lime kilned), and engineered (fines removed). The other major category of pigments is that composed of calcium carbonate. Calcium carbonate pigments are either ground calcium carbonate (GCC) or precipitated calcium carbonate (PCC). PCC is similar to engineered clay. Titanium dioxide is an expensive white pigment; plastic pigments such as polystyrene (PS) and hollow sphere plastic pigments also find use.

The binder performs the important task of anchoring the coating layer to the substrate surface. The binder also provides the coating layer with the necessary strength to avoid mechanical failure during printing. It is important that the binder forms a film under normal drying conditions. The binders used for media coatings can either be natural polymers such as starch, or synthetic polymers such as the latex copolymer styrene-butadiene. Other commonly used synthetic binders include acrylic latex, polyvinyl alcohol, polyvinyl acetate, and photographic gelatins. Latex binders are generally on the order of one tenth of a micron in diameter, much smaller than typical pigments. The widespread popularity of styrene-butadiene is due to its excellent balance of properties as well as favorable economics. Latex binders have several advantages over natural polymers including improved strength, good gloss, high ink gloss, high solids

content with low viscosity thus minimal effects on coating mix viscosity, and good machine runnability even at high solids concentration. Latex polymers do not contain ester linkages and are thus less susceptible to bacterial attack than natural polymers. Latex binders (especially copolymers) can be specifically designed to meet a whole variety of coating and printing demands. (Hayes, 1994)

The three types of inkjet media commercially available today are surface sized, matte coated, and glossy coated media. While the first two types are almost exclusively paper-based, glossy coated media can have any base layer described earlier. Surface sized media is uncoated and is capable of producing a medium quality output; while matte coated media gives a better output with bright, vibrant colors. However, coated glossy media gives the highest photographic-quality color output (Ryu, 1999).

The prevalent types of glossy inkjet media are cast-coated, swelling (swellable), and microporous. Cast-coated media is disadvantaged by its generally low optical density, low gloss, and susceptibility to deformation of its paper base. Swellable and microporous media oftentimes have a paper base layer covered by a polyethylene layer which is impermeable to ink, thus protecting its paper base.

Swellable media have resin-rich coatings which typically contain water-swelling polymers such as gelatin, poly-vinyl alcohol (PVOH), and poly-pyrrolidone (PVP). As the name implies, the resin coatings of swellable media absorb ink by a swelling mechanism. (Chapman, 1999)

Microporous media coatings are primarily composed of amorphous silica and/or alumina, with a polymeric binder such as PVOH (Ryu, 1999). The coatings are formulated to be above the critical pigment volume concentration (CPVC). The CPVC is

defined to be the point at which just enough binder is present to completely fill the voids between the pigment particles (Asbeck, 1949). The CPVC is of great importance since the physical and optical properties of coatings change dramatically at this point. However, the amount of binder used in such a coating must be low enough to maintain the microporous void volume. Also, a non-swelling polymer is used so as to not hinder the absorption capability of the coating. In such a highly porous network, capillary absorption is the mechanism by which ink is absorbed (Chapman 1999).

1.3. Inkjet Ink

Inkjet inks have to satisfy the constraints set by both the firing process and the desired level of print quality. Inks used with thermal inkjet technology are required to withstand high temperatures, whereas those inks used with piezo-electric technology are not. The other design consideration is to achieve the highest possible print quality.

The inks used in inkjet printing are in the liquid phase to ease the jetting process, with viscosities ranging from 1 to 10 mPas. This small viscosity is necessary due to the tiny nozzle diameters and drop volumes and rapid cycle times; thermal DOD printers reach frequencies of up to 12000 drops per second (Le, 1999). While 36000 drops per second is now achievable in inkjet printing, most of the color printing uses 2-3000 drops per second. The inks have to be able to wet the media with minimal delay and with as little spreading as possible to have good dot definition. There are also many demands on the final printed product, such as being able to withstand the effects of weathering and the harmful radiation in sunlight (Anderson, 2004).

and weathering damage. However, dye-based inks have a wider color-gamut than pigmented inks. For this reason, pigments have traditionally only been used for black inks. Dye-based inks have remained the top choice for producing color, although much research has been concentrated on developing pigmented inks that can also produce the brilliant color images typical of dye.

In the colloidal size range, from 10 nm up to about 10 microns, inter-particle forces and Brownian motion become important. The particles involved in inkjet printing fall in this size range. In this size realm, the area of the particle surfaces per unit volume is important. In coating or printing processes this is true because the suspensions must be stable and must flow during application. In terms of stability, preventing irreversible agglomeration or sedimentation is a major concern. In the colloidal size range, attraction will occur between any like materials. To gain stability, intermolecular and inter-particle forces are manipulated to be repulsive, enough to overcome the van der Waals forces.

The attractive van der Waals forces are weak compared to covalent attractive forces but very significant when added over the whole mass of a particle. The attractive London-van der Waals dispersion force between two particles with equal radii has been represented by Suzuki et al. (1969) as

$$F_{attr} = \frac{rA}{12h^2} \frac{\lambda(\lambda + 22.232h)}{(\lambda + 11.116h)^2} \quad (1.2)$$

where r is the sphere radius, h is the gap, A is the Hamaker constant, and λ is the retardation length (100nm). The electrostatic repulsive force between two particles with equal radii may be represented as (Hogg et al., 1966)

$$F_{rep} = 2\pi r \kappa \epsilon \epsilon_0 \psi^2 \left[\frac{e^{-\kappa h}}{1 + e^{-\kappa h}} \right] \quad (1.3)$$

where κ^{-1} is the Debye double layer thickness, ϵ is the dielectric constant of the medium, ϵ_0 is the permittivity of a vacuum, ψ is the surface potential of the charged particles, and h is the particle-particle surface separation distance. The potential energy of interaction is the sum of the van der Waals and electrostatic forces.

An appropriate combination of ionic strength, surface potential, and Hamaker constant allows for a large energy barrier whose magnitude is several times the kinetic energy of the particles. This desirable circumstance leads to good stability of the solution. Potential decreases with distance, and at the primary minimum coagulation occurs. When a potential energy secondary minimum is present, flocculation occurs at this relatively large distance. The particles attached at this distance are stable; however, the loose flocs can easily be redispersed.

The Debye double layer thickness defines the region of influence of the repulsive force. At high ionic strengths the double layer is small; therefore suspension components behave as hard spheres. At low ionic strengths, the influence of the electrostatic forces increases and thus extends to larger particle-particle distances. Dispersed pigment systems, such as inkjet ink or paper coatings, generally contain a large number of dissolved ions. The consequently high ionic strength presents a problem: the double layer is compressed; hence particles get closer to one another. The energy barrier is therefore reduced and may even disappear in some cases. The solution to this problem has been the addition of polymers to supplement the insufficient electrostatic forces with steric stabilization. (Hiemenz, 1997)

Polymers can adsorb onto particles in solution and cause stabilization. This can change the particles' effective surface charge in addition to creating a steric layer that

promotes stability. A polyelectrolyte can be used—a polymer with ionizable functional groups such as -COOH . Adsorbed polymers can uncoil if charged groups repel each other. The solvent is a significant factor in the behavior of the polymer. A poor solvent may allow an adsorbed polymer to lay flat on the particle surface whereas a good solvent will promote the polymer to coil out away from the particle surface. In the event of having a good solvent yet poor adsorption, the polymer chains cannot fit between the gaps of the particles. The osmotic pressure gradient that develops is characteristic of this situation and is known as depletion flocculation. The desirable situation occurs when a good solvent is combined with good adsorption; this leads to bridging flocculation—a sterically stable solution.

1.4. Print Quality

How nice a printed sheet appears visually is termed “print quality”. A sharp, clean, glossy image can be visually pleasing to the eye and is said to have a high print quality. In inkjet printing, the media, ink, and capability of the printer are all crucial elements that determine what level of print quality can be achieved.

The non-impact nature of inkjet printing endows it with a unique set of print quality attributes. The most common problems encountered are drop coalescence, bleeding, dot spread, banding, smearing, and fading. Capillary diffusion into pores by wicking into unprinted regions causes bleeding. Closely related is lateral dot spreading. This leads to a larger dot size than intended, which is often referred to as dot gain. Banding refers to the emergence of undesirable light and dark patterns in the printed image; this is due to misfiring or clogged nozzles in the print head. A significant hazard

to be avoided is smearing. A printed sheet must be adequately dry before any handling or surface contact is allowed. This clearly necessitates the need for a low drying time. Image fading is a result of exposure to harmful environmental agents. Light fastness and water fastness, defined as resistance to color loss due to atmospheric/ultraviolet radiation and water exposure, respectively, are also important attributes.

If the problems discussed above can be kept to a minimum, high print quality then becomes possible. The factors that determine the print quality of a printed sheet of coated paper are numerous and complex. These factors are primarily properties of the coating layer such as brightness, opacity, gloss, surface roughness, absorptivity, surface strength etc. The brightness and gloss of a printed image is generally determined by how rough the surface of the printing medium is. A rough surface will scatter light in several directions, whereas a smooth surface will reflect more of the light in the specular direction. This will in turn make an image appear brighter. Another key factor in image quality is absorption. When ink is printed onto a substrate each drop should ideally remain a tight, symmetrical dot. If ink absorbs into the media in a non-uniform way, the dot will feather and spread out in an irregular fashion. The dot will thus cover a slightly larger area than desired, and the result is the creation of an image that appears fuzzy, particularly at the edges of the objects and text. Plain copy paper is not designed to enable high print quality; it is an uncoated media with a relatively high absorptivity, thus making it prone to feathering and low print quality when a high resolution image is printed onto it. That is why high quality coated photo media are used to achieve good image quality when printing high resolution images. The media coating has a low

absorptivity which keeps the ink on the surface in an ideally symmetrical dot. The small pores of the coating layer do not allow penetration of the pigment particles into that layer.

1.5. Ink-Media Interactions

The processes which occur at the ink-media interface ultimately control the resulting image quality. The ink-media interactions, which occur immediately after an ink droplet has been fired from its nozzle, can be classified into three events: impact on the substrate, wetting, and absorption. In addition to absorbing into the media, water is simultaneously lost via evaporation. The loss of water from the applied ink layer through these two processes is termed dewatering. The events that occur during dewatering will be discussed in this section.

Upon impact with a non-absorbent substrate, a droplet spreads radially into a pancake shape. The rate of spreading is controlled by the inertia of the droplet and by the viscous effects, which work in opposition to each other (Middleman, 1995). When the kinetic energy of the droplet is dissipated, the droplet reaches its maximum flat diameter. Once the retracting surface tension forces balance the spreading and the surface energy is dissipated, the droplet assumes an equilibrium shape.

On an absorbent substrate, the rate of absorption may also affect the initial shape. A rapid absorption rate may even prohibit the formation of an equilibrium shape. However, a substrate with a relatively slow absorption rate can be modeled as being a non-absorbent substrate, which is a good approximation for most coated media. This is true due to the time scales involved. The time required for the kinetic energy dissipation of a low-velocity droplet is just a few milliseconds, whereas the process of absorption

may occur on a much larger time scale such as seconds or tenths of seconds (Oliver, 1984).

A droplet of liquid placed on a solid substrate generally assumes an equilibrium shape once the interfacial forces balance each other. Figure 1.1 illustrates this idealized concept.

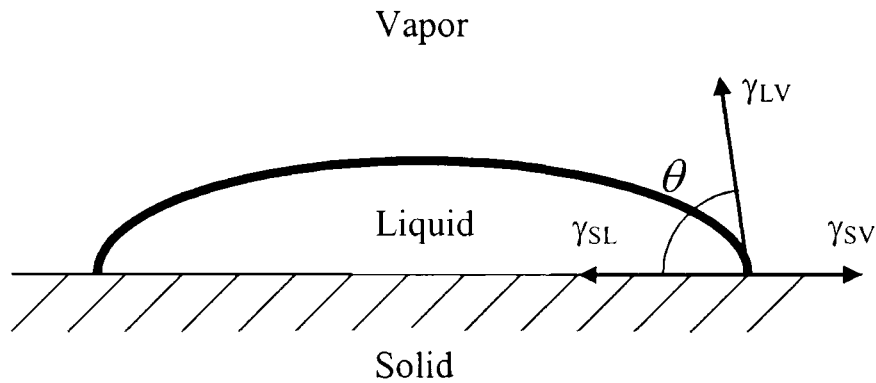


Figure 1.1. Idealized contact angle on a smooth solid surface

The angle made by the gas-liquid interface at the solid-liquid boundary, measured from inside the liquid phase, is called the contact angle (θ). The three forces acting at this point are interfacial tension forces and are represented each with a sigma, with S, L, and V denoting solid, liquid, and vapor phases respectfully. For example, σ_{LV} is the liquid-vapor interfacial tension acting along the perimeter of the droplet. The Young and Dupre equation (Adamson, 1967) represents the force balance as

$$\sigma_{LV} \cos \theta = \sigma_{SV} - \sigma_{SL} \quad (1.4)$$

A contact angle of greater than 90° is the result of a non-wetting liquid such as mercury on glass; whereas a contact angle of less than 90° results in wetting. A contact

angle of 0° is the result of complete wetting. Absorption into the pores will be determined by the contact angle.

The process of liquid absorption by porous media can be modeled as the spontaneous penetration into a capillary due to surface tension (Middleman, 1995). When idealizing porous media as a collection of many vertical cylindrical pores, the capillary pressure that forces fluid into the pores is expressed by the Young-LaPlace equation as

$$\Delta P = \frac{2\sigma}{R} \cos \theta \quad (1.5)$$

where σ is the surface tension of the liquid and R is the capillary radius. The effect of gravity has been neglected in this equation. Assuming low velocity Newtonian flow, the Poiseuille equation gives the average velocity of the liquid in the capillary as

$$\frac{dL}{dt} = \frac{R^2 \Delta P}{8\mu x} \quad (1.6)$$

where L is the length of capillary that is wetted, and μ is the liquid viscosity. Integrating Eq.(1. 7) gives

$$L = \sqrt{\frac{R\sigma \cos \theta}{2\mu} t} \quad (1.8)$$

which is the Lucas-Washburn equation. A more useful application of this relationship expresses the fluid volume V absorbed per unit area A . If the number of pores per unit area N_p is known, the void fraction ε is calculated as

$$\varepsilon = N_p \pi R^2 \quad (1.9)$$

The total liquid volume (TLV) absorbed per unit area is therefore

$$TLV = \varepsilon L = \varepsilon \sqrt{\frac{R \sigma \cos \theta}{2 \mu}} t \quad (1.10)$$

This is the Lucas-Washburn equation in its simplest form, expressed in terms of void fraction, which applies to cylindrical capillaries. In reality, the pores in most every media are anything but vertical, cylindrical, and isolated from one another. Pores generally interconnect to form highly complex networks. A number of relationships have been developed to account for these factors. (Agbezuge, 1998)

To account for the non-ideal pores, LePoutre (1978) added a tortuosity factor τ into the Lucas-Washburn equation. The resulting expression became

$$TLV = \frac{\varepsilon}{\tau} \sqrt{\frac{R \sigma \cos \theta}{2 \mu}} t \quad (1.11)$$

This is the Lucas-Washburn equation in its most common form. While it may not account for any of the complexities described above except for the non-straight nature of the pores, this equation is often a sufficient approximation for certain types of porous media.

1.6. Gloss

Gloss is an important optical property in the evaluation of print quality, with a higher value giving the perception of good quality. Gloss is a measure of the surface reflection of light in the specular direction; that is, the angle equal to the incident angle. High gloss values are achieved when a surface does not scatter much light in the non-specular direction, which implies a higher fraction of incident light reflected in the specular direction. In contrast, a surface reflecting light in all directions will produce the

sensation of a non-shiny or matte appearance. Figure 1.2 illustrates the concept of diffuse and specular reflection.

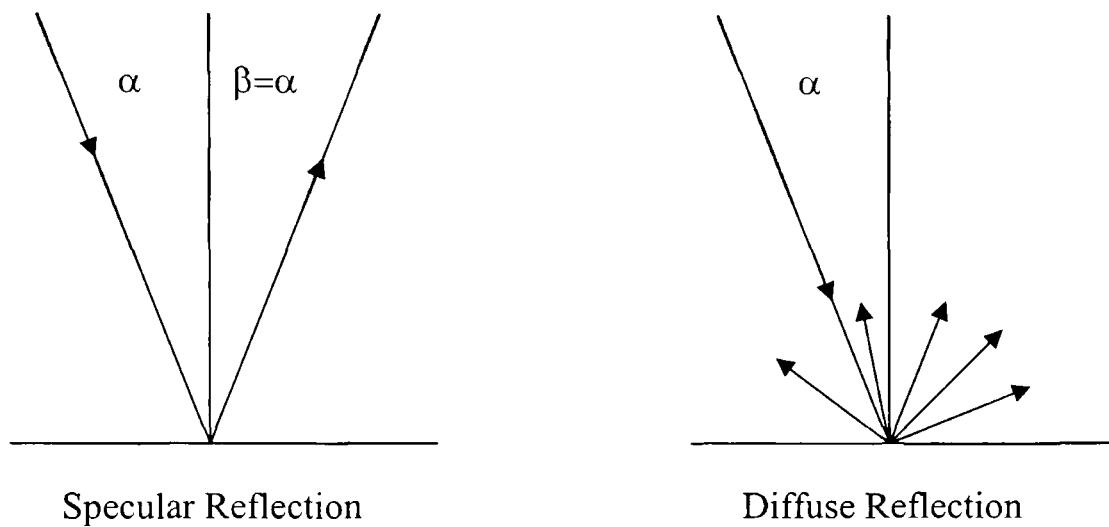


Figure 1.2. Specular (mirror-like) and diffuse (scattering) reflection

Gloss is affected by both the topography of the surface and its refractive index (Preston et al, 2003). In inkjet printing, the topography of the printed surface is influenced by factors such as the type and quantity of ink used, print mode, and media properties such as roughness and porosity. The refractive indices of the ink and media coating layers are the key determinant of how light will interact with these layers. The Fresnel equation has been developed to describe reflection as a function of refractivity, absorption of the materials, wavelength of incident light, and irradiation angle. With the assumption that refraction is the dominant factor, the Fresnel equation for reflection, with an irradiation angle of 90 degrees, can be simplified to

$$R = \left(\frac{n_2 - n_1}{n_2 + n_1} \right)^2 \quad (1.12)$$

where R is reflectance, and n_1 and n_2 are the refractive indices of two contacting layers (such as air and an ink layer). This expression illustrates that the greater the difference between the two refractive indices, the greater is the reflection and, accordingly, the level of gloss.

Despite numerous studies on ink and coating gloss development, the mechanisms which control the process are not well established (Aspler, 1991). Gloss development has been studied for many of the various printing techniques. A study of the dependence of ink gloss development on ink absorption for offset printing revealed that immediately after the nip printing event, the rate of leveling of the ink layer defects, their magnitudes, the printing speed, and ink film thickness affected the gloss development. It was found that the print gloss increased over time as the defects leveled out. The large defects, produced by thick inks, leveled slowly (Glatter, 1997).

Another study found that the coating absorbency to be strongly dependent on coating pigment size, pigment surface area, and binder content. The pore size of the coating was found to be proportional to the pigment diameter; while the volume of pores was inversely dependent on the binder content. The smaller pigments produced smaller pores, faster ink setting, and lower print gloss. It was concluded that smaller coating pigments may increase media gloss but produce lower print gloss. (Donigian, 1997). A study of offset printing revealed that high print gloss could be obtained on coatings with small pores on the surface, yet with large internal pore volume. (Arai, 1998). In an attempt to correlate the gloss uniformity of offset-printed samples with the local media

roughness, Beland (2000) found that roughness was insufficient in predicting the local reflectance and thus a nonlinear correlation was obtained.

The dependence of specular reflection on the incident angle, wavelength, and surface roughness is expressed in the following equation as

$$\frac{I}{I_0} = f(n,i) \exp\left[-(4\pi\sigma \cos i / \lambda)^2\right] \quad (1.13)$$

where I and I_0 are the specularly reflected and incident light intensities, respectively, $f(n,i)$ is the Fresnel coefficient of specular reflection as a function of refractive index, n , and the angle of incident light, i , σ is the standard deviation of the surface roughness, and λ is the wavelength of incident light (Stover, 1990). For the TAPPI 75⁰ gloss, the angle of 75⁰ can be inserted into equation (1.13). For paper coatings with similar refractive indices, the TAPPI 75⁰ gloss can be assumed to be primarily dependent on surface roughness. Factors that influence roughness include: pigment particle size, binder level, drying conditions of binder films, and calendaring. Smaller pigment size has been shown to increase coating gloss of monodispersed pigments. The gloss of coated media also increases with increasing coat weight, but gloss values level off at high coating weights. Supercalendering can improve gloss values by flattening the coating surface; however, this technique cannot remove microscopic surface irregularities. (Lee, 1974)

A study by Shirke (2002) investigated the factors that affect gloss development of ink jet prints. This earlier investigation concluded that the gloss of dye-based inks on porous media is controlled by media roughness; initially the gloss of pigmented inks on porous media is determined by a combination of pigment size and wet media roughness. It was also concluded that the gloss is determined by the events that occur within 30 ms after printing. Over a longer time period, the gloss on porous media was found to stay

relatively constant while the gloss on swellable media after complete drying is often higher than the wet gloss due to consolidation of the polymer coating due to the loss of water.

The research presented in this thesis is an extension of the work by Shirke (2002) and can be divided into three segments. The first part of this research involves the broad investigation of ink/media combinations. The focus of this effort is aimed at gaining a fuller understanding of the gloss development of a print and what influence the substrate has on this development. The second part deals with understanding the influence on print gloss of chemicals present on the substrate. The last part involves the understanding of the influence of the ink pigment load and image fill percentage on gloss.

Chapter 2

EXPERIMENTAL PROCEDURE

In this chapter, the ink/media properties that were investigated, along with the experiments conducted in that investigation will be explained. This research has several dimensions yet the primary focus is on gloss. This chapter introduces the importance of obtaining dynamic gloss values (the development of such gloss) as well as static gloss (final gloss values). It will be shown that the events involved with ink setting occur rapidly, on the millisecond scale, and that we have the capability to observe these events quite accurately.

This chapter also introduces the concepts involved with liquid absorption and the Bristow wheel apparatus which is used to measure this property. The mechanics of ink absorption into a given substrate will prove to be crucial in our understanding of ink setting and gloss development.

This discussion will conclude with a short list of other devices/experimental procedures that were employed in this research, all of which are vitally important to our understanding of gloss development.

2.1. Static Gloss

The final gloss value of a printed sample is an important bit of information in the characterization of that sample. The term “final” refers to a value where the gloss is fully developed. On most media, the level of gloss may appear to reach its final value within just a few minutes of printing. However in most cases, it may require 24 hours or more

for the events of gloss development to fully cease. Therefore, in this work “final” gloss values were not recorded until at least several days after printing. Static gloss values were also recorded within five minutes of printing and referred to as “5 min.” gloss values. These 5 minute gloss values are taken for long-term gloss development comparison with the final values.

The static gloss values are recorded using a Micro-TRI-gloss meter from BYK-Gardner USA. This device is capable of testing gloss values at 20, 60, and 85 degrees. For high-gloss samples, only the 20-degree gloss values are recorded. The high quality inkjet photo media used in these experiments can peak out the gloss meter at 60 and 85 degrees.

The gloss meter is calibrated using black glass with a refractive index of 1.567. The black glass is used because it absorbs any light which enters it. This is necessary because gloss is defined to be a surface phenomenon. The percentage of light that reflects off this smooth surface is the calibration standard value. Therefore, it is possible to obtain a gloss value higher than 100 if that sample has a refractive index higher than 1.567. This will be observed later in the research. Black ink pigments, for example, can have a refractive index in the range of 2-3. Any secondary reflection at the ink/media interface can also add to the level of gloss if that reflected light is not absorbed and thus exits the ink layer in the specular direction. Gloss values higher than 100 are often confusing to people until it is understood how the gloss meter is calibrated. The legitimacy of using black glass comes into question; however, if a mirror was used for the calibration standard, the measured gloss values of samples would consequently be small

and less distinguishable. Roughly 95% of the light that strikes the black glass is absorbed with only 5% reflected at the surface.

The gloss meter has the ability to compile data and return an average value and standard deviation for a set of measurements. This feature is used to determine all static gloss values presented in this research. Each static gloss value in this work represents the average of twenty to thirty recordings at various locations of the sample.

2.2. Dynamic Gloss

A vital element in the study of gloss development is the measurement of gloss during the initial few seconds after printing. This crucial time period is when the controlling factors of gloss development are most dominant. In order to capture the gloss dynamics at very short time scales, a setup was used by which the gloss could be continuously monitored with a high data acquisition frequency.

The apparatus that we designed to capture the dynamic gloss is composed of a modified inkjet printer (HP 970 Cxi series), a 5mW, 680nm laser source, laser detector (1,000 Hz), 10V voltmeter/gain, and a computer. Modified PCL files control the printer and a Visual Basic program is used to acquire data. Figure 2.1 is a schematic of this apparatus.

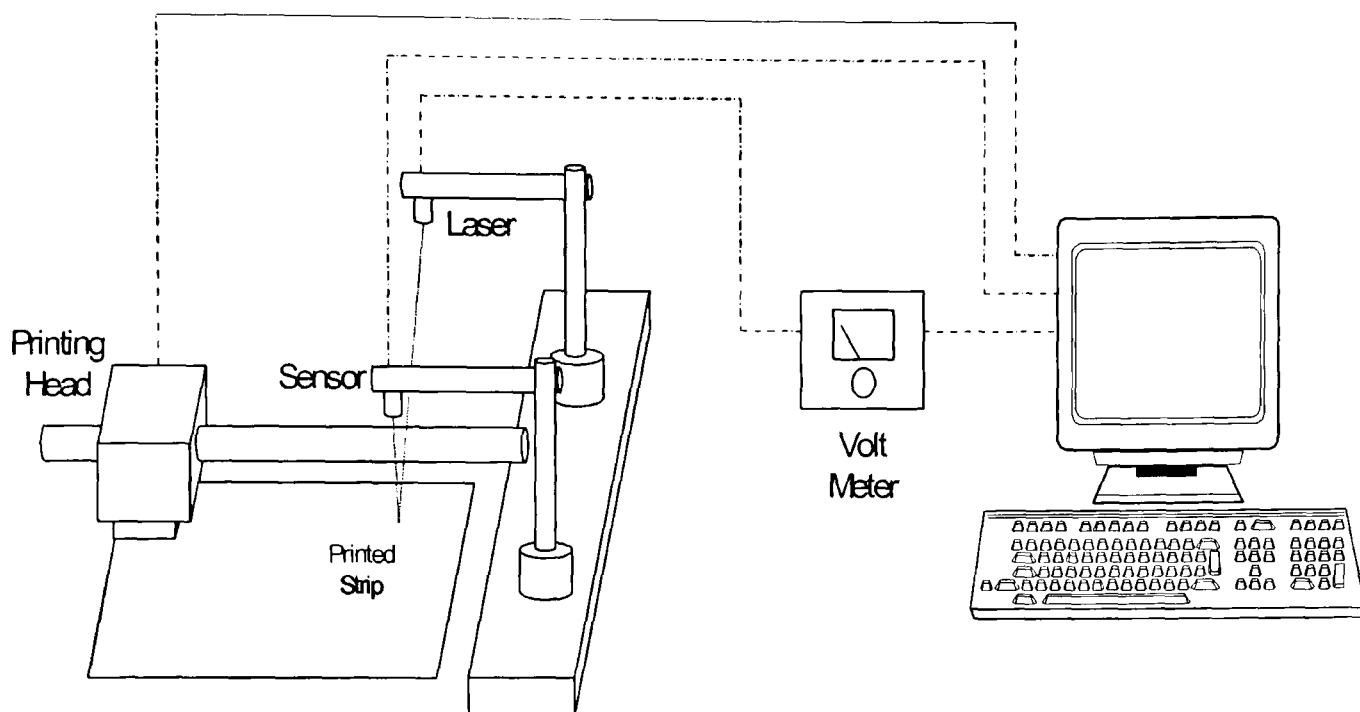


Figure 2.1. Schematic of dynamic gloss device

The process of obtaining dynamic gloss data is initiated by the user in the computer program. The printer is instructed to gather up a single sample sheet and print a 10mm by 90mm rectangular strip upon it. The laser source is positioned to strike the printed sample with a beam of light at an angle of 20 degrees from the normal. The laser detector is setup to collect the incident beam and then send this data to the voltmeter/gain and then on to the computer. Data is recorded once the laser beam is not deflected by the exiting print head. On average, it takes about 15-20 ms from the moment a droplet impacts the substrate to the moment that the laser first hits that location. The first meaningful data points are available once the print head has completely cleared the path of the laser beam (about five or six ms after the first detectable signal), due to the width of the beam. Experiments were carried out in a dark room to avoid erroneous results due to ambient light.

The amount of ink that is printed in the rectangular strip is determined by which PCL file is used. PCL files have been modified to direct a certain level of ink onto the media in a certain configuration. The ink level is characterized as a certain fill percentage. The PCL files we have available are: 100%, 75%, 50%, 25%, 12.5%, and 6.25% fill. The 100% fill PCL file produces a print where the printed region is completely covered with ink just to the point where ink droplets do not overlap. However, due to ink spreading and imperfect printing, overlapping ink dots are observed in addition to the occasional print defect of an unprinted stripe. Decreasing the fill percentage decreases the level of ink that is printed as the ink dots are placed further apart in a regular pattern. Much more information about a certain ink/substrate interaction can be learned by examining several different ink fill percentages instead of just one.

2.3. Absorption Rate

The rate of absorption for a given liquid/substrate combination is another

important characterization property. A Brinell wheel apparatus is used in this

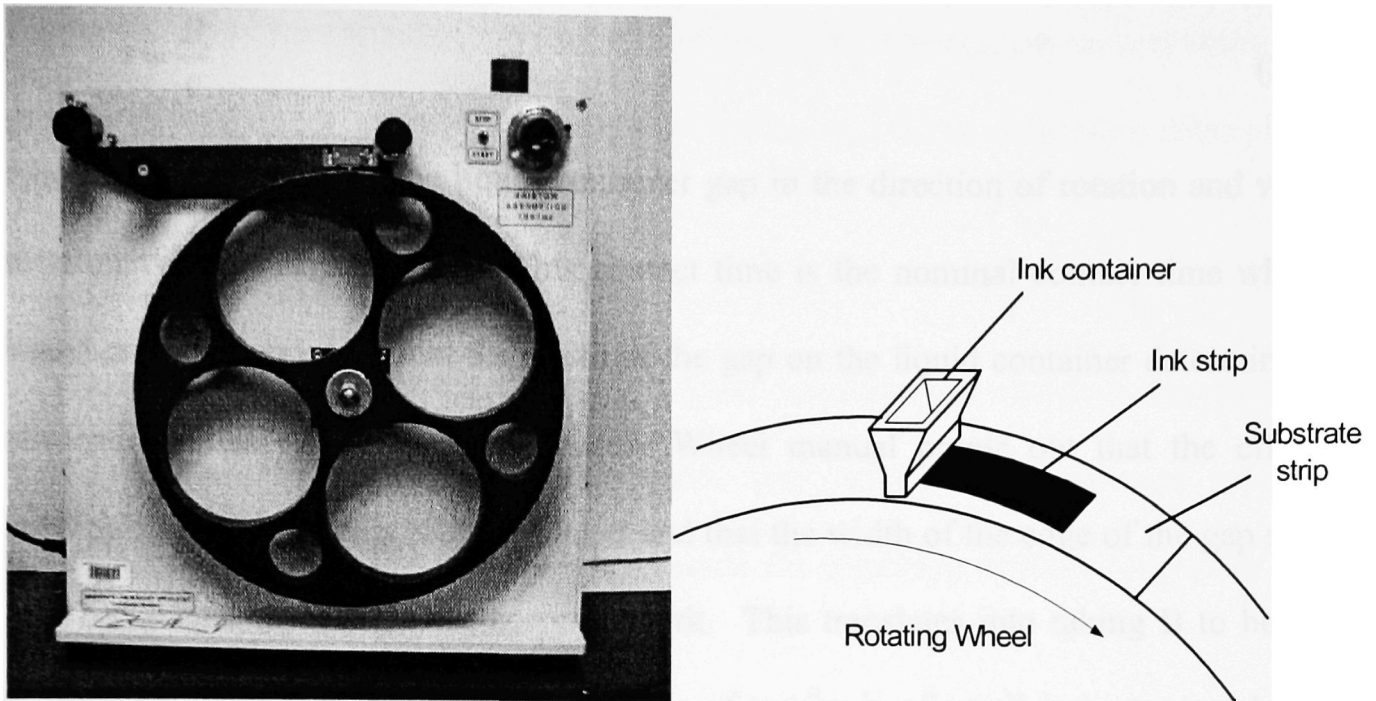


Figure 2.2. Bristow apparatus with close-up of testing process

To use the device, the substrate is cut into a strip and affixed to the speed-adjustable wheel. A small measured quantity of liquid—dyed water or ink—is carefully added to the liquid container; usually 10 or 20 microliters depending on the substrate and liquid used. With the wheel rotating at the desired speed, the ink container is lowered to the sample where the liquid exits the container through a one millimeter gap which is 15 millimeters in length. By measuring the area of the track of ink that is left on the substrate, the quantity of liquid transferred per unit area (TLV—Total Liquid Volume) for a certain contact time can be attained. The TLV is calculated as

$$TLV = \frac{V}{L_t w} \quad (2.1)$$

where V is the liquid volume transferred, L_t is the approximate length of the liquid track left on the substrate, and w is the length of the liquid container gap. The contact time is calculated as

$$t = \frac{B}{v} \quad (2.2)$$

where B is the length of the liquid container gap in the direction of rotation and v is the rotation velocity of the wheel. This contact time is the nominal contact time which is based on the assumption that the width of the gap on the liquid container determines the absorption time. However, the Bristow Wheel manual points out that the effective absorption time is usually slightly longer and that the width of the edge of the gap should also be taken into account for accurate work. This translates into taking B to be three millimeters instead of one millimeter. This of course is of small importance when the device is used for the comparison of different media and/or inks.

After a series of tests at a range of rotation speeds, the measured TLVs can be plotted against the square-root of contact time. Figure 2.3 shows typical Bristow absorption plots.

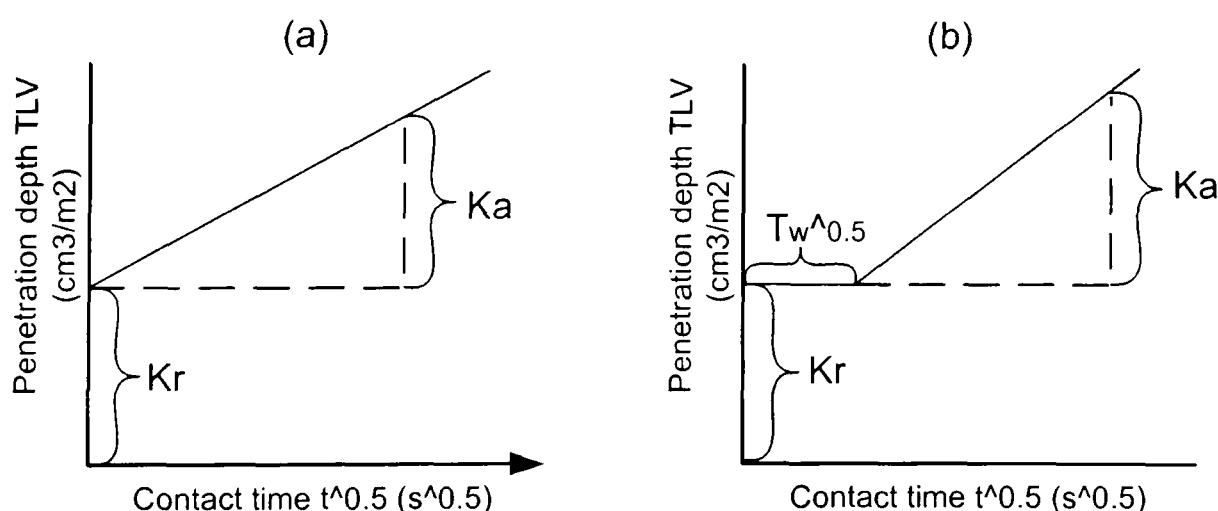


Figure 2.3. Typical Bristow results

The slope K_a is the absorption coefficient which reflects the absorption rate. The intercept K_r is the roughness coefficient which characterizes the sample's surface

roughness. The initial horizontal portion of curve (b) corresponds to a wetting delay, during which only the surface pores are filled and no significant absorption takes place.

2.4. Stylus Profilometer

Since the focus of this research is gloss, roughness is clearly a key factor and highly important. To many people, gloss and surface roughness are essentially interchangeable. We have two means available for acquiring average roughness values for a surface, mechanically and optically.

The first method of testing surface roughness uses a basic mechanical stylus profilometer. An Alpha-step 200 profilometer from Tencor Instruments is used to scan the surface of a sample with a diamond tip stylus. The apparatus carefully measures the topography of a surface and returns an average roughness value. The scan length, scans per micron, and stylus force can all be adjusted to achieve the most appropriate results for a given sample and the desired level of accuracy. In this research, the parameters of the profilometer were set to the following: stylus force, 7 mg; scan length, 400 μm ; 5 scans per micron. Due to the commonly wide variability in surface structure, it is highly recommended to perform many tests at several locations along a sample to ensure a representative average roughness value. Profilometry is the standard method of determining surface roughness and has been used by many for years.

2.5. Confocal Microscope

A newer and more reliable method for attaining average roughness values for a surface involves using a confocal microscope. This optical method of testing surface

roughness has the advantage of providing more precise results, and doing so without the physical contact that occurs with a mechanical stylus which can damage a sample.

Confocal microscopy takes advantage of the phenomenon of fluorescence. A high intensity laser is used to provide the excitation light. The laser is sent to a dichroic mirror which reflects light shorter than a certain wavelength. Mirrors scan the laser across the sample which fluoresces. The emitted light gets descanned by the mirrors, sent through the dichroic mirror, and is then focused onto a pinhole. The pinhole is conjugate to the focal point of the objective lens of the microscope, thus it is a confocal pinhole. With a confocal pinhole, the microscope is efficient at rejecting the fluorescent light which is out of focus. With a small depth of field, a very clean image of sample is produced; this allows for accurate surface roughness calculations.

In this research, the scans were performed using a 10X objective dry lens with an N.A. of 0.4. The confocal microscope that was used has the following parameters: total magnification, 100X; excitation wavelength, 633 nm; lateral resolution, 633 nm; axial resolution, 1.266 μm ; z stack depth, 22 μm ; area of scans 639 μm^2 .

2.6. Porosimeter

The pore size distribution is obtained with a device that forces mercury into the small pores (PoreSizer 9320 from Micromeritics Instrument Corporation). This porosimeter can test pore diameters ranging in size from about six nanometers up to 360 microns. The PoreSizer measures the volume distribution of pores in materials by mercury intrusion/extrusion. Mercury has a very high surface tension, thus when in contact with a solid mercury assumes the minimum surface area and largest radius of

curvature at a given pressure. An increase in pressure on the mercury causes the radius of curvature of mercury contacting the solid to become smaller. When the radius of curvature of the mercury is equal to that of the pore, mercury fills the volume of the pore. By closely monitoring the respective volumes of mercury which enter the sample for each step increase in pressure, a pore size distribution profile for the sample can be obtained. Figure 2.4 shows a typical mercury porosimetry result for a coated substrate.

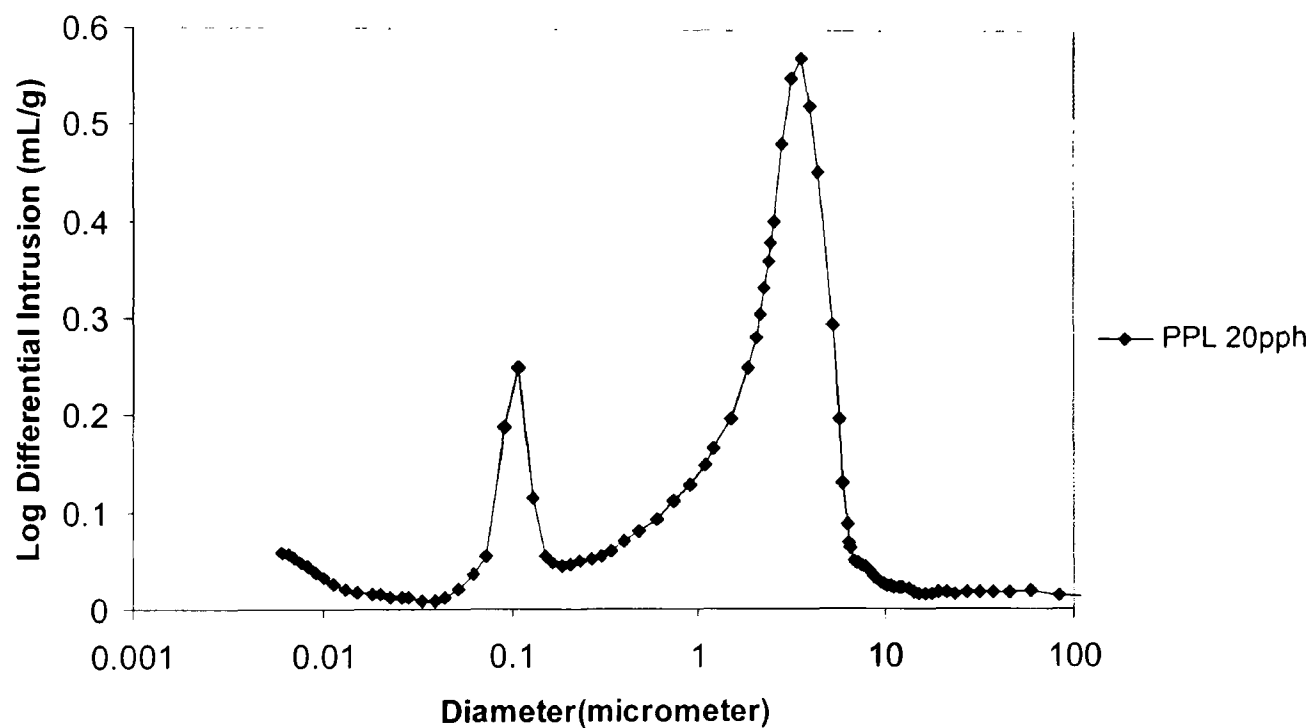


Figure 2.4. Mercury porosimetry result for a coated substrate

The peaks in the plot above represent the highest concentrations of pore sizes in the distribution. The large peak on the right side and the smaller peak on the left side correspond with the pore distributions in the base layer and coating layer, respectfully. Mercury porosimetry therefore offers an accurate method of finding the average pore sizes in the layers of a substrate. One artifact of this method, however, is inaccuracy due

to constrictions in the pores. Upon retraction of the mercury, pore constrictions are evident when mercury is trapped in the sample

In addition to pore size distribution, the volume void fractions can also be calculated based on experimental data. For example, the void fraction of the coating layer is

$$\varepsilon = \frac{V_V}{V_V + V_S} \quad (2.3)$$

where V_V is the void volume of the coating and V_S is the solid volume of the coating. V_V is calculated as

$$V_V = (V_T - V_b)(W_P + W_C) \quad (2.4)$$

where V_T is the total intrusion volume of mercury per unit weight of the entire sample (mL/g), V_b is the intrusion volume of mercury per unit weight of the base paper, W_P is the base weight of the base layer (g/m²), and W_C is the base weight of the coating. V_S is calculated as

$$V_S = \frac{W_C}{\rho_C} \quad (2.5)$$

where ρ_C is the density of the coating.

2.7. Draw-Down Coater

For certain experiments, it was necessary to modify the sample media with chemicals. This was performed manually using a 49733 rod draw-down coater from RK Print-Coat Instruments Ltd. This device uses a wire-wound rod fixed on a rack to evenly distribute a liquid coating solution onto a substrate. The rack is driven by an adjustable speed motor.

Any number of different slurries and solutions can be applied to a substrate with this apparatus. In this research for example, media were modified with ionic solutions to test the effect those ions may have on print gloss. Also, non-reactive styrene-butadiene latex solutions (Dow 620NA, Dow Chemical Co.) were applied to media samples to modify their rates of absorption without altering the electronic nature of the media.

Chapter 3

INFLUENCE OF SUBSTRATE TYPE ON GLOSS

This chapter reports the influence that substrate type has on print gloss. Several media and ink combinations were investigated to further our understanding of the mechanisms of gloss development. New insights were gained into the influence that the substrate has on this development. It was hypothesized that the unprotected fibers in paper-based media could swell and damage the coating layer, roughening the media surface and thus lowering gloss. The development of gloss on these media was investigated to explore this theory.

3.1. Media Description

Five different types of microporous media were tested. For simplicity, the five commercially available media will be referred to as:

- 1.) Media A – paper-based, Hewlett-Packard Photo Paper, Glossy (C1846A)
- 2.) Media B – paper-based, Hewlett-Packard Brochure and Flyer Paper (C6817A)
- 3.) Media C – plastic-based, Hewlett-Packard High Gloss Film (C3836A)
- 4.) Media D – photo-based, Epson Premium Glossy Photo paper (S041286)
- 5.) Media E – photo-based, Canon Photo Paper Pro (F51-3261-400)

Information about the five media samples are tabulated below. The TLVs were taken using the Bristow device at a contact time of 1.0 second. The static gloss values were recorded at a geometry of 20 degrees. The coating pore diameters and volumes

were estimated from the porosimetry plots in Figures 3.1 through 3.5. More specifically, the coating pore volumes were taken as an estimated difference along the cumulative curves.

Table 3.1. Media data

Media	Basis Weight (g/m ²)	TLV-1sec (mL/ m ²)	Sheet Gloss (20 ⁰)	Coating Pore Diameter (nm)	Coating Pore Volume (mL/g)
A	176.7	34.19	22.9	12	0.09
B	164.5	12.01	13.9	30, 200	0.14
C	231.4	27.78	40.2	15	0.19
D	252.6	24.69	15.7	20	0.10
E	240.0	28.99	30.9	20	0.12

Table 3.1 highlights the important differences between the five media samples. The contact time of one second for the TLV data was chosen because this essentially represents the capacity value of the media. The 20-degree gloss values reported is the unprinted sheet gloss. The plastic-based media C has the highest sheet gloss. The low sheet gloss of media D is surprising since media C, D, and E are all capable of producing high print gloss. Coating pore diameter and volume will be shown to be related to print gloss.

Mercury porosimetry was used to obtain the respective pore size distributions. The important information regarding pore size is contained in the log differential curves. These results are shown in Figures 3.1 through 3.5.

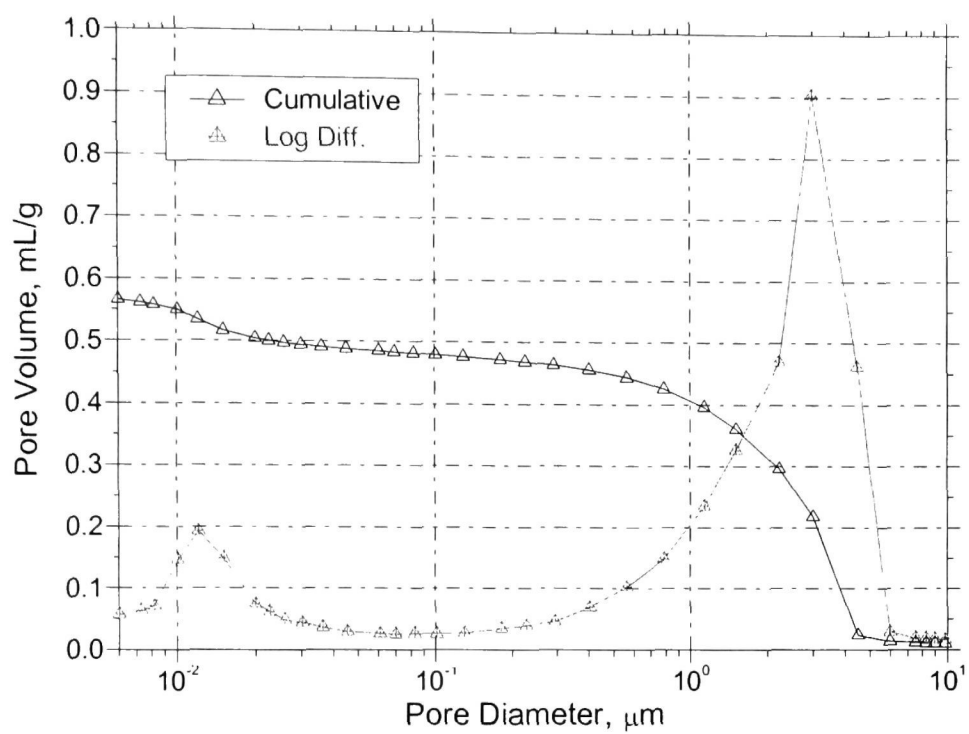


Figure 3.1. Pore size distribution of media A

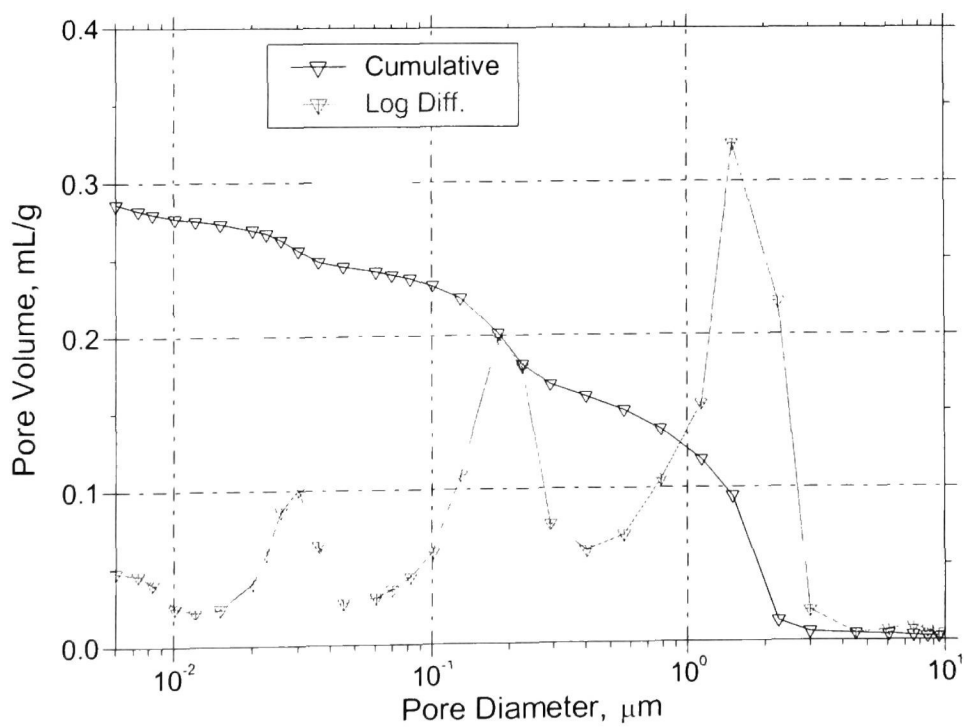


Figure 3.2. Pore size distribution of media B

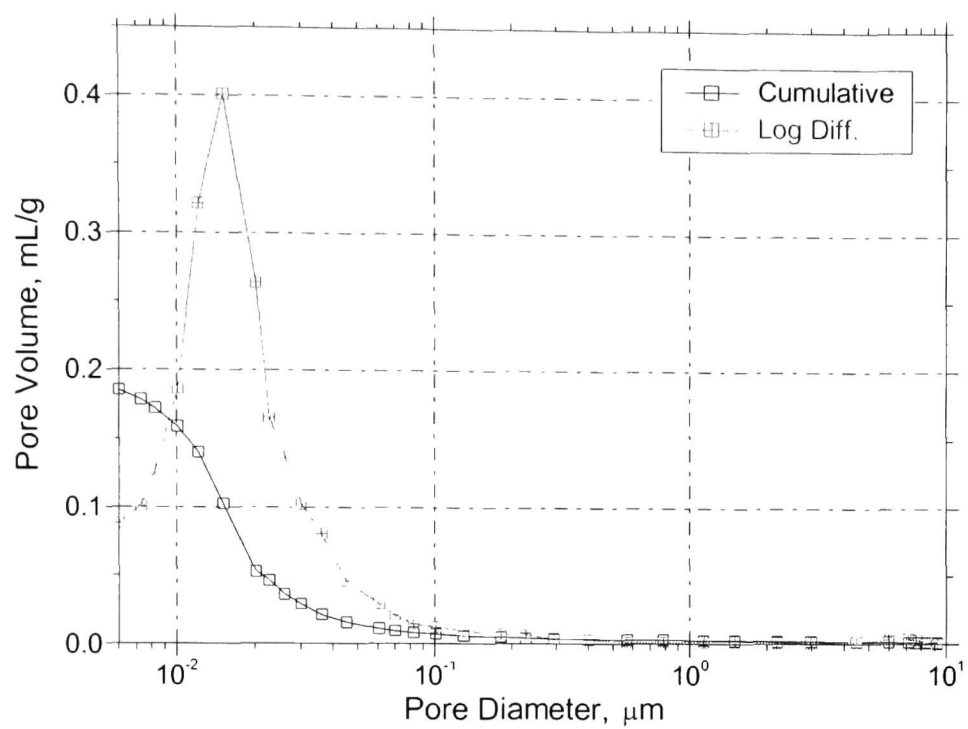


Figure 3.3. Pore size distribution of media C

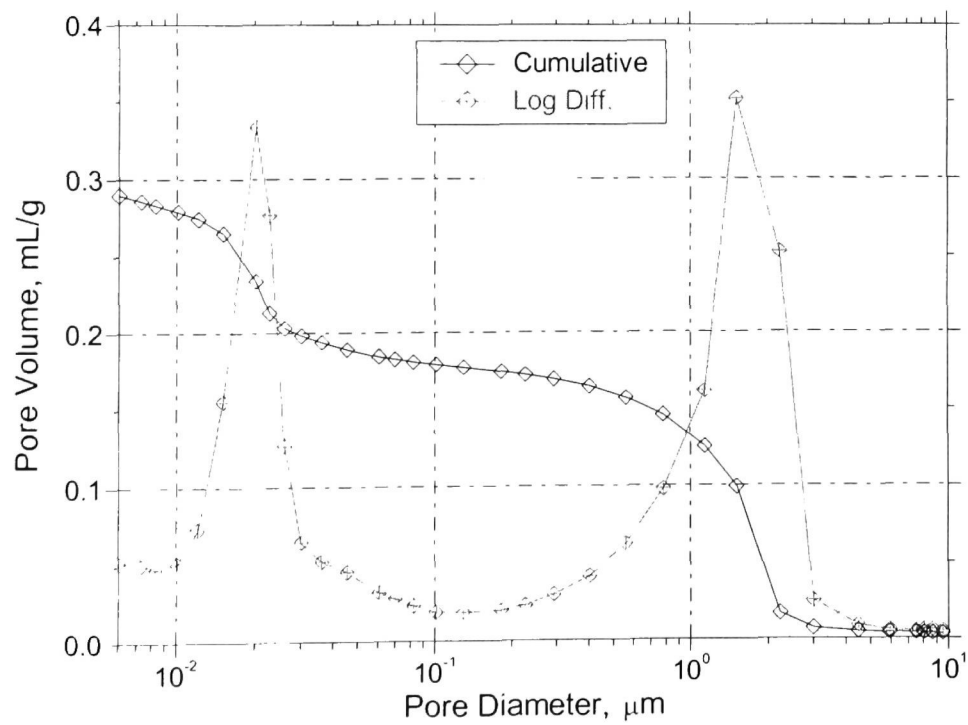


Figure 3.4. Pore size distribution of media D

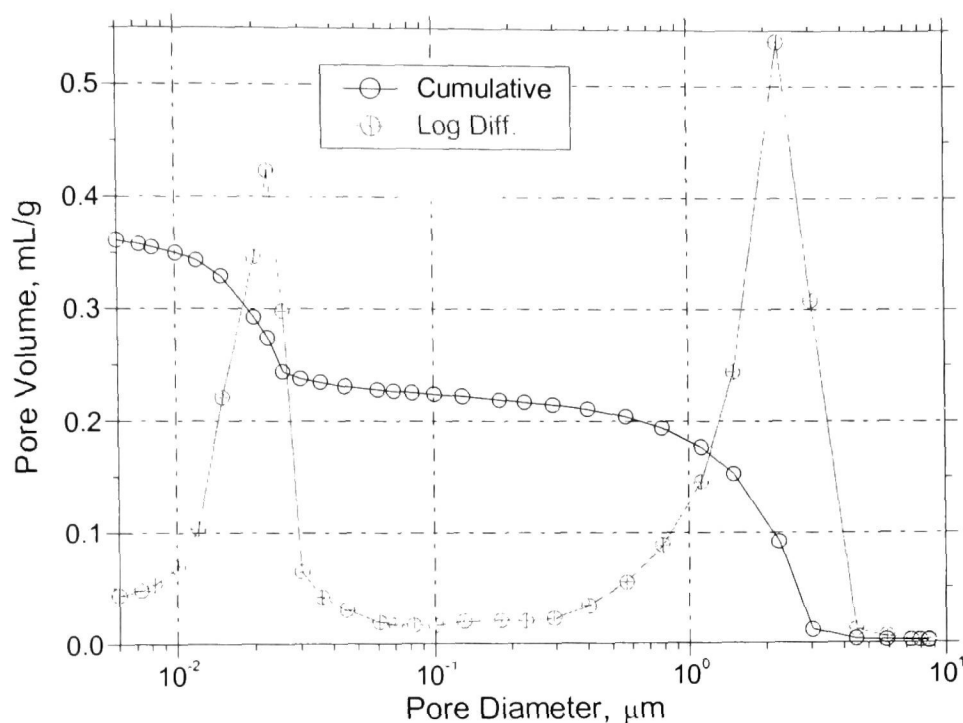


Figure 3.5. Pore size distribution of media E

The large peak on the right in Figures 3.1-3.2 and 3.4-3.5 is indicative of paper as the base layer of media A, B, D, and E. Figure 3.1 shows the predominant pore size of the paper base layer of media A to be about three microns in diameter. The small, almost undetectable peak on the left indicates the presence of a coating layer with a pore diameter of about 12 nm. The small size of this peak compared to the base-layer peak also implies that the paper base is the primary absorber. Figure 3.2 indicates that media B has a paper base layer with a predominant pore diameter of about two microns. The two peaks to the left indicate the presence of two distinct pore sizes of 30 and 200 nm respectively. The predominant pore size of media C in Figure 3.3 is shown to be about 15 nm in diameter. The fact that no peak is present on the right side of the plot reveals the absence of paper in media C. The large peak on the left of Figures 3.4 and 3.5

indicates a sharp pore size. The closeness in size between the peaks of the base layer and coating layer in Figures 3.4 and 3.5 is characteristic of photo-based media. The protective coating layer is responsible for absorption; the base layer of media D and E is not intended to aid absorption. Table 3.1 summarizes the pore size of the coating layer.

3.2. Ink Description

Four different inks were used in the original work. The following notation will be used to specify the various inks used in this research:

- 1.) Ink A1 – pigmented, black
- 2.) Ink B1 – pigmented, magenta
- 3.) Ink B2 – pigmented, black
- 4.) Ink C1 – dye-based, black

In the ink notation, the letter designates an ink ‘group’—those with the same vehicle (water and other components). Following the letters are numbers which distinguish

3.3. Static Gloss Results

Static gloss values were recorded for all of the ink/media combinations. General trends emerged in the data therefore only select results will be shown. Figure 3.6 shows the static gloss values for ink A1 printed on the five media at 100% fill.

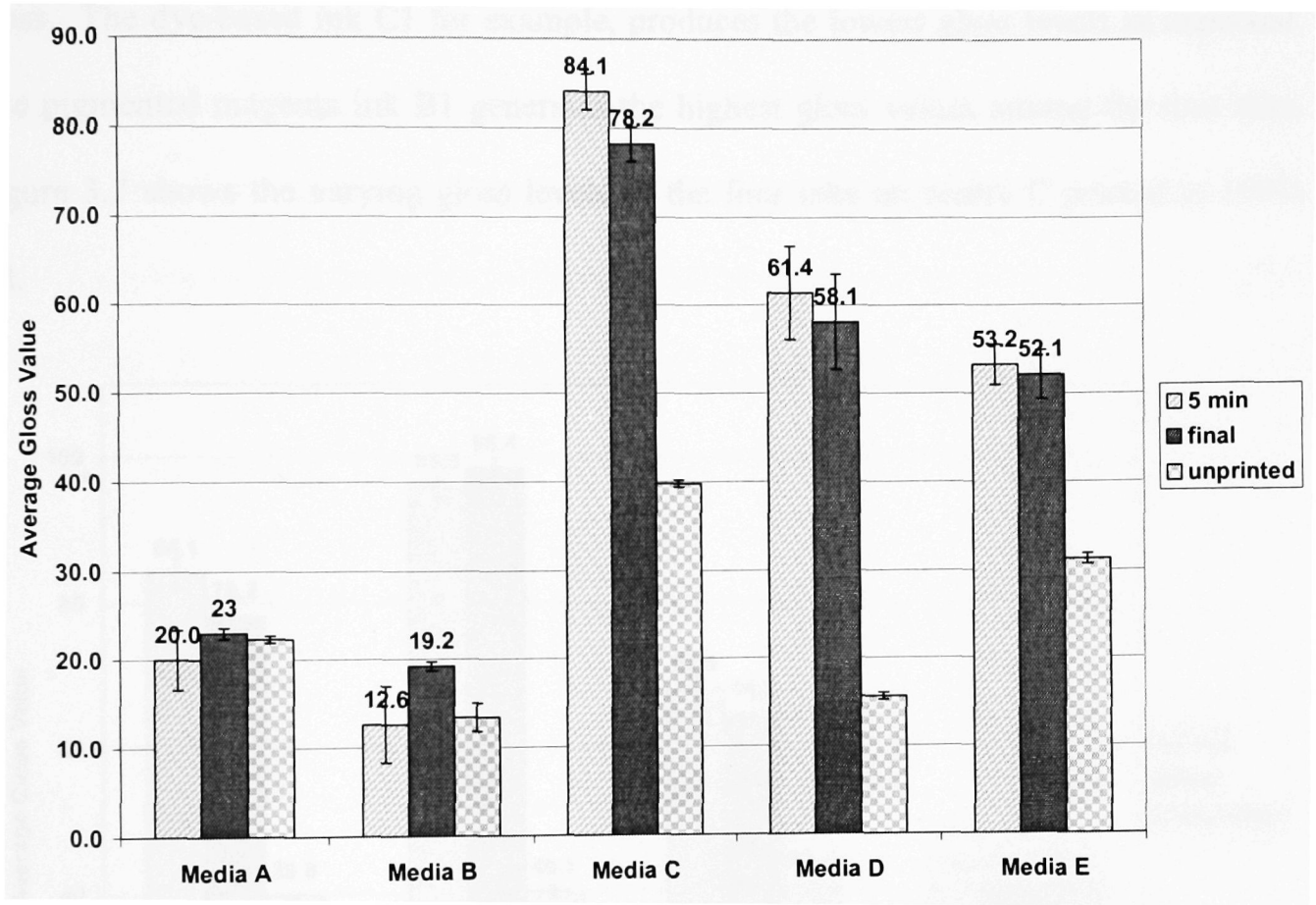


Figure 3.6. Static gloss results for ink A1

Figure 3.6 illustrates that for ink A1, the plastic-based media C produces the highest gloss values, followed by the two similar photo-based media D and E, with low gloss values reported for the paper-based media A and B. A correlation may be made between coating pore diameter and volume, and print gloss. The small pore diameter and large pore volume of media C could be responsible for the high print gloss. These results match those found by Arai (1998) discussed in chapter one, where a study of

offset printing revealed that high print gloss could be obtained on coatings with small pores on the surface, yet with large internal pore volume.

The order of ranking among the five media in terms of static gloss is observed with the other three inks as well. The other inks, however, generate different levels of gloss. The dye-based ink C1 for example, produces the lowest gloss levels as expected. The pigmented magenta ink B1 generates the highest gloss values among the four inks. Figure 3.7 shows the varying gloss levels of the four inks on media C printed at 100% fill.

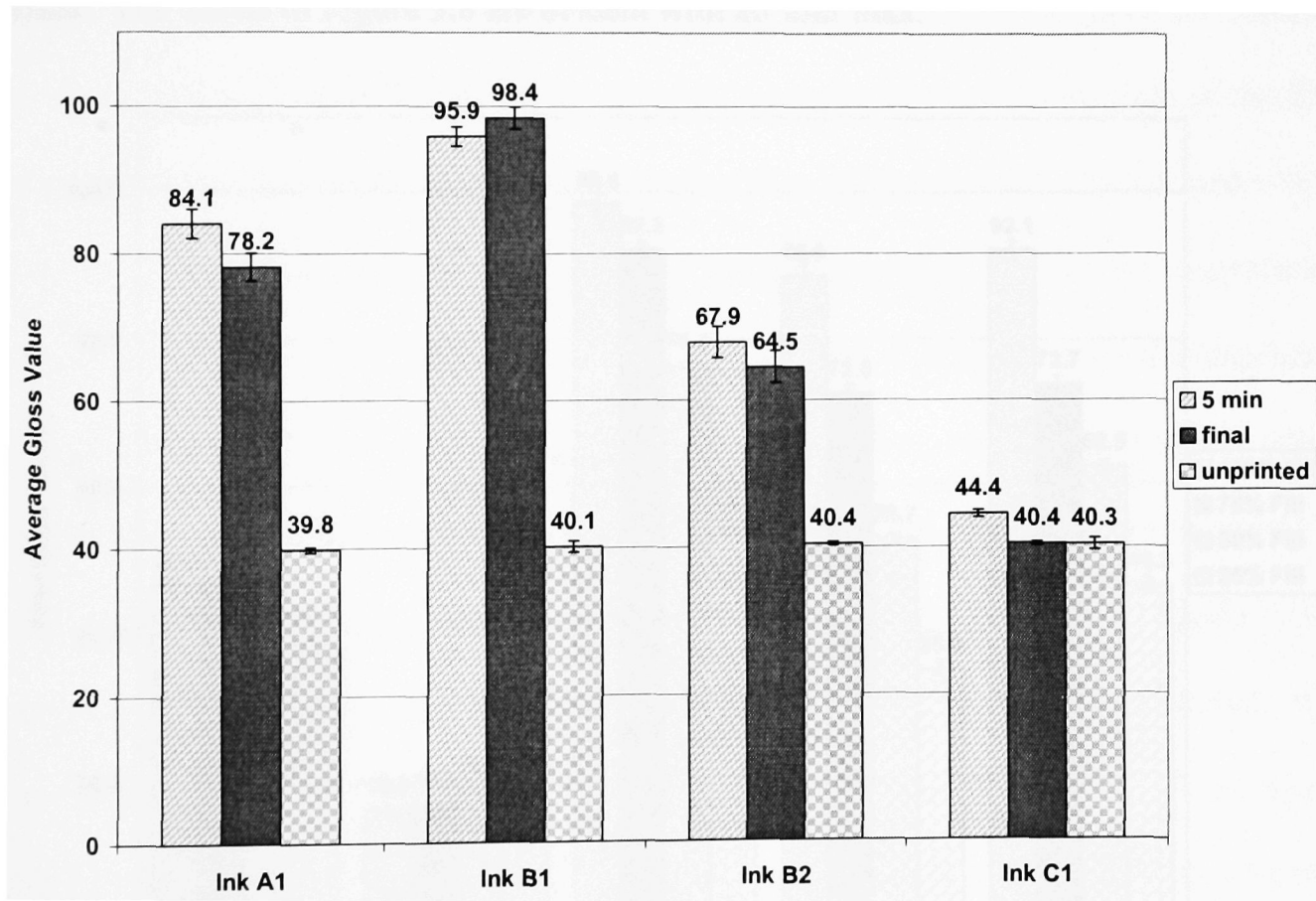


Figure 3.7. Static gloss results for media C

While ink B1 dominates the others in terms of gloss, the closely related ink B2 generates much lower gloss values. The only difference between these two inks is their respective

pigments; their binder and other components are exactly the same. This fact suggests that the ink's pigment is important in the development of gloss.

The inks were also printed at different fill percentages; in addition to 100% fill, 75%, 50%, and 25% fill levels were also printed for comparison. Figure 3.8 shows the final gloss results for ink B1 on the five media for the range of fill percentages. Gloss values decrease with decreasing fill percentage for media C, D, and E. Gloss values of the low-gloss paper-based media are not affected much by the level of ink in the print. This suggests that the substrate is the controlling factor in gloss for these low-gloss media. The trends in Figure 3.8 are evident with all four inks.

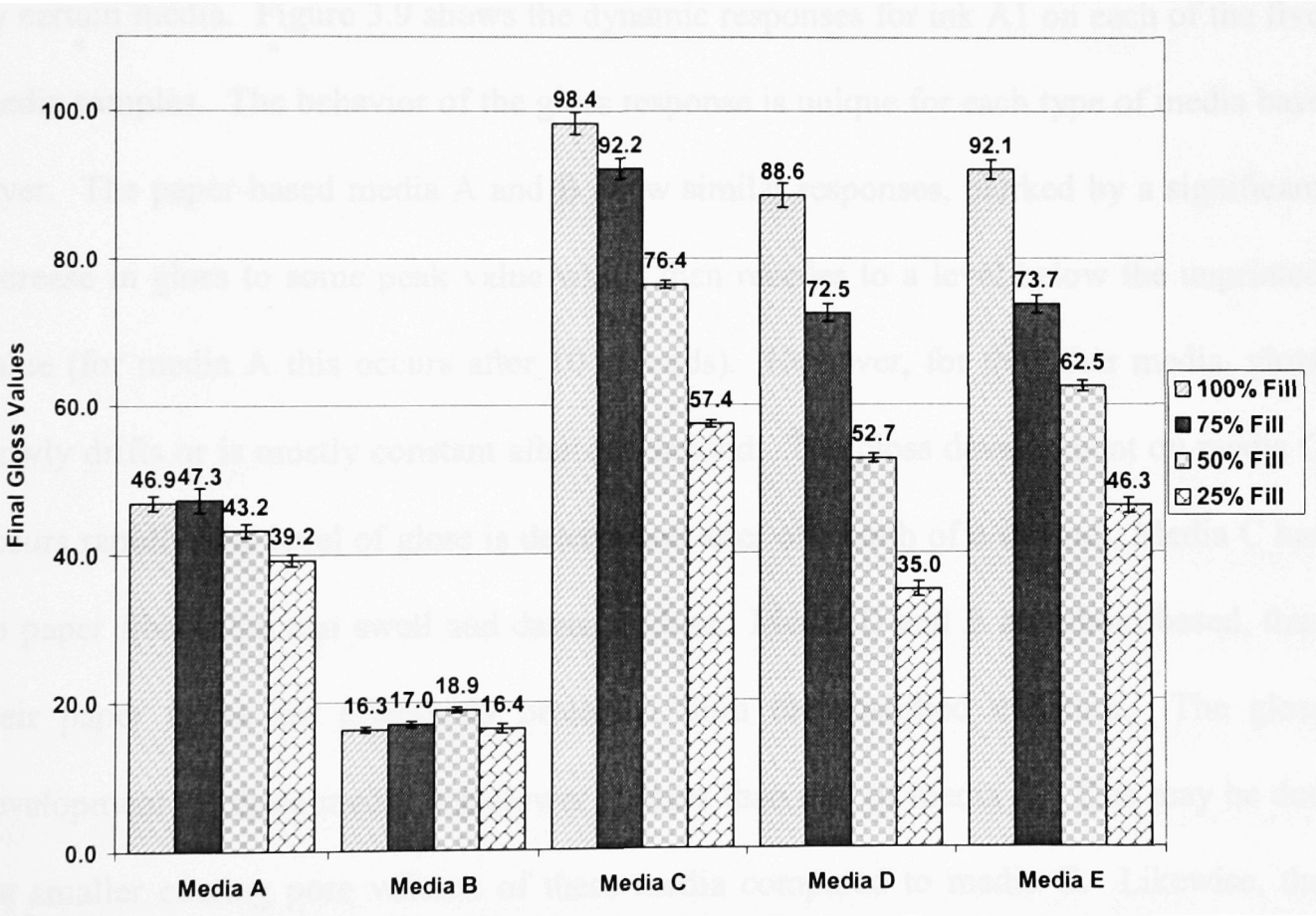


Figure 3.8. Final gloss results for ink B1 for the range of fill percentages

3.4. Dynamic Gloss Results

Since the events of leveling occur very rapidly, the results are best shown on a logarithmic scale. The dynamic gloss response curves are plotted out to ten seconds, a point by which most of the activity has occurred. The voltage observed by the sensor is plotted versus time. Calibration between gloss and voltage is required for each substrate because adjustments in sensor position are required to obtain data for the different media. Once the sensor is moved a new calibration is needed. Voltages are reported in the results since our interest is the events of gloss development.

The dynamic response curves help explain why high levels of gloss are attained by certain media. Figure 3.9 shows the dynamic responses for ink A1 on each of the five media samples. The behavior of the gloss response is unique for each type of media base layer. The paper-based media A and B show similar responses, marked by a significant increase in gloss to some peak value which then recedes to a level below the unprinted value (for media A this occurs after 10 seconds). However, for the other media, gloss slowly drifts or is mostly constant after one second. The gloss development on media C occurs rapidly; the level of gloss is determined after one tenth of a second. Media C has no paper fibers that can swell and damage gloss. Media D and E are photo-based, thus their paper fibers are effectively protected from the absorbed moisture. The gloss development on these media is a slower process than that of media C. This may be due the smaller coating pore volume of these media compared to media C. Likewise, the rapid response of media C is likely due to rapid absorption by small pores aided by a large pore volume.

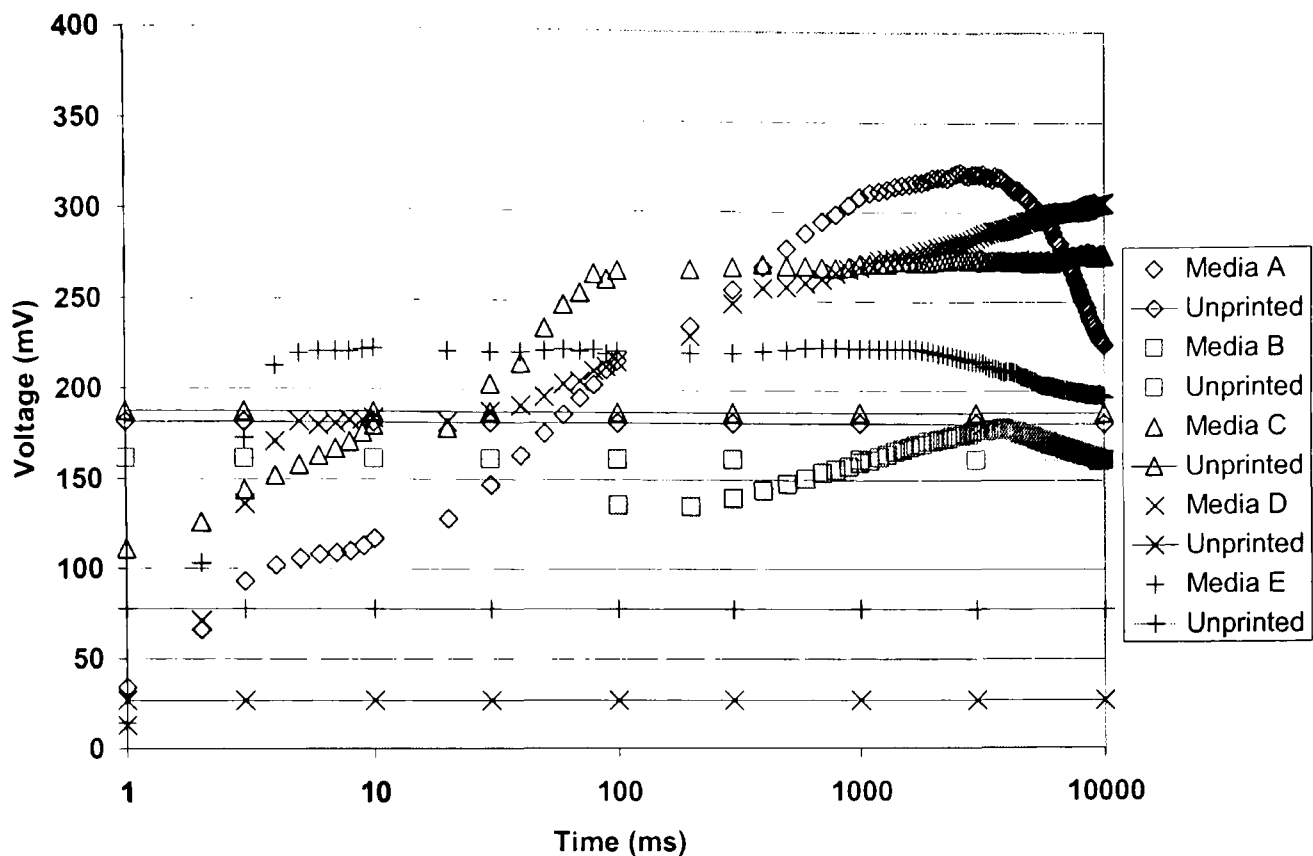


Figure 3.9. Dynamic gloss results for ink A1

The initial increase in gloss of the paper-based media must be due to ink film leveling. Upon printing, the ink begins to level which results in an ink/air interface that is smoother than the coating layer surface. Meanwhile the ink is draining into the media. The reason for the sudden decline in gloss is two-fold. First, the loss of water from the ink layer leads to a point where the continuous aqueous surface is no longer present as the highest particles begin to emerge; this point is called the First Critical Concentration (FCC) in the application of water-based coatings to paper (LePoutre, 1989). Gloss continues to decrease as the dewatering process continues. Second, the ink vehicle drains through the permeable coating layer into the base layer where it encounters the unprotected paper fibers. The paper fibers readily absorb this moisture which causes

them to swell and push up into the coating layer. The non-uniformity of the fibers causes the coating layer to distort. The distortion of the coating layer increases the surface roughness which decreases the level of gloss. The deformation of the coating layer is permanent; that is why the final gloss values of the paper-based media sink to a level below that of the unprinted media. Figure 3.10 is a representation of paper-based media and the result of fiber swelling due to absorbed moisture.

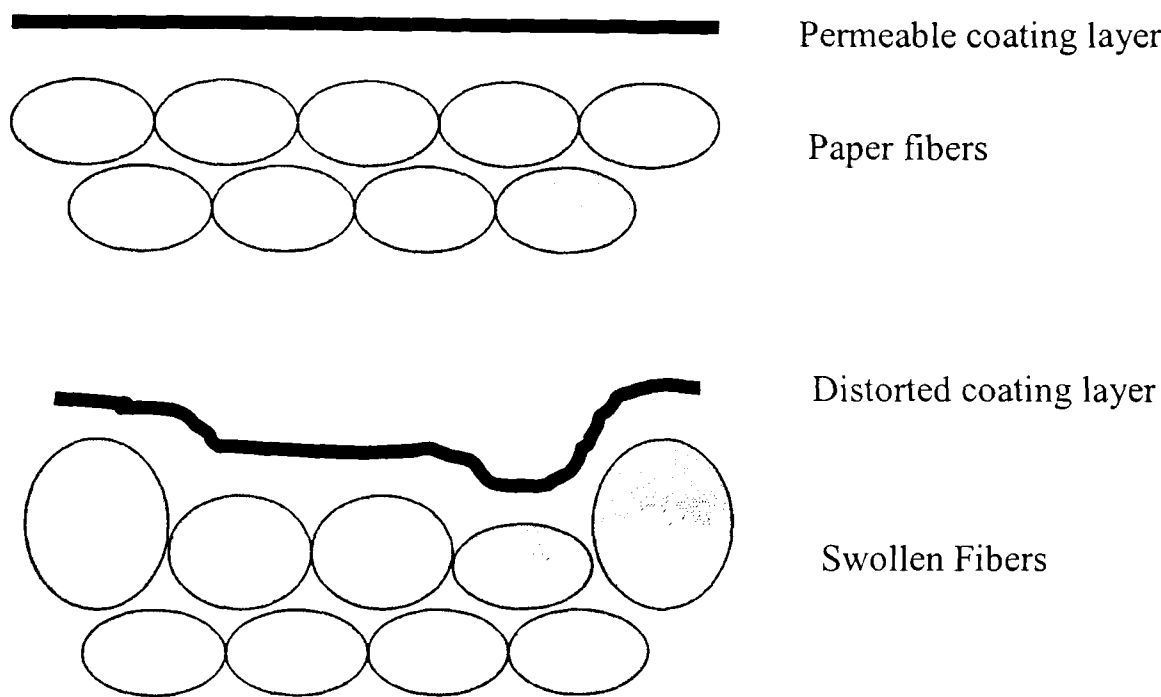


Figure 3.10. Paper-based media and fiber swelling

3.5. Summary

Results show that a wide range of final print gloss values exist for the five media. Plastic-based media C produced the highest print gloss while paper-based media A and B gave the lowest gloss values. Variation in print gloss was also observed among the four inks as well. The dye-based ink C1 consistently produced lower print gloss than the pigmented inks. The magenta ink B1 gave the highest gloss values. For the high-gloss

media C, D, and E, decreasing fill percentage decreased gloss values. This decrease in gloss was not observed in the low-gloss media A and B; this suggests the substrate is the controlling factor in gloss for these two media.

The gloss development characteristics of the media are determined primarily by the composition of the base layer. The print gloss on paper-based media reaches a maximum before receding to a level below that of the unprinted sample. This overall decrease in gloss from the unprinted to the final gloss value is due to fiber swelling. The unprotected paper fibers in the base layer absorb the moisture from the ink layer and swell, irreversibly distorting the coating layer. The plastic-based media C contains no paper fibers that can swell and damage gloss. The gloss development on this media occurs very rapidly; within 0.1 second. This is likely due to rapid absorption due to small pores yet large pore volume. The paper fibers in the photo-based media D and E are effectively shielded from moisture; this allows high gloss. The gloss development on these media, however, is slower than that of media C—a suspected consequence of slower absorption and smaller pore volume.

It is generally thought that slower absorption leads to better leveling and thus higher gloss. The rapid gloss development on media C is attributed to fast absorption, however, the highest print gloss is obtained with media C. It is therefore suggested that the general rule relating gloss and absorption may not apply to such a system. The concept of leveling may be irrelevant in such a fast-setting system due to the low viscosity of the ink. Such a low viscosity allows leveling to occur on the order of about 20 ms; this is small compared to the 100 ms for gloss development.

Chapter 4

INFLUENCE OF SURFACE CHEMISTRY ON GLOSS

The primary concern of this chapter involves how ionic species on the media surface influence gloss. Any pigment dispersion needs to be stabilized to produce a desired outcome. The key question relates to the ability of chemicals on the media to influence the print gloss. It is suspected that certain ions influence gloss by destabilizing the ink layer. The focus of the remaining chapters also is centered upon plastic-based media; therefore media C will be used exclusively during the remainder of this research.

4.1. Ink Description

Additional inks were used in the subsequent research, they are:

- 1.) Ink D1 – pigmented, black
- 2.) Ink D2 – pigmented, grey
- 3.) Ink D3 – pigmented, magenta
- 4.) Ink D4 – pigmented, yellow
- 5.) Ink D5 – pigmented, cyan
- 6.) Ink E1 – pigmented, black
- 7.) Ink F1 – pigmented, black
- 8.) Ink G1 – pigmented, black

All the inks listed above are not commercial products, therefore no other information regarding them can be provided.

4.2. Influence of Calcium Chloride

Solutions of calcium chloride were prepared for a range of molarities: 0.01 M, 0.1 M, 0.2 M, 0.5 M, and 1.0 M. These solutions were applied with the draw-down coater using a fine wire wound rod. This range of molarities was used to determine what level is required to affect print gloss. Table 4.1 shows the resulting coat weights for the application of these solutions. The coat weight of the 0.01 M sample was too small to be measured accurately.

Table 4.1. Average coat weight of calcium chloride-treated solutions

Molarity (M)	Average Coat Weight (g/m ²)
0.01	
0.1	0.27
0.2	0.95
0.5	2.70
1.0	4.00

In Figure 4.1, the results for ink B2 show that gloss is not affected until solutions of 0.5 M or higher are applied. For lower molar solutions, the observed increase in gloss may be a result of the smoothening of the media surface due to the addition of the small ionic crystals. However, not all inks behaved similarly on these treated samples. Figure 4.2 shows how ink E1 is unaffected by calcium chloride for the range of molarities.

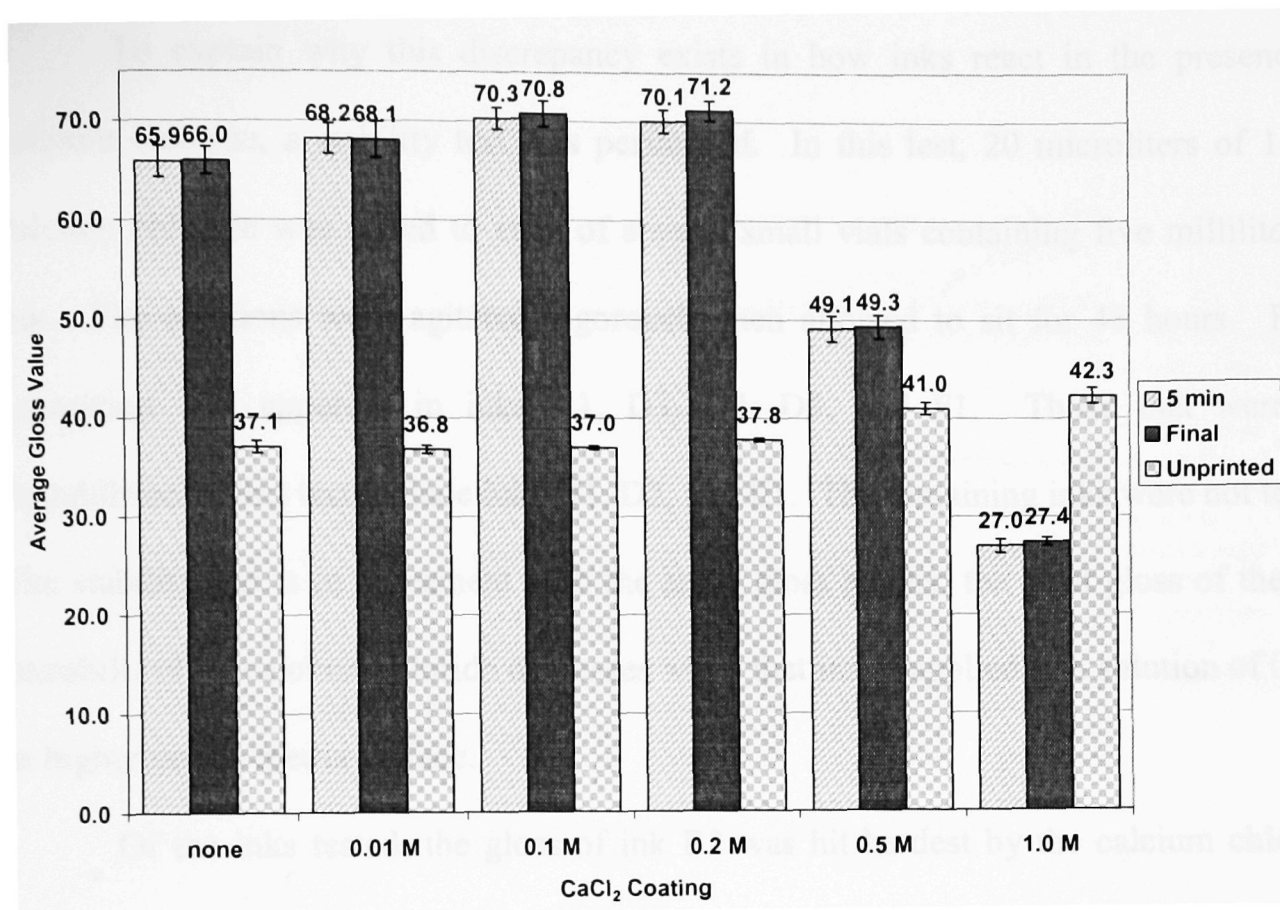


Figure 4.1. 20-degree static gloss results for ink B2 on CaCl₂-treated media C

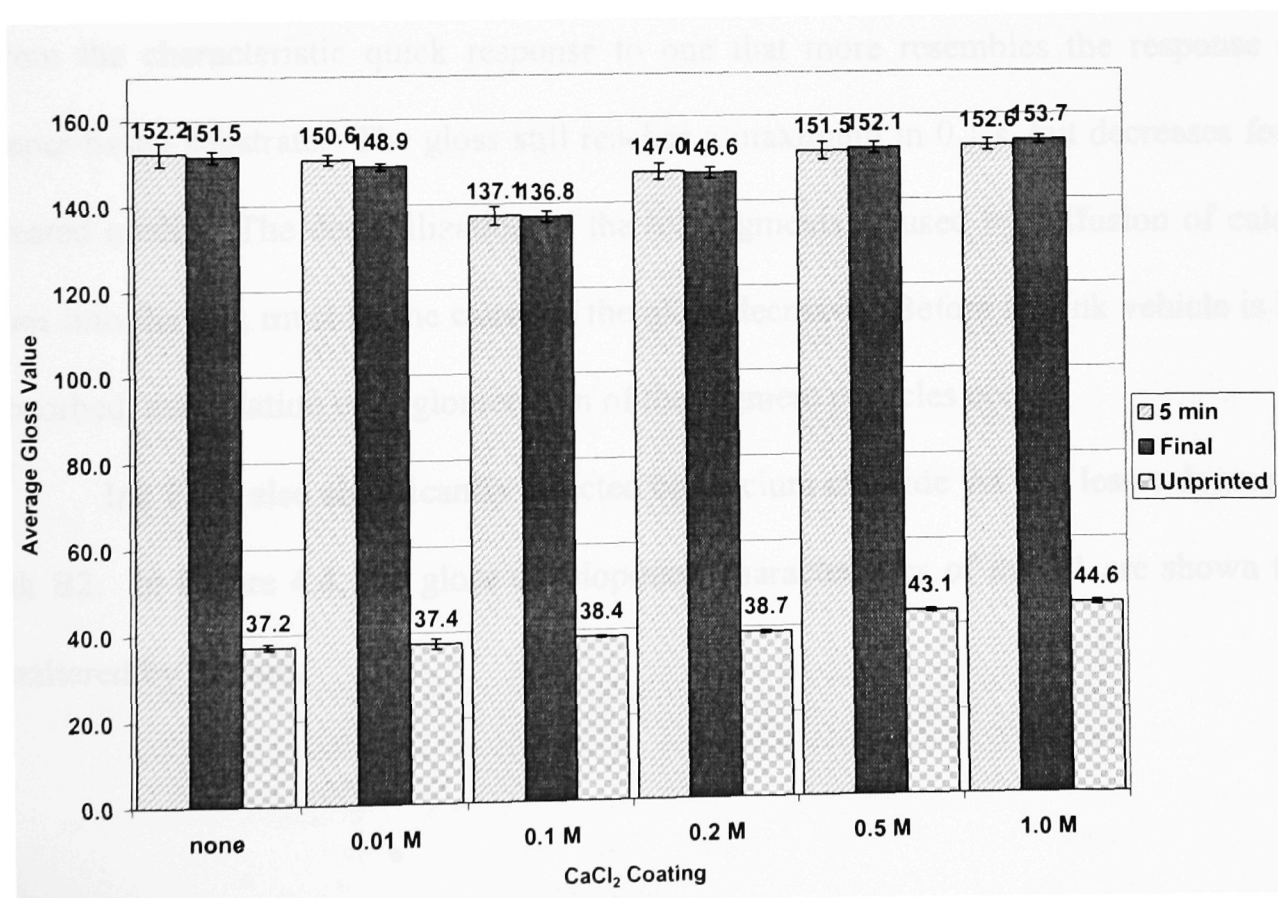


Figure 4.2. 20-degree static gloss results for ink E1 on CaCl₂-treated media C

To explain why this discrepancy exists in how inks react in the presence of calcium chloride, a stability test was performed. In this test, 20 microliters of 1.0 M calcium chloride was added to each of several small vials containing five milliliters of ink. The solutions were agitated vigorously then allowed to sit for 48 hours. Phase separation was apparent in inks A1, D3, D4, D5, and F1. Those that were not destabilized in this test include inks D1, D2, and E1. The remaining inks were not tested. The stability test is in agreement with the static gloss results; the print gloss of the inks destabilized by calcium chloride decreases when that ion is applied as a solution of 0.5 M or higher on the media surface.

Of the inks tested, the gloss of ink B2 was hit hardest by the calcium chloride. Figure 4.3 illustrates how the gloss development of ink B2 is altered by the presence of this ion. As the level of calcium chloride increases, the dynamic gloss curves transition from the characteristic quick response to one that more resembles the response of a paper-based substrate. The gloss still reaches a maximum in 0.1 s, but decreases for the treated media. The destabilization of the ink pigments, caused by diffusion of calcium ions into the ink, must be the cause of the gloss decrease. Before the ink vehicle is fully absorbed, coagulation or agglomeration of the pigment particles occurs.

Ink F1 is also significantly affected by calcium chloride yet to a lesser degree than ink B2. In Figure 4.4, the gloss development characteristics of ink F1 are shown to be unaltered by the ion.

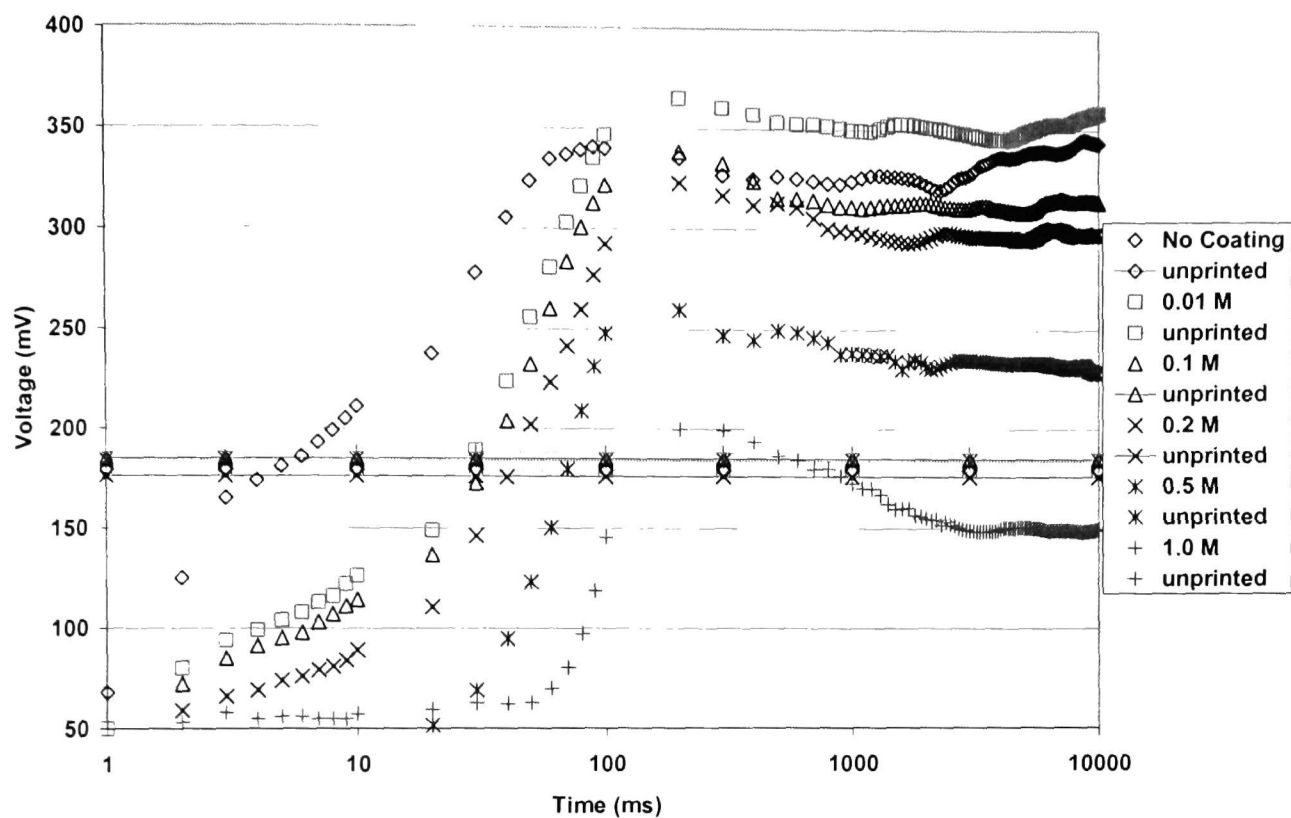


Figure 4.3. Typical responses of ink B2 on CaCl_2 -treated media C

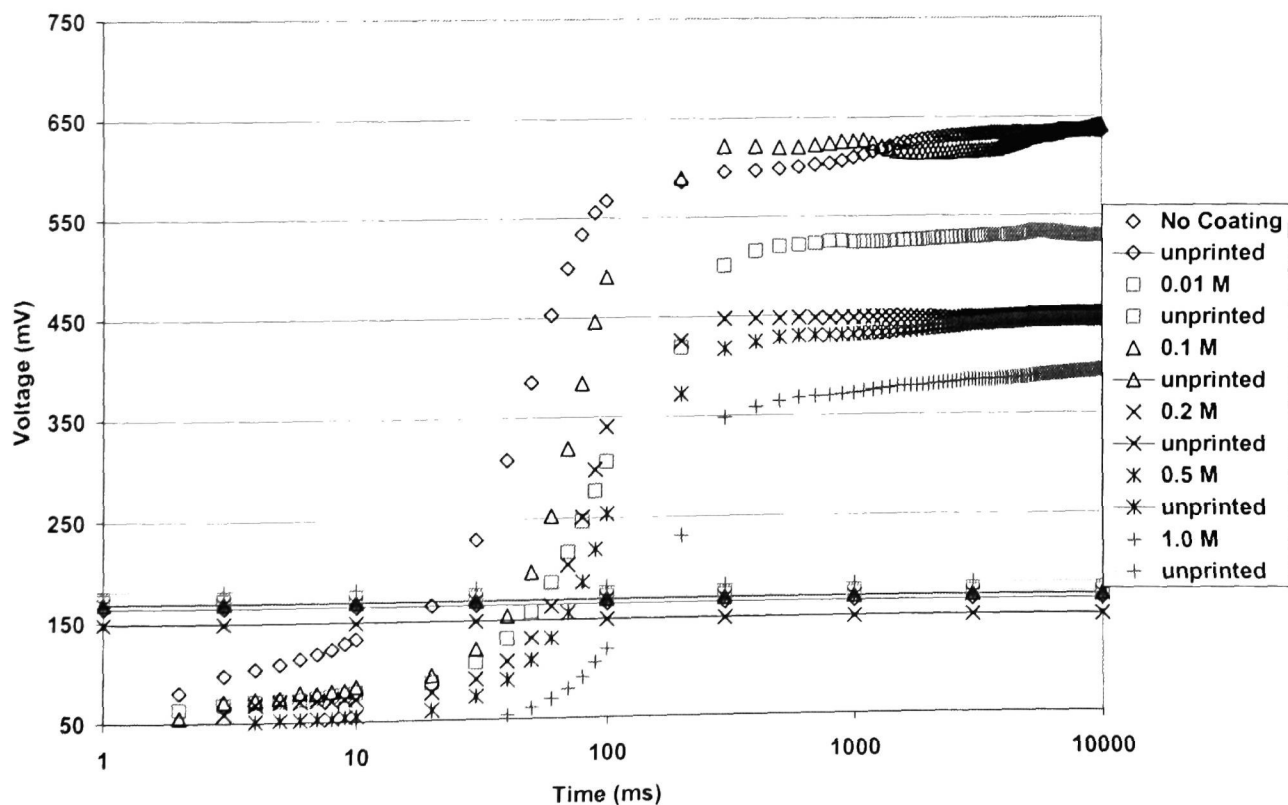


Figure 4.4. Typical responses of ink F1 on CaCl_2 -treated media C

4.3. Influence of Other Ions

It was determined from the experiments with calcium chloride that a 1.0 M solution was sufficient for an ion to significantly affect gloss if an ink can be destabilized by that ion. Therefore, 1.0 M solutions were used for the additional chemicals: sodium chloride, aluminum chlorohydrate (ACH), and boric acid. The average coat weights of the treated samples are shown in Table 4.2

Table 4.2. Average coat weight of treated samples, 1.0 M solutions

Chemical	Active Ion(s)	Average Coat Weight (g/m ²)
Calcium Chloride	Ca ²⁺	4.00
Sodium Chloride	Na ⁺	7.45
Aluminum Chlorohydrate	AlO ₄ [Al ₃ (OH) ₆] ₄ ⁷⁺	6.42
Boric Acid	H ⁺ ; BO ₃ ⁻	2.63

Figures 4.5-4.8 show the static gloss results for various inks on treated samples. For ink A1, sodium chloride harshly affects gloss similarly to calcium chloride. ACH, however, significantly increases gloss. A considerable increase in sheet gloss is also observed for the ACH-treated samples. Boric acid has little effect on final gloss. Ink B2 is similarly affected—except sodium chloride affects gloss less dramatically than calcium chloride. While the print gloss of ink D1 is basically unaffected by these ions, the closely related ink D2 is affected; even ACH is shown to decrease gloss.

In all cases, the Boric acid seems to have little influence. Sodium chloride and calcium chloride, for most cases, decrease the gloss. The reason for this decrease seems to be the destabilizing of the ink causes flocs or non-uniform pigment distributions that

lead to a rough surface. However, the results with ACH are hard to understand. For inks A1 and B2 the gloss actually increases when ACH is on the surface. For the D-group inks, the gloss decreases, but the decrease for ink D1 is small. ACH should be a strong flocculation agent and should damage gloss for all of these systems. Perhaps the pH of the system must be correct for ACH to be active.

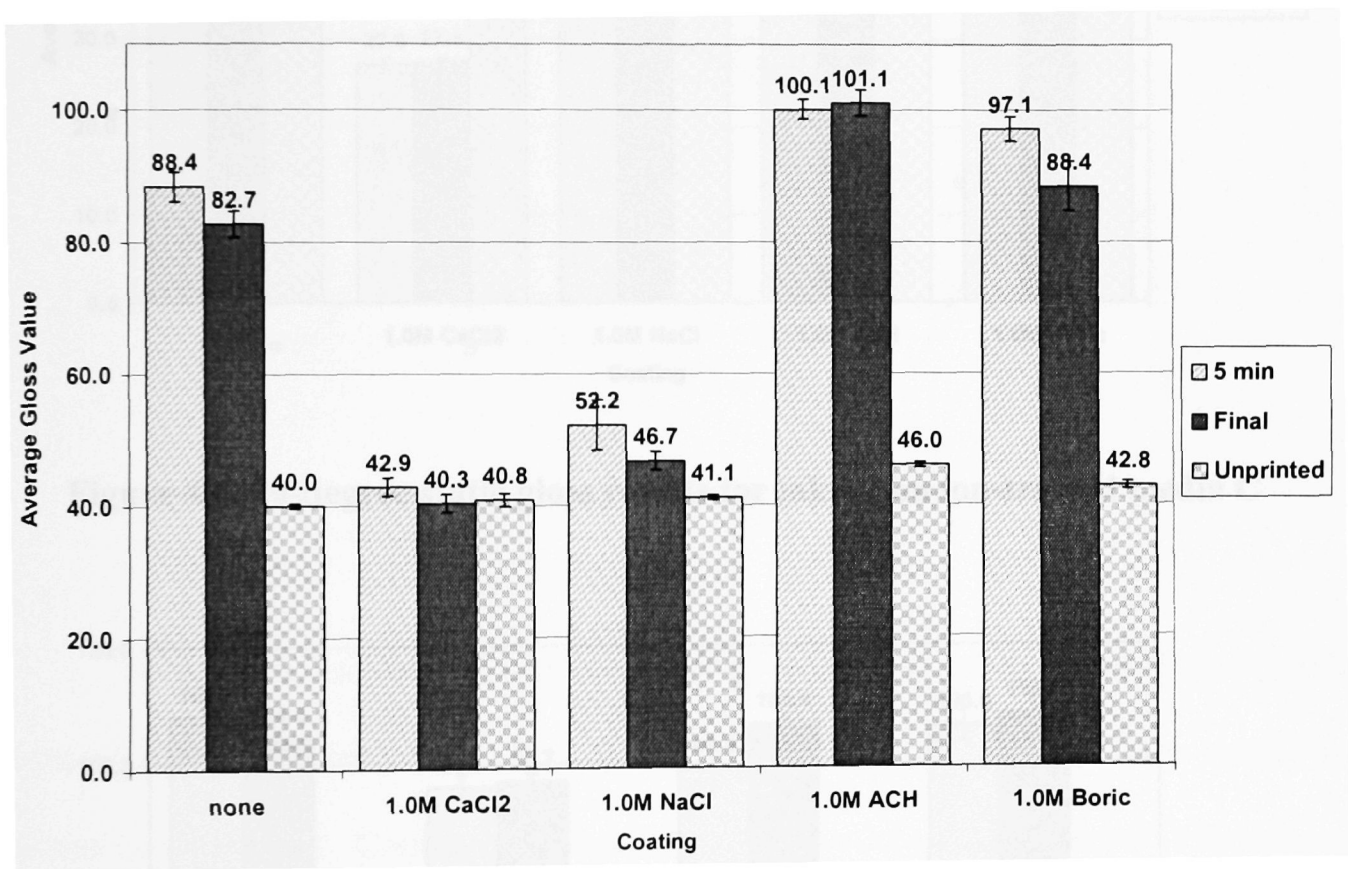


Figure 4.5. 20-degree static gloss results for ink A1 on ion-treated media C

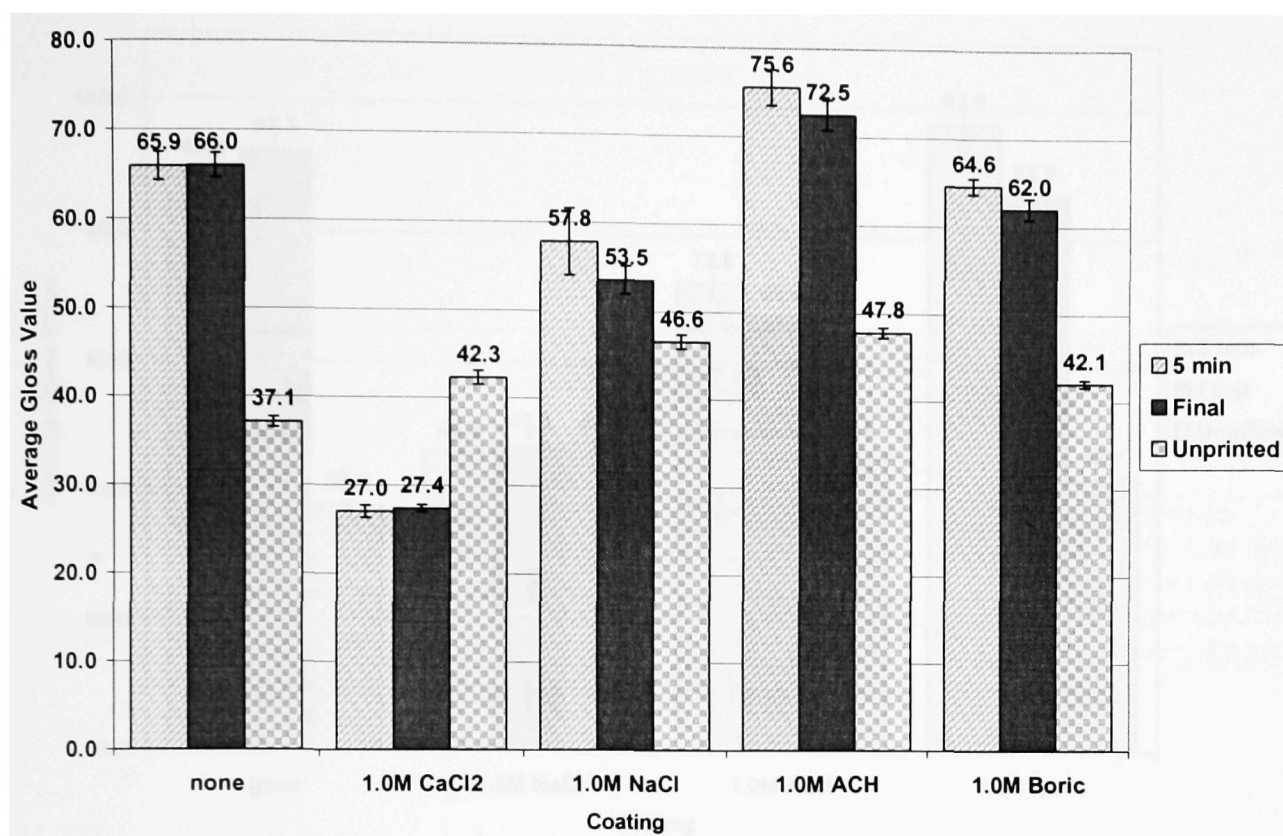


Figure 4.6. 20-degree static gloss results for ink B2 on ion-treated media C

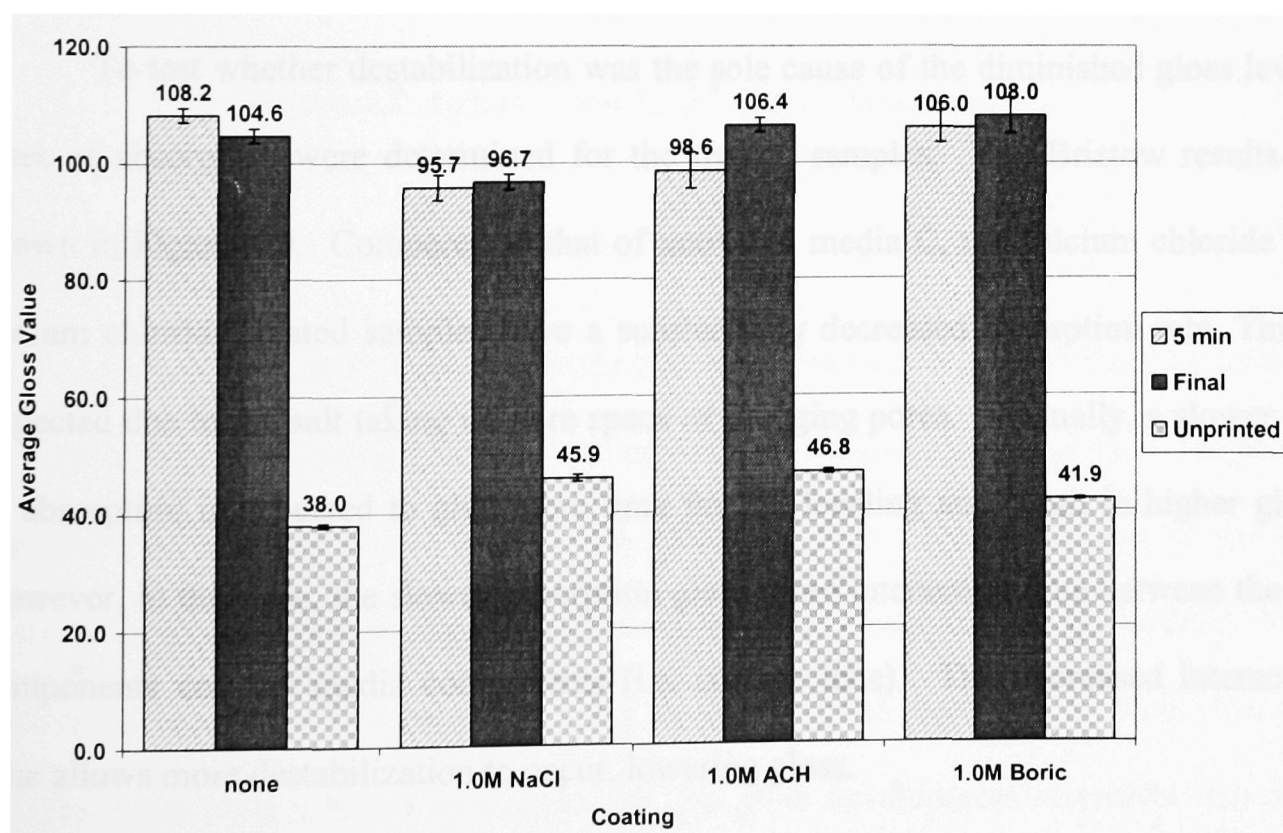


Figure 4.7. 20-degree static gloss results for ink D1 on ion-treated media C

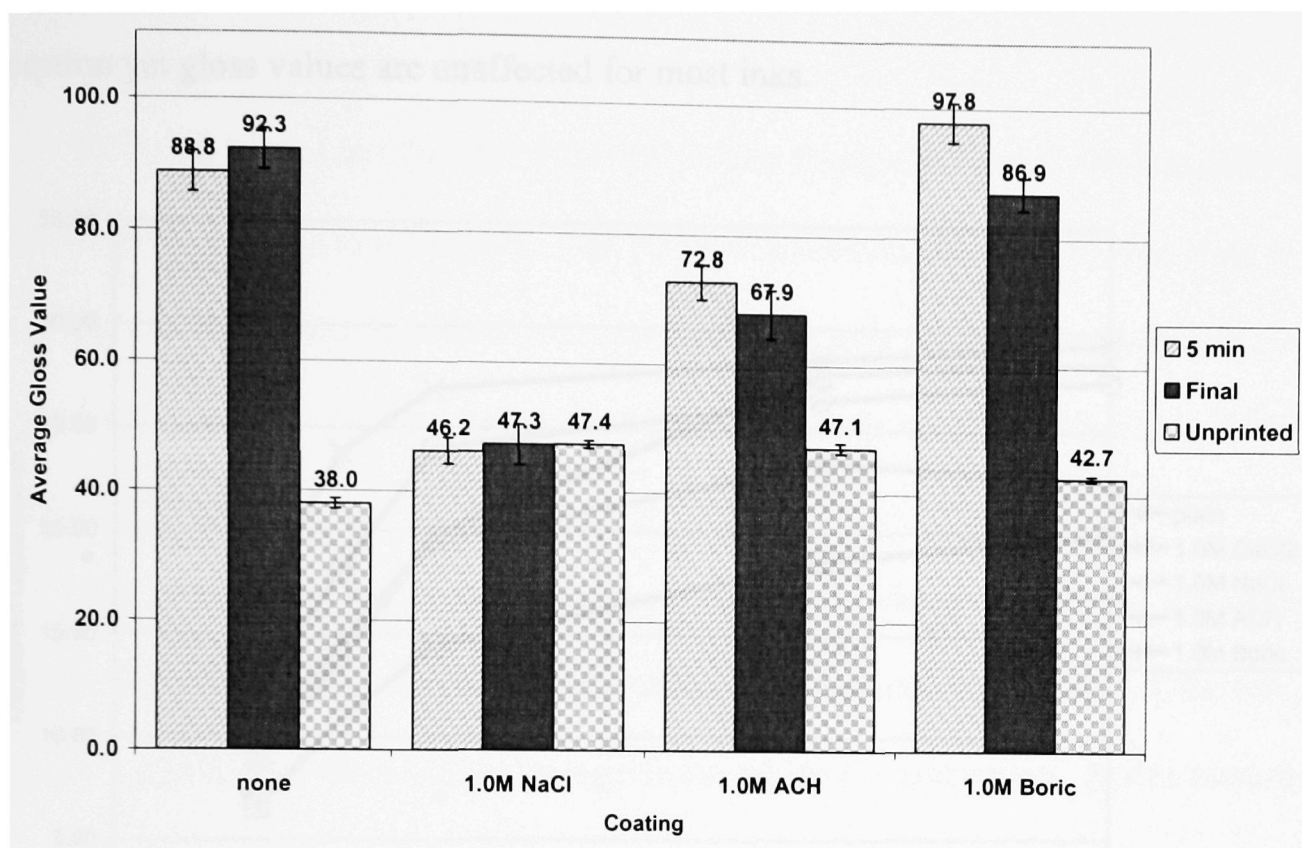


Figure 4.8. 20-degree static gloss results for ink D2 on ion-treated media C

To test whether destabilization was the sole cause of the diminished gloss levels, rates of absorption were determined for the treated samples. The Bristow results are shown in Figure 4.9. Compared to that of untreated media C, the calcium chloride and sodium chloride treated samples have a substantially decreased absorption rate. This is expected due to the salt taking up pore space or plugging pores. Normally, a slower rate of absorption is expected to give more time for ink leveling and result in higher gloss. However, in this case, the slower absorption gives more interaction time between the ink components and the media components (i.e. surface ions). This increased interaction time allows more destabilization to occur, lowering gloss.

Since these treatments lower gloss for most inks, this must be due to destabilization of the ink. ACH decreases absorption rate similar to sodium chloride yet

the gloss is affected quite differently. The boric-treated samples have an increased rate of absorption yet gloss values are unaffected for most inks.

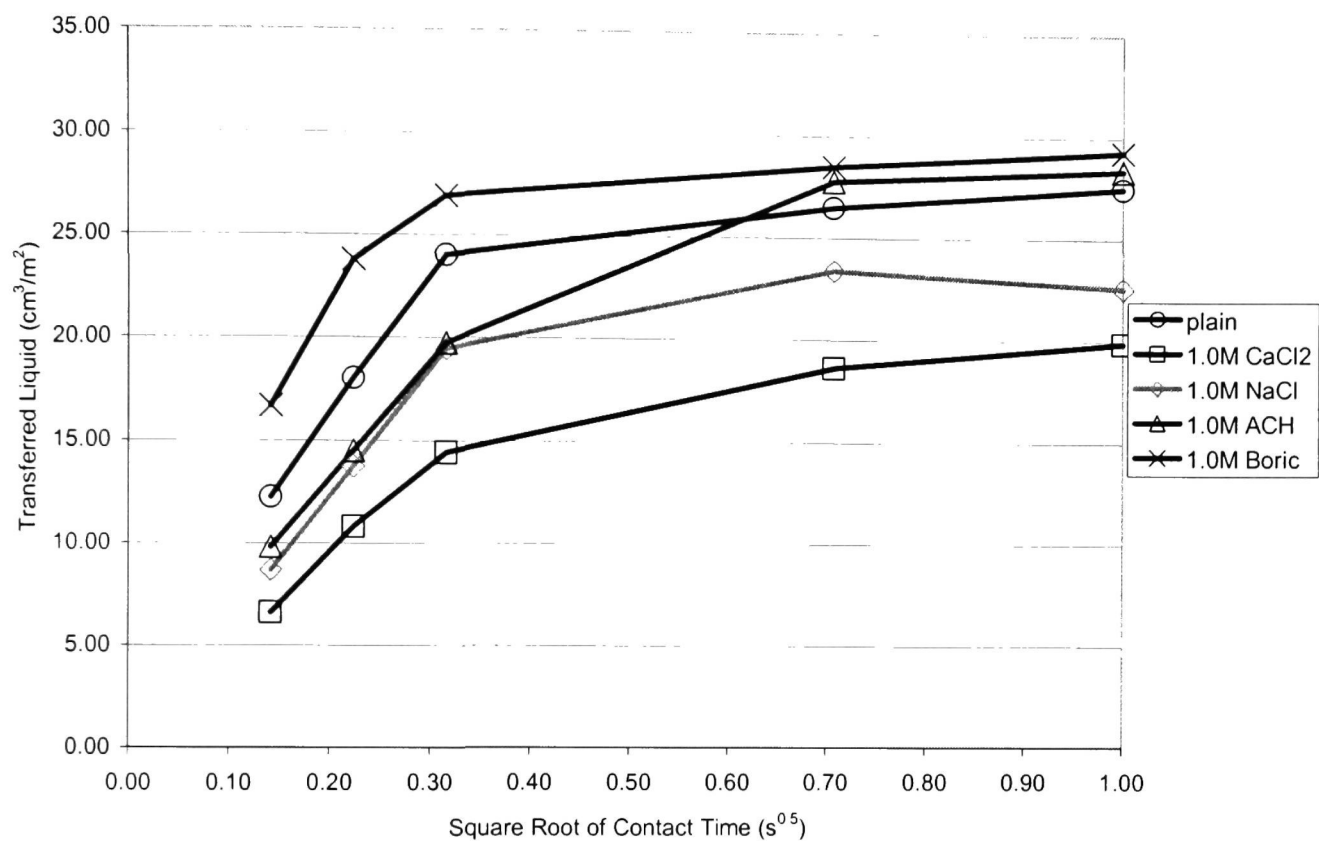


Figure 4.9. Bristow results for ion-treated samples

4.4. Summary

The results of this chapter illustrate how some inks can be destabilized by ions on the media surface, lowering gloss. It was proved that the decrease in gloss is due to ink destabilization and not due to the altered absorption rate. Destabilization of the ink causes flocs or non-uniform pigment distributions which leads to a rough surface. This destabilization is shown to affect the gloss development of these inks as well. For the inks which are most affected by a given ion, the gloss development resembles that of a paper-based substrate with a peak in gloss followed by a decrease to a level below that of

the unprinted gloss. The lesser affected inks show no altered gloss development characteristics.

Different ions affect the inks differently. The strong Ca^{2+} ion in calcium chloride is shown to affect gloss most harshly. The Na^+ ion in sodium chloride affected gloss to a lesser degree. ACH was expected to be damage gloss as a strong flocculant; however, results show this not to be the case for most inks. The boric acid had very little effect on gloss for all inks.

The printed ink flux is far lower than the ink absorbing capacity of the media. The absorbing rate is very fast when the media is not saturated with ink. If the ink is absorbed immediately, there will be no significant ink/media interaction. In this scenario, the added ions will not have significant impact on gloss. When the ink flux is close to the saturation point of the media, absorption rate is slow and there will be more interaction time between the ink and media components. The result is that gloss will be affected more significantly. This situation is realized when the added salts effectively clog pores and reduce absorption rates, as shown in Figure 4.9. Calcium chloride is shown to reduce rates of absorption the most, while also affecting gloss most harshly. The role of absorption rate in pigment flocculation, however, is secondary to the fact that certain inks can be destabilized by a given ion while others cannot.

Chapter 5

INFLUENCE OF INK PIGMENT LOAD AND IMAGE FILL PERCENTAGE ON GLOSS

One issue that can cause a decrease in quality of a printed sample is different gloss values of different regions of the image. While a high level of gloss is desirable, non-uniformity is not. Uniformity is perhaps more important than the absolute level of gloss. Light color inks were found to have high gloss values at 50% fill compared to 100% fill while most other inks have the opposite behavior. The goal of this chapter is to understand this issue.

5.1. Ink D Group

The focus of this chapter is confined to the ink D group, explicitly inks D1 and D2. These two inks are similar in composition; they share the same vehicle and even have identical pigments. To achieve the grey color of ink D2, a lesser amount of pigment is used in its production compared to that of ink D1. With these two closely related inks, one would expect them to have similar print properties. The static gloss results of these two inks are shown in Figures 5.1 and 5.2. Figure 5.1 shows that ink D1 behaves normally, that is, as ink fill percentage decreases so do the gloss values. Ink D2, however, is shown to have a gloss spike at 50% fill in Figure 5.2. This behavior of increasing gloss values from 100% to 50% fill is not reported in the literature and does not match what was found in Chapter 3 for a number of ink-media combinations.

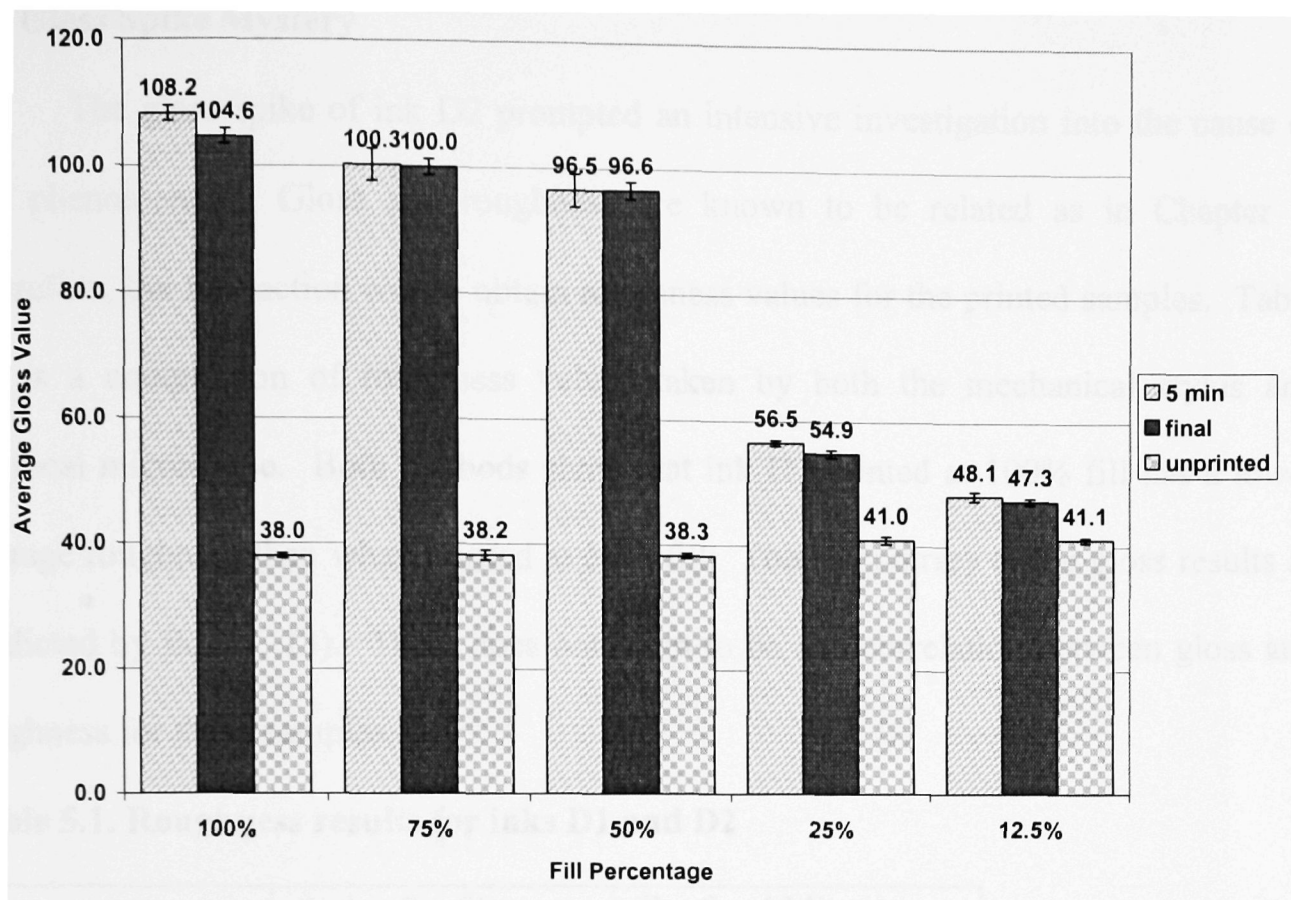


Figure 5.1. 20-degree static gloss results for ink D1 on media C

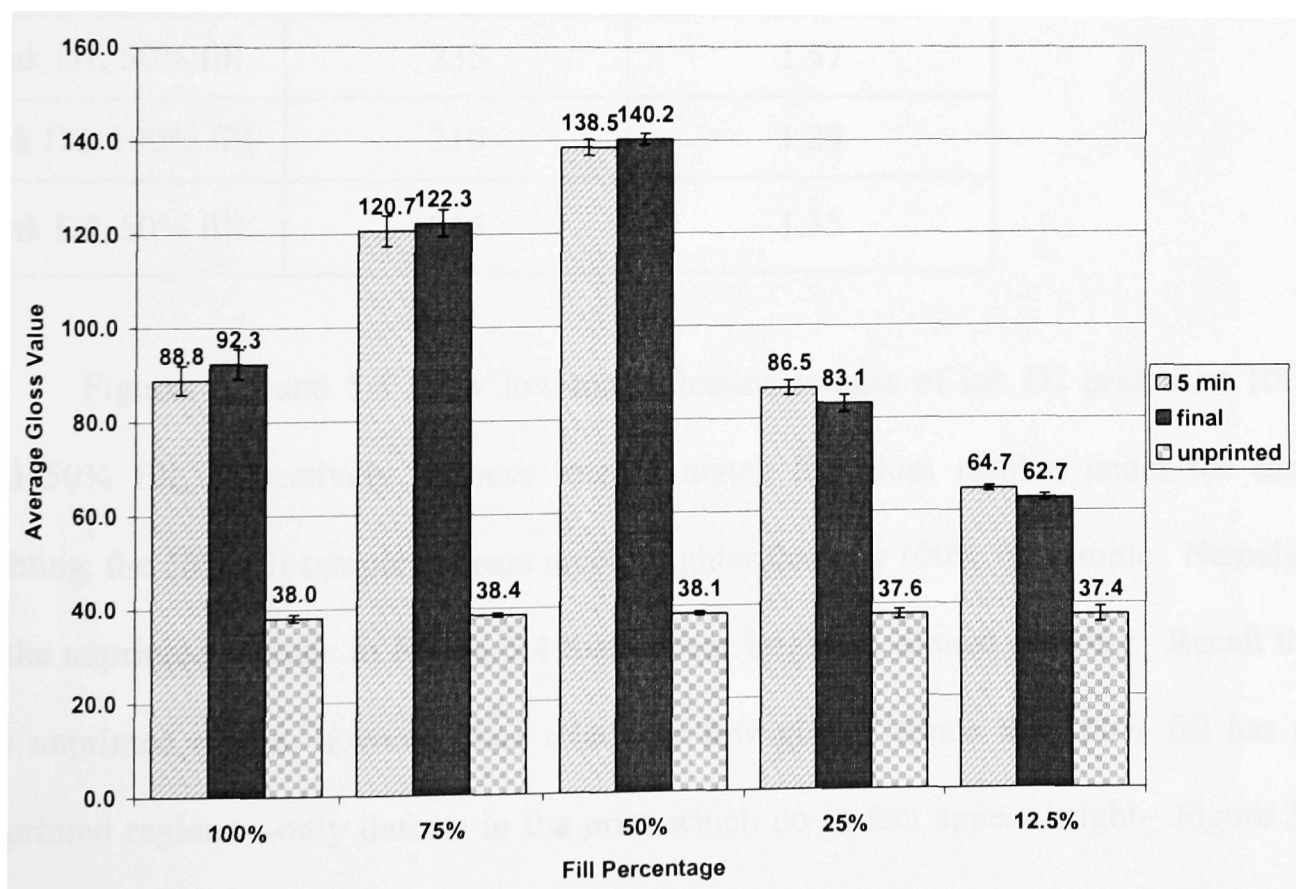


Figure 5.2. 20-degree static gloss results for ink D2 on media C

5.2. Gloss Spike Mystery

The gloss spike of ink D2 prompted an intensive investigation into the cause of this phenomenon. Gloss and roughness are known to be related as in Chapter 1. Therefore, the first action was to obtain roughness values for the printed samples. Table 5.1 is a compilation of roughness values taken by both the mechanical stylus and confocal microscope. Both methods show that ink D2 printed at 100% fill has a lower average roughness than when printed at 50% fill. This is contrary to the gloss results as predicted by Eq. (1. 13). There does not seem to be any correlation between gloss and roughness for these samples.

Table 5.1. Roughness results for inks D1 and D2

Sample	Stylus Profilometer (nm)	Confocal Microscope (μm)
Ink D1, 100% fill	278	1.07
Ink D1, 50% fill	235	1.57
Ink D2, 100% fill	210	1.25
Ink D2, 50% fill	265	1.35

Figures 5.3 and 5.4 show low-magnification images of ink D2 printed at 100% and 50% fill, respectively. These images match the gloss results; under the same

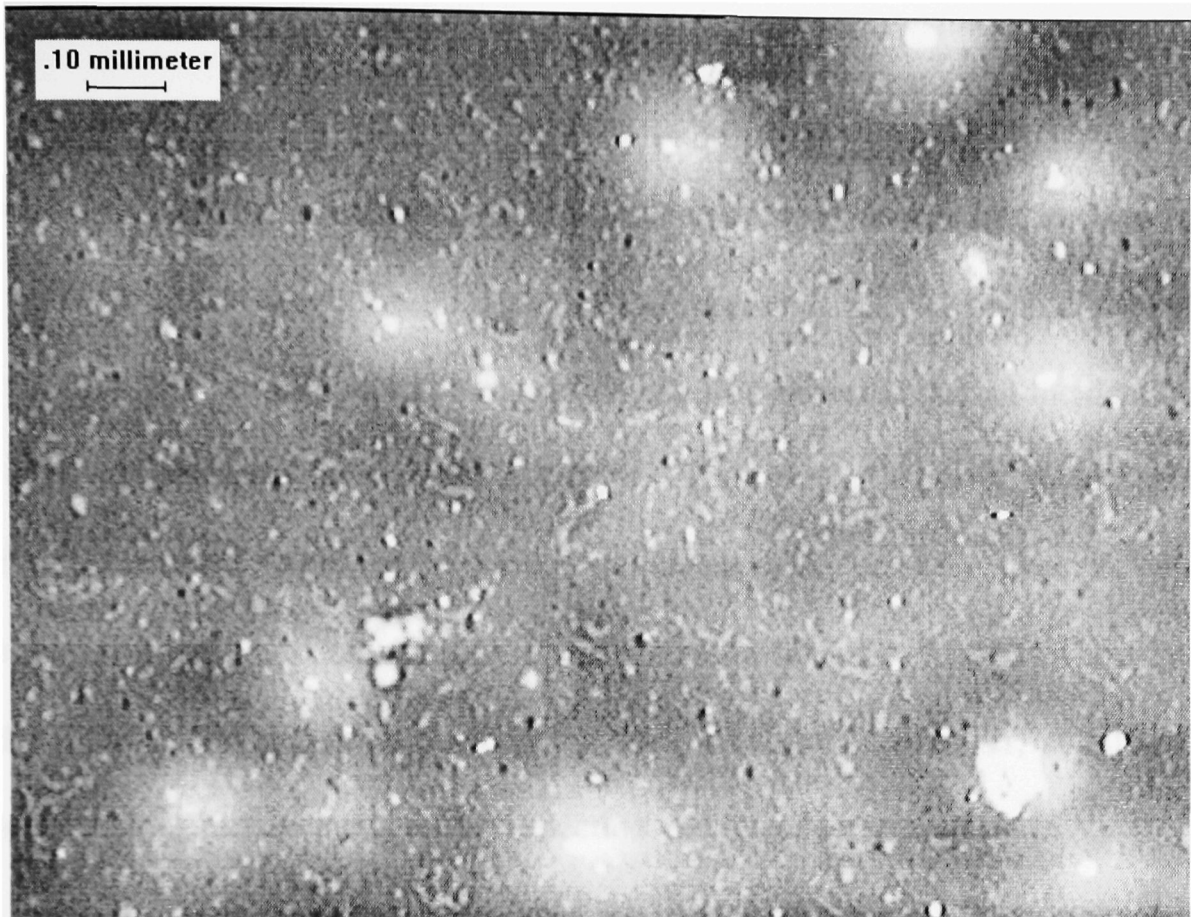


Figure 5.3. Magnified image of ink D2, 100% fill, on media C

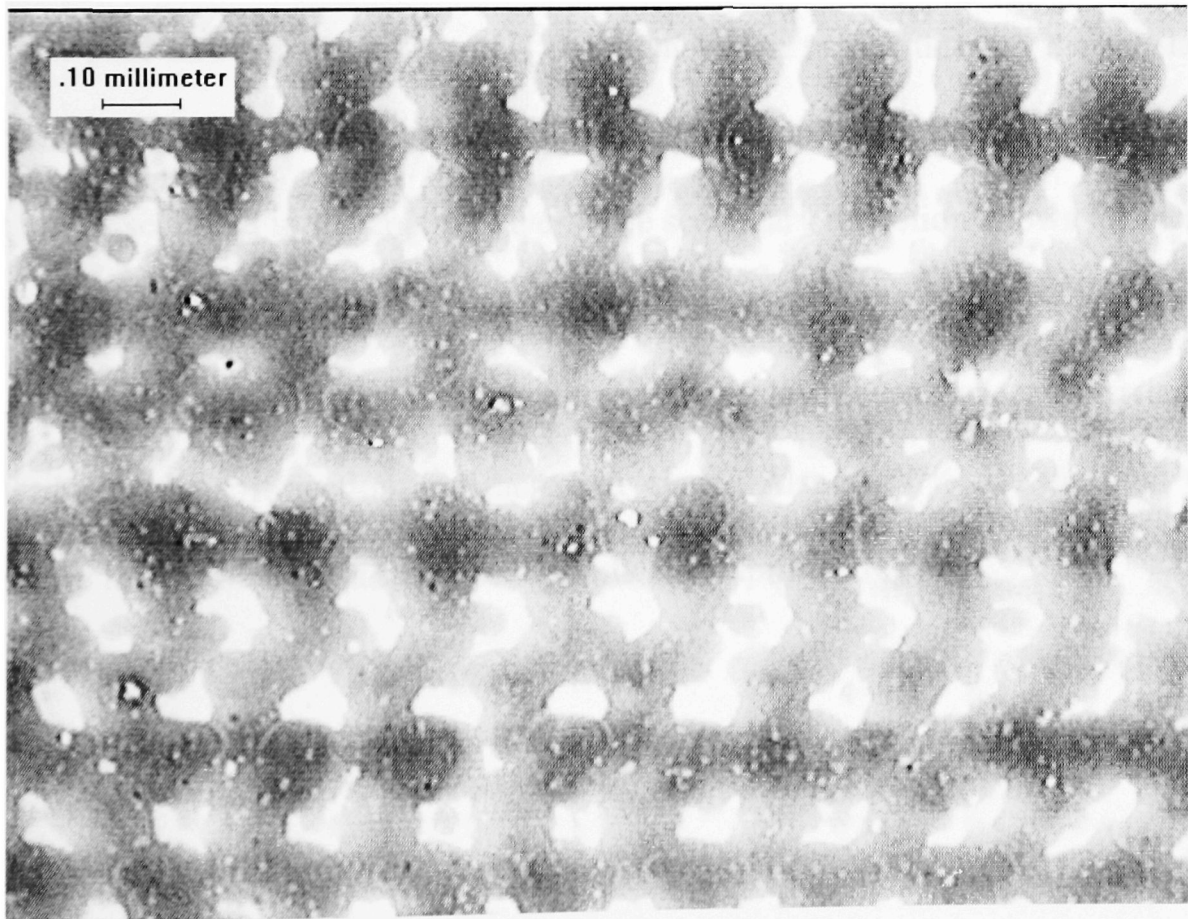
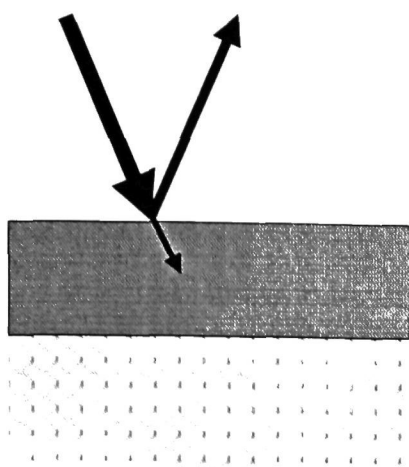


Figure 5.4. Magnified image of ink D2, 50% fill, on media C

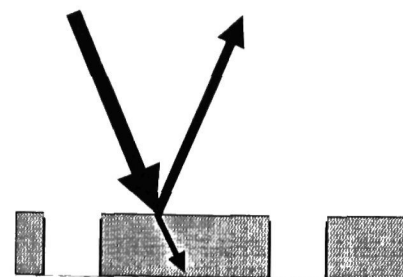
5.3. Optical Phenomena

Figure 5.5 is an attempt to represent the potential mechanisms and light pathways. Figures 5.5 (a) through (d) illustrate the difference between a dark ink, such as ink D1, and a light ink, such as ink D2. Figure 5.5 (a) represents ink D1 printed at 100% fill. With the high level of pigment present in this ink, it is expected that an incident beam of light does not penetrate through the ink layer. The level of gloss of such a sample is therefore determined solely by the surface roughness of the print, i.e. specular reflection at the ink/air interface. The situation is unchanged at 50% fill, illustrated in Figure 5.5 (b); the light cannot penetrate through the dark ink layer. However, at 50% fill, the unprinted regions reduce the specular reflection and thus decrease gloss.

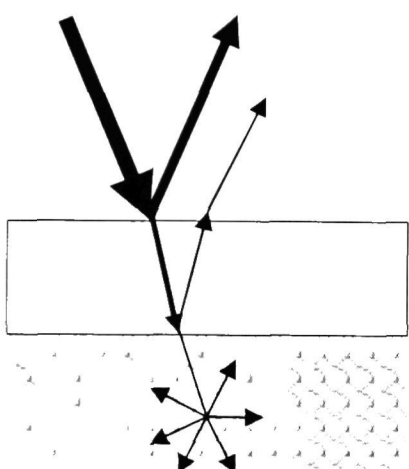
The behavior changes when a light ink is used. Figure 5.5 (c) represents ink D2 printed at 100% fill. Ink D2 contains less pigment than ink D1; the result is that a light beam can pass through the ink layer. The light which passes through the ink layer is either reflected back toward the ink/air interface (secondary reflection), or enters the media and is scattered in the coating layer. The secondary reflection allows for increased gloss since the reflection is in the specular direction. At 50% fill, less light is absorbed in the ink layer and light can pass through the smaller ink layer even easier. The result is an increased secondary reflection and increased gloss. Also at 50% fill, the light that is scattered in the media now has easy exit points, the unprinted regions.



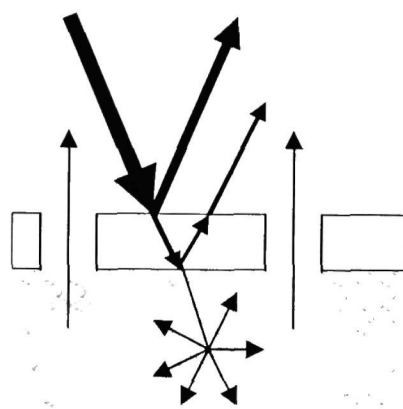
(a) dark ink, 100% fill



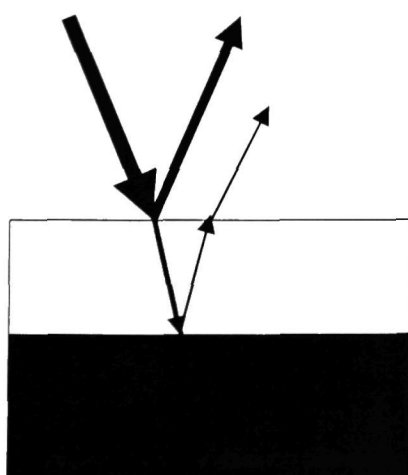
(b) dark ink, 50% fill



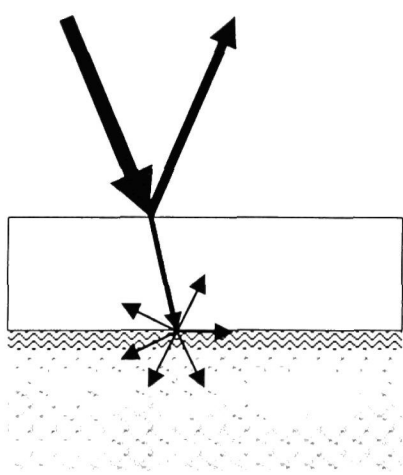
(c) light ink, 100% fill



(d) light ink, 50% fill



(e) light ink on
dyed media



(f) light ink on
roughened media

Figure 5.5. Theoretical light interaction with a print for various cases

The unprinted regions of the sample printed with ink D2 at 50% fill allow the scattered light in the media to exit easily—this mechanism is likened to a flashlight. The result of this “flashlight” effect is observed Figure 5.4 where the unprinted regions appear bright. When this image was first taken it seemed obvious that the gloss spike must be due to the bright unprinted regions of the 50% fill sample. To test this theory, an experiment was performed where the coating layer of the media was dyed black with two applications of the black dye-based ink C1. The black dye had no effect on the properties of the media (i.e. gloss or absorption). Its purpose was to absorb light which enters the coating layer, disallowing the escape of that light through the unprinted regions. Ink D2 at 50% fill was then printed upon the dyed media; Figure 5.5 (e) is a representation of this situation and Figure 5.6 is low power image captured of this sample. Compared to Figure 5.4, it is clear that the unprinted regions are no longer emitting much light. Interestingly however, when the gloss values were recorded for the dyed sample they were the same as for the untreated sample. The gloss values are shown in Figure 5.7. This fact proves that the suspected cause of the gloss spike, the bright unprinted regions, is in fact not the cause of the increased gloss at 50% fill. An explanation for this observation is that the light that escapes through the unprinted regions is scattered and traveling in many different directions. The gloss meter only records light traveling in the specular direction. Therefore, while the unprinted regions may appear very bright, this scattered light does not add to the gloss of the sample.

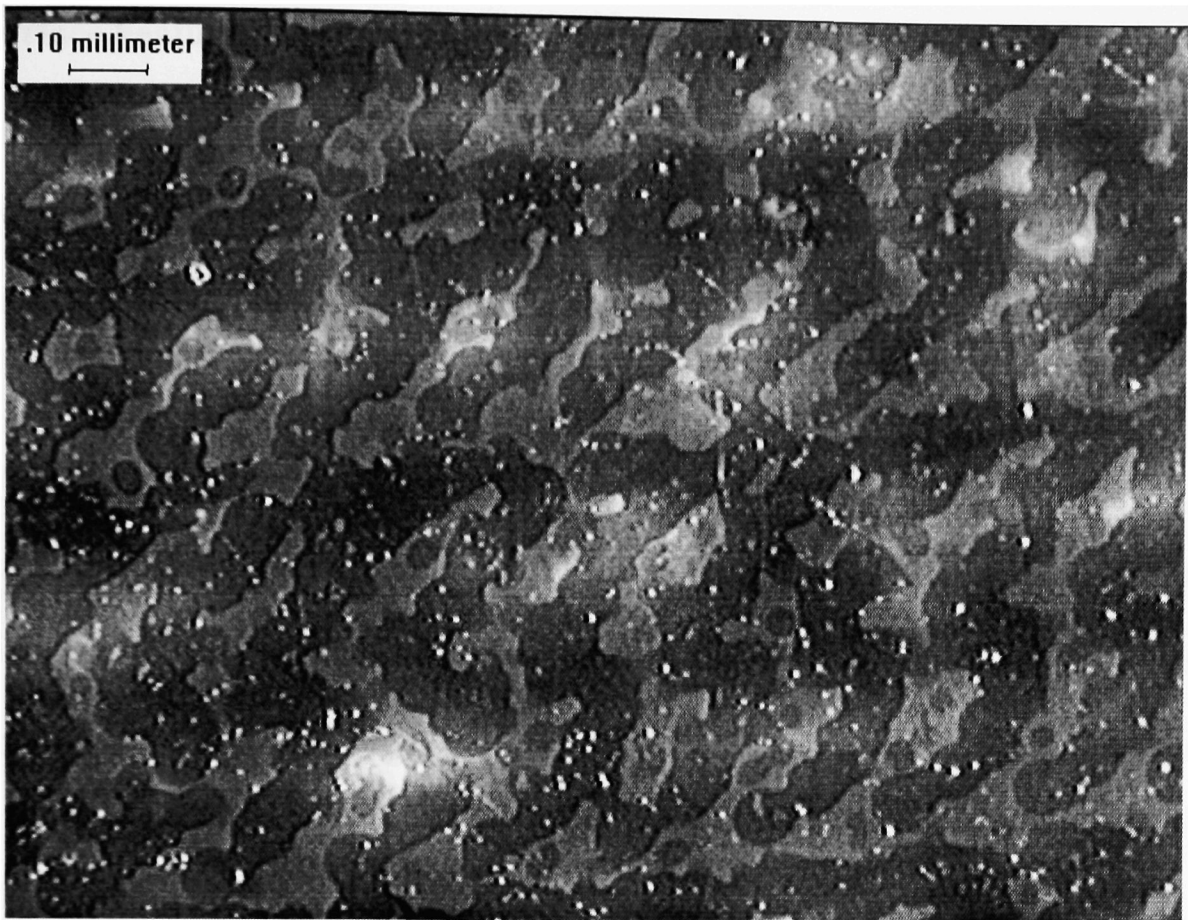


Figure 5.6. 50% ink D2 on dyed media C

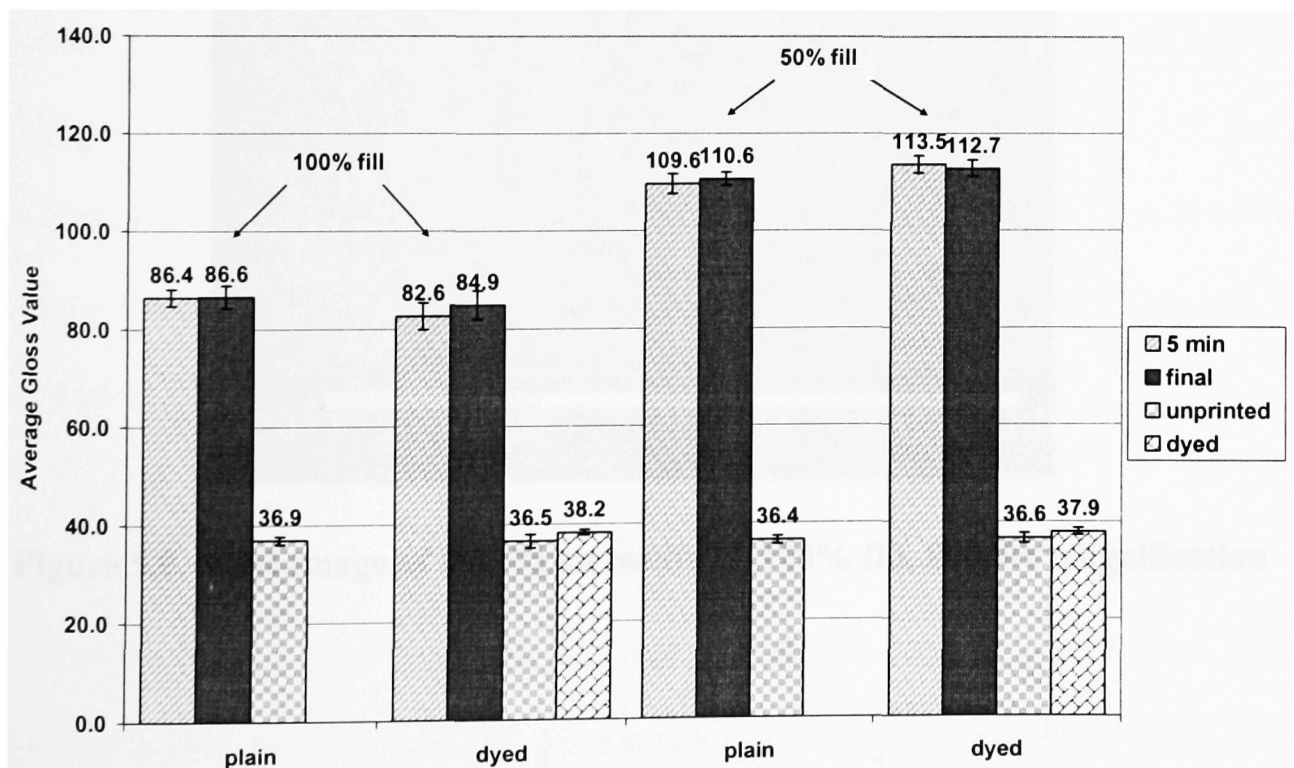


Figure 5.7 20-degree gloss results for ink D2 printed on untreated and dyed media C

5.4. Surface Features

Further investigation of ink D2 revealed more differences between samples printed at 100% and 50% fills. Scanning electron microscopy was used to obtain high magnification images of the sample surfaces. Figures 5.8 and 5.9 are SEM images of ink D2 at 100% and 50% fills, respectively. At 80000x magnification the ink pigments are visible. The striking difference in these images is the presence of relatively spheres at the surface of the 50% fill sample, Figure 5.9. These large spheres also appear to be present in the 100% fill sample, Figure 5.8, yet mostly submerged in pigments. These spheres are polymeric beads which are added to the coating as a spacer to control the sheet to sheet friction.

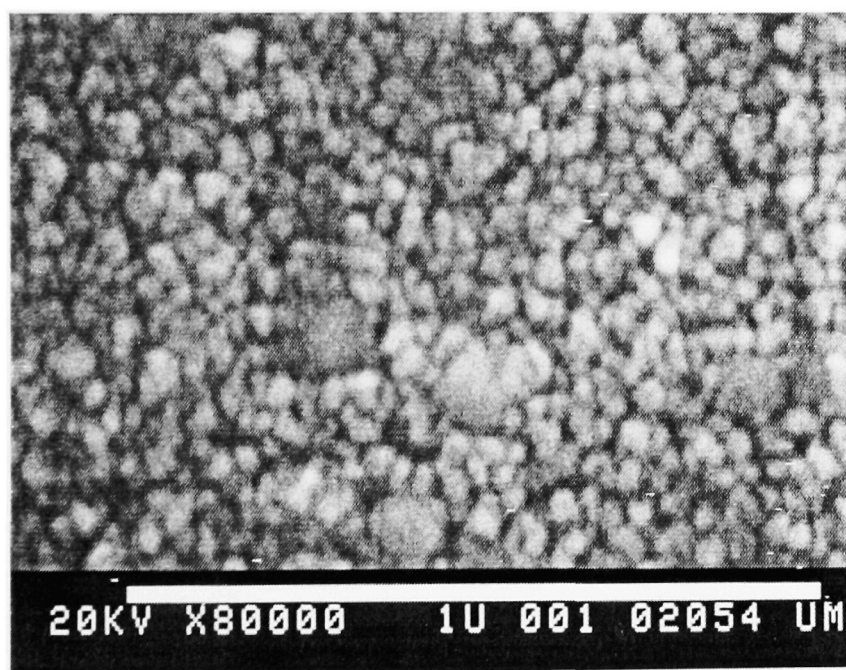


Figure 5.8. SEM image of ink D2 on media C, 100% fill, 80000x magnification

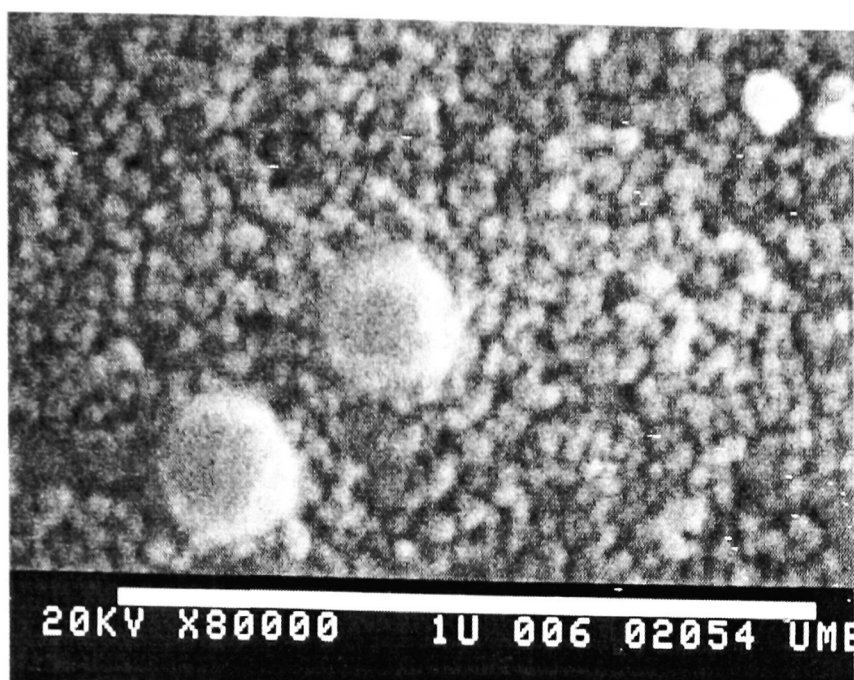


Figure 5.9. SEM image of ink D2 on media C, 50% fill, 80000x magnification

The presence of the polymeric beads at the surface of the 50% fill sample is peculiar considering the high gloss of the sample. Any particle will interact with light, however, since the concentration is so low (percent coverage), these beads will have no significant impact on gloss. The polymeric beads on the surface of the 50% fill sample may contribute a bit to the roughness of the sample, but the difference in bead location is certainly not the explanation for the large difference in gloss between the 100% and 50% fill samples.

5.5. Other Surface Treatments

Before it was discovered that the large spheres present in Figures 5.8 and 5.9 are polymeric beads, it was thought that those spheres were binder flocs. Even at that time it was realized that the supposed binder flocs were most likely not responsible for the gloss spike of ink D2, however, an experiment was conducted to confirm that belief. The

media surface was treated with a layer of binder (ink D vehicle and binder printed at 100% fill) to provide an over-abundance of binder flocs. The gloss results are shown in Figure 5.10. As expected, the gloss spike at 50% fill remained. This was thought to prove that the binder flocs were not responsible for the gloss spike. Knowing now the identity of the spheres, the results in Figure 5.10 basically conclude that the binder in general has no role in the gloss spike.

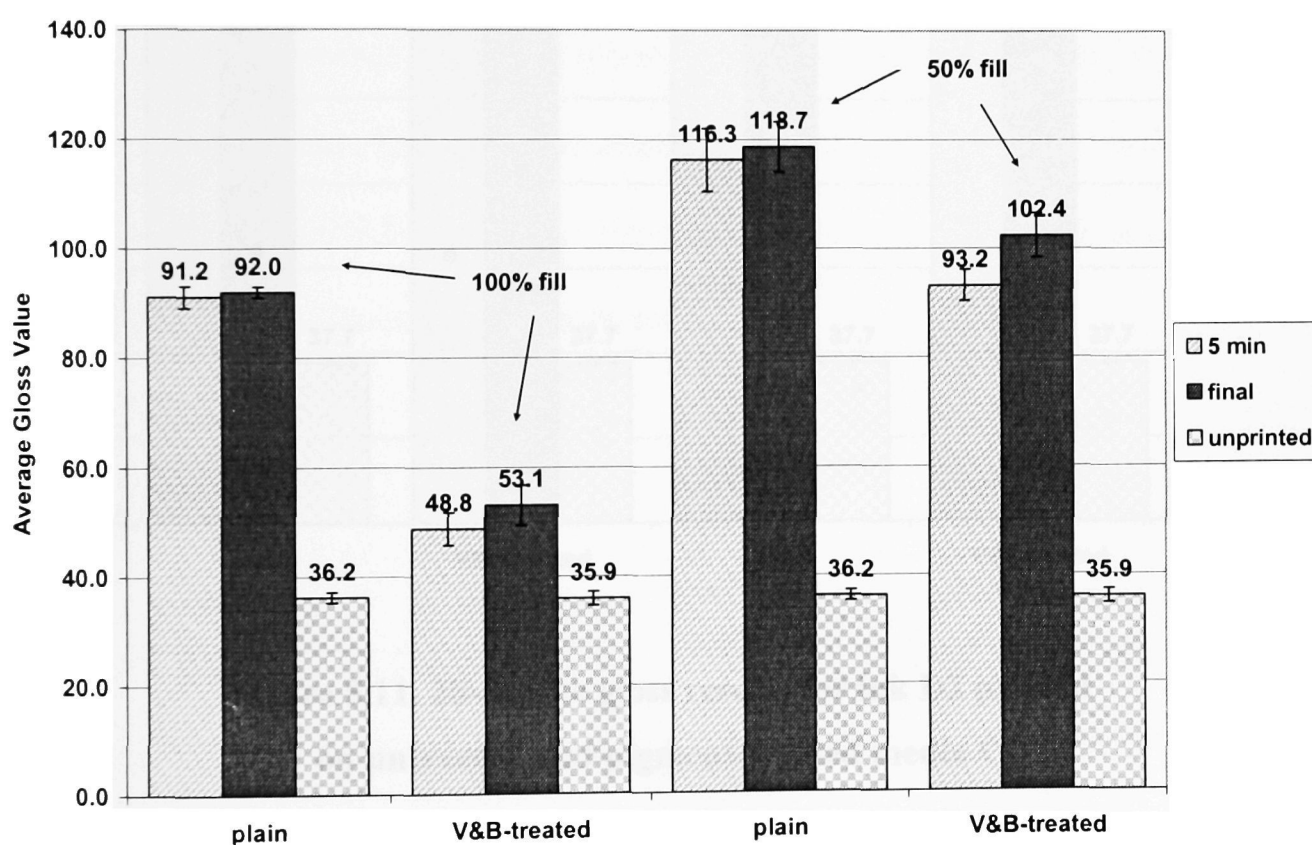


Figure 5.10. 20-degree gloss results for ink D2 printed on untreated and binder-treated media C

The final surface treatment applied to media C was a solution of ink D vehicle and pigment, printed at 100% fill. The premise of this experiment is that the secondary reflection at the ink/media interface, if present, can add to the gloss of a sample—this is depicted in Figure 5.5. The addition of a thick layer of pigment to the media surface

should absorb any light that enters it and eliminate any secondary reflection at the ink/media interface that may occur. The gloss results in Figure 5.11 show that the pigment-treatment eliminates the gloss spike at 50% fill.

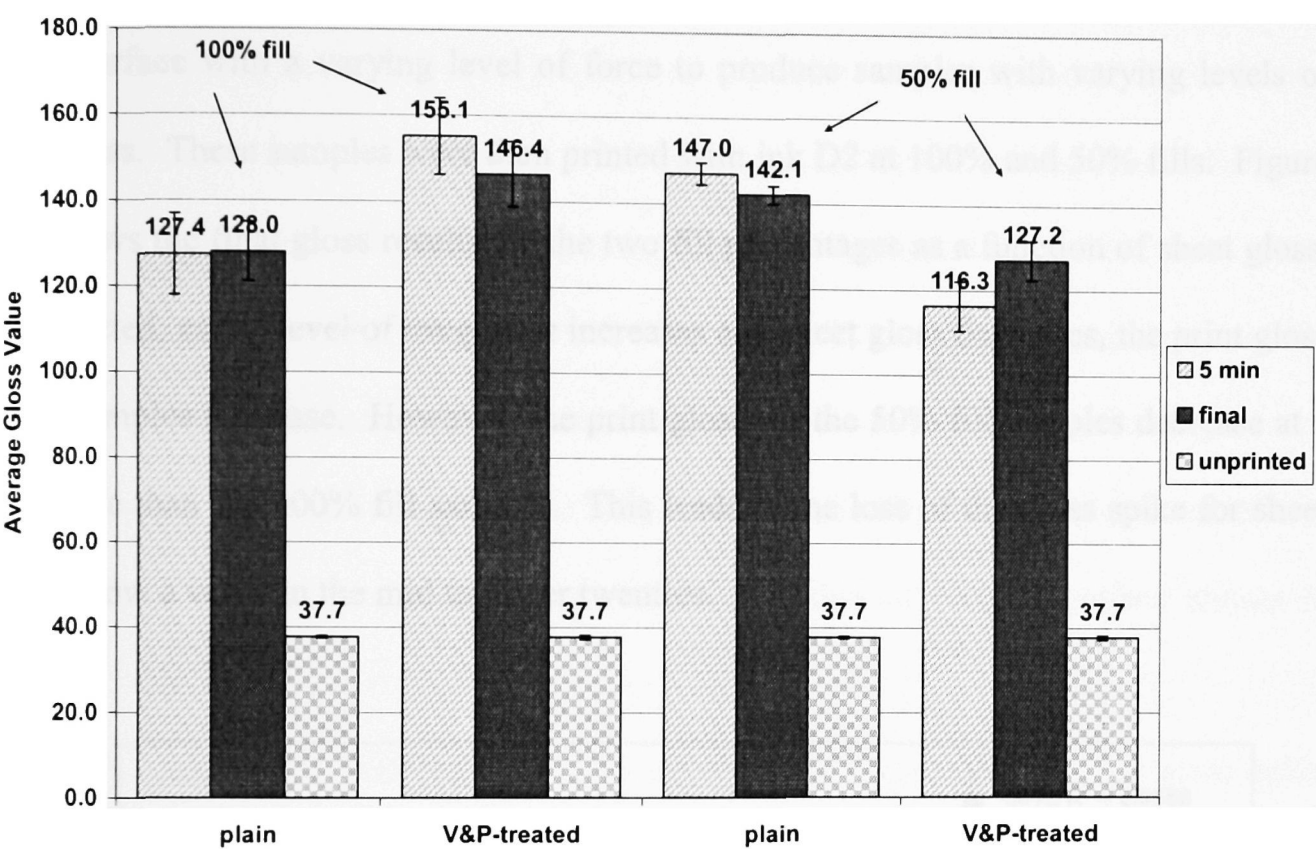


Figure 5.11. 20-degree gloss results for ink D2 printed on untreated and pigment-treated media C

The results in Figure 5.11 suggest that the secondary reflection at the ink/media interface is most likely responsible for the gloss spike. Ink D2 printed on the pigment-treated media results in a thicker layer of pigment, similar to what is found with ink D1 where there is no gloss spike.

5.6. Roughened Media Surface

One last experiment was performed to reinforce the theory that the secondary reflection at the ink/media interface is responsible for the gloss spike associated with ink D2. Samples of media C were roughened by pressing rough white plastic film against the media surface with a varying level of force to produce samples with varying levels of sheet gloss. These samples were then printed with ink D2 at 100% and 50% fills. Figure 5.12 shows the final gloss results for the two fill percentages as a function of sheet gloss. As expected, as the level of roughness increases and sheet gloss decreases, the print gloss of the samples decrease. However, the print gloss for the 50% fill samples decrease at a faster rate than the 100% fill samples. This leads to the loss of the gloss spike for sheet gloss below a value in the mid to upper twenties.

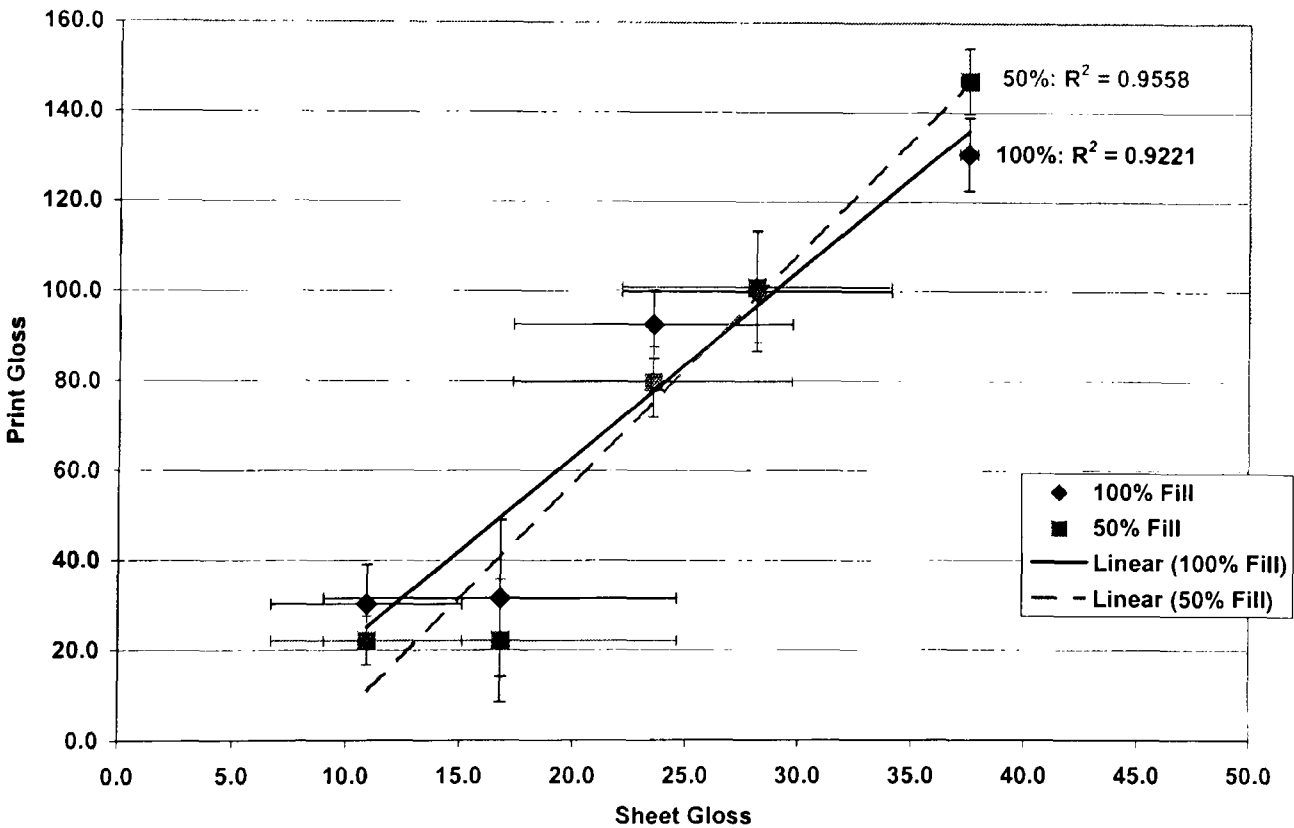


Figure 5.12 20-degree final gloss values of ink D2, 100% and 50% fill, vs. sheet gloss

The roughening of the media surface is intended to reduce the secondary reflection of the print, as depicted in Figure 5.5 (f). It was hypothesized that the high gloss of 50% fill sample is due to a high level of secondary reflection, a consequence of a lesser amount of pigment compared to ink D1 and thinner ink layer compared to 100% fill. The gloss of the 100% fill sample was expected to be more dependent on the primary reflection than the secondary reflection since the thicker ink layer absorbs more light. This experiment of media roughening validates the hypothesis. The gloss of the 50% fill sample is more dependent on the secondary reflection, therefore, as the secondary reflection is reduced, the gloss of the 50% fill samples decrease at a faster rate than that of the 100% fill samples. It is therefore concluded that the gloss spike exhibited by ink D2 is caused by the secondary reflection at the ink/media interface shown in Figure 5.5 (d).

The conclusion that the secondary reflection is responsible for the gloss spike with certain light colored inks has an important implication in ink manufacturing. To avoid the problem of the gloss spike associated with these inks, instead of using less pigment in these inks and letting the white media dilute the color, a white pigment should be used, such as TiO_2 . The white pigment should scatter light and decrease the secondary reflection. The use of a pigment like this should not be difficult and should eliminate this issue.

5.7. Summary

In this chapter, the focus of this research was narrowed to inks D1 and D2, two similar inks that behave very differently. The observed gloss spike of ink D2 at 50% fill

could not be explained in the literature, thus experiments were devised to help us understand this issue. The mystery deepened when results showed that ink D2 had a higher roughness at 50% fill than at 100% fill. The expected relationship between gloss and roughness is of course opposite to these results. Low-magnification images of these samples revealed that the unprinted regions of the 50% fill sample appeared bright. It was intuitively suspected that the bright unprinted regions were responsible for the gloss spike, however, an experiment proved that theory to be incorrect. Another difference between the 100% and 50% fill samples was observed in high-magnification SEM images. Polymeric beads, once thought to be binder flocs, were found to be located predominantly at the surface of the 50% fill sample while mostly buried in pigments in the 100% fill sample. It was explained how the high gloss of the 50% fill sample could persist despite the large surface features due to the low surface coverage of the beads. It was assumed that the differing location of the beads was not responsible for the gloss spike of ink D2.

It was hypothesized that the secondary reflection at the ink/media interface may be responsible for the gloss spike. The elements of this theory are illustrated in Figure 5.5. It was suspected that the lower level of pigment found in ink D2 compared to D1 allows more light to pass through the ink layer. At 50% fill, enough light could get through the ink layer to create an appreciable secondary reflection which adds to gloss. An experiment was conducted to test the theory and the results suggested it to be valid. A second experiment confirmed these results. It was therefore concluded that the secondary reflection at the ink/media interface is responsible for the gloss spike of ink D2 at 50% fill. To achieve light colored inks without the gloss spike problem, a solution to

this problem would be the addition of white pigments to the ink which scatter light, instead of simply using a lesser amount of the colored pigment. A white pigment such as TiO_2 is inexpensive and should pose no difficulties in an inkjet application.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

As in any adventure, one hardly ever ends up at a point where they had originally planned. New discoveries create new paths to follow. Sometimes these paths are productive and novel ideas arise. The research presented in this thesis brought forth new and exciting results. Chapter 3 detailed an investigation of the substrate's influence on gloss and the results validated a theory on fiber swelling. Chapter 4 explored new territory in looking at the influence of media surface chemistry on gloss. Chapter 5, however, became one of those new paths as the result of an unexpected discovery. The outcome of that investigation was a novel idea with an important implication in ink manufacturing.

Chapter 3 introduced some key points about gloss development and what influence the substrate itself has on gloss. Experiments showed how pigmented inks could produce much higher print gloss than dye-based inks, how gloss decreased with decreasing fill percentage, and the importance of protecting the paper fibers in paper-based media to achieve high gloss. The observed gloss development of paper-based media indicated how the unprotected paper fibers would absorb moisture and swell, distorting the coating layer and damaging gloss. It was evident that the substrate was the controlling factor in print gloss for the low-gloss media. The inks had a larger influence on gloss with the high-gloss media. The gloss development of the photo-based media, where the fibers are effectively protected, did not exhibit the decline in gloss. The gloss development of the plastic-based media was shown to be a rapid process with the final

gloss determined in just 0.1 second. This fast response is thought to be due to the small pore diameter and large pore volume of the media. The high level of gloss is achieved despite the rapid absorption rate due to the low viscosity of inkjet inks; the low viscosity allows very rapid leveling. The research discussed in Chapter 3 was fairly complete and the objectives were met. Future work could take a step beyond the basic investigation performed here and test many more inks and media. Different colored inks could be printed together to explore how they influence one another in terms of gloss.

Chapter 4 discussed the effect of surface chemistry on gloss by investigating selected chemical treatments. The key result from that chapter was that certain ions can destabilize the ink layer, forming flocs or a non-uniform pigment distribution which leads to a rough surface and lower gloss. Some inks were affected by the ion treatments while others were unaffected. The different ions affected gloss to a varying degree. The Ca^{2+} and Na^+ ions affected gloss most harshly. Aluminum Chlorohydrate was expected to also affect gloss harshly, however, this was found not to be the case. Boric acid had very little effect on gloss for all inks. Decreased absorption rate may allow more pigment flocculation to occur due to increased interaction time between pigments and ions; however, this effect is secondary to the fact that certain inks can be destabilized while others cannot. Unfortunately, time limitations only allowed a small, strategic sampling of chemicals. Much more research should be devoted to this subject as many unanswered questions remain. Such as why an ion may affect certain inks harshly yet have no effect on others, or why ACH did not affect the inks as expected. Testing new ions and new inks may reveal even more questions.

Chapter 5 explored the gloss spike mystery that was discovered with ink D2. This is a problem in ink manufacturing because one issue that can cause a decrease in quality of a printed sample is different gloss values of different regions of the image. Many experiments were performed to find the cause of the gloss spike, and it was concluded that the secondary reflection at the ink/media interface is most likely responsible. To produce light colored inks, such as the grey ink D2, ink manufacturers often just use less pigment in the formulation. With less pigment to absorb and scatter light, in the case of printing at 50% fill the secondary reflection becomes appreciable in terms of gloss. It was suggested that instead of using less pigment to achieve light colored inks, manufacturers could add a white pigment such as TiO_2 which would scatter light and reduce the secondary reflection. Future work could test and refine this proposed solution.

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APPENDIX

Visual Basic Data Acquisition Code

This computer program was used with the dynamic gloss apparatus described in chapter 2.2. It was generously provided by Prof. John C. Hassler, a now retired faculty member of the Chemical Engineering department at The University of Maine.

```
' PrintTest – Author: Prof. John C. Hassler, (The University of Maine)
' To use the printer control file, I had to
' read it in in BINARY, and then use the WIN32 API
' to bypass the printer driver. The API methods are from
' Knowledge Base articles Q154078 and Q138594
' This version includes the ComputerBoards code.
```

Option Explicit

```
' --- for the WIN32 API calls ----\
```

```
' raw print spool API
```

Private Type DOCINFO

 pDocName As String

 pOutputFile As String

 pDatatype As String

End Type

Private Declare Function ClosePrinter Lib "winspool.drv" (ByVal _

```

    hPrinter As Long) As Long

Private Declare Function EndDocPrinter Lib "winspool.drv" (ByVal _
    hPrinter As Long) As Long

Private Declare Function EndPagePrinter Lib "winspool.drv" (ByVal _
    hPrinter As Long) As Long

Private Declare Function OpenPrinter Lib "winspool.drv" Alias _
    "OpenPrinterA" (ByVal pPrinterName As String, phPrinter As Long, _
    ByVal pDefault As Long) As Long

Private Declare Function StartDocPrinter Lib "winspool.drv" Alias _
    "StartDocPrinterA" (ByVal hPrinter As Long, ByVal Level As Long, _
    pDocInfo As DOCINFO) As Long

Private Declare Function StartPagePrinter Lib "winspool.drv" (ByVal _
    hPrinter As Long) As Long

Private Declare Function WritePrinter Lib "winspool.drv" (ByVal _
    hPrinter As Long, pBuf As Any, ByVal cdBuf As Long, _
    pcWritten As Long) As Long

' Performance counter API's

Private Declare Function QueryPerformanceCounter Lib "kernel32" _
    (lpPerformanceCount As Currency) As Long

Private Declare Function QueryPerformanceFrequency Lib "kernel32" _
    (lpFrequency As Currency) As Long

Private secFreq As Currency, secStart As Currency, secEnd1 As Currency

```



```

' --- end Winapi declares ---

' --- begin CB declares ---

Private ULStat As Integer

Private ChanNo As Integer, CBCount As Long

Const BoardNum As Integer = 0

Const CBRange As Integer = UNI10VOLTS

' --- end CB declares ---


' ***** set the rate and number of points here *****

Const Msec As Single = 1

Const NumPoints As Integer = 30000

' *****

Private InDat(NumPoints) As Integer

Private Ix As Integer

Private BinData(10000) As Byte, bTemp As Byte

Private Sub cmdExit_Click()

Unload Me

End

End Sub

-----

Private Sub cmdFileOpen_Click()

Dim FName As String, TmpString As String, FilHandle As Integer

Dim i As Integer, j As Integer

```

```

With cdbFile

.InitDir = "C:\HP Printer Files\"

.ShowOpen

FName = .FileName

End With

If FName = "" Then

    txtShow.Text = "No file specified."

    Exit Sub

Else

    txtShow.Text = FName & vbCrLf

    FilHandle = FreeFile

    ' Must read file as binary since it has control char.

    Open FName For Binary As FilHandle

End If

Ix = 0

txtShow.Text = txtShow.Text & "Begin input loop." & vbCrLf


Do While Not EOF(FilHandle)

    Ix = Ix + 1

    Get #FilHandle, , BinData(Ix) ' Binary, one byte at a time

    DoEvents

Loop

txtShow.Text = txtShow.Text & "Finished reading." & vbCrLf

```

```
txtShow.Text = txtShow.Text & "Number of bytes =" & Ix & vbCrLf
```

```
Close FilHandle
```

```
End Sub
```

```
-----  
Private Sub cmdPlot_Click()
```

```
' Collect and plot the data
```

```
picPlot.Cls
```

```
Dim MaxX As Integer, MaxY As Integer
```

```
MaxX = picPlot.ScaleWidth
```

```
MaxY = picPlot.ScaleHeight
```

```
Dim i As Integer, X As Integer, Y As Integer
```

```
Dim px(NumPoints) As Integer, py(NumPoints) As Integer
```

```
For i = 1 To NumPoints
```

```
    px(i) = (CSng(i) * MaxX / NumPoints)
```

```
    py(i) = (1 - InDat(i) / 4095) * MaxY
```

```
    picPlot.PSet (px(i), py(i))
```

```
DoEvents
```

```
Next i
```

```
End Sub
```

```
-----  
Private Sub cmdPrint_Click()
```

```
Dim i As Integer
```

```
Dim lhPrinter As Long
```

```

Dim lReturn As Long

Dim lpcWritten As Long

Dim lDoc As Long

Dim sWrittenData As String

Dim MyDocInfo As DOCINFO

lReturn = OpenPrinter("HP DeskJet 970C Series", lhPrinter, 0)

If lReturn = 0 Then

    MsgBox "The Printer Name you typed wasn't recognized."

    Exit Sub

End If

MyDocInfo.pDocName = "AAAAAAA"

MyDocInfo.pOutputFile = vbNullString

MyDocInfo.pDatatype = vbNullString

lDoc = StartDocPrinter(lhPrinter, 1, MyDocInfo)

Call StartPagePrinter(lhPrinter)

txtShow.Text = txtShow.Text & "Sending data to printer." & vbCrLf

For i = 1 To lx

    bTemp = BinData(i) ' send one byte at a time by reference

    lReturn = WritePrinter(lhPrinter, bTemp, _

        Len(bTemp), lpcWritten)

Next i

lReturn = EndPagePrinter(lhPrinter)

```

```

lReturn = EndDocPrinter(lhPrinter)

lReturn = ClosePrinter(lhPrinter)

txtShow.Text = txtShow.Text & "Finished." & vbCrLf

Call GetData

End Sub

```

```

Sub GetData()

txtShow.Text = "Start Getdata." & vbCrLf

Screen.MousePointer = vbHourglass

DoEvents

CBCount = NumPoints

Dim i As Integer, Delta As Currency

' Uses Windows API call to the performance counter.
' Appears to be good for sub-msec resolution. This
' gives a very accurate sampling at 1 msec.

Delta = Msec * secFreq / 1000

' wait until printer does something

Dim Temp1 As Integer, Temp2 As Integer

Temp2 = 0

ULStat = cbAIn(BoardNum, ChanNo, CBRange, Temp1)

Temp1 = Temp1 + 200

Do While Temp2 < Temp1

```

```

    ULStat = cbAIn(BoardNum, ChanNo, CBRange, Temp2)

Loop

' now collect data

    QueryPerformanceCounter secStart

    secEnd1 = secStart + Delta

For i = 1 To CBCount

    ULStat = cbAIn(BoardNum, ChanNo, CBRange, InDat(i))

    Do

        QueryPerformanceCounter secStart

        Loop Until secStart > secEnd1

        secEnd1 = secEnd1 + Delta

    Next i

    txtShow.Text = txtShow.Text & "End Getdata." & vbCrLf

    DoEvents

    Screen.MousePointer = vbDefault

End Sub

-----

Private Sub cmdSave_Click()

    Dim FName As String, TmpString As String, FilHandle As Integer

    Dim i As Integer, j As Integer

```

```

AutoRedraw = True

With cdbFile

.InitDir = "\\Grad01\PSSP\amol\Project\gloss\newprinter"

.ShowSave

FName = .FileName

End With

If FName = "" Then

    txtShow.Text = "No file specified."

    Exit Sub

Else

    txtShow.Text = FName & vbCrLf

    FilHandle = FreeFile

    Open FName For Output As FilHandle

End If


For i = 1 To NumPoints

    Print #FilHandle, InDat(i)

Next i

txtShow.Text = txtShow.Text & "Finished saving." & vbCrLf


Close FilHandle

End Sub

```

```
Private Sub Form_Load()
```

```
AutoRedraw = True
```

```
lblHeader.Caption = "HP Printer Test V. 1.10"
```

```
ULStat = cbDeclareRevision(CURRENTREVNUM)
```

```
ULStat = cbErrHandling(PRINTALL, DONTSTOP)
```

```
    If ULStat <> 0 Then Stop
```

```
QueryPerformanceFrequency secFreq ' frequency of timer
```

```
End Sub
```


BIOGRAPHY OF THE AUTHOR

Aaron W. Clark was born in Bangor, Maine on June 12, 1979. He was raised in Hermon, Maine, where he received his primary and secondary education. He enrolled at the University of Maine in 1997 where he obtained the Bachelor of Science in Chemical Engineering and Bachelor of Arts in Mathematics in 2002. After graduation, he remained at the University of Maine to begin his graduate study in Chemical Engineering. He is a candidate for the Master of Science degree in Chemical Engineering from The University of Maine in August, 2004.