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Enhanced Print Performance of Water-Based Rotogravure Inks through Rheological Balance

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ENHANCED PRINT PERFORMANCE OF WATER-BASED ROTOGRAVURE INKS THROUGH RHEOLOGICAL BALANCE

by

Rurou Mai

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Rurou Mai

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Rurou Mai, M.S.

Western Michigan University, 2006

Water-based inks have been of more and more interest to the printing and ink industry. Compared with solvent-based inks, water-based inks have more complex formulations because of their higher surface tensions, lower drying speed, foaming problems, pH balance, and different rheological properties. This work explores the significant effects of various rheology modifiers, including non-associative and associative thickeners, on the rheological properties of a water-based rotogravure ink system. Particular emphasis is given to thickening efficiency, pH stability, particle size, system compatibility, temperature stability, and printability on vinyl substrates. Wire-wound lab rods and a Moser Sheet-fed Gravure Proofing Press were employed to produce printed samples for characterizing the performance of the formulated inks. The purpose of these investigations was to acquire a better understanding of the effect of rheology modifiers' on the water-based ink system, as well as to provide useful information for rheology modifiers selection in order to achieve better print quality for water-based ink systems.

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CHAPTER I

INTRODUCTION

Rotogravure is a very old and widely utilized printing process that has been employed in numerous applications, such as publication and packaging. Over the years, gravure has also become well-established in other less known areas including decorative laminates, vinyl products, and commercial wall covering products.

Prior to the environmental concerns for VOCs (volatile organic compounds), printers utilized solvent-based inks, which provide excellent print quality at a low cost. However, solvent-based inks contain organic solvents such as alcohols, esters, ketones, and toluene, etc. Researchers have shown that the emission of VOCs leads to the formation of photochemical smog (ozone) by reacting with oxides of nitrogen, other pollutants and sunlight. Photochemical smog affects human health [Annon[1], 2005].

Once the concerns were raised, governments began to place stricter environmental regulations on printers, requiring them to reduce and finally eliminate the emission of VOCs. This resulted in a ripple effect throughout the supply chain. Printers began to explore the use of alternative technologies, and ink formulators started to create water-based systems with zero, or near zero, percent VOCs. Through decades of work, many areas have now been successfully transitioned from solvent-based inks to water-based inks. According to the National Association of Printing Ink Manufacturers' (NAPIM), water-based inks have made major inroads in the flexo packaging market. While there has been some entry into the gravure market, water-based inks still have made little headway. NAPIM reported that in 1999, water-based gravure inks held five percent of the packaging market [Annon[2], 2000].

One of the reasons for the slow progress in water-based gravure ink development is its slower drying speed, which limits the print speed in rotogravure. Another reason is the difference in chemistry between these two categories of materials. For a solvent-based ink, the resins not only act as the vehicle for the pigment, but also build the rheology of the system that can be easily controlled during press runs. With the integration of water, the chemistry is drastically shifted: the rheology of the system is no longer controlled by the primary polymeric component in the ink and is therefore unstable during the printing process; thus, rheology additives must be employed in order to achieve product consistency. Also, the inherent higher surface tension of the water-based system leads to difficulties in replacing the solvent-based system.

The aim of this research is to investigate the rheological properties of water-based gravure inks based on acrylic or polyurethane chemistry for vinyl wall covering products, study the effect of different rheological modifiers on the water based ink system, and provide guidelines for rheology modifier selection.

CHAPTER II

LITERATURE REVIEW

Overview of Rotogravure Printing

Rotogravure is typically designed for repetitive printing functions associated with high print quality, complex graphic demands, and long runs such as publication and packaging applications.

The rotogravure printing unit contains several fundamental parts: the engraved cylinder, the impression roller, the doctor blade, and the ink pan [Annon[3], 2004].The engraved cylinder functions as an ink acceptor, where ink is applied onto its surface by spraying or immersion. It is made in a three-layer structure with an iron core that provides mechanical stability, a copper layer where the image will be engraved, and an outside layer made of chrome to enhance the resistance to abrasion. Images are engraved into cells to various depths on the surface of the cylinder by chemical etching, electromechanical engraving, or laser engraving. The doctor blade is used to eliminate the excess ink applied onto the engraved cylinder and to ensure that the ink is remaining only in the engraved cells. The rubber coated impression roller brings the substrate in contact with the inked engraved cylinder resulting in ink transfer and helps move the substrate through the press.

Rotogravure printing is used in three main product areas: publication, packaging, and product gravure. Publication printing includes magazines, catalogs, newspaper inserts, and other commercial advertisements. Packaging includes the production of flexible packaging, such as flexible food packages, folding cartons, labels and gift wrappers. The product gravure describes everything other than what cannot be classified as publication or packaging printing. Typical of these products are curtains, tablecloths, ceiling tiles, vinyl fabrics for outdoors furniture, and wall and floor coverings.

Rotogravure is always a great choice for printers; it is the highest speed and most consistent process of all. Today, technological advances in gravure have helped it become a more competitive process. Gravure can print very fine screen resolution and has the ability to print fine type and line work, with even greater improvements coming via laser engraved cylinders as well as using extremely accurate electromechanical engraving. It has excellent reproducibility independent of operators' skills due to the simplicity of the process. Providing the automatic wash-up system that allows for faster job changeovers, the gravure process is more flexible than ever and now is considered for high-quality, short-run jobs. Finally, the latest development is the lightweight, chrome-coated, nickel sleeve systems in which sleeves are engraved and floated directly onto a gravure cylinder [Tremper, J. et al, 2002]. This technology solved the weight issues associated with traditional gravure cylinders and lowered the cost of shipping and handling.

Solvent-based Inks Vs. Water-based Inks

Printing inks have been known for several centuries. An ink is a liquid containing various pigments and/or dyes used for coloring a surface to render an image or text. Solvent-based inks have been used most extensively in gravure printing during the past decades until the Environmental Protection Agency issued regulations for clean up and to protect the environment. These systems contained VOCs as a suitable solvent to formulate printing inks for desired properties such as adhesion to low surface energy substrates including plastics and metallized films, water and alcohol resistant properties, rub fastness, press stability, print quality, and fast drying speed. In the late1970s, environmental pressures to reduce solvent emissions provided a stimulus to packaging converters and ink suppliers to develop water-based technology. However, the transition from solvent-based to water-based system would be a difficult task. Though a lot of the required properties have been successively achieved in the solvent-based inks, there are some difficult areas for water-based inks. First, water has a much higher surface tension in comparison to organic solvents. This results in poor ink transfer for water-based inks. Also, water-based inks tend to foam more than solvent-based inks. Foaming becomes an issue during press runs, where print quality may deteriorate. Another problem is that the viscosity of water-based inks is less stable to the condition changes experienced during press runs. A drop in the pH can cause an increase in viscosity; on the other hand, a rise in temperature can result in a decrease in viscosity of the inks. These changes in turn lead to color inconsistency or poor performance during printing [Hrehorova, E et al, 2005].

To overcome all of these problems, ink formulators have needed to add many different additives to the water-based systems. This leads to a more complicated formulation in water-based inks. Table 1 summarizes the differences in formulations of solvent-based and water-based inks.

Table 1

Solvent-based ink and water-based ink composition

Material employed	Solvent-based	Water-based
Polymer(s)	+	+
Solvent(s)	+	+
Rheology additive	-	+
Coalescent	-	+
Wetting additive	-	+
De-foamer / Anti-foamer	-	+
Wax	+	+
Dispersing additive	-	+
Emulsifier	-	+
Flattening additive	+	+

History of Water-based Inks Manufacture

As we know, consistent color and graphic reproduction, excellent chemical and physical properties, easy control of ink application, and fast drying speed of solvent-based inks contribute to excellent quality and fast printing speed of gravure. For water-based inks, improvements in ease of use, performance factors, and chemical resistance properties have been critical in maintaining this advantage of gravure printing. To fulfill these requirements, water-based inks have come a long way.

The 1970's were the trial years for water-based technology. Due to the limited raw materials available at the time, these early water-based inks could include as much as 20% solvent, and they had many shortcomings such as unacceptable odor, viscosity instability with some pigments, poor water resistance of dried inks, poor printability, foaming, and substrate wettability problems. Significant progresses were made in water-based inks during 1980's with the development in polymer technology and other areas. The introduction of new resins provided better gloss, adhesion, and water resistance and improved performance of water-based inks; various new emulsions offered improved drying speed; new surfactants allowed water-based inks to be formulated with low surface tension and improved flow properties; new defoamers were able to reduce the level of foaming. The quality of water-based inks continued to improve during the last decade. Water-based inks today have less than 5% VOCs, will not foam, will be pH stable, and will have good gloss, water resistance, rub resistance, and adhesion [Podhajny, R.M., 2003]. They have penetrated into all printing sectors and dominated in the corrugated, folding carton, multi-wall bags, and low to medium film flexography market, although they are used less in rotogravure printing due to the limitation of dry speed and press stability.

Printability of Water-based Gravure Inks on Non-paper Substrates

Substrate wetting is defined as the replacement of adherent air at the substrate surface by a liquid coating or ink material [Helien, W., 2003]. Fluid surface tension is determined by the intermolecular force of attraction between adjacent molecules, and surface tension determines whether an ink, coating, or adhesive will wet and spread over, or retract from, a solid surface [Janule, V.P., 2001]. If a liquid is to wet a solid surface, its surface tension must be lower than the surface energy of the solid. As shown in Table 2, water has a much higher surface tension than that of the polymer films such as LDPE, polyester, and PVC. In such cases, wetting becomes an issue for water-based inks, and wetting defects such as cratering, crawling, Bernard cells, or poor adhesion can occur.

However, the most important property in designing and measuring formulations is dynamic surface tension, rather than equilibrium surface tension, since dynamic surface tension directly impacts the quality of spreading and adhesion [Janule, V.P., 2001]. In a highly dynamic application process such as the gravure printing process, even when the surface energy of substrate is relatively high, spreading and adhesion might still have problems if the wetting is too slow. Uneven ink-lay, poor ink transfer, or some other print defects may result.

The printability of water-based inks on non-porous substrates is poor due to their high surface tension. Another reason is the low surface energy smooth surface of non-paper substrate. Two methods have been used to improve printability of water-based inks on non-porous films: raising the surface energy of the substrate, or lowering the surface tension of the ink. Raising the surface energy of the substrate can be done through cleaning, which removes contaminants, or through surface treatment such as corona discharge, flame treatment, and caustic wash. These treatments change the chemical compositions and morphology of the surface, and enhance the adhesion properties and printability, since adhesion occurs through chemical interactions as well as mechanical interlocking between the surface and inks. Lowering the surface tension of the inks can be achieved by using additives made for this purpose.

Table 2

Surface tensions of some solvents and surface energies of some polymer films at 293K

Solvents / polymers	Surface tension mN/m	Surface energy mN/m	
		Untreated	Treated
Water	72.6	-	-
Methanol	22.6	-	-
Ethanol	22.3	-	-
Propan-2-ol	21.4	-	-
Ethyl ethanolate	23.9		
LDPE/HDPE	-	31	38-40
OPP 29	-	36-40	
Polyester	-	43	48-54
Nylon 6,6	-	46	-
Polyvinylchloride (PVC)	-	41.9	-
PTFE	-	19	-

The printability of an ink system on a particular substrate can be predicted by measuring the dynamic contact angle. The contact angle is measured from the solid-liquid interface and through the liquid to the tangent drawn at the solid interface. The dynamic contact angle is the contact angle

[Rebros M., et al, 2006] measured as a function of time, which indicates the spreading of the ink drop on a specific surface. This method is particularly suitable for comparing the surface tensions of aqueous solutions of various surfactants, or of clear solvent-borne coatings, but in some cases do not give reliable data for pigmented systems because the presence of pigment hinders lamella stability.

Water-based Gravure Inks Requirements

There are some basic and fundamental requirements for water-based gravure inks considering their press properties and end-use properties. For example, wall covering gravure printing is generally performed on vinyl surfaces, and it requires the printed patterns to be reproduced repetitively. Therefore, water-based inks for this function must meet the following requirements.

- Health and safety requirements and low odor
- Good print quality
- Diluteable
- High color strength
- Good ink transfer and flow properties
- Non-foaming
- pH stability and good press stability
- Good resolubility
- Ease of de-inking
- Fast drying
- Adequate adhesion to a particular substrate
- Good water resistance; toughness and rub fastness of the print

Components of Water-based Ink Formulations

There are three basic ingredients in a water-based gravure ink: colorant, vehicle, and additives. These components impart color and adhesion and meet the necessary requirements of the inks. Some components and their functions in water-based systems are given in Table 3. Each of them will be discussed in detail further.

Table 3

Components of water-based inks used in gravure printing

Components	Functions	Percentage (%)	Literature source
Colorants: Organic pigments Inorganic pigments Dye Metallic pigments	Impart colors	 9-10 20-30	[Kirshnan, et al, 1999], [Wallstrom, E. et al, 1996], [Krishnan, et al, 1992], [Batlaw, R. et al, 1995]
Resins / Polymers: Water-soluble polymers Polyvinyl alcohol (PVA) Acrylic copolymers Emulsions: Acrylic copolymers Polystyrene polyester Styrene-acrylic Polyurethane Vinyl chloride-acrylate	 Pigment dispersion Impart adhesion rheology control	 5-30 5-50	[Krishnan, et al, 1999], [Wallstrom, E. et al, 1996], [Krishnan, et al, 1992], [Batlaw, R. et al, 1995]
Additives Wax De/Anti-foamers Wetting agents Rheology modifiers	 Rub resistance Foaming control Pigment dispersion Rheology modification	 0.01-10 0.01-5 0.01-5 0.01-5	[Kirshnan, et al, 1999], [Wallstrom, E. et al, 1996]
Coalescents Alcohol Alkaline material	Improve film forming	< 5%	[Kirshnan, et al, 1999], [Wallstrom, E. et al, 1996]

Colorant

The colorant imparts color to a surface. The colorant used in water-based gravure inks can be organic pigments, inorganic pigments, metallic pigments, and dyes. Organic pigments are those which can be derived form carbon-bases materials, and inorganic pigments contain no carbon atoms. A generic name and constitution number is given to each of the pigments according to their chemical composition, hue, and the sequence in which the color was registered, using the international Color Index System developed by the Society of Dyers and Colorists (SDC) and the Association of Textile Chemists and Colorists (ATCC) [Laden, P., 1997]. Careful and proper selection of pigments for each water-based system can convey better color strength, viscosity stability, and print gloss to the inks.

Vehicle

The vehicle is the liquid portion of the ink, which contains resins, polymers, drying oils and solvents. These compositions are the backbone of any ink system that determine the ink film's stiffness, drying rate of inks, adhesion to a particular substrate, print gloss, resistant properties, and appropriateness to a particular printing process. Their main functions includes: disperses pigment to develop color strength, gloss, and transparency of inks; controls flow; binds and carries pigments to substrates through a particular printing process; and forms a continuous film on the printed surface.

Usually, two or more polymers are combined to capture the desired properties or applications [Krishnan et al, 1999]. Polymers utilized in water-based formulations can be divided into two groups: polymer solutions and polymer emulsions.

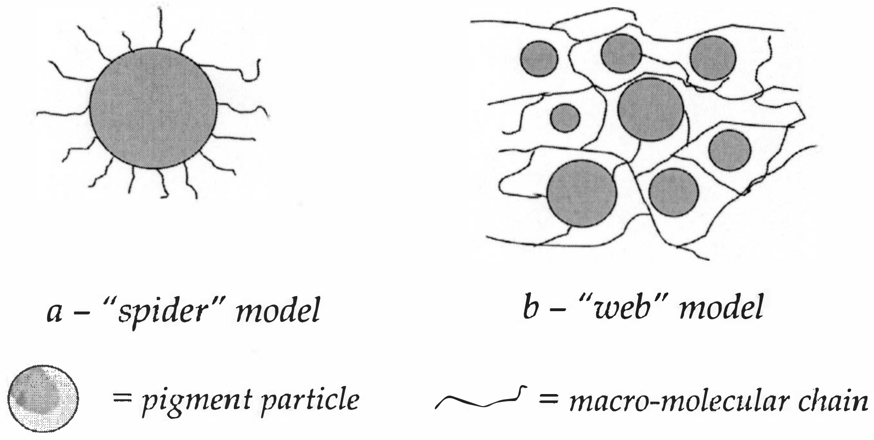
Polymer Solutions

These polymers produce a clear solution in an aqueous medium and do not scatter light. During the drying process, the aqueous phase evaporates, and a compact film is developed as a result of the mobility, flexibility and the entanglement of the lengthy polymer molecules [Sharma M.K., 1991]. Polymer solutions can be classified into three categories:

- Water-Soluble polymers
- Acid-Soluble polymers
- Alkaline-Soluble polymers

Water-soluble polymers are polymeric materials that dissolve and/or swell in water. These include the naturally available polymers such as starches, alginates and dextrins, and the synthetic polymers polyvinyl alcohol (PVA), polyacrylamides (PAA), and polyvinyl methyl ethers (PVME), etc. Acid-soluble polymers are materials whose compositions allow them to dissolve and/or swell in an acidic medium. This category includes acrylate copolymers. Alkaline-soluble polymers dissolve and/or swell in water in the presence of an alkaline substance with a pH greater than 7. This group includes styrene-maleic copolymers, acrylic copolymers, shellac, and acidic polyesteramides.

Polymer solutions are non-film formers and poor drying materials, but they enhance the ability of water to wet the pigment particles, and thus improve pigment dispersion and create a glossy film The complete wetting out of the primary sized pigment particles mostly depends on the interaction between the pigment particles and the binder system. The chemical nature of resins affects the efficiency and quality of the pigment dispersion. This can be illustrated in two models: "spider" and "web" model. The schematic illustration for the two mechanisms is shown in Figure 1. When resin precursor consisting of linear and relatively small macromolecules is involved, pigment particles are likely to have one end of the molecular chains of the resin precursor attached to their surface while have the other end of the molecular chains of the resin precursor extending away from the pigment particles forming the "spider" system. On the other hand, when the resin precursor is composed of highly branched, relatively large macromolecules, the pigment particles are likely to be embedded in a network forming the "web" system. It is likely that a "spider" system will be easier to disperse than a "web" system because external mechanical energy is easier to direct into pigment particles in the "spider" system, but the "web" system is better for storage stability.



a – "spider" model

b – "web" model

Figure 1. "Spider" and "Web" model of pigment dispersion system [Lin, L., 2003]

Polymer Emulsions

Polymers of this group are water immiscible and suspended in an aqueous medium in the form of fine particles forming a colloidal system. These emulsions appear translucent or milky, depending on the size of their particles. Aqueous polymer emulsions developed for water-based coatings, paints, and inks are usually prepared by an emulsion polymerization process. This group includes acrylic copolymers, polystyrene, styrene-acrylic copolymers, vinyl acetate copolymers, and polyurethanes. They are usually 30-55% solid in an aqueous medium with a relatively low viscosity. This high solid content at low viscosity provides a high coating weight deposited from a relatively thin film.

Polymer emulsions are film formers. They provide adhesion to substrates and give the ink film toughness, resistance properties, and durability. For example, in water-based formulations, polymer emulsions do not wet pigments, but they play an important role in the film forming mechanism. This process is illustrated in Figure 2. During the drying process, the dispersed polymer particles get closer due to evaporation of water. Finally, these polymer particles touch each other, and under suitable conditions, the particles fuse to form a continuous film [Sharma M.K., 1991].

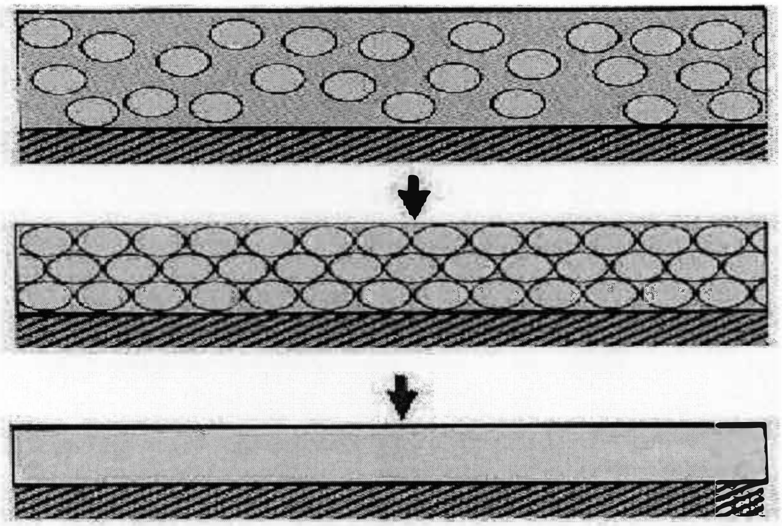


Figure 2. Schematic of film forming process [Annon[5], 2000]

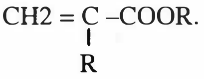
Acrylic Chemistry

Acrylic polymerization techniques have evolved over the past several decades to encompass a wide array of procedures and composition combinations that impart very specialized performance attributes to water based inks and coatings [Laden, P., 1997]. Acrylic polymers cover a wide range of physical properties, depending on the monomers selected and the methods of polymerization. When designing polymers for high speed gravure, end use properties such as rewettability, dry speed, printability and high shear rheology must be considered [Laden, P., 1997]. The ability to remain stable when combined with other polymers and ink ingredients is also an important performance criterion for acrylic polymers.

Table 4

Monomers used for polymers preparation [Sharma M.K., 1991]

Monomers	Glass Transition Temperature (Tg °C)
Methyl Acrylate	9.0
Butyl Methacrylate	20.2
Vinyl Acetate	28.0
Styrene	100.
Methyl Methacrylate	105.5
2-Ethylhexyl Acrylate	-60.0
N-Butyl Acrylate	-56.5
Ethyl Acrylate	-24.4

Acrylic chemistry starts with the basic acrylic formula:  $\mathrm{CH2} = \underset{\underset{R}{|}}{C} - \mathrm{COOR}$. This vinyl type monomer is capable of undergoing a number of molecular changes, and they are all characterized by the fact that they have two reactive groups, the carbon- carbon double bond and the end group, which may be a carboxyl, nitrile, ester, and aldehyde, etc. These reactive groups can react quite easily with other materials and form monomers used to prepare polymers for different end uses. Some of the monomers utilized in polymer preparation are listed in Table 4. These monomers can combine with themselves through polymerizations, which react at the place of their double bonds. This process results in a much higher molecular weight than the monomer, depending on the condition of polymerization and the requirement of its end use.

Polymerization in acrylic chemistry can be classified into three categories:

- Polymerization in bulk
- Polymerization in solution
- Polymerization in heterogeneous systems

Bulk polymerization is generally used to make cast rods, sheets, and tubes. Polymerization in solution is valuable where the product is used in solutions such as in some coating, inks and adhesives, and it produces the most water-resistant film. These products are usually of a lower range of molecular weights. Heterogeneous polymerization is a process when a monomer is mixed with water in which it breaks up into many small monomer pockets or droplets [Horn, M.B., 1960]. This method can be further divided into three types: (a) Emulsion polymerization, (b) Suspension polymerization, (c) Granular polymerization. Emulsion polymerization is carried out by dissolving in water an emulsifier and water-soluble catalyst [Horn, M.B., 1960]. Monomers and surfactant are dispersed by agitation, and the batch is then heated and polymerized. In this process, temperature, method of addition of monomer, and additives can be varied to produce different emulsions. Nowadays, advanced surfactant technology helps to yield excellent emulsions of very small particle size, high solid content at low viscosity, and electrolytic stability.

Acrylic polymers are the most successful of all waterborne technologies available and used extensively in water-based coatings, adhesives, and printing inks. They can be classified into four categories:

- Alkali soluble resins: typically, they are styrene acrylic. These resins are insoluble in water in their acid forms, but are soluble when alkaline materials are added. They are highly efficient wetting and grinding agents that are used in pigment dispersions and overprint varnishes to improve stability, resolubility, color strength, gloss, and transparency.

- Acrylic emulsions: impart key application properties to inks and overprint varnishes (OPVs) and are utilized as letdown vehicles to control rheological properties and provide final properties to the ink or OPV. Some acrylic emulsions exhibit near-Newtonian rheology and maintain their viscosity stability even under the high shear conditions of the printing process, and their lower polarity contributes to faster water release than with acrylic solution. Also, they become completely insoluble upon drying, which improves water resistance of ink films.
- Colloidal emulsions and solutions: are used extensively in low-cost inks for porous substrates, such as corrugated board and multi-wall kraft bags, where high gloss or adhesion to film is not required [Laden, P., 1997].
- Acrylic specialty polymers: designed for high performance applications.

In selecting acrylic resins and emulsions to formulate water based gravure inks, careful consideration must be given to balance their desired properties. For example, higher T_g emulsions usually provide better gloss, dry speed, hardness, and heat resistance, but low T_g polymers are excellent film formers with advantages such as flexibility, adhesion to non-porous substrate, and water resistance. In alkali soluble resin selection, it is important to consider their molecular weight. The higher is the molecular weight, the higher the viscosity, and the better the pigment dispersion.

Vinyl Acrylic Copolymer (VAC) Chemistry

Polymers made from only one monomer are called homopolymers. They have a definite set of physical characteristics. However, this normally cannot satisfy all the requirements of their end-use properties as printing inks ingredients. For example, conventional soft acrylic binders, having a single, low T_g polymer type, usually produce tacky films lacking in block resistant properties, and surface hardness; on the other hand, rigid acrylic emulsions create brittle films. To achieve satisfactory property, the copolymerization process, which allows for the presence of two or more different polymers simultaneously in one particle, combines different properties.

Vinyl acrylic copolymers include all copolymer of vinyl acetate with acrylic and methacrylic acids and their esters, which are manufactured by the copolymerization of an alkyl acrylate, such as ethyl, 2-ethylhexyl and butyl acetate, with a vinyl acetate monomer. Vinyl acetate emulsions cover a wide range of compositions, and vary in adhesive characteristics. Their compositions are usually dictated by the end-use properties such as flexibility, tack, resistance properties, adhesion, and temperature stability. The acrylate concentration in the composition is usually in the range of 15-25%, but can be higher. The commonly preferred co-monomers are 2-ethylhexyl acrylate and butyl acrylate.

VACs provide good low temperature film formation, binding capacity, durability, good gloss and adhesive ability. They are usually designed for use in adhesives, coatings and as a binder in printing inks [Horn, M.B., 1960; Boyce, et al, 1993].

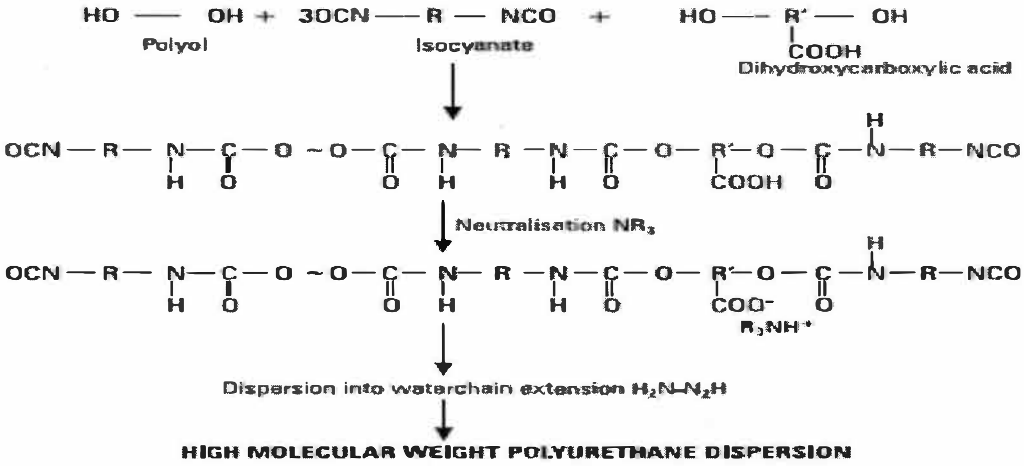
Polyurethane Chemistry

Polyurethanes were first invented by Otto Bayer in 1937 in an attempt to create an alternative fiber to compete with Nylon [Roesler and Hergenrother, no date]. With the need to move forward to water-based systems, the polyurethane chemistry coupled with their ability to be dispersed into water has resulted in the development of water-based polyurethane dispersions (PUDs). PUDs are reacted urethane polymers whose raw materials are typical of any urethane chemistry.

There are a number of approaches to manufacture PUDs including the “acetone process”, “melt dispersion”, and “pre-polymer mixing process” [Manock, H.L., 2000]. The pre-polymer mixing process has the advantage of avoiding the use of large amounts of solvent. In this process, PUDs are synthesized in the following way: first, the selected raw materials, difunctional polyol and di-isocyanate, are reacted together to form an isocyanate-terminated pre-polymer; then, carboxyl groups can be added to the PU backbone at this stage, typically by the addition of DMPA (dimethylpropionic acid); next, the carboxyl groups are neutralized by tertiary amine – triethylamine; finally, dispersion into water and chain extension [Moss, M., 1997]. This process is summarized in Table 5.

Table 5

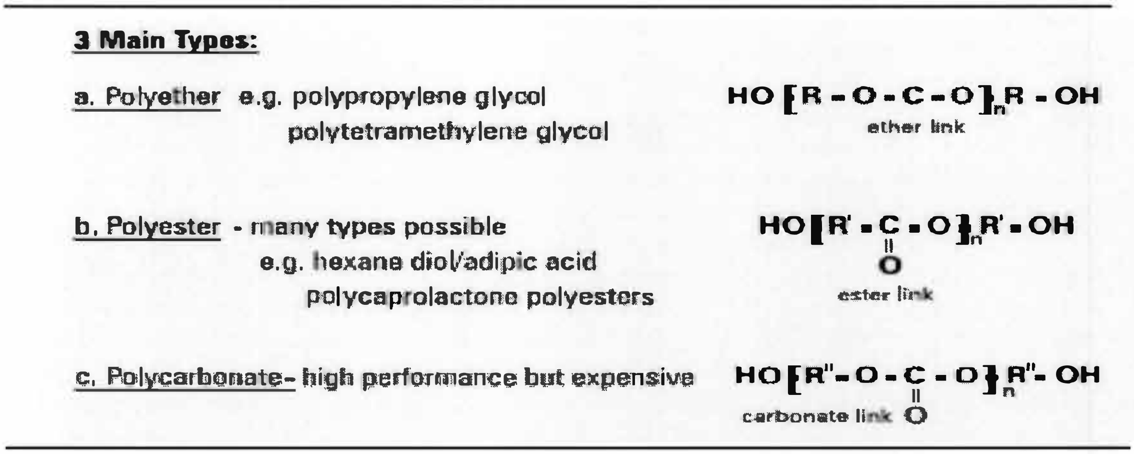
Pre-polymer mixing process [Manock, H.L., 2000]



The resultant properties of PUDs are mostly determined by the choice of raw materials that form the polymer's backbone. These properties include molecular weight, particle size, pH and viscosity, amorphous characteristics, chemical resistance, and adhesive ability. Linear polymers, resulting from di-isocynate monomers and diols, are usually weak in water and solvent resistance. Based on the polyol selection, PUDs can be divided into three main types, which have different properties. The structure of the three types of polyol is shown in Table 6. Polyester-based PUDs offer a wide range of properties from high to low modulus, solvent resistance, adhesion, good UV resistance and reasonable hydrolysis resistance. Polyether-based PUDs provide good low temperature flexibility, hydrolysis resistance and reasonable adhesion. Polycarbonate and polycarbonate ester are used in high performance applications that demand tailored toughness, adhesion, hydrolysis and UV resistance [Manock, H.L., 2000].

Table 6

Polyol selection [Manock, H.L., 2000]



3 Main Types:

a. Polyether e.g. polypropylene glycol polytetramethylene glycol	$HO[R-O-C-O]_nR-OH$ ether link
b. Polyester - many types possible e.g. hexane diol/adipic acid polycaprolactone polyesters	$HO[R'-\overset{\overset{\displaystyle O}{\parallel}}{C}-O]_nR'-OH$ ester link
c. Polycarbonate- high performance but expensive	$HO[R''-O-\overset{\overset{\displaystyle O}{\parallel}}{C}-O]_nR''-OH$ carbonate link

The level of dimethylpropionic acid (DMPA) is also a critical factor in determining the properties of PUDs, since it controls dispersibility and the resulting particle size. An increase in the concentration of DMPA results in an increase in water sensitivity of the dried polymer film, but with this increase, the particle size decreases.

With such diversities, the chemistry offers many options to improve the performance of PUDs. These exceptional performances make PUDs suitable for a wide range of coating and printing ink applications.

Additives

Through the resin system alone, it is impossible to achieve a workable formulation for water-based inks. Many problems including pH instability, variation in viscosity, poor substrate wettability, and poor film formation need to be solved with the addition of certain additives. These include waxes, anti-skinning agents (antioxidants), defoamers, additives that promote rub resistance, water resistance, proper rheology, and many others [Laden, P., 1997].

Defoamers/Antifoamers

Foam is a stable dispersion of a gas in a liquid medium that results when a surfactant layer forms around air bubbles and entrains them with it [Zeng, Jianren, 2004]. Deformer and antifoamer products play an important role in degassing and stabilizing coatings. Foam control agents can be divided into two types:

- Defoamers: destroy the already formed foam, eliminate the macro-foam.
- Antifoamers: agents that inhibit foam forming [Schnell R. R. et al, 2004].

Defoamers and antifoamers are used predominantly in water-based coating and ink systems. On the basis of the constituents of defoamers or antifoamers, they can be further classified into silicone-containing and silicone-free defoamers, water-based emulsions and solvent containing solutions.

Surfactants

An effective ink free of defects can be ensured only if the surface tension of the ink is less than the surface energy of the substrate [Kunjappu, J. T., 2000]. The introduction of surfactants can bring down the surface tension of the water-based system. Surfactant molecules can migrate to the solvent surface. They take-up an orientation in which the polar head groups are directed toward the solvent surface, and the hydrocarbon chains protrude out to the air. This leads to the reduction in surface tension, and thus the ink achieves better substrate wettability.

A surfactant is a surface active agent, a material of fairly low molecular weight that is amphiphilic in nature [Hahn, L., 2004]. It possesses both hydrophilic and hydrophobic parts. Based on the nature of hydrophilic group, surfactants are divided into three classes:

- Nonionic: head group is hydrophobic and the "tail" is hydrophilic.
- Cationic: possessing positive charge in the head group.
- Anionic: possessing negative charge in the head group.

However, the use of surfactants in some cases can seriously affect the water sensitivity of the ink film, as well as the adhesion characteristics. Surfactants that remain on the interfaces of the polymer particles will create hydrophilic channels through the film, which may cause undesirable effects such as water transport through the film to the substrate [Buckmann, A.J.P. et al, 2003]. Also, ionic surfactants are generally avoided in ink formulations because associations of these surfactants and polymers can alter the rheological characteristics of the ink system.

Water-based Gravure Ink Rheology

The study of the flow of fluids (liquids or gases) is known as rheology [Eldred, N.R. and Scarlett, T., 1990]. Resistance is offered when one part of a fluid (liquid or gas) is moved past another. The "resistance to flow" is called the viscosity, which is the most commonly sought after rheological quantity. To define the rheological features of most printing inks, the term Newtonian, dilatant, and pseudoplastic (non-Newtonian, thixotropic) will be used.

- Newtonian: the viscosity of the system does not depend on the shear gradient applied.
- Dilatant: viscosity rises with increasing shear (which is normally extremely undesirable in surface coating).
- Pseudoplastic (non-Newtonian thixotropic): the viscosity decreases with increasing shear gradient and then, when the external forces decline, returns immediately (non-Newtonian) or with a certain delay (thixotropic) to approximately its original value [Sauer, F., 2004].

Water-based gravure inks are complex colloidal suspension systems that combine ingredients such as pigment, additive, polymer, and emulsion. The interactions between these component particles cause the formation of network structures in suspension, and the degree of interaction and the strength of these structures are expressed in the rheological properties of a system. Each of these components by itself may or may not have Newtonian characteristics, but together, the mixture shears in unique, nonlinear ways.

The rheological properties of inks play a central role in the distribution of ink on the printing plates, in the penetration of ink into the surface structure of printing papers and in the splitting of the ink film at the exit of the printing nip [Pangalos, G. et al, 1985]. In the gravure printing process, the ink flow between the two rigid cylinders is compressed, stretched, sheared, fractured, and transferred to the surface of substrates in seconds. Therefore, the inks must be able to flow in and out the cells fast and uniformly when contacted with the cylinder and the substrate. With a high viscosity, the cells filling and emptying is difficult, and deep cells will give uneven, mottled printing; on the other hand, with too low of a viscosity, a dilution factor will occur that leads to poor ink transfer, which will give poor optical density and affect image fidelity. Furthermore, low viscosity may also cause sedimentation problems of an ink during storage.

The rheology of printing inks has great effects on ink transfer; therefore, different printing processes have different viscosity requirements. Some viscosity requirements of a printing system are shown in Table 7. For water-based gravure inks, the ability to maintain a viscosity is complicated. This is not only due to the fact that alkaline materials are involved in the formulations, which will affect the ink viscosity when they evaporate, but also the shear thinning may affect the stability of emulsions. Shear thinning, which is the most common non-Newtonian effect, is the tendency of some materials to decrease in viscosity when they are driven to flow at a high shear rate, such as by higher pressure drop [Morrison, F. A., 2001]. Viscosity as a function of rate of shear [Hermans, J. J., 1953] was first observed by Hatschek [Hatschek, E.J., 1911] and confirmed by Sibree [Sibree, J.O., 1930]. The special feature of emulsions has been well summarized by Sumner [Sumner, O.G., 1950] as following: When an emulsion is caused to flow, deformation of the droplets may occur, and this will reduce the apparent viscosity of the emulsion as a whole. This effect will be most pronounced at a high rate of shear, for high volume concentrations of disperse phase, for relatively large droplets, and for a disperse phase of low viscosity [Hermans, J. J., 1953].

Table 7

Ink viscosity of some printing processes [Podhajny, R.M., 1998]

Printing process	Ink viscosity (poise)
Lithographic & offset	100-600
Letterpress	10-100
Flexography	1-4
Rotogravure	0.5
Ink Jet	0.02-0.1

Viscoelasticity Basics

Viscoelastic materials are those, which are neither purely elastic (obey Hooke's Law) nor purely viscous (obey Newton's Law) but exhibit both characteristics simultaneously, depending upon the situation with which they are faced [Saunders, G., 1992; Hrehorova, E. et al, 2005]. Water-based gravure inks are considered viscoelastic materials, they may generate normal stresses associated with the elasticity during flow, and such normal stresses may affect the printing operation providing a lifting force on the printing nip. Viscoelasticity measurement reveals the state of the dispersion at small deformation.

Elastic or Storage Modulus, G'

The storage modulus, or dynamic rigidity, G' is defined as the component of the stress in phase with the strain divided by the strain amplitude [Gupta, R. K., 2000]. It measures the amount of energy stored within a sample structure per cycle of deformation. The sample structure depends on the interactions between the different component within the system; thus, the value of G' reflects both the strength of each interaction and the number of interactions. The elastic modulus G' of viscoelastic materials normally exhibits linear response with low applied stresses; however, this relationship is seen to break down if the system is forced to undergo large deformation.

Viscous or Loss Modulus, G"

The loss modulus, G", is defined as the component of the stress out of phase with the strain divided by the strain amplitude [Gupta, R. K., 2000]. It measures the energy dissipated per cycle of deformation. G" also depends on the structure of the suspension system and the interactions between particles in the system.

Loss Tangent, tan δ

Loss Tangent, tan δ measures the ratio of energy loss to energy stored in a sinusoidal cyclic deformation. δ, the phase angle,

$$\tan \delta = G'' / G' \qquad (1)$$

For purely viscous materials, the stress and strain will be out of phase by ninety degrees, i.e., the phase angle shift equal to 90°. In contrast, purely elastic materials will have a phase angle shift equal to 0°. And for most other materials, for example, coatings, inks, and adhesives, phase angle shift falls between the two extreme values ($0° < \delta < 90°$). Phase angle shift close to 0° represent material with elastic (solid-like) behavior, whereas close to 90° indicates more viscous (fluid-like) material.

Rheology Modifiers

In gravure printing, the engraved cylinder is immersed in the ink fountain and is rotated at a high speed. This high shear rate is transferred to the ink and reduces the viscosity of the ink. It is therefore highly desired to be able to formulate inks in such a way as to optimize their flow behavior on the press [Pangalos, G. et al, 1985]. The inks should possess optimum rheological behavior that can prevent sedimentation and flocculation at low shear rate and enhance ink transfer and leveling at a high shear rate. Such inks must be formulated with the help of rheology modifiers. In the early years, the most commonly used rheology modifiers were natural clays and organoclays. Recently, more effective rheology modifiers such as non-associative and associative polymers were developed to optimize the flow properties of water-based inks.

Rheology modifiers, commonly referred to as thickeners or viscosifers, have more influence on a system than simply altering the thickness or viscosity of the compound. Rheology additives range from organically modified clays to organics products like castor oil derivatives, diamides, hydrophobically modified polyether polyols (PEPO), hydrophobically modified polyurethanes (HEUR) and hydrophobically modified acrylic acid copolymers (HASE) [Avci, Sel, 2003]. These additives play a major role concerning storage and application properties of liquid systems.

Non-associative Thickeners

Non-associative thickeners comprise water soluble polymers with a high molecular weight, which dissolve in the aqueous phase and create strong linkage with neighboring water molecules [Kalenda, P., 2002]. This group includes cellulose ether, polycarboxylic acid salts, polysaccharides, and alkali swellable emulsions (ASE), which are liquid products generally commercialized at low concentration of 25-30% of dry matter, easily soluble, and pH dependent. ASE thickeners can provide excellent low-shear rate viscosity; thus, they are usually recommended for water-based interior/ exterior paints and water-based printing inks. However, they might have a negative influence on gloss, corrosion resistance, and leveling at different applications. The structure of a non-associative thickener is shown in Figure 3.

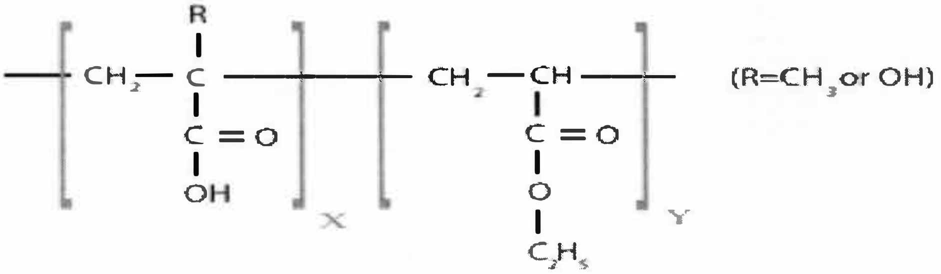


Figure 3. The Structure of non-associative thickeners (ASE) [Annon[6], 2005]

The thickening effect of the non-associative rheological additives is based primarily on hydrodynamic volume exclusion (HDV) mechanism. In solution, a substance occupies some volume with the solution, thereby excluding the possibility of any other substance occupying that same volume. As more solute is added, less volume is available within the solution, which will cause an increase in solution viscosity [Verstrat, D. W., no date]. As shown in Figure 4, addition of alkali to the polymer emulsion results in neutralization of the carboxylic acid groups, generating an anionic charge at the acid sites along the polymer chain. The like charges repel one and another and uncoil the polymer, which results in an extremely large increase in the hydrodynamic volume of the neutralized ASE polymer, which is responsible for the significant build in solution viscosity.

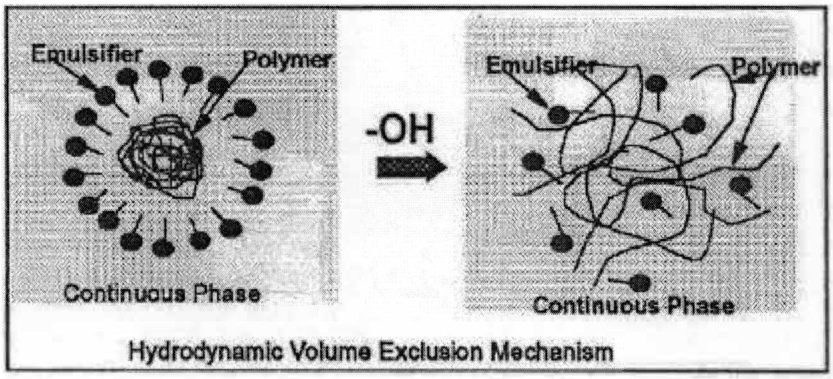
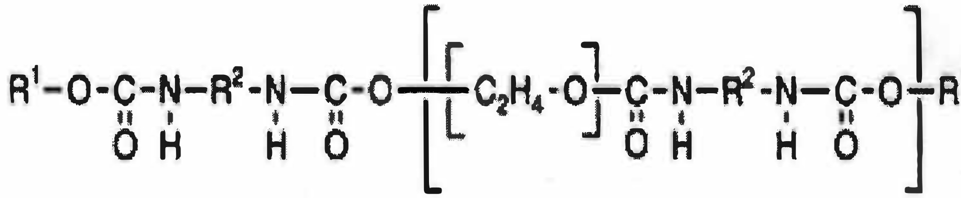


Figure 4. Thickening mechanism of non-associative thickeners (ASE) [Verstrat, D. W., no date]

Associative Thickeners

Associative thickeners are low-molecular weight polymers, soluble in water, which are modified by hydrophobic groups [Kalenda, P., 2002]. This group includes the hydrophobically modified polymers such as HASE and HEUR, which now are widely used in water-based coating and printing ink systems. HASE have a liquid form (milky appearance), a concentration of about 30%, and a pH between 2.5 and 4.5. Their structures are shown in Figure 5 and Figure 6.



$$R^1-O-\underset{\overset{\parallel}{O}}{C}-\underset{\overset{|}{H}}{N}-R^2-\underset{\overset{|}{H}}{N}-\underset{\overset{\parallel}{O}}{C}-O-\left[\left[C_2H_4-O\right]-\underset{\overset{\parallel}{O}}{C}-\underset{\overset{|}{H}}{N}-R^2-\underset{\overset{|}{H}}{N}-\underset{\overset{\parallel}{O}}{C}-O\right]-R^1$$

Figure 5. The structure of hydrophobically modified ethylene oxide urethane rheology modifier (HEUR) [Annon[6], 2005]

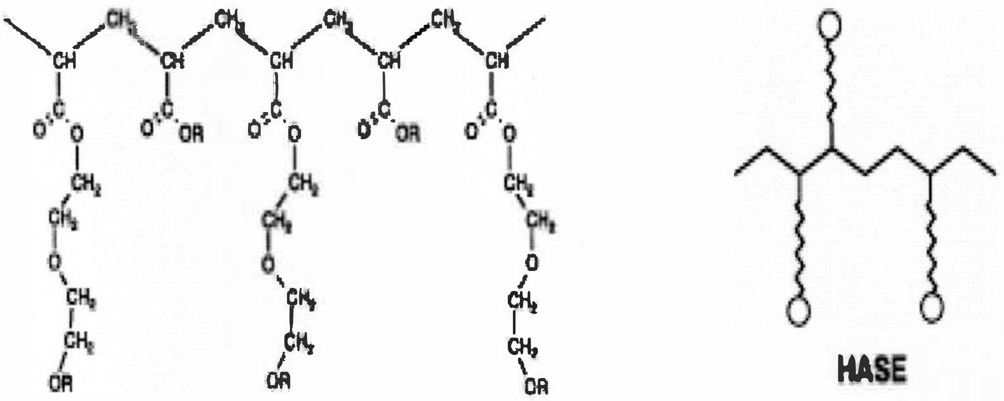


Figure 6. The structure of hydrophobically modified alkali swellable emulsion (HASE) [Annon[6], 2005]

The thickening effect of associative thickeners (HEUR) is based on the interaction of the hydrophobic components of the thickener molecules with components of the coating such as latex particles, pigments, and extenders. The hydrophilic segments of the thickener remain in the aqueous phase (shown in Figure 7). As a result of the interaction, a three-dimensional reversible physical cross-linking occurs in the dispersion, which has a major influence on the flow properties of such a system [Sauer, F., 2004]. The results of the study performed by Miller et al. [Miller et al, 2000] show that the neutralization behavior of a HASE thickener is similar to that illustrated for ASE thickeners. Associative thickeners are attractive in that higher viscosities at high shear rates lead to good film build during application, and their lower viscosities at lower shear rates is desirable for improved flow and leveling. A smoother ink film surface could result in higher gloss of a print surface.

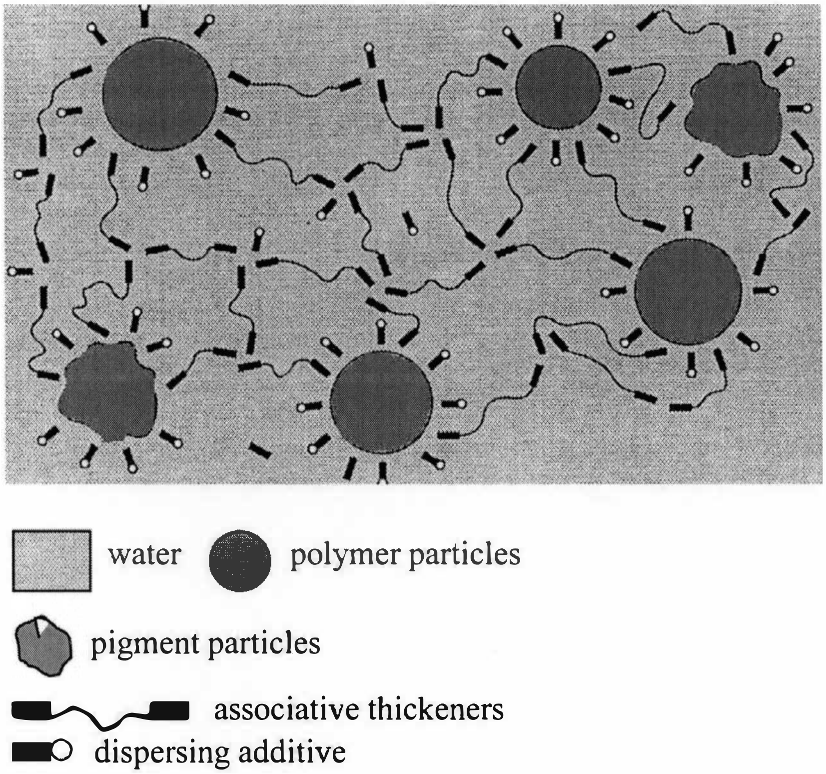


Figure 7. Thickening mechanism of associative thickeners (HEUR) [Kalenda, P., 2002]

Clays and Organoclays

Naturally occurring clays are hydrophilic in nature the clay particles swell and separate into individual clay platelets when they are dispersed in water. Due to platelet interaction, a three-dimensional "house of cards" structures are developed [Avci, Sel, 2003]. This structure provides thickening properties so that clays may be utilized in water-based gravure inks systems to improve the rheological properties of the inks.

The organoclays have been successfully used for more than 50 years in a variety of ink applications [Avci, Sel, 2003]. They contribute to improved rheological properties of inks. To make an organoclay, the smectite clay is reacted with a quaternary ammonium compound. The quaternary amine ions can exchange with the sodium cations on the surface of the clay. The organic component is then firmly bonded to the clay surface, and the salt product is washed out.

Selection of Thickeners for Water-based System

The most important rheological criteria for selecting thickeners for water-borne gravure inks is that a thickener must provide adequate thickening at low velocity gradients, which is important for sedimentation of pigments during the storing period, flow and leveling after application of the ink. It should be noted that if hydro-surfactants are also added into water based systems, the viscosity enhancement due to the hydrophobic modification may be completely lost at sufficiently high levels of surfactant addition.

CHAPTER III

PROBLEM STATEMENT

The main purpose of this project is to investigate the problem associated with the rheological properties of water-based gravure inks for vinyl wall covering products used by OMNOVA. The problem is described as following: the inks, based on vinyl chloride emulsion systems, are thermally unstable and shear unstable which cause irreversible shifts in viscosity during press runs. This leads to an inconsistent performance and causes color value variations. Rheology modification of the ink is considered one of the solutions.

The goal of this research is to study the effect of different rheological modifiers in the water-based inks, and provide useful information for rheology modifier selection. The properties that need to be examined will be:

- Viscosity efficiency
- pH value profile
- Rheology behavior
- Particle size profile
- Solid content of inks
- Ink performance test

CHAPTER IV

EXPERMENTAL

Materials Used in Water-based Gravure Inks

Pigment Dispersions

- Black dispersion from OMNOVA Solutions
- Blue dispersion from OMNOVA Solutions
- Vehicle (emulsion and polymer): a semi-finished product provided by Noveon containing Vycar460X95, surfactants, defoamers/antifoamer, flat reagents, and other additives.

Rheology Modifiers

Non-associative Thickeners

- ASE 95: Rohm & Hass. pH is 3.0, must be neutralized. Imparts a long, leggy viscosity.
- ASE 60: Rohm & Hass. pH is 3.0. Non-associative thickener. Water-phase thickener. Builds low-shear viscosity. Provides “buttery” feel.

Urethane Associative Thickeners

- RM-8W: Rohm & Hass. Solvent-free and lower solids version of RM-825 and RM-8. Easier incorporation and handling.
- RM-2020: Rohm & Hass. Use in interior / exterior flat through gloss paints. Ready to use in an all water solution and imparts Newtonian rheology. Use as co-thickener

with KU efficient HEUR.

- RM-825: Rohm & Hass. KU-efficient, especially with small particle size and gloss binders. Works well in interior/exterior flat through gloss paints.
- DSX 1514: COGNIS. Non-ionic rheology-additive for aqueous systems, low structural viscosity.

Acrylic Associative Thickeners

- TT 678: Rohm & Hass. pH value is 7, can be used in water-based and solvent-based solution.
- TT 615: Rohm & Hass. Base-activated and more shear-thinning than Acrysol TT-935. Recommended in interior flat through sheen, satin paints.
- TT-935: Rohm & Hass. pH is 3.0, must be neutralized to impart viscosity efficiency.
- 20KR019: Union Carbide Corporation.
- 20KR021: Union Carbide Corporation.
- 20KR026: Union Carbide Corporation.

Design of Experiment

Preparation of Inks

Clears

Varying levels of thickeners were first added into the water-based vehicle system to test for efficiency and to observe their effects on the system. A clear mixture composed of 97 – 99% vehicle mixture and 1 – 3% rheology modifier (level used is shown in Table 8) was prepared and mixed for 10 – 15 minutes using Lightnin Labmaster High Speed Mixer at 600 rpm. Samples were sealed and stored for particle size, pH value, and viscosity measurement.

Table 8

Rheology modifiers and their tested level in the water-based vehicle system

Test	Type	Name		Level used (Weight %)		
1	HEUR	RM-8W	Rohm & Hass	1	2	2.5
2	HEUR	RM-2020	Rohm & Hass	1	2	3
3	HEUR	RM-825	Rohm & Hass	1	2	2.5
4	HEUR	DSX 1514	Cognis	1	1.5	2
5	HASE	TT 615	Rohm & Hass	1	2	-
6	HASE	TT 678	Rohm & Hass	1	2	2.5
7	HASE	TT 935	Rohm & Hass	1	2	-
8	HASE	20KR019	Union Carbide Corporation	1	2	-
9	HASE	20KR021	Union Carbide Corporation	1	2	-
10	HASE	20KR026	Union Carbide Corporation	1	2	2.5
11	ASE	ASE 60	Rohm & Hass	1	2	2.5
12	ASE	ASE 95	Rohm & Hass	1	1.5	2

Blue Inks

A mixture of 30% blue pigment dispersion, 65 – 70% vehicle mixture, and a selected level of rheology modifiers was mixed for 10 – 15 minutes using Lightnin Labmaster High Speed Mixer at 600 rpm. Ink formulations are shown in Table 9. Samples were sealed and stored for further study.

Table 9

Blue ink formulations

	Blue Pigment Dispersion (g)	Extender (g)	Rheology Modifier (g)	RM concentration (Weight %)
Blank	300	700	0	0
RM-825	300	683.9	16.1	1.61
DSX-1514	300	690.9	9.6	0.96
TT-678	300	686.0	14.0	1.40

Black Inks

A mixture of 35% black pigment dispersion, 60 – 65% vehicle mixture, and a selected level of rheology modifiers was mixed for 10 – 15 minutes using Lightnin Labmaster High Speed Mixer at 600 rpm. Ink formulations are shown in Table 10. Samples were sealed and stored for further study.

Table 10

Black ink formulations

	Black Pigment Dispersion (g)	Extender (g)	Rheology Modifier (g)	RM concentration (Weight %)
Blank	350	650	0	0
RM-825	350	633.7	16.3	1.63
DSX-1514	350	640.3	10.3	1.03
TT-678	350	633.7	16.3	1.63

Viscosity Measurement

The most common method of manual measuring of viscosity is by using efflux cups such as Shell cups and Zahn cups. Viscosity is recorded as the time required for the liquid draining out of the cup. The Shell cup (shown in Figure 8 right) viscosity cups are simple, reliable devices for measuring viscous fluids. They are available in eight different sizes (#1, #2, #2.5, #3, #3.5, #4, #5, and #6) for viscosity ranges from 0.3 to 7000 cps (cps = Centistokes x S.G.). The Zahn cups (shown in Figure 8 left) are also useful for measuring the viscosity of liquids such as paint, lacquer varnish, and inks. Five cups (#1, #2, #3, #4, and #5) are available for viscosity ranges from 18 to 1725 cps. In this research, either Zahn cups or Shell cups were used to perform the viscosity profiles measurement of the different water-based systems. Before the viscosity measurement, the pH values of all tested mixtures were adjusted to 9 – 10 by adding 20% solution of 2- amino – 2- methyl – 1 – propanol, which has a pH value around 11.8.

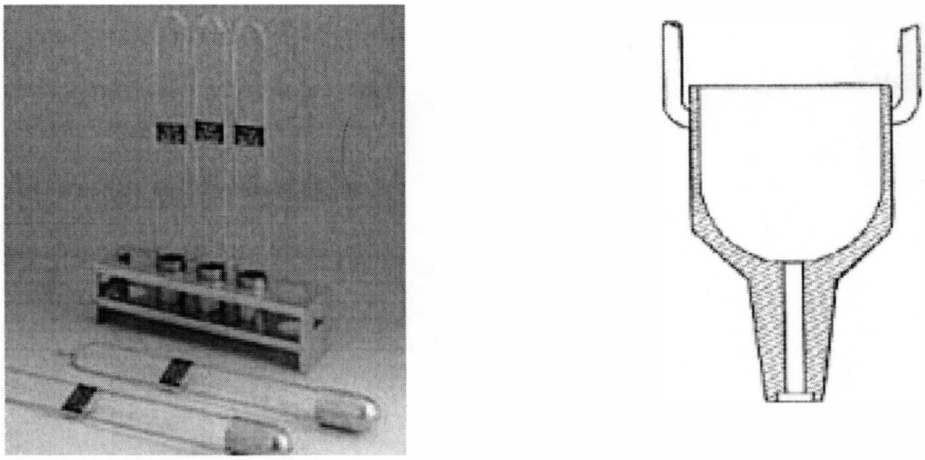


Figure 8. Zahn cups and Shell cup [Annon[7], 2005; Annon[8], 2005]

Rheology Measurement

In the ink industry, the viscosity is the most frequently determined property. But in some cases, two inks having the same viscosities may produce different print quality. Therefore, further rheological behavior studies are required. Rheological properties were determined using a TA Advanced Rheometer AR 2000 (Figure 9 left) with a standard concentric cylinder system (or cup and bob system, Figure 9 right). Concentric cylinder systems are generally used for low viscosity samples that cannot be held within the gap of cone and plate or parallel plate system.

In all of the rheology measurements, the samples were first exposed to a conditioning step which ensured the samples were at the correct temperature and the residual normal force was at an acceptable level. Except in the temperature ramp test, the geometry was maintained at the constant temperature using circulating water bath (25°C ± 0.1°C). Following the conditioning step was a two-minute equilibrium period. The rheology measurements techniques used were as follows:

- Oscillation stress sweep test: constant frequency of 1 Hz was applied and the amplitude of the stress was incremented from 0.001 to 1000 Pa. By performing an amplitude stress sweep, the linear viscoelastic region (LVER) was then determined.

- Oscillation frequency sweep test: from the amplitude sweep test, a stress or strain was selected from the LVER and incorporated into the oscillation frequency sweep test. During the frequency sweep test, the fixed amplitude of the stress was applied while the frequency was changing from 100 Hz to 0.001 Hz.
- Steady state flow test: in this mode, the material was subjected to a controlled increasing shear rate and the resultant viscosity was measured.
- Temperature ramp test: in this measurement, a fixed shear rate was applied (400 s^{-1}) while the ink's temperature was increased from 20°C to 45°C using a circulating water bath.

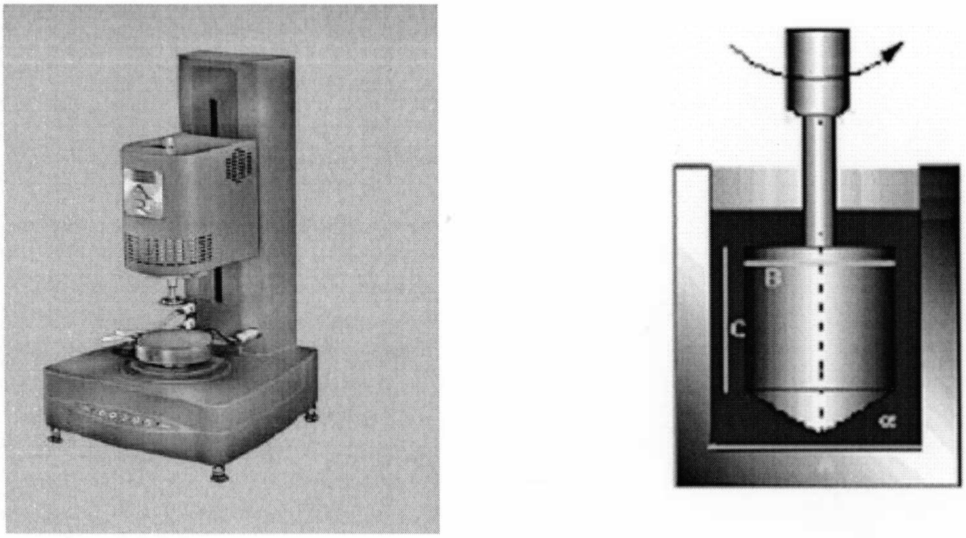


Figure 9: TA instrument AR 2000 and concentric cylinder system [Annon[9], 2005]

Shear Thinning Index

This measurement employs the use of Brookfield Viscometer, Model DV-III. The Brookfield viscometer determines viscosity by measuring the force to turn the spindle in the solution at a given rate. The test method determines the apparent viscosity and the shear thinning properties of non-

Newtonian materials. According to ASTM standard D2196-99, the Shear Thinning Index is the value that the apparent viscosity at a low rotational speed divided by the viscosity at a speed ten times higher. Typical speed combinations are 2 and 20 rpm, 5 and 50 rpm, and 6 and 60 rpm [ASTM Standard, 1999]. In this research, the thinning index of the formulated water-based gravure inks will be characterized at 6 and 60 rpm using spindle No.3 at 25 C°.

pH of Inks

pH value affects the viscosity of the water-based system, so it is necessary to monitor this value under different temperature. pH values were measured by using the AmericalTM pH I. pH meter (American Scientific Products).

Particle Size Measurement

Particle size affects ink performance and its viscosity. A smaller particle size held within a narrow range will show improved performance in gravure transfer and rewettability [Helien, W., 2003]. Also, a lower particle size indicates a lower molecular weight polymer, which has better compatibility including viscosity stability, with a wide range of polymers [Helien, W., 2003]. The Particle Sizer Submicron 370 NICOMP analyzer, which is based on dynamic light scattering (DSL), was employed in particle size measurement. Light from a laser is focused into a glass tube or cuvette containing a diluted suspension of particles. Each of these particles scatters light in all directions. The intensity of the light scattered by a single, isolated particle depends on its molecular weight and overall size and shape, and also differences in the refractive indices of the particle and the surrounding solvent [Sesetyan, T., 2002; Frimova, A., 2005]. The pH value of the tested system was control at 9-10.

Temperature Stability

In this process, the Shell cup (#5) viscosity of ink samples was measured before they were sealed into HDPE containers. The following procedure was repeated:

- Samples were placed in an oven at the temperature of 120 °F for three days. After cooling down to room temperature (75 °F), samples were checked for viscosity and particle size.
- Samples were left in the oven for four more days and were checked for viscosity and particle size again.
- Samples were left in oven for 7 more days and were checked for viscosity and particle size.

Drawdown

In this process, ink will be transferred from the grooves of a wire-wound rod directly on the surface of the vinyl wall paper substrate. The diameter of the wire, in the wound form, regulates the thickness of the ink film. The diameter of the rod and wire vary in size depending on the type of application. Rod size 6 or 8 can produce an ink film thickness similar to gravure printing.

Moser Sheet-fed Gravure Proofing Machine

The Moser proofing machine was employed to simulate more realistic printing conditions for the printability study of water-based inks. A circulating water bath was used to maintain a consistent temperature at 25°C. It is equipped with a hollow electromechanically engraved cylinder, which serves as the image carrier. The screening is 150 lpi, and printing speeds was set at 60 m/min.

After formulations were evaluated based on their rheological behavior, pH stability, and printability on the substrates using drawdown, several optimum performance rheology modifiers were added into the water-based gravure inks to tailor the inks, which would be printed on the vinyl using the Moser sheet-fed gravure proofing machine. The inks were run on the Moser to evaluate the rheological behavior and the performance of the ink.

Ink Performance Test

All printed samples were tested for ink performance by measuring their reflective density using the X-Rite SpectroDensitometer 530. The densitometer measures the difference between light projected onto (through) the sample and the amount of light reflected back (or transmitted by sample). The density related to reflectance as follows:

$$\text{Density} \quad D = \log 10 \; 1/R \qquad (2)$$

Where reflectance $R = R_1/R_w$

R_1 = Intensity of light reflected from print

R_w = Intensity of light reflected from white paper

CHAPTER V

RESULTS AND DISCUSSION

Effect of Rheology Modifiers on the Water-based Ink System

During the first phase of this research, experiments were conducted on the water-based vehicle system to obtain the basic data such as efficiency, effects of the twelve rheology modifiers on pH value and on particle size of the water-based gravure system.

Effect on Low Shear Viscosity

Figure 10 presents the low shear (Zahn Cup #2) viscosity results for the twelve rheology modifiers. It is evident from the Figure 10, that the non-associative thickener, ASE-95, from Rohm & Hass, is the most efficient thickener, whereas the urethane associative thickener, RM-2020, also from Rohm & Hass, is the least efficient one.

The high number of acid groups in the acrylic emulsion polymer accounts for the high efficiency of the ASE thickeners' low shear viscosity. ASE thickeners thicken by means of neutralization of acid groups along the polymer chain, causing charge repulsion. Based on the HDV mechanism, the expanded acid portions of the polymer occupies more volume with the solution and thus less volume is available within the solution, causing an increase in solution viscosity. Maximum viscosity can be achieved if all acids groups are completely neutralized.

HEUR and HASE thickeners are associative polymers with hydrophobic portions. These hydrophobic portions link to the hydrophobic component particles in the ink system by ion-dipole interactions and create a three-dimension network structure. Some of them such as DSX-1514, TT-615, and RM-825 provide a fairly high level low shear viscosity and a strong viscous state as it will be presented in later discussion in rheological behavior.

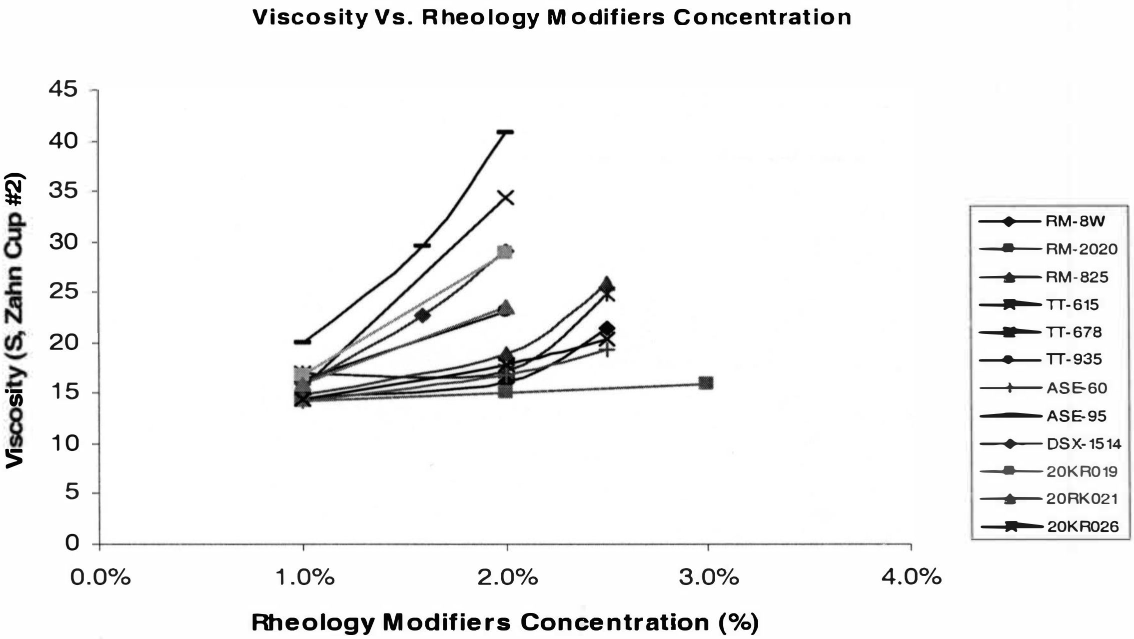


Figure 10: Efficiency of rheology modifiers in the water-based gravure ink system

pH of Inks

Although all of the above thickening processes are initiated by a change in pH, it was observed that pH value of the system changed differently with the addition of each thickener. As shown in Figure 11, TT-615, TT-935, ASE-60, 20KR019, 20KR021, and 20KR026 lowered the pH value of the system greatly. RM-8W, RM-2020, RM-825, TT-678, and DSX-1514 maintained a more consistent pH value of the system.

Rheology modifiers are added directly into the vehicle / pigment formulation with good mixing. During addition of non-associative thickeners, the viscosity of the formulation will begin to increase immediately, whereas the pH value of the system displays a decrease because of the neutralization between the acid portions of the polymer and the alkali groups in the system.

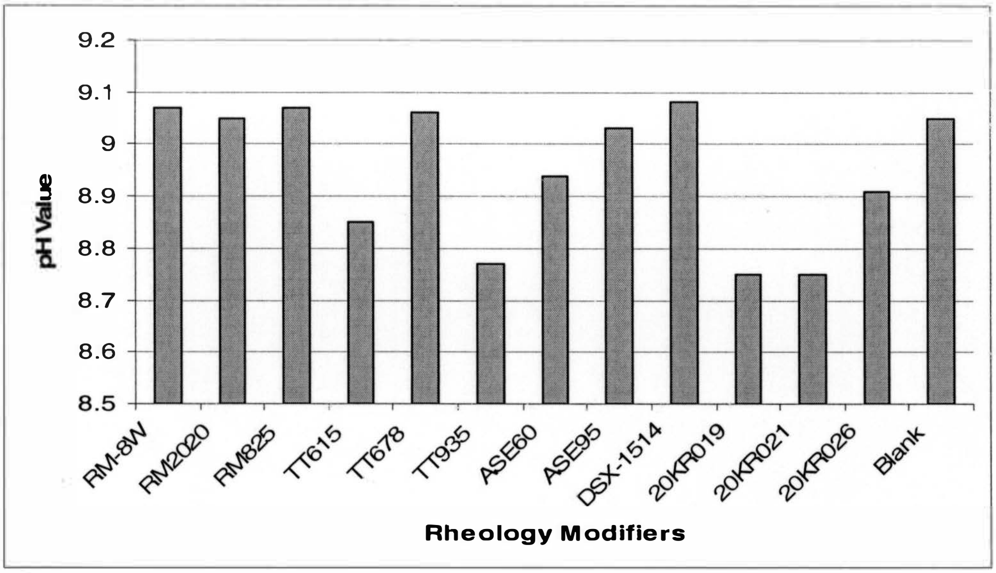


Figure 11: Influence of rheology modifiers on pH value of the water-based system

Particle Size of Inks

A decrease in pH value might pose a negative effect on particle size, In Figure 12, a major increase in particle size was observed with the addition of TT-615, TT-935, ASE-60, ASE-95, 20KR019, 20KR021, and 20KR026 into the system. Furthermore, after storage, it was observed that some rheology modifiers such asASE-95, TT-615 and TT-935 can cause flocculation or separation of polymer and solvent layer in the system. Particle size is one of the most important factors that affect print quality in gravure printing. A smaller particle size held within a narrow range will show improved performance in gravure transfer and rewettability [Helien, W., 2003]. Therefore, when choosing rheology modifiers for a system, we need to balance thickening efficiency and system compatibility.

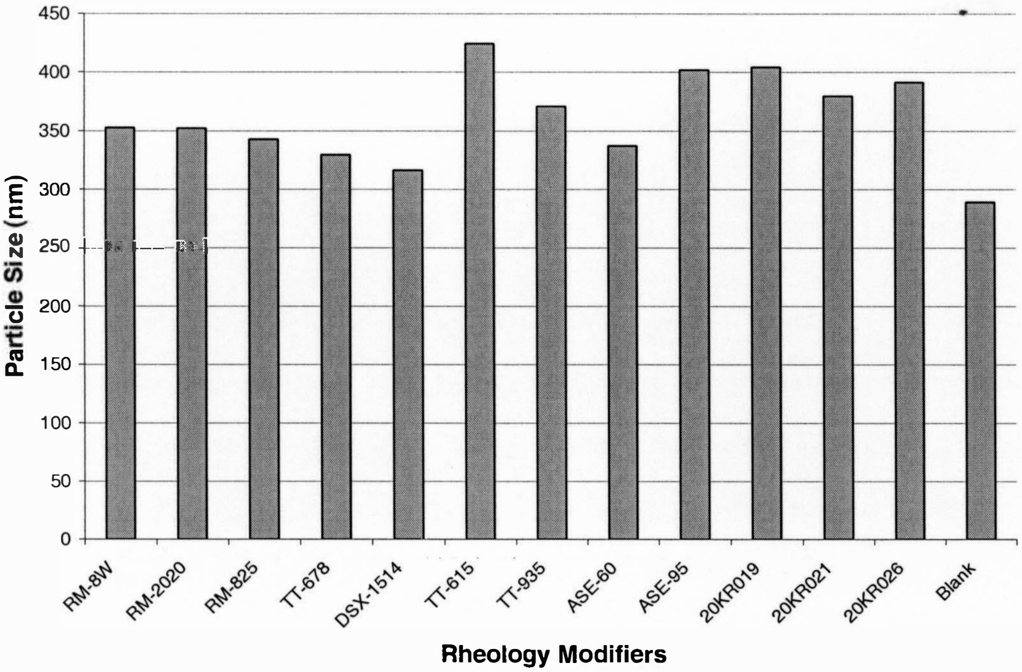


Figure 12: Influence of rheology modifiers on particle size of the water-based system

Rheological Behavior of Inks

Based on their thickening efficiency and their effects on the system, three rheology modifiers including RM-825, DSX-1514, and TT-678 were chosen for further study. A different amount of these rheology modifiers were added to obtain an equal shell cup viscosity. The level of additions are shown in Table 9 and 10. Oscillation stress and frequency sweep tests were run on the water-based inks to determine the amount and strength of interaction between ink components.

Oscillation Test

Oscillation measurements involve subjecting the material to a sinusoidal stress wave and measuring the resultant strain of this wave form in the material. If the material is purely elastic (solid like), then the stress and strain waves will be in-phase and follow Hooke's law. And if, the material is purely viscous (fluid like), then stress and strain will be 90°C out-of-phase. The behavior of a semisolid is defined as a combination of elasticity and viscosity, and the elasticity part of the system was measured as storage modulus G', and the viscosity part was measured as loss modulus G".

Stress Sweep Test

Stress sweep tests were conducted under dynamic oscillatory conditions with a constant frequency of 1 Hz and over a stress range of 0.001 to 1000 Pa. Under low stress, the bonds between ink components are distorted, but not broken. As expressed by the G' values, they remained unchanged. After a certain point of stress, the network structure formed by the component particles in the system starts to break down, and the elastic modulus G' starts to decrease. The stress at which the modulus G' starts decreasing can be regarded as a critical stress. The characteristic critical value of each formulation reflects the strength of the structure formed by component particles such as pigment, binder, and thickener particles. Therefore, the stress sweep test not only defined the range of linear viscoelastic region (LVER), but also the critical stress of an ink system. The length of the LVER of the elastic modulus, G', can be used as a measurement of the stability of a suspension structure, since structural properties are related mostly to elasticity. A longer LVER indicates a better dispersed and more stable system.

Figure 13 and 14 show the elastic modulus, G', and the viscous modulus, G", as a function of stresses applied at a constant frequency of 1 Hz. It is evident that G" is greater than G' for all tested inks, which means that they are more viscous than elastic. The loss tangent values, defined as G" / G', which is close to 90° C; also indicate that the viscous modulus is the dominant feature in all formulations. An ink is movable enough to allow good flow and leveling from the recessed cells of a rotogravure cylinder when the viscous modulus is dominant.

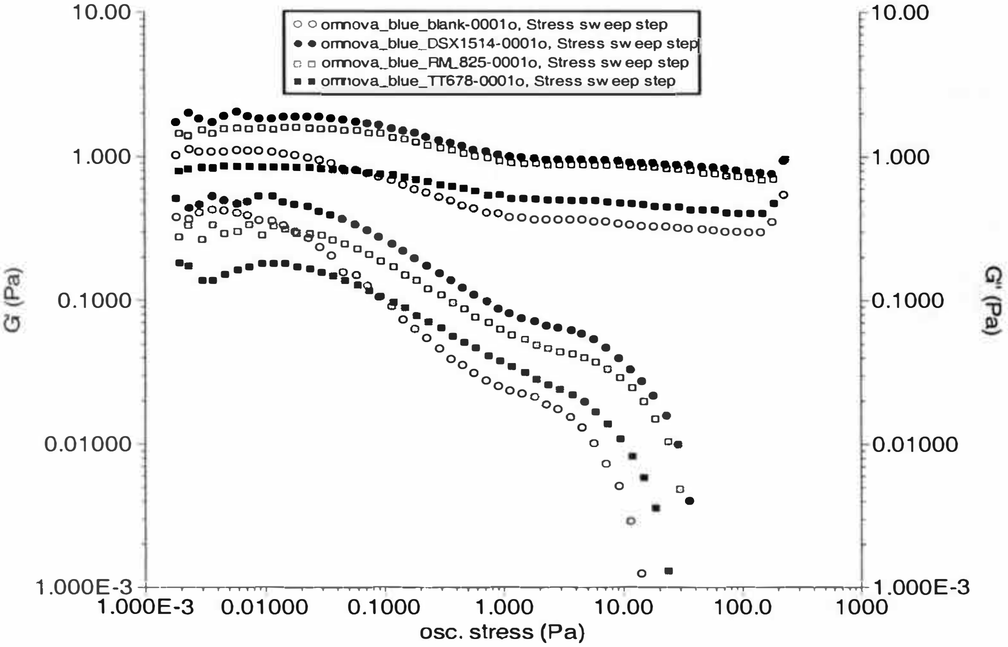


Figure 13: Comparison of viscoelasticity of blue inks to stress (Stress sweep test)

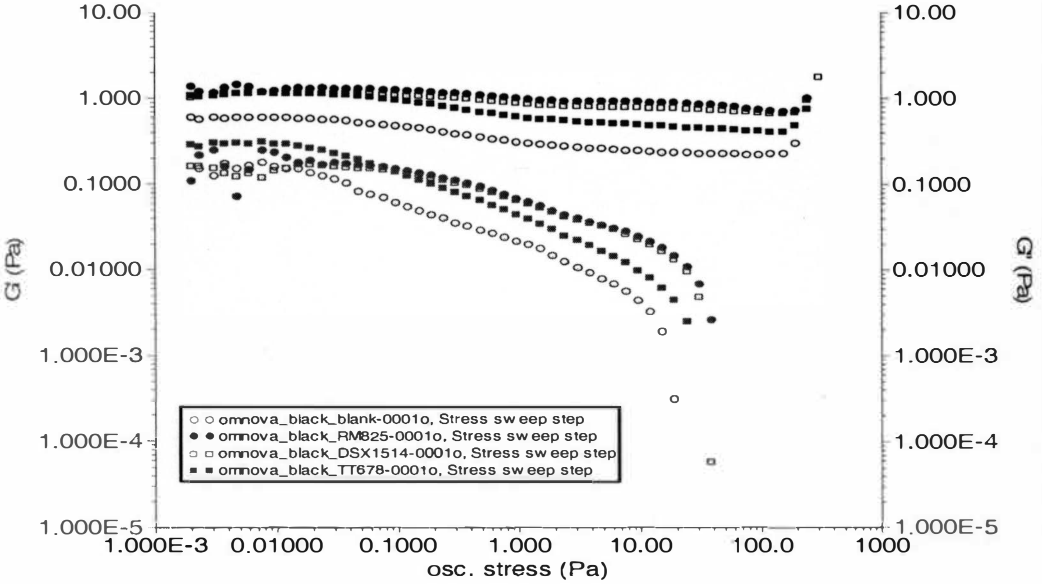


Figure 14: Comparison of viscoelasticity of black inks to stress (Stress sweep test)

It was observed that the rheological behavior of all tested inks exhibited similar trends. As shown in Figure 13 (blue inks) and Figure 15 (black inks), the viscous modulus G" of all tested samples does not change too dramatically with applied stress. The elastic modulus G' of all black inks are linear up to an oscillation stress around 0.01 – 0.2 Pa, which are the critical stresses, then the elastic moduli G' have a sudden decrease after the critical stress values, indicating a disruption in the ink's structure. For the blue inks, the presence of two linear stages in the elastic modulus G' curves suggests that there are two kinds of structures of varying strength in the suspension system. It is obvious that the ink without any rheology modifier has the shortest LVER and the lowest G' and G' value. A longer LVER means a better dispersed and more stable suspension system. Therefore, it can be concluded that with the addition of rheology modifier, a suspension system is more stable since all the tested inks were prepared under the same conditions. Obviously, the three-dimension network structure formed between the rheology modifier and ink component particles helped to stabilize and strengthen the system.

Table 11 and 12 show the critical oscillation stress value and elastic modulus (G') for all tested blue and black inks (see appendices 1 - 8 for onset point calculation). As they present, the ink with rheology modifier RM-825, DSX-1514, or TT-678 has higher critical stress value, which means greater number of interaction between ink components. Again, this indicates that with the addition of rheology modifiers, the network structure of the suspension is stronger and thus needs higher stress to break the bonds.

Table 11

Stress sweep test results for blue inks

	σ_c [Pa]	G' [Pa]
Blank	5.743	0.01168
RM-825	9.311	0.03540
DSX-1514	10.90	0.04410
TT-678	7.738	0.02052

Table12

Stress sweep test results for black inks

	σ_c [Pa]	G' [Pa]
Blank	0.01321	0.1723
RM-825	0.1711	0.1517
DSX-1514	0.1977	0.1393
TT-678	0.1267	0.1588

Frequency Sweep Test

Frequency sweep tests were performed at the stresses determined to be in the LVER by the stress sweep tests. They enable the viscoelastic properties of samples to be determined as a function of timescale. The elastic modulus (G') and the viscous modulus (G") can be obtained from these tests.

Figure 15 and 16 show a strong time dependent behavior of the elastic and viscous moduli, since the slope of G' and G" for all tested samples are rather sharp. As demonstrated in Figure 15 and 16, all of the inks were linearly viscoelastic at low shear stress in the range of frequencies from 0.01 Hz to 100 Hz, and the viscous component G" is greater that the elastic component G' over the whole range of applied frequencies. The results of the frequency sweep tests support the oscillation stress sweep test, which indicated that viscous features are dominant in all formulations. The elastic and viscous modulus of all inks increased with frequencies showing their dependence on frequency. Since all the tested inks contained the same pigment and binder, the magnitude of their elastic and viscous modulus at low shear was purely a function of different types of thickeners. It was observed that the ink without rheology modifier had lower G' and G" values compared to the formulations with rheology modifier.

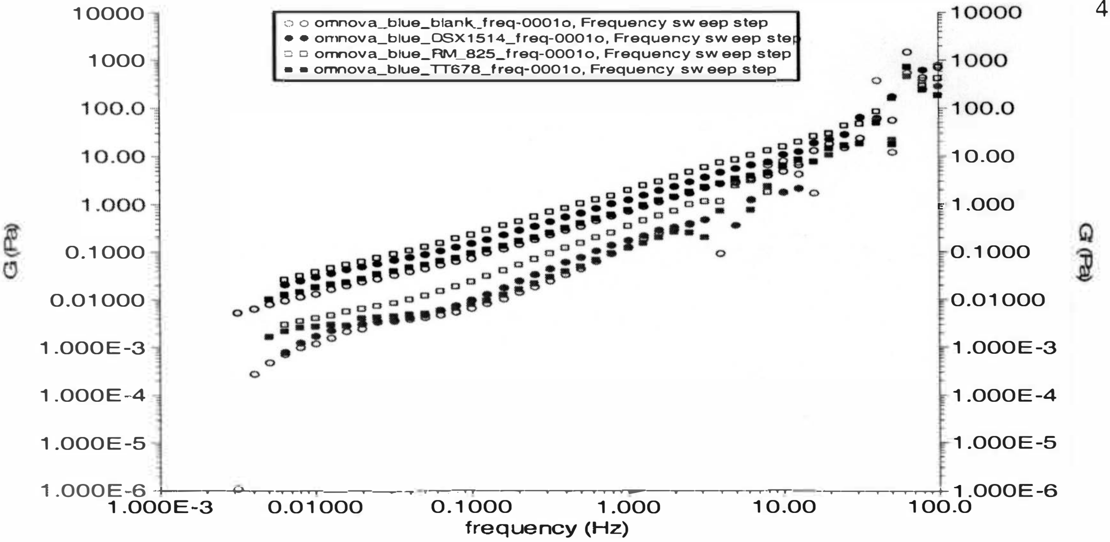


Figure 15: Comparison of viscoelasticity of blue inks to frequency (Frequency sweep test)

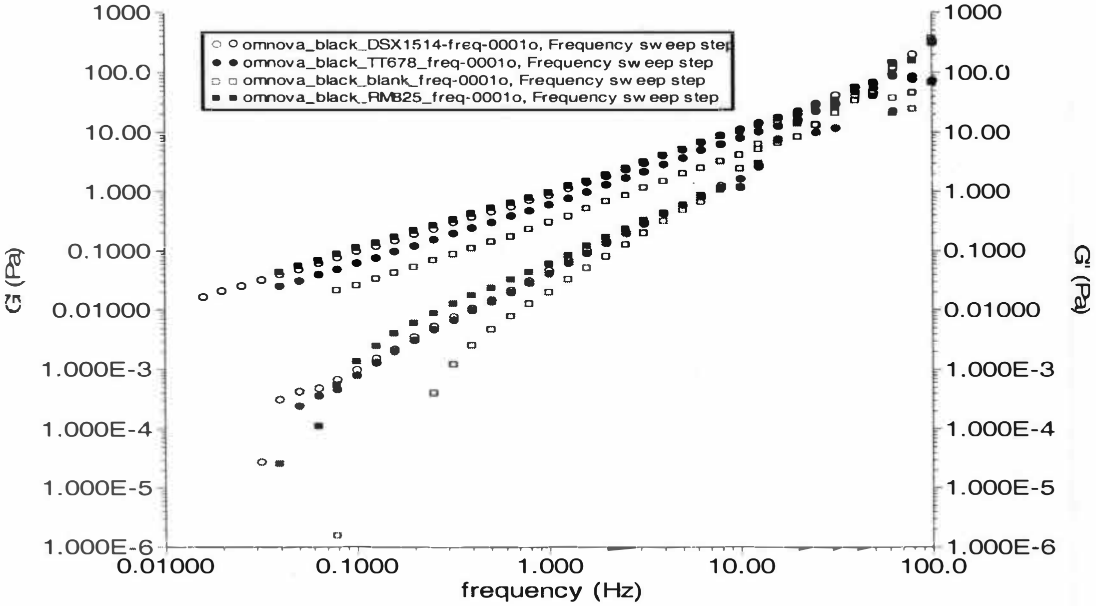


Figure 16: Comparison of viscoelasticity of black inks to frequency (Frequency sweep test)

Flow Test

Steady State Flow Test

Shear rates associated closely with the application processes such as ink transfer and distribution. During the gravure printing process, when the image cylinder rotates and transfers ink onto the surface of the substrate, high shear rates are applied on the ink. For easy application and obtain good print quality, inks should be shear thinning; however, they need to maintain an appropriate viscosity to prevent spreading and smearing during printing.

Steady state shear experiments were carried out on the AR 2000 Rheometer (TA Instrument) at a temperature of 25°C. Viscosity is the measurement of a material's resistance to flow. In Figure 17 and 18, the viscosity is plotted as a function of shear rate on logarithmic coordinates for all the tested inks. It is obvious that all the inks display a shear-thinning behavior. The addition of rheology modifier into the system tends to increase the viscosity at low shear rates. As shear rate increases, the viscosity decreases and appears to approach a limiting value. The limiting value also increases with the addition of rheology modifier into the system. Therefore, it can be concluded that the addition of rheology modifier has given the ink system more structure and changes its shear behavior.

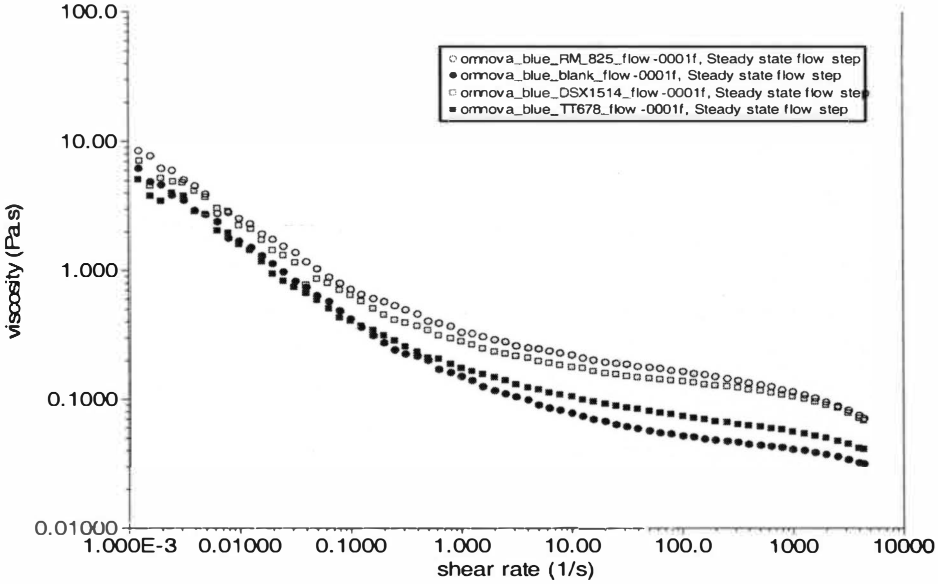


Figure 17: Viscosity as a function of shear rate of the four blue inks (Steady state flow test)

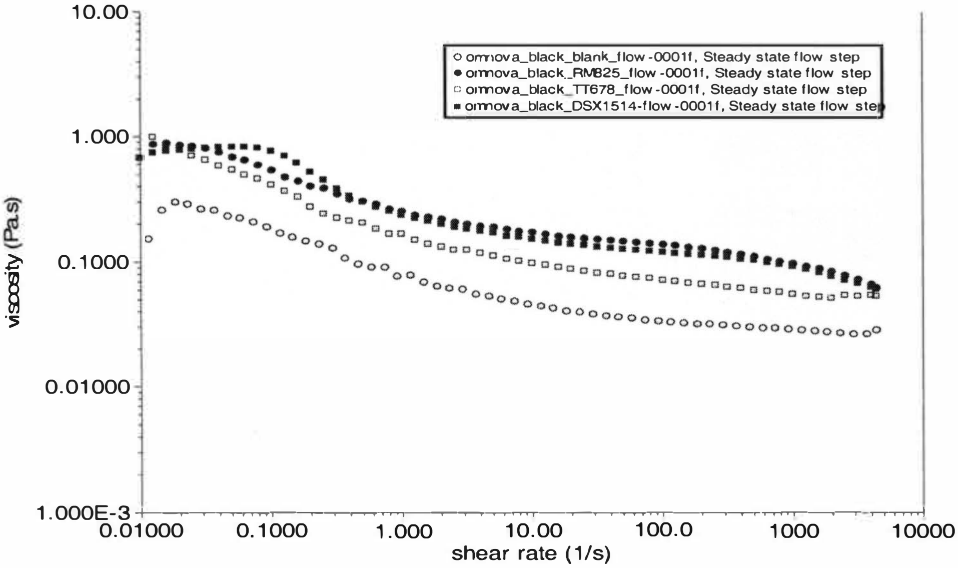


Figure 18: Viscosity as a function of shear rate of the four black inks (Steady state flow test)

Temperature Ramp Flow Test

One of the main characteristics on interest to users of printing inks is the flowability (viscosity) at the temperature of the printing process. Figure 19 and 20 show the viscosity versus temperature obtained from flow measurement with a controlled stress rheometer (AR 2000, TA Instrument). A circulating water bath chamber was used to rapidly raise the ink's temperature during evaluation from 20°C (room) to 45°C (press temperature).

From the curves it is obvious that all inks display decreasing viscosity with increasing temperature. It is evident that with the addition of rheology modifier, the viscosity of the inks has a higher viscosity at room temperature, which can help solve a sedimentation problem during storage at low viscosity. As temperature increases during the printing process, the viscosity of all inks decreases and approach a limiting value at the printing nip. Again, the limiting value of the ink with rheology modifier is higher than that of the control. An Arrhenius plot of viscosity and temperature is a plot of log y (or ln y) over 1/T (or 1/kT). This produces a straight line (see appendices 9 & 10).

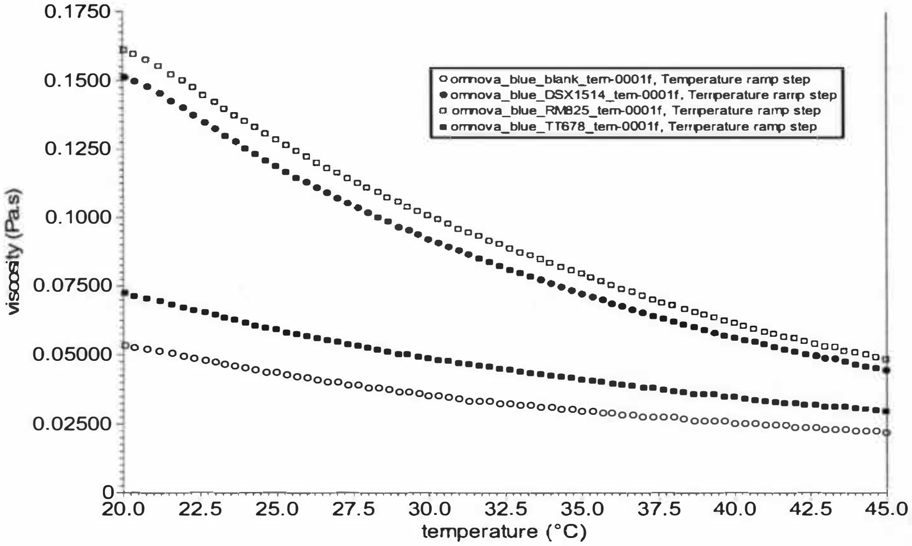


Figure 19: Viscosity as a function of temperature of blue inks (Temperature ramp flow test)

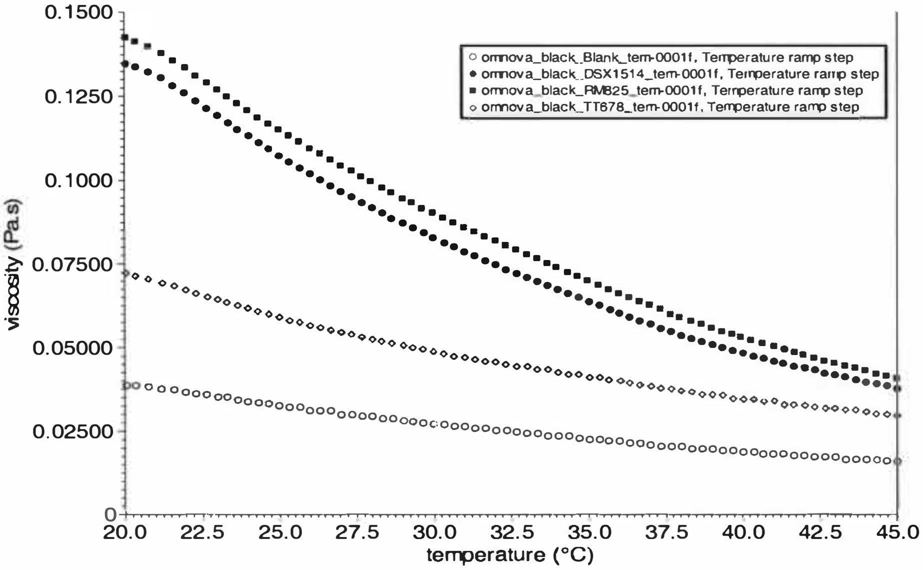


Figure 20: Viscosity as a function of temperature of black inks (Temperature ramp flow test)

Shear Thinning Index

The Shear Thinning Index was calculated by dividing the apparent viscosity measured at 6rpm rotational speed by the viscosity measured at 60rpm rotational speed. All measurements were made at a temperature of 25°C. A shear thinning index equal to 1.0 indicates Newtonian flow behavior (see Newtonian definition). The shear thinning index measures the shear thinning properties of the inks.

Table 13

Shear thinning index of extender systems (systems contain only binder, emulsion, and additives, without pigment)

	Viscosity at 6 rpm (cP)	Viscosity at 60 rpm (cP)	Shear Thinning Index
Blank	187	63	2.97
RM-825	367	118	3.11
DSX-1514	400	135	2.96
TT-678	733	177	4.14

Table 14

Shear thinning index of blue inks (with / without rheology modifier)

	Viscosity at 6 rpm (cP)	Viscosity at 60 rpm (cP)	Shear Thinning Index
Blank	267	78	3.42
RM-825	400	223	1.79
DSX-1514	267	153	1.74
TT-678	367	173	2.12

Table 15

Shear thinning index of black inks (with / without rheology modifier)

	Viscosity at 6 rpm (cP)	Viscosity at 60 rpm (cP)	Shear Thinning Index
Blank	217	68	3.19
RM-825	450	213	2.11
DSX-1514	417	180	2.32
TT-678	533	237	2.25

A higher index number means more shear thinning of the ink. As shown in Tables 13 – 15, almost all of the tested inks show a lower shear thinning index with rheology modifiers addition.

Ink Performance

RM-825, DSX-1514, and TT-678 were selected to add into the water-based rotogravure ink formulation to study rheology modifiers' effect on ink performance. Ink performance was characterized in terms of reflective density of the printed samples. As presented in the Table 16 and 17, it was observed that the addition of these four rheology modifiers did not change the pH value of the system; also the particle size did not change significantly. On the other hand, the viscosity of the ink system has increased greatly with the addition of these rheology modifiers. This increase in viscosity could benefit the ink transfer and the system had improved performance, which was reflected in slightly higher print densities.

Table 16

Blue inks properties and performance

Rheology Modifier	pH Value	Particle Size (nm)		Solid Content (%)	Viscosity (Shell #5, S)	Reflective Density (C)
		Diam	SD			
Blank	9.2	281.3	70	36.2	10.8	1.01
RM-825	9.2	301	76	35.9	22.3	1.09
DSX-1514	9.2	297.1	152.5	34.8	23.5	1.11
TT-678	9.2	286	135.3	34.0	22.5	1.07

Table 17

Black inks properties and performance

Rheology Modifier	pH Value	Particle Size (nm)		Solid Content (%)	Viscosity (Shell #5, S)	Reflective Density (C)
		Diam	SD			
Blank	9.0	315.6	127.4	32.5	10.0	1.01
RM-825	9.0	342.7	76	33.8	21.3	1.07
DSX-1514	9.0	349.3	135.4	33.0	22.5	1.09
TT-678	9.0	351.6	152.6	32.3	22.0	1.03

Temperature Stability

Previous work by Erika Hrehorova found that viscosity varies during press runs and affects color consistency [Hrehorova, E., et al, 2005]. Therefore, it is important that ink systems have the ability to maintain consistent viscosity during press runs. Viscosity inconsistency of water-based gravure ink can be caused by many factors such as evaporation of amines, pH value change, and temperature. Temperature is one of the most important factors that affect ink viscosity.

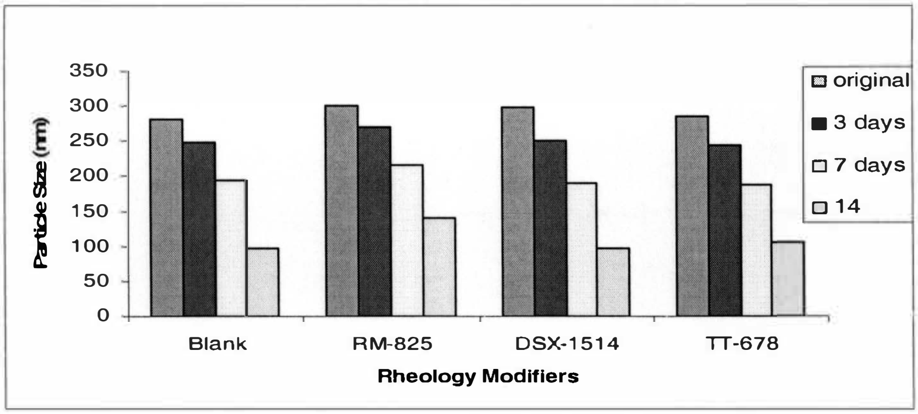


Figure 21: Temperature stability investigation (Particle size of blue inks)

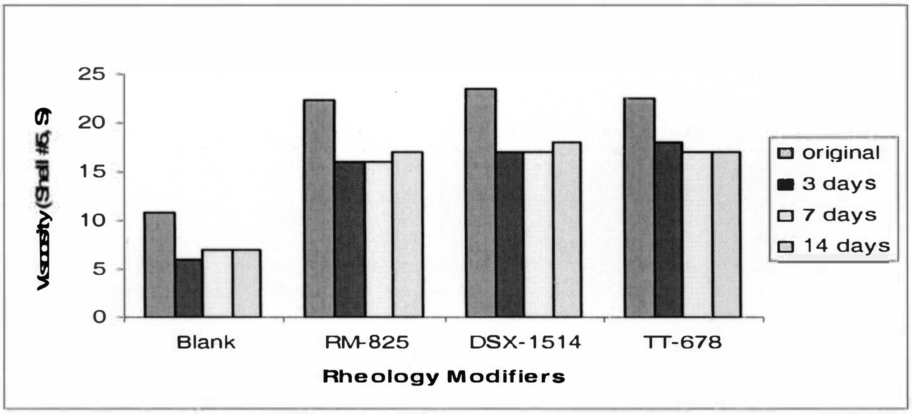


Figure 22: Temperature stability investigation (Viscosity of blue inks)

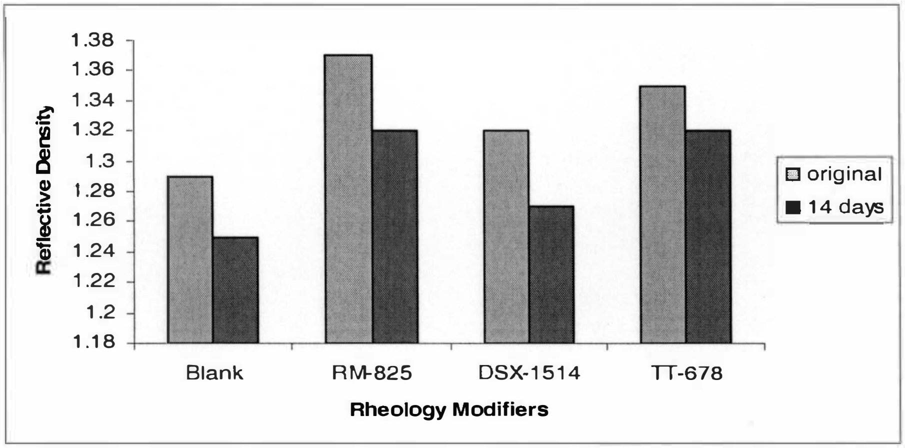


Figure 23: Temperature stability investigation (Reflective density)

In this project, the temperature stability test was performed on the blue inks. The test method was provided by OMNOVA Solution that simulated the temperature conditions encountered during a gravure press run. Samples were placed at the temperature of 120 °F and room temperature (75 °F) back and forth for a period of fourteen days. Samples were checked for viscosity and particle size. It was found in this research that the addition of rheology modifiers did not help improve the temperature stability (viscosity and particle size stability) of the water-based system. The results are shown in Figure 21 and 22. The viscosity of the system decreased when temperature increased, and the particle size decreased as temperature increased. The possible explanation for these changes could be the higher temperature can cause degradation of the resins in the system. Lower viscosity leads to the lower print density of the printed samples (Figure 23). Further studies should be performed on rheological properties of the binder system.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

The two most popular groups of rheology modifiers employed in water-based gravure ink systems are non-associative and associative thickeners. These rheology modifiers have more influence on a system than just simply altering the thickness or viscosity of the mixture. They also might have great impact on the rheological behavior, pH value, particle size, and storage stability of an ink system. These impacts will finally affect the ink performance on press.

Twelve different rheology modifiers were studied in this experiment. Their viscosity efficiency, pH stability, particle size, rheology behavior, and temperature stability in the system were measured. Wire-wound lab rods and a Moser Sheet-fed Gravure Proofing Machine were employed to produce printed samples which were used to characterize the performance of the formulated inks.

It was observed that the different rheology modifiers evaluated in the water-based gravure inks had significant effects on the viscosity and rheological behavior of the inks. Regarding the low-shear viscosity, ASE-95 appeared to be the most efficient among the tested thickeners, whereas RM-2020 being the least efficient one. Although the addition of some rheology modifiers did increase the ink viscosity, they affected the pH values of the water-based system significantly. It was observed that the addition of TT-615, TT-935, ASE-60, 20KR019, 20KR021, and 20KR026 lowered the pH value of the system greatly and thus created a less stable system. It was found that ASE-95, TT-615 and TT-935 caused the system to flocculate and separate after storage for one week.

Particle size analysis showed that the addition of all the evaluated rheology modifiers increased the particle size of the suspension system. A major increase in particle size was observed with the addition of TT-615, TT-935, ASE-60, ASE-95, 20KR019, 20KR021, and 20KR026. The increase in particle size was probably due the decrease in pH value of the system which caused the clustering of the pigment particles in the system.

Based on the studies on thickening efficiency, pH value, and particle size, it was preliminarily concluded that the three rheology modifiers RM-825, DSX-1514, and TT-678 were suitable for the water-based gravure system. Experiments were performed to study the inks containing these rheology modifiers.

The rheological behavior studies showed that all the formulated inks were found to be viscoelastic under the conditions tested. The viscous modulus G" is greater than the elastic modulus G' for all tested inks, which means that they are more viscous than elastic. Results from oscillation stress sweep test and frequency sweep test showed that with the addition of rheology modifiers, the ink had a higher critical stress value, higher viscous modulus G", and higher elastic modulus G'. It can be concluded that a suspension system is more stable, since the three-dimension network structure formed by the rheology modifier with ink component particles helps stabilize and strengthens the system.

The results from steady state shear and temperature ramp experiments also indicated that all the tested ink exhibited shear-thinning behavior and the viscosity decreased with temperature. However, with the addition of rheology modifiers, the limiting values of the system increased.

Overall, with the addition of rheology modifier of RM-825, DXS-1514, and TT-678 into the water-based system, the ink exhibited improved rheological behavior and ink performance. The reflective density of the print samples confirmed this conclusion in an experimental scale. The shear-thinning index of all tested inks close to 1 also indicated good runability of the formulated inks.

However, these rheology modifiers did not help improve temperature stability of the system. Both ink viscosity and particle size decreased with temperature increased. Further consideration should be given to rheological behavior of binders used in the system.

REFERENCES

Annon[1]: VOC Report, accessed April 2005 at http://www.printnet.com.au/verve/_resources/VOC_Report_-_members.pdf

Annon[2]: Ink World Feature Story: Water-Based Inks. Ink World Magazine, February 2000. http://www.inkworldmagazine.com/articles/2000/02/waterbased-inks.php

Annon[3]: From Engraving to Printing – How Gravure Printing Works. July 2004. http://www.specialchem4coatings.com/resources/articles

Tremper, J. et al: Gravure: Can It Fight Flexo? Gravure Magazine, August 2002. http://www.gaa.org/pdfs/gravuremag/ _vs_Flexo.pdf

Hrehorova, E., Pekarovicova, A., and Fleming, P.D.: Spot Color Consistency for Product Gravure. Proceeding of the 57th TAGA Annual Technical Conference, Toronto, Ontario, April 2005.

Podhajny, R.M.: Has Water-based ink technology peaked? http://www.findarticles.com.

Helien, W.: Overcoming Substrate Wetting Problems. Dec 17, 2003. http://www.specialchem4coatings.com

Janule, V.P.: Formulation Problem Solving with Dynamic Surface Tension Measurement. Paint and Coating Industry, Feb 22, 2001. http://www.pcimag.com/CDA/Archives/1aee0e95856a7010VgnVCM100000f932a8c0

Rebros M., Fleming, P.D., and Joyce, M.K.: UV-Inks, Substrates and Wetting. 2006 Coating & Graphic Arts Conference, Atlanta, GA. April 24-27, 2006

Kirshnan, et al: U.S. Patent, 5, 972,088. (October 26, 1999).

Wallstrom, E. et al: U.S. Patent, 5,534,049. (July 9, 1996).

Krishnan, et al: U.S. Patent, 5,098,478. (March 24, 1992).

Batlaw, R. et al: U.S. Patent, 5,389,130. (February 14, 1995).

Laden, P.: Chemistry and Technology of Water-based Inks. Edition 1997, pp 190-207.

Sharma, M.K.: Advance in Water-based Coating and Printing Technology. Surface Phenomena and

Additives in Water-Based Coatings and Printing Technology, Edited by Sharma, M.K., Plenum Press, New York, 1991, pp1-10.

Lin, L.: Mechanisms of Pigment Dispersion. Pigment & Resin Technology. 2003, Volume 32, Number 2, pp 78-88.

Annon[4]: The Weatherability of Acrylic Gloss Paints. Paint Quality Institute, 2000. http://www.paintquality.com.au/press/newspaper/BOAPT02.html.

Horn, M.B.: Acrylic Resins. Reinhold Publishing Corporation, New York, 1960, pp 28.

Horn, M.B.: Acrylic Resins. Reinhold Publishing Corporation, New York, 1960, pp 123 -148.

Boyce, et al: U.S Patent, 5,208,285, (May 4, 1993).

Roesler, R.R. and Hergerrother, R.P.: Two Component Coatings. Bayer Corporation. No date.

Manock, H.L.: New Developments in Polyurethane and PU/Acrylic Dispersions. Pigment & Resin Technology, 2000, Volume 29, Number 3, pp 143-151.

Moss, M.: Polyurethane Dispersion for Adhesive Applications. Pigment & Resin Technology, 1997, Volume 26, Number 5, pp 296-299.

Zeng, Jianren: New silicone Foam-Control Agents for Waterborne Coatings. Jan 26, 2004. http://www.specialchem4coatings.com.

Schnell R. R. et al: Selection Defoamers: Defoamers and Antifoamer Products Play an Important Role in Degassing and Stabilizing Coatings. Polymers Paint Colour Journal, May 2004. V194, i4476 pp 22(3).

Kunjappu, J. T.: Surfactants in Ink Chemistry. Ink World, July 2000. V6, i7 pp 44.

Hahn, L.: Polymer-surfactant interactions: Modes of Association and Methods of Analysis. Ink World, March 2004. V10, i3 pp 65(7).

Buckmann, A.J.P. et al: Self Crosslinking Polymeric Dispersants Used in Emulsion Polymerization. Nov 3, 2003. http://www.specialchem4coatings.com.

Eldred, N.R. and Scarlett, T.: What the Printer Should Know about Ink. Graphic Arts Technical Foundation, 1990, pp48.

Sauer, F.: a New Approach to Understanding Rheological Additives. Paint and Coating Industry, Jan 2004. http://www.pcimag.com/CDA/ArticleInformation/features/BNP__Features__Item/0,1846,127045,00.html.

Pangalos, G. et al: Rheological Properties of News Inks. Journal of Rheology, 1985, 29(4), 471-491.

Morrison, F. A.: Understanding Rheology. Oxford University Press, New York, Oxford, 2001. pp3.

Hermans, J. J.: Flow Properties of Disperse Systems. Amsterdam, North – Holland Publishing Company; New York, Interscience Publishers, 1953, pp 54.

Hatchek, E.J., Koll. Zschr. 8, 34. 1911.

Sibree, J.O., Trans. Faraday Soc. **26**, 26. 1930.

Sumner, O.G., Nature **165**,182 (abridged report). 1950.

Hermans, J. J.: Flow Properties of Disperse Systems. Amsterdam, North – Holland Publishing Company; New York, Interscience Publishers, 1953, pp 39.

Podhajny, R.M: The Importance of Viscosity in Printing Ink Systems – Column. Paper, Film, & Foil Converter, May 1998. http://www.highbeam.com/doc/1G1-20897717.html

Saunders, G.: The Rheological Evaluation of the Inks, Ink & Print, 1992, v10, n2, pS 1 (4).

Gupta, R. K.: Polymer and Composite Rheology. West Virginia University, Morgantown, West Virginia, 2nd Edition, 2000, p 6.

Avci, Sel: Rheological Additives Selection for Printing Inks. Ink World, September 2003. V9 i9 p 96 (6).

Kalenda, P.: Application of Associative Thickeners to Water-borne Coatings. Pigment and Resin Technology, 2002, Volume 31, Number 5, pp 284-289.

Annon[6]: Rheology, accessed April 2005 at http://www.specialchem4coatings.com/tc/rheology.

Verstrat, D. W.: Formulating with Associative Rheology Modifiers. http://www.alcochemical.com/techsupport/whitepapers.asp

Miller C. M. et al: Determination of the Thickening Mechanism of a Hydrophobically Modified Alkali

Soluble Emulsion Using Dynamic Viscosity Measurements. Associative Polymers in Aqueous Media, by Glass, J. E. American Chemical Society, Washington, DC, 2000, pp 338-350.

Annon[7]: Zahn Cup accessed April 2005 at http://www.geneq.com/catalog/en/zahn_cup.html.

Annon[8]: Shell Cup, accessed April 2005 at http://www.viscosity.com/html/viscosity_cup.htm.

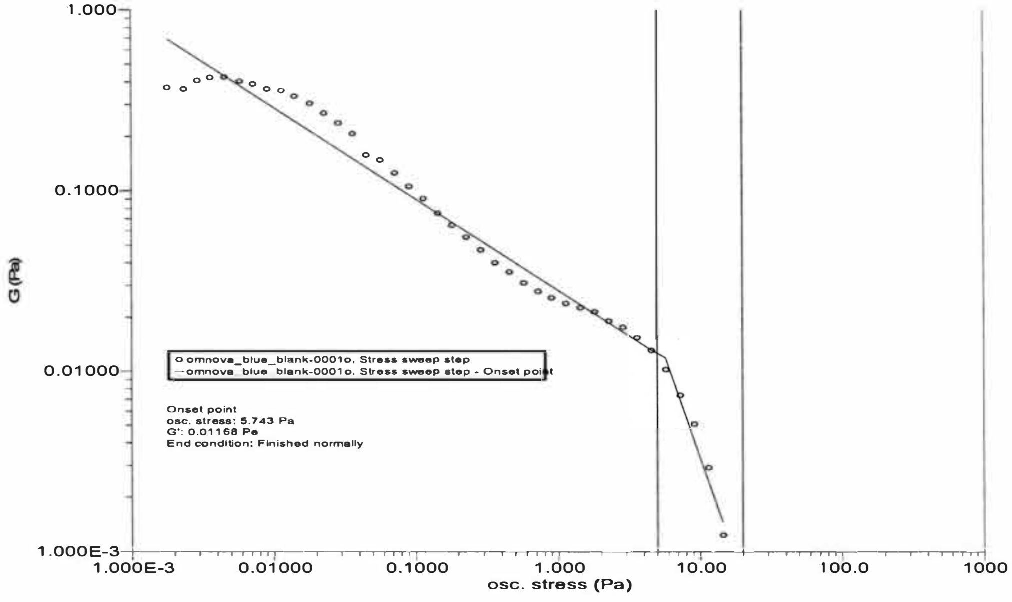
Annon[9]: TA Instrument AR 2000 Rheometer, accessed April 2005 at http://www.tainstruments.com/product.asp?n=1&id=35

Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield type) Viscometer. Annual Book of ASTM Standards, Section 06, 01, Designation: D 2196-99, pp 234-237.

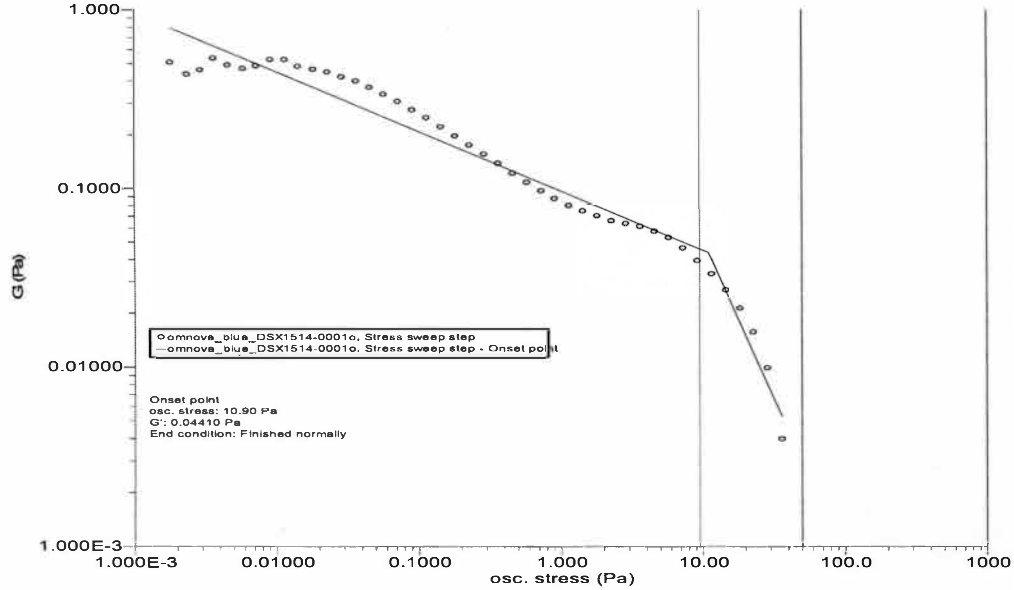
Sesetyan, T.: The Ink Challenge. Label and Narrow Web, May/June 2002.

Frimova, A., Pekarovicova, A., Fleming, P.D., and Pekarovic, J.: Ink Stability during Printing. TAGA J., 2, December 2005.p122

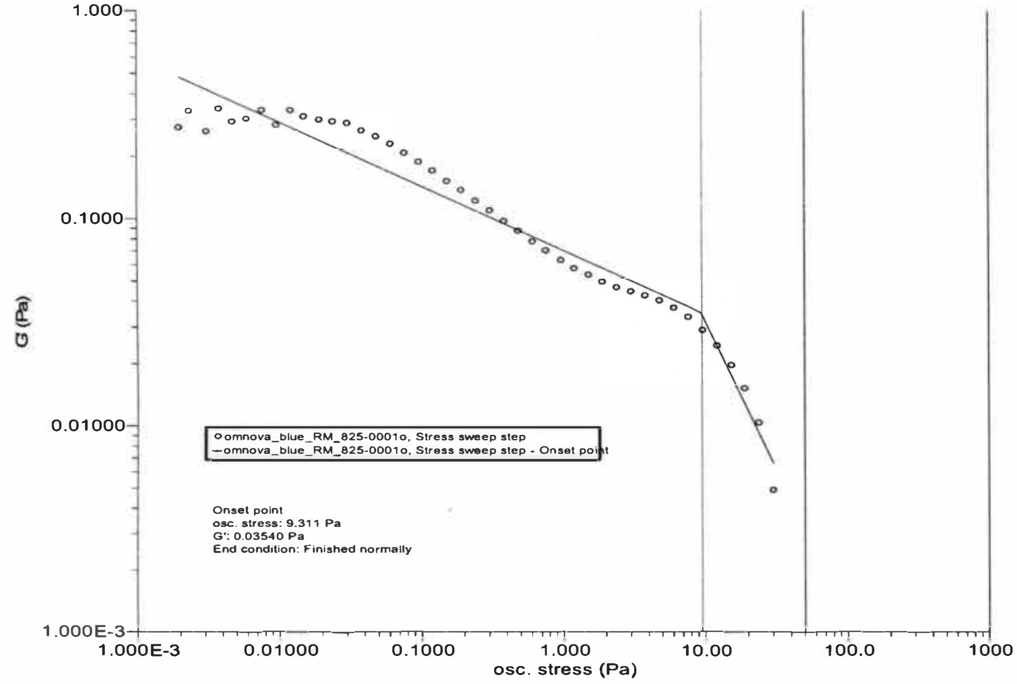
APPENDICES



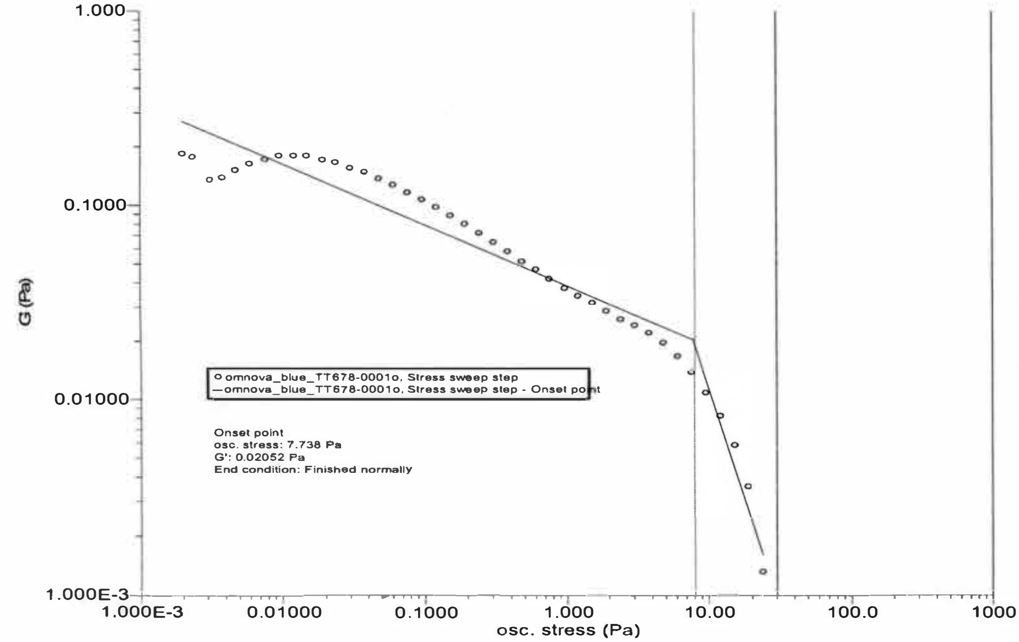
1. Onset point of blue ink without rheology modifier



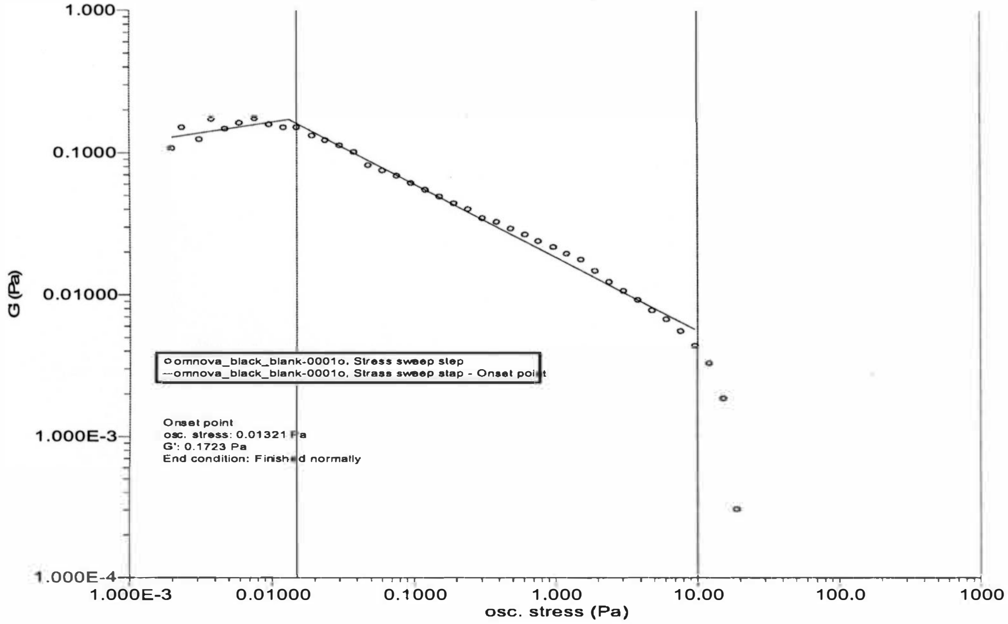
2. Onset point of blue ink with addition of rheology modifier DSX 1514



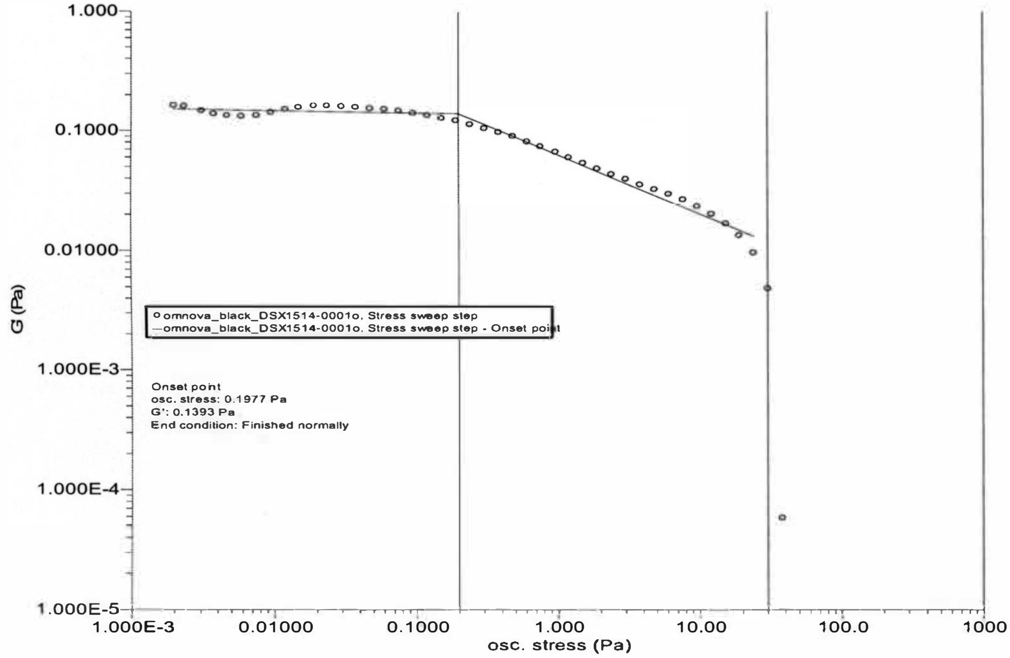
3. Onset point of blue ink with addition of rehology modifier RM 825



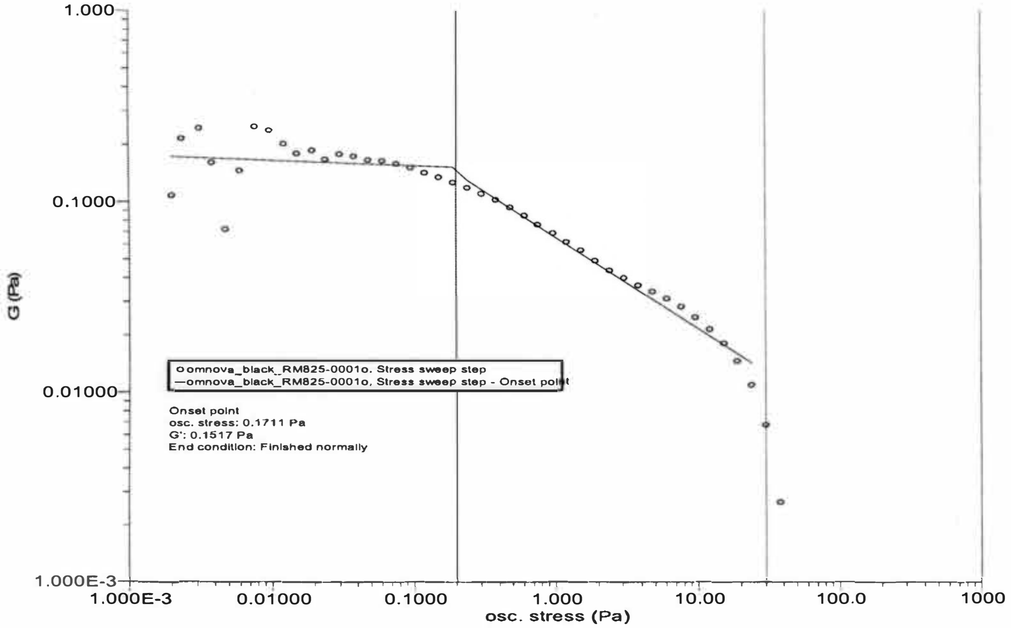
4. Onset point of black ink with addition of rehology modifier TT 678



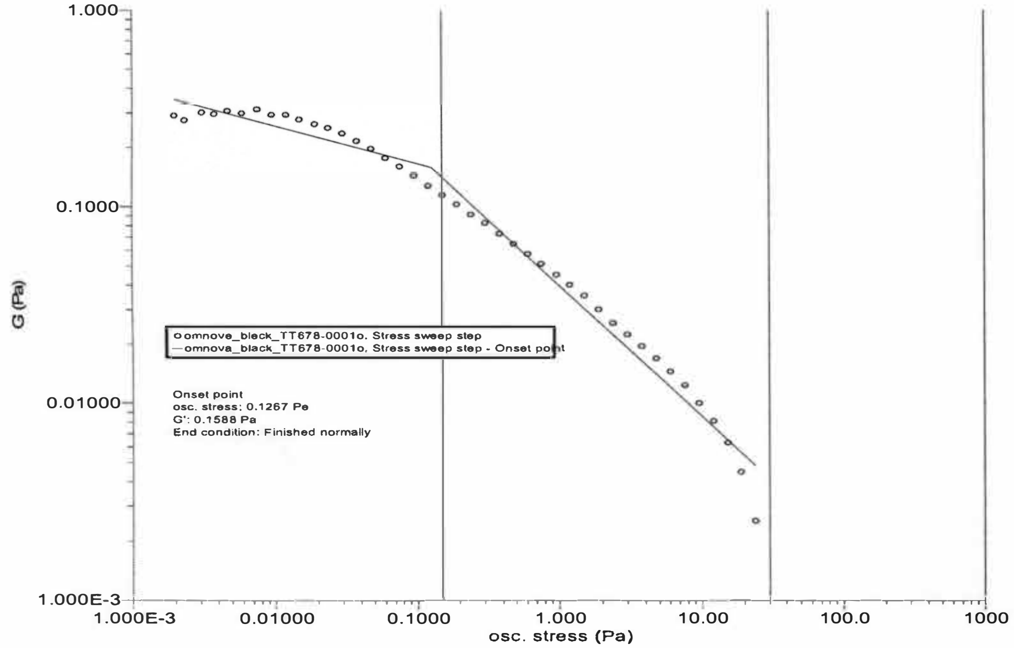
5. Onset point of black ink without rheology modifier



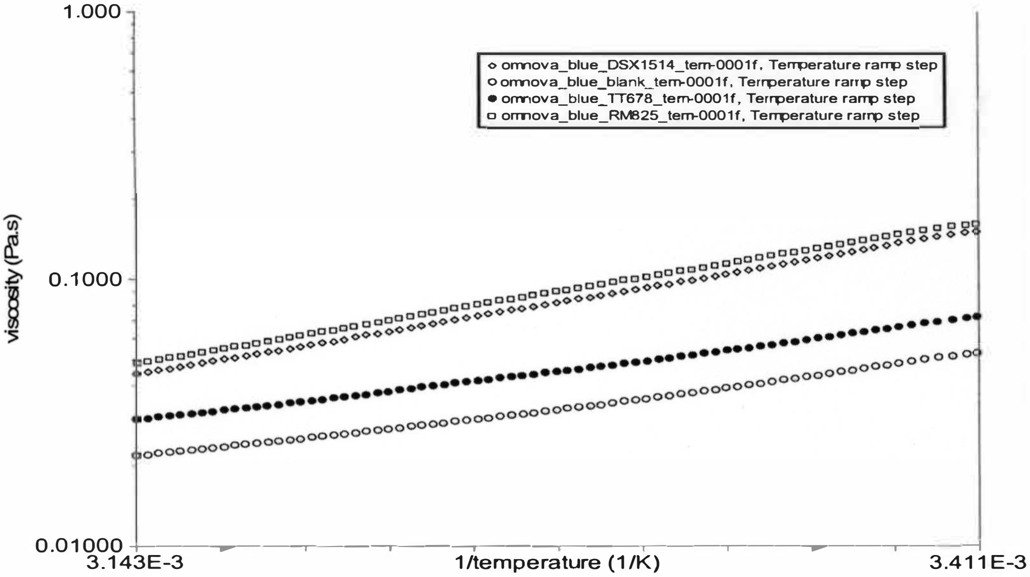
6. Onset point of black ink with addition of rheology modifier DSX 1514



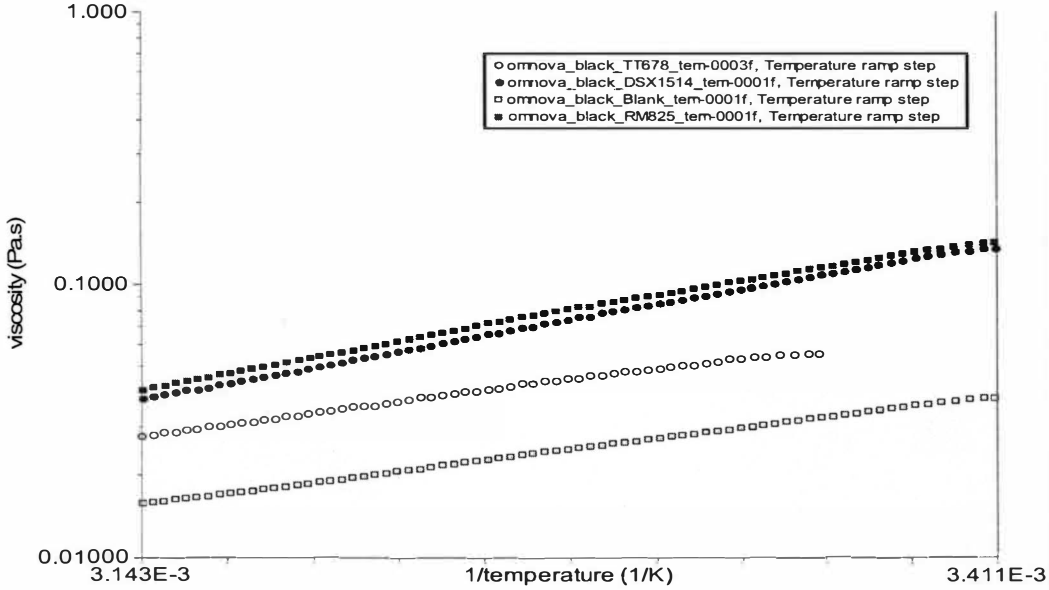
7. Onset point of black ink with addition of rheology modifier RM 825



8. Onset point of black ink with addition of rheology modifier TT 678



9. Viscosity as a function of temperature of blue inks (Arrhenius plot)



10. Viscosity as a function of temperature of black inks (Arrhenius plot)