Rheology Modifiers in Water-based Rotogravure Inks

RuRou Mai*, Alexandra Pekarovicova*, and Paul D. Fleming III*

Keywords: associative and non-associative thickener, water-based rotogravure ink, printability, stability, rheology

Abstract

Recently, water-based inks have been of more and more interest to the printing and ink industry, because of their environmental benefits. 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. The transition from solvent-based to waterborne inks has been facilitated by advances in both the chemistry and the printing technologies employed. With the new development in rheology modifiers and their increasing application in water-based gravure inks, a more complete investigation of their chemistry, thickening mechanism and effects on water-based gravure ink systems is necessary. This paper 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 (viscosity profiles of each rheology modifier in a model system), pH stability, particle size, system compatibility, temperature stability, and printability on vinyl substrates. Wire-wound lab rods and a Moser Sheet-fed Gravure Proofing Machine were employed to produce printed samples for characterizing the performance of the formulated inks. The purpose of these investigations is to acquire a complete understanding of rheology modifiers' effects on the water-based ink system, as well as to help select appropriate rheology modifiers for water-based ink systems in order to achieve better print quality.

---

* Department of Paper Engineering, Chemical Engineering and Imaging
Western Michigan University
Kalamazoo, MI 49008

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 entrenched 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 mostly solvent-based inks, which provide excellent print quality at a low cost. However, solvent-based inks contain organic solvents such as alcohol, ester, ketone, and toluene, etc. These compounds will affect the overall environmental quality and human health. Researchers have shown that the emission of VOCs lead to the formation of photochemical smog (ozone) by reacting with oxides of nitrogen, other pollutants and sunlight (Allen et. al, 2005).

Once the concerns were raised, governments began to place stricter environmental regulations on printers, requiring them to reduce and finally eliminate the emissions 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 of 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 (Ink World, 2000). 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 (Ink World, 2000).

One of the reasons for the slow progress in water-based gravure ink development is the difference in chemistry between these two types of materials. For a solvent-based ink, the resins not only act as the dispersion vehicle for pigments, 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 printing processes. Alkaline materials are involved in the formulations, which will affect the ink viscosity when they evaporate and change the pH value of the system. Furthermore, the emulsions used in water-based systems have extremely low viscosity.

Rheological properties of printing inks play a central role in the distribution of ink on the printing substrates and in the splitting of ink film at the exit of the printing nip. In the gravure printing process, the ink flow between the two rigid cylinders is compressed, stretched, sheared, fractured, and then transferred to the surface of substrates in seconds. Therefore, the ink must be able to flow in and out of the cells fast and uniformly when contacted with the cylinder and the substrate. The performance of an ink can be evaluated by its non-Newtonian viscosity profile. With a too high of viscosity, the cells' filling and emptying is difficult, and deep cells will give un-even printing; on the other hand, with a too low viscosity, a dilution factor will occur and lead to poor ink transfer, which will give poor optical density and may also cause sedimentation problems. In order to achieve optimum print quality and product consistency, rheology modifiers must be employed in a water-based gravure ink to improve its rheology properties.

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 presses. This research examines twelve commonly used thickeners in a comparative analysis of their efficiency in a water-based gravure ink system and observes their effects on ink properties. Wire-wound lab rods and a Moser sheet-fed gravure proofing press were employed to simulate the printing trials. Ink performance was characterized in terms of print density. Selection of rheology modifiers for a water-based rotogravure system is also discussed based on these investigations.

Experimental

Ink Components

Pigment Dispersions: Blue pigment dispersion was provided by **Penn Color**.

Vehicle Mixture: a semi-finished water-based mixture containing emulsion (Vycar 460X95), surfactants, de/antifoamers, flat reagents, and other additives was provided by **Noveon**.

Rheology Modifiers: Non-associative thickeners and associative thickeners as listed in **Table 1**.

Ink Preparation

Clears: Varying levels of thickeners were added into the water-based system to test for efficiency and to observer their effects on the system. A clear mixture of 97 – 99% vehicle mixture and 1 – 3% rheology modifier (level used is shown in **Table 1**) 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 1: Rheology Modifiers and Their Tested Levels

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	1	2	-
9	HASE	20KR021	Union Carbide	1	2	-
10	HASE	20KR026	Union Carbide	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 2**. Samples were sealed and stored for further study.

Table 2: Blue Ink Formulations

	Blue Pigment Dispersion (g)	Extender (g)	Rheology Modifiers (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	1.4

Ink Test

Low-shear Viscosity: The most common method of low-shear viscosity measuring on press is by using efflux cups such as Shell cups or Zahn cups. Viscosity was recorded as the time required for the liquid draining out of the cup (Viscosity Measurement and Shell Cup Introduction, 2005). Eight different sizes

(#1 - #6) for viscosity ranges from 0.3 to 7000 cps were available in Shell cup serials.

pH value: The pH value of each formulation was measured by using the Americal^{TM} pH I. pH meter (American Scientific Products).

Particle Size: Particle size measurement was performed using the Particle Sizer Submicron 370 NICOMP analyzer, which is based on dynamic light scattering (DSL). 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, 2002 and Frimova, 2003).

Rheology of Inks: The rheological behavior of the formulated inks was investigated using the TA Advanced Rheometer AR 2000. Concentric cylinder systems are generally used for lower viscosity samples. The conical end (DIN) was selected in this research. A stress sweep test was performed to characterize rheological behavior of an ink. A constant frequency of 1Hz was applied and the amplitude of the stress was incremented from 0.1 to 1000 Pa.

Temperature Stability: In this process, the 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 cooled 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.
- Report data.

Printing

Drawdown: In this process, ink was transferred from the grooves of a wire-wound rod directly on the surface of the 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.

Moser Sheet-fed Gravure Proofing: The Moser proofing machine was employed to simulate more realistic printing conditions for ink performance studies. It is equipped with a hollow electromechanically engraved cylinder, which serves as the image carrier. The screening is 150 lpi, and the printing speed was set to 60 m/min.

Substrates: Commercial vinyl wall covering material was provided by **OMNOVA Solutions**.

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:

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

Where reflectance $R = R_1/R_w$
R_1 = Intensity of light reflected from print
R_w = Intensity of light reflected from white paper

Results and Discussion

Non-associative thickeners comprise water soluble polymers with a high molecular weight, which dissolve in aqueous phase and create strong linkage with neighboring water molecules (Kalenda, 2002). The thickening effect of the non-associative rheological additives is based primarily on the 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 (Verstrat, 2005). As more solute is added, less volume is available within the solution, which will cause an increase in solution viscosity (Verstrat, 2005). Alkali Swellable Emulsions (ASE), which are the most common non-associative thickeners used in water-based systems, thicken by means of neutralization of acid groups along the polymer chain. With an increase in pH and subsequent neutralization, the acid portion of the polymer expands caused by charge repulsion. ASEs provide excellent low-shear rate viscosity; however, they might have a negative effect on gloss and cause flocculation due to thickening effect.

Associative thickeners are low-molecular polymers, soluble in water, which are modified by hydrophobic groups (Kalenda, 2002). This group includes the hydrophobically modified polymers such as HASE and HEUR, which are widely used in water-based coating and printing ink systems. The thickening effect of this group is based on the interaction of the hydrophobic components of the thickener molecules with the hydrophobic components in a coating, such as emulsion and pigment particles. As a result of this interaction, a three-dimensional reversible physical cross-linking occurs in the dispersion, and a noticeable effect is an increase in viscosity.

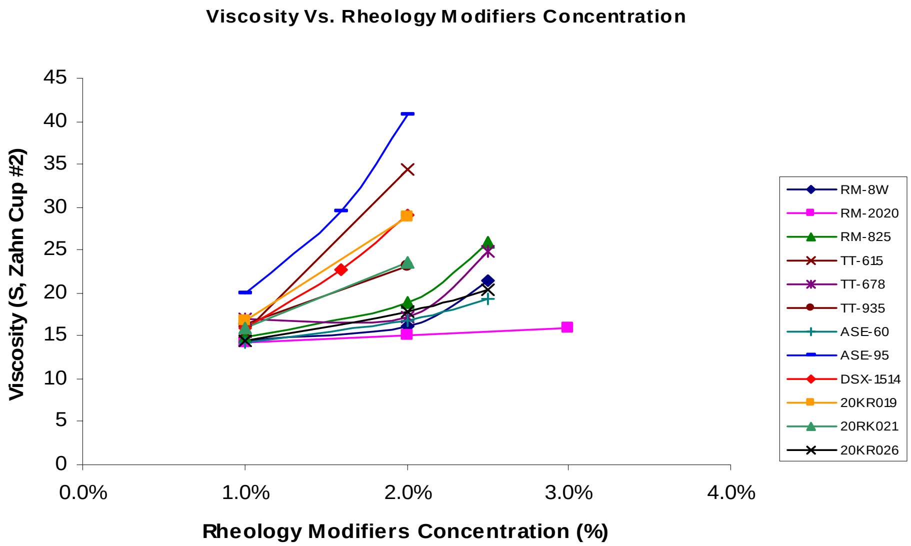

Figure 1. Efficiency of Rheology Modifiers

Figure 1 presents the efficiency of the twelve rheology modifiers, with ASE-95 being the most efficient thickener, whereas RM-2020 being the least efficient thickener. However, it was also observed that pH value and particle size of the system changed differently with the addition of each thickener.

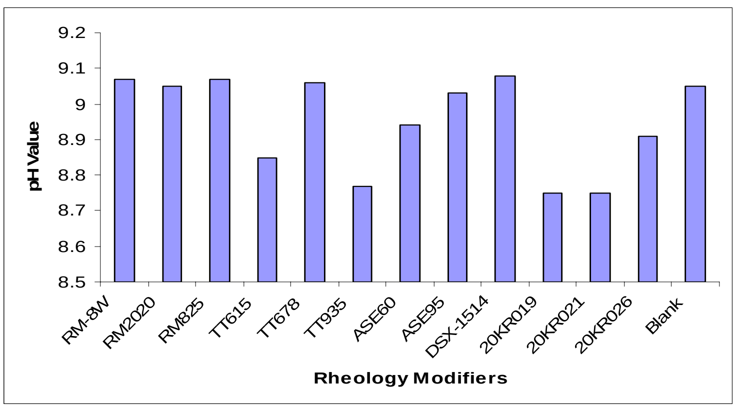

Figure 2. ***pH values Vs Rheology Modifiers***

As shown in **Figure 2**, TT-615, TT-935, ASE-60, 20KR019, 20KR021, and 20KR026 lowered the pH value of the system greatly. This is not desired in water-based gravure ink systems because a decrease in pH value can cause a negative effect on particle size, which is one of the most important factors that affect print quality. A smaller particle size held within a narrow range will show improved performance in gravure transfer and rewettability.

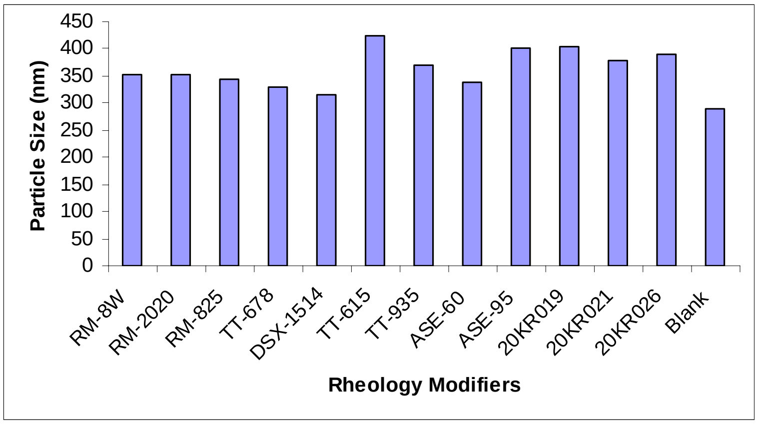

Figure 3. ***Particle Size Vs Rheology Modifiers***

In **Figure 3**, 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. Therefore, when choosing rheology modifiers for a system, we need to balance thickening efficiency and system compatibility. 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.

In the gravure printing process, the ink flow between the two rigid cylinders is compressed, stretched and sheared; therefore, the application of ink on a substrate is a time dependent flow process, and its performance is related to the rheology of the ink. Printing inks are considered as viscoelastic materials, which exhibit both elastic and viscous properties. The oscillation mode is used to characterize the rheology of these materials. The elastic or storage modulus, G', represents the amounts of energy from the oscillation that can be stored within the sample structure; the viscous modulus or loss modulus, G", represents the energy lost during the oscillation. The value of G' reflects the strength of the interaction between the different components of the tested sample. These two properties fully describe the dual nature of a viscoelastic material and together they give the total resistance made by the sample in oscillatory motion known as the complex modulus (Saunders, 1992 and Hrehorova, 2004).

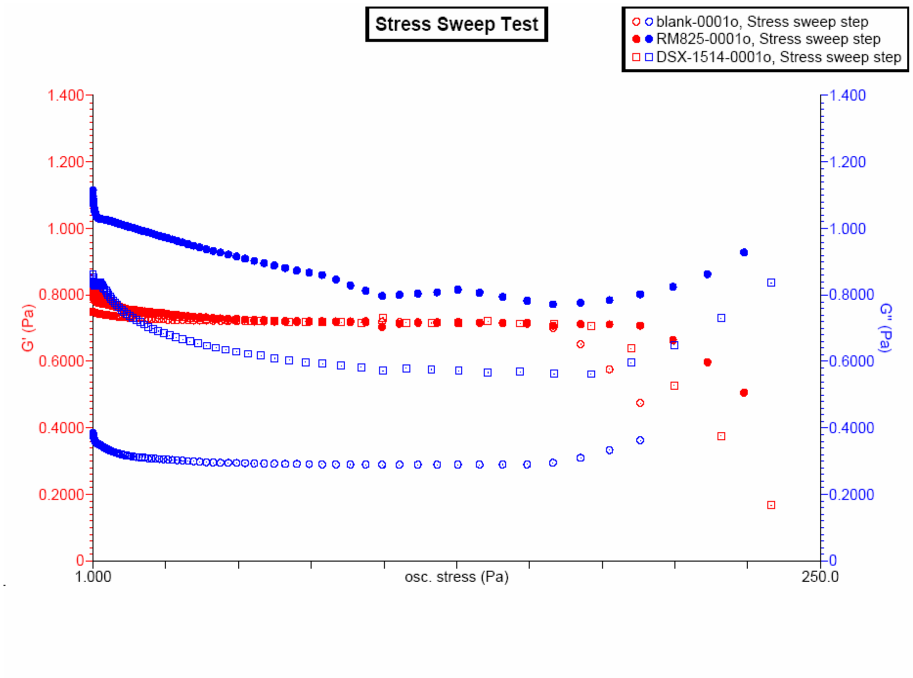

Figure 4. Stress Sweep Test

As shown in **Figure 4**, the inks with rheology modifiers (RM-825 and DSX-1514) have higher critical oscillation stresses, viscous moduli G' and elastic moduli G" than the ink without modifiers. The higher value of G' indicates greater interaction between ink components. Therefore, it can be concluded that with the addition of rheology modifiers, forming the three-dimension structure in an ink system results in a stronger structure.

RM-825, DSX-1514, and TT-678 were selected to add in the blue water-based rotogravure ink to study rheology modifiers' effect on ink performance. Ink performance was characterized in terms of reflective density of the printed samples. As presented in **Table 3**, 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, and the system had improved performance, which was reflected in higher print densities.

Table 3: Blue Ink Properties and Performance

Rheology Modifier	pH Value	Particle Size (nm)		Total Solids (%)	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

Another objective of this research was to investigate whether the rheology modifier can improve temperature stability of the water-based rotogravure ink system. Previous work found that viscosity varies during press run and affects color consistency; therefore, it is important that ink systems have the ability to maintain consistent viscosity during press runs. Rheology of inks is obtained through a combination of binder (polymers and emulsions), pigments, and additives, but primarily a result of the binder system used in the formulations. Researchers have shown that the temperature coefficient of viscosity for printing inks is about -3 or -4% per degree Fahrenheit. This means that a temperature increase of 15 °F will reduce the viscosity of the ink by around 50% (Eldred, 1990).

It was found in this research that the addition of rheology modifiers did not help improve the temperature stability of the water-based system. The results are shown in **Figure 5** and **Figure 6**. The viscosity of the system decreased when temperature increased, and the particle size decreased as temperature increased. Lower viscosity leads to the lower print density of the printed samples (**Figure 7**). Further studies need to be performed on rheological properties of the binder system.

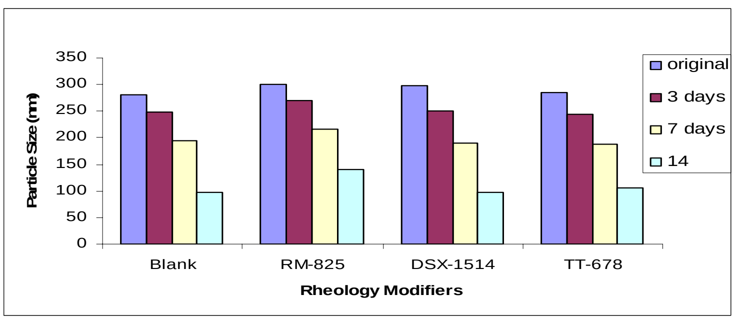

Figure 5. Temperature Stability Investigation: Particle Size

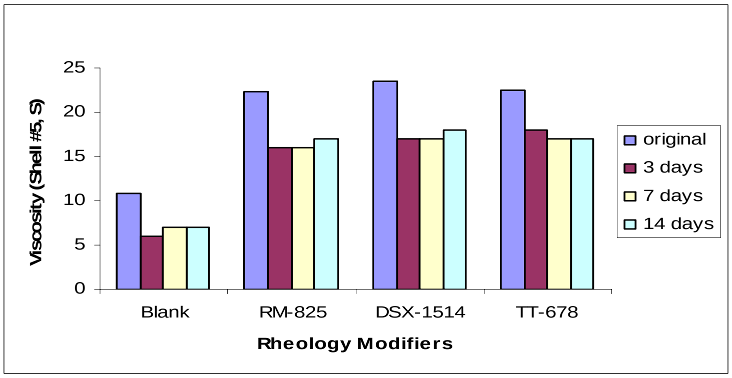

Figure 6. Temperature Stability Investigation: Viscosity

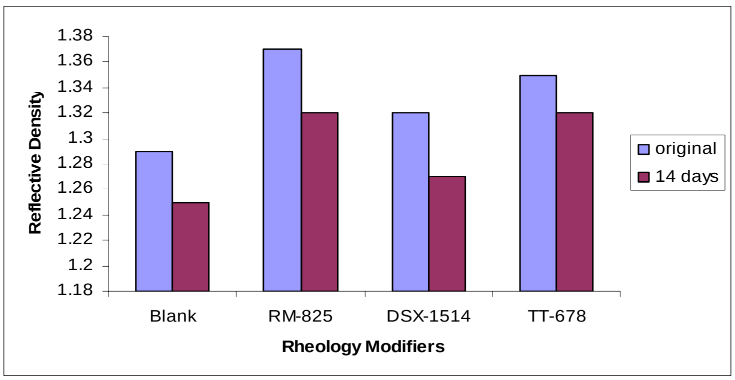

Figure 7. Temperature Stability Investigation: Reflective Density

Conclusion

Twelve different rheolgy modifiers were investigated for viscosifying efficiency and their effects on the water-based rotogravure ink system. Regarding low-shear viscosity, ASE-95 appeared to be the most efficient among the tested thickeners, whereas RM-2020 being the least efficient one. 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 less stable system. Particle size also increased greatly with the addition of these rheology modifiers. ASE-95, TT-615 and TT-935 even caused the system to flocculate after storage.
The investigation indicated that RM-825, DSX-1514, and TT-678 were suitable for the water-based rotogravure ink system. They increased the ink viscosity significantly and thus improved ink performance on the press (higher print

density). And at the meantime, they did not change the pH value of the system and did not affect the particle size significantly after their addition.

However, 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

Allen, D. et. al "Variable Industrial VOC Emissions and their Impact on Ozone Formation in the Houston Galveston Area", accessed May 2005 at http://www.epa.gov/ttn/chief/conference/ei13/uncertainty/allen.pdf

Ink World Feature Story: Water-Based Inks. Ink World Magazine, February 2000

Viscosity Measurement, accessed May 2005 at http://www.andweighing.com/and.nsf/html/Measuring+Viscosity

Shell Cup Introduction, accessed May 2005 at http://www.viscosity.com/PDF/8_1_2_04_Shell_Cup_Intro.pdf

Sesetyan, T. 2002 "The Ink Challenge," Label and Narrow Web, May/June, accessed November 2005 at http://www.labelandnarrowweb.com/articles/2002/05/the-ink-challenge.php

Frimova, A. 2003 "Particle Size Analysis of Commercial Printing Inks and Their Press Stability and Printability," (MS Thesis, Western Michigan University)

Kalenda, P. 2002 "Application of Associative Thickeners to Water-borne Coatings," Pigment and Resin Technology, vol. 31, no. 5, pp. 284-289

Verstrat, Daniel W. "Formulating with Associative Rheology Modifiers," accessed May 2005 at http://www.alcochemical.com/techsupport/whitepapers.asp

Saunders, G. 1992 "The Rheological Evaluation of the Inks," Ink & Print, vol. 10, no. 2, pS 1 (4).

Hrehorova, E. 2004 "Spot Color Consistency for Product Gravure" (MS Thesis, Western Michigan University)

Eldred, N.R. and Scarlett, T. 1990 "What the Printer Should Know about Ink" (Graphic Arts Technical Foundation), 2nd ed., pp. 48.