Spot Color Consistency for Product Gravure

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Keywords: spot color, water based ink, color stability, aging, rheology, rotogravure

Abstract

With any type of printing, controlled and consistent ink conditions, such as temperature, viscosity and pH of water-based inks are essential to achieve a consistent print quality. The performance of water-based gravure spot color inks during the printing trials simulated on the laboratory scale, using a Moser sheet-fed gravure proofing press, was investigated. The viscosity and pH profiles of water-based gravure inks were monitored. Changes in the rheological behavior of the tested inks after different dwelling time of inks on the press and changes in the flow properties were observed. Viscoelastic behavior of the tested inks showed that the strength of ink's structure is time-dependent. Color stability during the printing trials was tested in terms of reflective spectra; CIE Lab color coordinates and color difference. The importance of viscosity and pH control of water-based gravure inks was shown. It was observed that even if the ink's pH drop is in the acceptable range for water-based inks, keeping it constant during the printing runs improves the color stability.

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Introduction

With any type of printing, color control is very important throughout the print run. It is important to ensure that the colors of the final product are consistent from the beginning of the run to the end.

One of the chief advantages of gravure printing is the ability to print continuous patterns. Gravure is used to print simulated wood grain paper for laminated furniture, wallboard, textiles, flooring and other product applications where uninterrupted patterns are required. It is widely used for vinyl applications such as pool liners, play pens, outdoors furniture, shower curtains, pocket planners and automotive interiors (Gillett, 2003).

Since the solvent typically constitutes from 30 to 70 wt. % of the gravure ink composition, the emission of volatile organic compounds (VOC) represents a significant environmental concern. Pressure from the government to reduce VOC is the major incentive for choosing water-based inks. Publication gravure is using solvent-based inks, but packaging inks are more likely to be water-based (Fischman, 1995). Product gravure uses both water-based and solvent-based inks (Nelson, 1992). The industry has used water-based inks successfully on medium-weight papers and on nonabsorbent substrates such as plastics, aluminum, and laminates.

Water – based gravure inks contain the same major components as solvent based inks: colorant, vehicle, and additives with the water as the solvent portion. Vehicles used in water-based inks are substantially different from those used in solvent-based inks. They are generally classified into three categories: water soluble, alkali soluble and acid soluble (Leach, 1998). Additives for water-based inks include alcohols, glycols, glycol ethers, silicones, plasticizers, defoamers, and solubilizing agents (ammonia and amines), in addition to waxes and surfactants. The alcohols or co-solvents are added in order to improve the printability of waterborne inks by reducing the surface tension, which can be also reduced by careful selection of surface-active agents (Laden, 1997). A volatile amine is also required, to neutralize the acidic resin system. The selection of amine and control of pH is as important as viscosity control. Premature release of the amine before the point of impression can result in a drop in pH and subsequent precipitation of the resin in the cells of the gravure cylinder. Furthermore, water-based systems are not as readily resolubilized as solvent systems. It is therefore possible that any precipitation will not be resolubilized within the next revolution of the cylinder in the ink duct Therefore unless carefully controlled, fluctuations in pH can lead to clogging of the gravure cells and ultimately to screening (Laden, 1997). The surface tension characteristics of the water-based system must also be considered since generally they are totally different from those of solvent based. These differences can lead to poor substrate wetting, which results in ink reticulation, crawling, and non-uniform ink flow from the cells (Krishnan, 1999).

In preliminary work (Frimova, 2003), it was found that during printing trails taking several hours, the ink particle size is diminishing on the press. This may cause differences in color values and printability features measured on printed substrates at the beginning of trial and after several hours of printing (Frimova, 2003). Another important property in the ink industry is the viscosity. Nevertheless, it is not always efficient to rely on a viscosity measurement alone, and further rheological behavior evaluation is required. Printing inks are a mixture of pigments, suspension agents, polymers, solvents, etc. Each of these items by itself may or may not have Newtonian characteristics, and when combined, they shear in unique, nonlinear ways (Pangalos, 1985). Moreover, the application of ink is a time dependent flow process and performance is closely related to its rheological properties (Pangalos, 1985, Sauders, 1992).

The present work deals with investigation of performance of water-based gravure spot color inks on press during the printing trials. Printing trials were simulated on the laboratory scale. A Moser sheet-fed gravure proofing press was employed to simulate the printing trials. The viscosity and pH profiles of water-based gravure inks were investigated. Changes in the rheological behavior of the tested inks after different dwelling time of inks on the press were studied in addition to color stability in terms of reflective spectra, CIE Lab color coordinates and color difference. The importance of viscosity and pH control of water-based gravure inks was shown

Experimental

Printing on the Moser Gravure Press:

The experimental approach to the problem of color stability was to run and test four different water-based spot color gravure inks (beige, brown, red and light green ink). All of the tested inks were printed on the Light Weight Coated Paper (LWC).

The Moser Sheet-fed Gravure Proofing Press was employed in this experiment. Printing speed during trials was set to 60 m/min and blade pressure was 36 psi. The image carrier was a hollow cylinder electromechanically engraved. Constant temperature was achieved by tempering the cylinder using Programmable Circulator (Thermostat) by VWR Scientific Products filled with silicone oil. The ink and cylinder temperature for the trials was kept constant at 23 ± 0. 5 °C. The viscosity of tested inks was adjusted to be 37 – 38 seconds when measured with Shell Cup #4, which corresponds to the viscosity of approximately 125 cP. The pH of tested water based inks was also monitored during the printing trials.

Each of the tested inks was run on the press for three time periods, 1, 2 and 3 hours. Samples were printed on LWC paper every 30 minutes. Two different printing conditions were used. The first condition was to evaluate changes in ink performance, rheological behavior, and printability during printing trials without pH control. The second condition was to determine importance of ink's pH control and its influence on color consistency. The pH was kept constant by adding 20% solution of 2-amino-2-methyl-1-propanol, which had a pH = 11.8.

Printing conditions were as follows:

1. Temperature constant, 23 °C
   Viscosity constant, 37 ± 0.5 sec (Shell Cup #4)
   pH changing

2. Temperature constant, 23 °C
   Viscosity constant, 37 ± 0.5 sec (Shell Cup #4)
   pH constant, 9.4 ± 0.05

Ink Testing:

Virgin and aged spot color gravure inks were tested for their particle size using the Particle Sizer Submicron 370 NICOMP analyzer, which operates based on dynamic light scattering (DLS). Light from a laser is focused into glass tube or cuvette containing a diluted suspension of particles. Each of the particles illuminated by the incident laser beam 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 (NICOMP, 1997).

The rheological behavior of virgin and aged spot color water-based gravure inks was studied using a TA Stress Rheometer AR 2000 equipped with instrument software (Rheology Advantage Instrument Control AR). Double gap concentric cylinder geometry was used to measure the low viscosity samples. The measuring cell **(Figure 1)** was maintained at the constant temperature using a circulating water bath (23 °C).

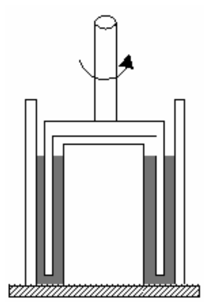

Figure 1: *Standard double concentric cylinders geometry used to measure the rheological behavior of the tested inks.*

Two types of oscillation tests were used in this experiment **(Figure 2):**

Stress Sweep Test – Stress sweeps were performed at a constant frequency of 1 Hz while incrementing the amplitude of the stress.

Frequency Sweep Test – Frequency sweeps were performed at fixed stress amplitude while the frequency was changed. The oscillation stress was set according to results from Stress Sweep Test. A stress in the linear viscoelastic range was selected for each sample.

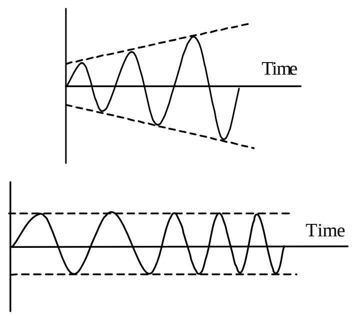

Figure 2: *Illustration of frequency and amplitude changes in Stress Sweep Test (Top), and Frequency Sweep Test (Bottom).*

Printability Testing:

All the printed samples were tested for printability by measuring their color in terms of reflective spectra and CIE Lab color coordinates. The X-Rite 530 SpectroDensitometer together with X-RiteColor Master Software was used in this experiment to measure reflective spectra and L*a*b* coordinates of the samples. The illuminant D50 and 2 degree standard observer were used. In order to establish color changes caused by changes in ink during the printing run, color difference was calculated as the difference between the virgin ink values and a printout at particular time period. For total color difference, ΔE, the general equation bellow was employed:

$$\Delta E = \sqrt{\left(\Delta L^*\right)^2 + \left(\Delta a^*\right)^2 + \left(\Delta b^*\right)^2}$$

Print gloss was measured using a Novogloss Gloss Meter with 75° angle geometry and delta gloss was calculated as the difference between ink gloss and paper gloss. Print gloss is usually measured at 60° angle, but our inks were of very low gloss due to the flattening additive, so the 75° angle was used.

Results and Discussion

Water-based inks are usually based on acrylic polymer chemistry, thus have to have some sort of amine included in the formulation to assure water solubility of the polymers and to keep the ink in a fluid solution form. When the amine evaporates, the ink properties change significantly. The acrylic resin starts to precipitate and solids have a tendency to agglomerate. As the water evaporates, the viscosity increases, solids tend to lump together, and colors get darker if they were neglected (Sesetvan, 2002).

It was observed that the pH of the tested water-based ink samples dropped considerably during the three hour printing trials from an average value of pH = 9.4 down to an average value of pH = 8.6 for all tested inks. The changes in pH of the tested inks were due to the evaporation of the amines present in the ink system, as well as, the addition of water to keep the viscosity constant.

By measuring the particle size of the tested inks, it was found that the particle size did not change significantly during the printing trials. The highest decrease in particle size was observed for the red ink, where particles decreased in size from 340 to 297 nm. A major decrease was observed during the first hour, which may be due to the redispersing of the particles in the systems and distraction of existing clusters or agglomerates by running on the press. **Figure 3** presents an overlay of the particle size distribution for the virgin and three hour aged red inks. It is evident that the distribution of the virgin ink is shifted to the higher particle size values. However, the particle size distribution of virgin ink is also wider than that of aged ink, which indicates that the particle size distribution of virgin ink is less uniform. **Table 1** summarizes the complete results from the particle size measurements.

Table 1: *Particle size of tested water-based inks aged for different time periods on Moser Gravure Press.*

		Virgin		1h		2h		3h	
		Diam. [nm]	**SD [nm]**	**Diam. [nm]**	**SD [nm]**	**Diam. [nm]**	**SD [nm]**	**Diam. [nm]**	**SD [nm]**
#1	**Beige**	280.5	62.5	280.9	64.9	280.5	69.5	279.3	43.6
#2	**Brown**	276.8	56.8	278.2	62.3	279.6	69.3	280.3	76.8
#3	**Red**	340.0	164.7	301.2	107.8	304.2	120.1	297.7	92.1
#4	**Green**	281.7	78.5	271.4	64.0	275.7	68.9	275.9	66.0

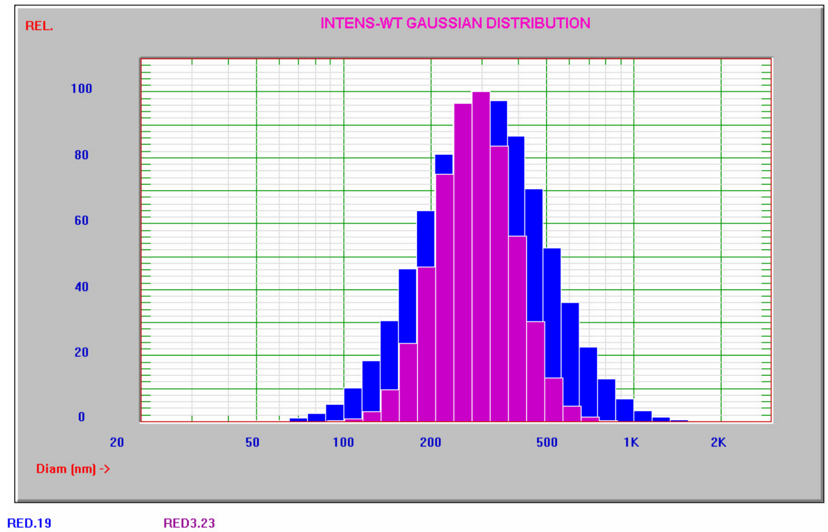

Figure 3: *Particle size distribution for virgin and three hours aged red ink (Particle Sizer Submicron 370 NICOMP analyzer – CW 380 Software Version 1.51a). Blue distribution is for virgin ink. Purple distribution is for 3 hours aged red ink.*

The rheological behavior of the tested inks was studied in terms of elastic and viscous modulus. 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). The elastic or storage modulus, G', represents the amount of energy from the oscillation that can be stored within the sample structure. The sample structure depends on the interactions between the different constituents of the sample. The value of G' reflects both the strength of each interaction and the number of interactions. The viscous modulus or loss modulus, G", represents the energy lost as frictional heat between the constituents of the sample during the oscillation sweep. This also depends on the molecular structure.

From the rheological measurements **(Figure 4)**, it was observed that the beige ink experienced similar changes in its rheological behavior as the red ink and brown ink's rheological changes are similar to those of the green ink **(Figure 5).** The stress sweep tests show the elastic modulus, G', of the virgin beige and virgin red ink to be linear up to an oscillation stress of 0.024 and 0.067 Pa, respectively, which is called the critical oscillation stress. The critical oscillation stress for all the tested inks was established by application of the Onset point model in the Rheology Advantage Data Analysis Software **(Figure 6).** When printing ink was already used for printing, G' curves change depending on the time they spent on printing press. Even after one hour of being on the press, a decrease in G' value as well as a decrease in critical oscillation stress σ_c occurs. This is due to the disruption in the interactions within the ink system with the shear experienced on the press. Comparison of the red and beige ink sets to the brown and green ink sets shows higher critical stress values indicating stronger interactions as well as a possibly slightly higher number of interactions within these inks. Again, due to shearing on press, the elasticity modulus decreases for both inks.

Considering the loss modulus G", it can be concluded that it does not change with applied stress. However, it is evident that the shear history experienced during printing caused the G" values to decrease.

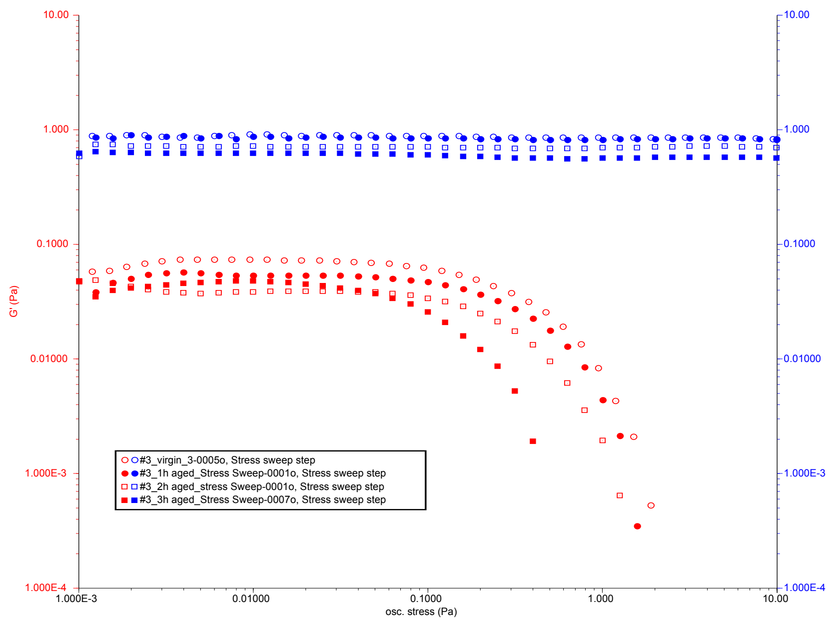

Figure 4: *Oscillation Stress Sweep test results for red ink.*

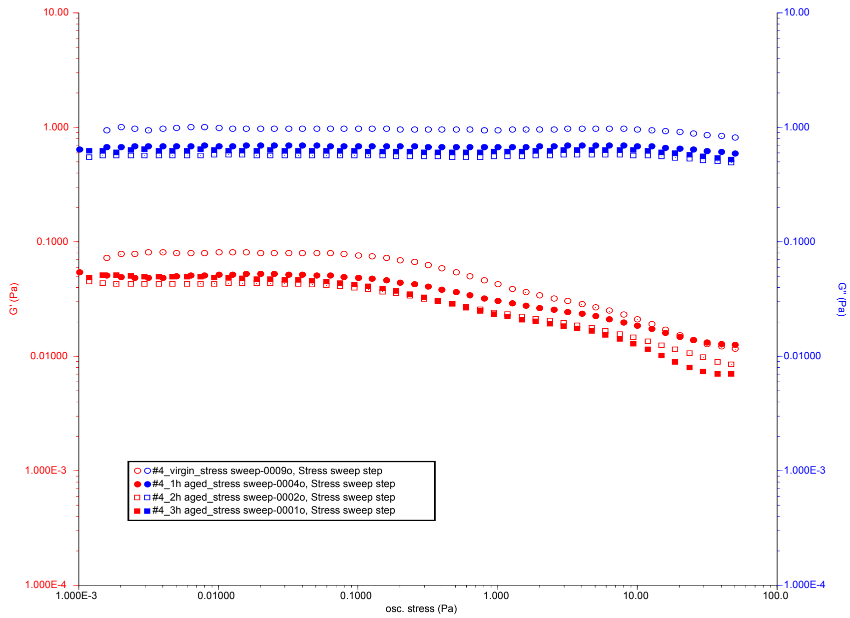

Figure 5: *Oscillation Stress Sweep test results for green ink.*

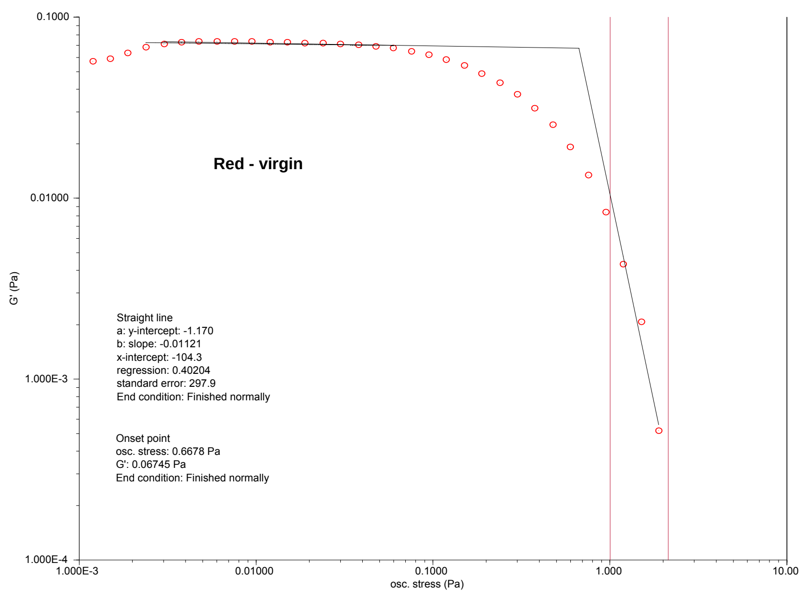

Figure 6: *Illustration of Onset Point Model application to establish critical stress value.*

Table 2 shows the changes in the critical oscillation stress and elastic modulus for all sets of virgin and aged inks. A tested high value of σ_c indicates that the structure in the ink is stronger. The higher value of G' indicates more structured ink. The weakest structure was observed with beige ink. Although, the critical stress value is relatively high for the virgin beige ink, it was observed that after three hours, the flow of beige ink becomes non-linear over whole range of applied stresses, which is to due to disruption of very weak structure of the ink once the ink is sheared on press. **Figure 7** shows the changes in critical stress for tested inks in graphical form.

Table 2: *Critical stress and elastic modulus for tested water based gravure inks.*

BEIGE	σ_c [Pa]	G' [Pa]	*RED*	σ_c [Pa]	G' [Pa]
virgin	0.245	0.035	**virgin**	0.668	0.067
1h	0.180	0.032	**1h**	0.563	0.050
2h	0.060	0.014	**2h**	0.423	0.040
3h	-	-	**3h**	0.150	0.051
BROWN			*GREEN*		
virgin	0.133	0.087	**virgin**	0.155	0.080
1h	0.095	0.065	**1h**	0.093	0.053
2h	0.074	0.058	**2h**	0.077	0.043
3h	0.069	0.048	**3h**	0.077	0.048

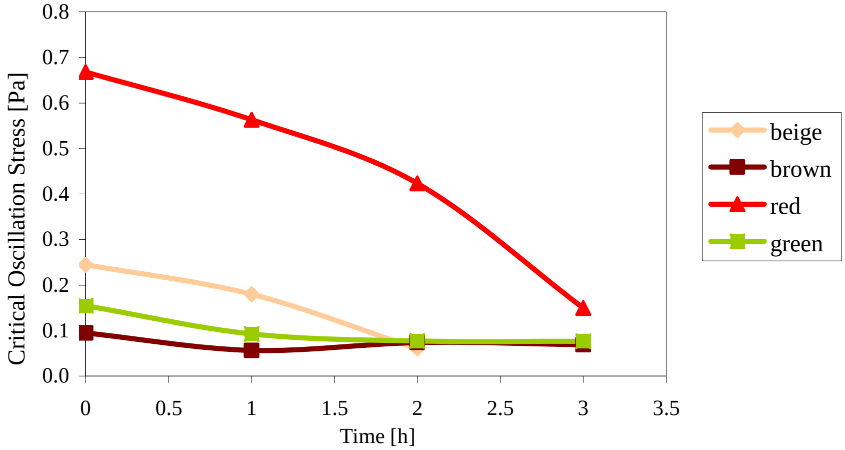

Figure 7*: The changes in critical stress for tested water based inks as a function of time the ink spent on the press.*

In addition, several changes or shifts in reflective spectra of tested inks were observed during the printing. Each of the tested inks shows more or less shift in the reflective spectrum after running on the press for different periods of time. The shift was mainly a slight increase in reflectance for all printed samples, which can be understood as fading of colors due to addition of water to adjust viscosity during the printing trials.

The most common method of evaluating of color change is the color difference calculation. The CIE $L^*a^*b^*$ color coordinates **(Table 3)** were used to calculate color difference between virgin ink print and ink at the particular time of the printing trial. The highest color difference was observed with red ink, and the lowest with brown ink. **Figure 8** shows the comparison between all the tested inks and their color difference during the printing trial.

Table 3: *The CIE $L^*a^*b^*$ color coordinates and color differences for samples printed at constant T, viscosity and varying pH.*

BEIGE				
	L^*	**a^***	**b^***	**Δ E**
virgin	85.9	0.7	14.0	
0.5 h	86.0	0.7	13.2	**0.9**
1 h	85.7	0.7	13.3	**0.8**
1.5 h	85.9	0.7	12.9	**1.2**
2 h	85.9	0.7	12.9	**1.1**
2.5 h	86.0	0.7	13.0	**1.1**
3 h	85.8	0.5	12.7	**1.3**

RED				
	L^*	**a^***	**b^***	**Δ E**
virgin	54.3	41.1	-6.8	
0.5 h	55.7	40.1	-7.1	**1.7**
1 h	55.8	40.2	-7.2	**1.7**
1.5 h	56.0	40.0	-7.2	**2.0**
2 h	56.6	39.8	-7.2	**2.6**
2.5 h	56.4	39.9	-7.2	**2.4**
3 h	56.9	39.5	-7.3	**3.1**

BROWN				
	L^*	**a^***	**b^***	**Δ E**
virgin	77.4	3.2	16.5	
0.5 h	77.8	3.1	16.1	**0.6**
1 h	77.7	3.1	16.1	**0.5**
1.5 h	77.9	3.1	16.0	**0.7**
2 h	78.1	3.0	15.7	**1.1**
2.5 h	78.2	3.0	15.7	**1.2**
3 h	78.1	3.0	15.7	**1.0**

GREEN				
	L^*	**a^***	**b^***	**Δ E**
virgin	76.6	-2.5	2.8	
0.5 h	77.2	-2.4	2.7	**0.6**
1 h	77.6	-2.4	2.7	**1.0**
1.5 h	77.8	-2.4	2.6	**1.2**
2 h	77.6	-2.4	2.7	**1.0**
2.5 h	77.4	-2.4	2.8	**0.8**
3 h	77.7	-2.4	2.7	**1.2**

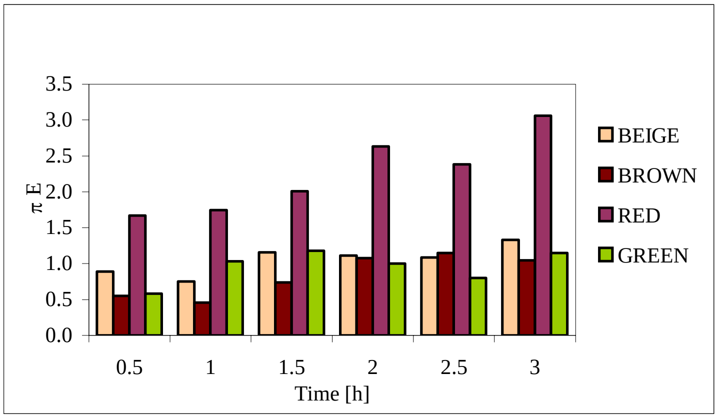

Figure 8: *Color difference for water based gravure inks printed at constant viscosity and temperature and varying pH.*

The second set of printing trials, where pH was kept constant in addition to the temperature and viscosity, shows the importance of maintaining the constant pH when using water-based inks. Manufacturer recommended pH of water-based inks is to be within the range of 8.5 – 9.5, but even if the pH of ink is within the acceptable range, the color stability is reduced as it was shown earlier. However, with constant pH of water-based inks during printing trials, the color difference decreased. The color difference for beige, brown and green inks was not very high without controlled pH and it can be stated that these changes with controlled pH are negligible. On the other side, constant pH helped to improve color consistency for red ink. The color difference decreased from unacceptable to the acceptable range of ΔE **(Figure 9).**

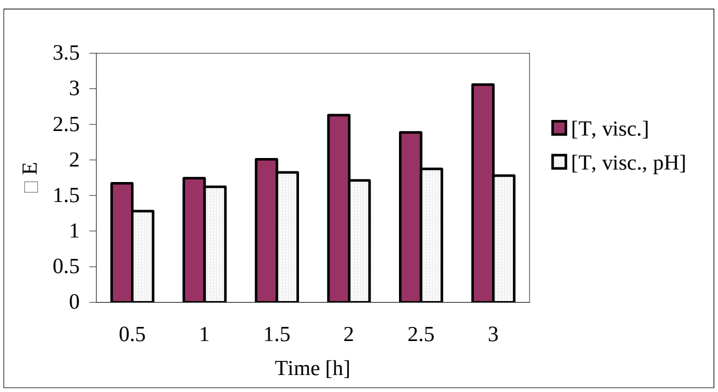

Figure 9: *Color difference for red ink during printing trials with varying and constant pH.*

Print gloss is associated with many properties and characteristics of the substrate as well as the printing ink. Since all the samples were printed on the same substrate (LWC paper), the print gloss change was determined only by changes in the printing ink characteristics.

Figure 10 displays Δ gloss values (difference between print gloss and paper gloss at 75°) for all tested inks as the function of the printing time. Rheological behavior of brown and green ink was similar and also the gloss pattern is similar. It is possible that some break down of the polymer structure occurred during printing, which affected ink leveling. When the leveling of ink film decreases, layer becomes rougher and consequently ink gloss will decrease. Similarly, the rheological behavior of beige and red inks was analogous; their gloss pattern is also similar.

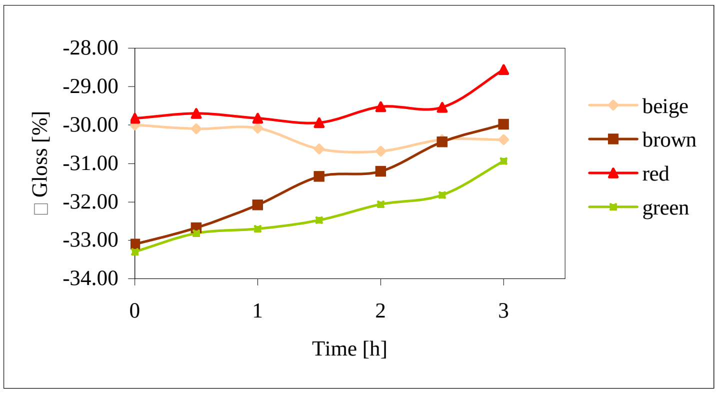

Figure 10: *Delta gloss for tested inks (measured with 75 degrees angle geometry).*

Conclusion

Four different water based gravure spot color inks were studied. Printing trials were performed on the Moser Sheet-fed Gravure Proofing Press. The inks were analyzed for their performance and printed samples were evaluated for their printability characteristics.

It was observed that pH of the water-based inks considerably declined during the three hour printing trials. These changes are due to evaporating of amines present in the ink system, as well as addition of water to keep the viscosity constant. Particle size analysis showed that simulated printing trials did not influence size of particle in the ink system. The highest change in particle size was observed with red ink within first hour of the trial, which can be due to redispersing and distracting of existing clusters and flocculates.

It was observed that the structure of inks gets weaker when prior shearing was applied on the press. The critical oscillation stress decreases with time the ink spent on the printing press. Results from frequency sweep tests showed that tested inks are very time dependent materials. The loss modulus G" is greater than the storage modulus over whole range of applied frequencies, indicating that the tested inks are more viscous than elastic, which is typical for fluid inks.

Color change in terms of color difference showed that beige, brown and green ink are in an acceptable range of color difference. The highest color difference was found for red ink. The importance of pH control of water-based inks was shown. Even if the ink's pH drop is in the acceptable range for water-based inks, keeping it constant during the printing runs improves color stability.

Overall, color consistency is very important in today's printing industry. The gravure printing process is very complex and there is a need to continuously improve color reproduction, engraving techniques and new printing ink formulations as well as substrates and their surface properties. Studying rheological behavior of inks can help to predict their press performance as well as it can help to reformulate inks in order to achieve specific properties.

Acknowledgement

Authors would like to thank Omnova Solutions, Inc. for financial support of this project.

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