RHEOLOGICAL ASPECTS OF WATER BASED WATERLESS INKS

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ABSTRACT

Continuous flow and oscillatory measurements of new, water washable, waterless inks were made in order to correlate their physical properties to ink gloss, printability and press performance. Two different offset paste ink systems were examined and the rheological parameters were obtained. Parameters such as tanδ and viscosity n were different for these two systems and related well to printability and press performance. The system with the best performance had a ratio of viscous (G") to elastic modulus (G') similar to that of the conventional paste inks. At low oscillation frequencies ink leveling and gloss development were observed. A more elastic behavior was observed at higher oscillation frequencies.

INTRODUCTION

Rheological features of inks determine plant throughput rate and printability (1). The purpose of this study was to initiate an investigation of rheological factors in manufacturability, press performance and printability of new ink systems.

The current printing ink technologies involve mainly flexography, gravure and lithography. Lithographic run lengths are medium to long and speeds can be high (3,000 fpm), flexo run lengths are short to medium and speeds moderate (1,000 fpm), and gravure run lengths are long to very long and speeds can be high (3,000 fpm). However the cost of the plate is very low for lithography (Al plate) and very high for gravure (engraved metal cylinder). Waterless lithography is a special lithographic printing process that uses no fountain solution compared to conventional lithography. In lithography a fountain solution (surface energy ~40 dynes/cm) is applied to the printing plate, spreads uniformly on the non-image area (72 dyne/cm) due to chemical affinity and forms droplets in the image area (2). These droplets emulsify with the ink. In waterless lithography the differential surface chemistry and energetics of the plate (22 dyne/cm for non-image vs 40 dynes/cm for image) help the ink to wet only its image areas, thus eliminating the use of fountain solutions (3). Fountain solutions cause many problems associated with printing press shut down and troubleshooting.

Print on-demand color work with runs up to 5,000 or 10,000 copies is growing fast in view of the digital revolution. This market fills the gap between conventional offset (>10,000 copies) and toner based printing (<500 copies).

This work is focused on waterless lithography and addresses the needs of that intermediate market by introducing the science and technology of a new family of environmentally friendly, water based and water washable paste inks. The emphasis is on the rheological aspects of these sheet-fed offset paste inks and means of testing to ensure good manufacturability, press performance and printability. Data acquired by continuous flow and oscillatory methods for better characterization of ink rheology will be discussed. Furthermore, models and correlations that have been developed to link structure-property relationships to print gloss will be presented. After all gloss is a very important aspect of printability.

Waterless lithography has a limited market due to the plate availability and cost, use of solvents in the pressroom and required control of the roller temperature during printing. The introduction of this new offset inks opens new opportunities for waterless lithography. There are no VOCs in the pressroom, control of the plate temperature is not as critical and plate costs could be potentially reduced (4). Furthermore, the new materials introduced in the formulations open unlimited possibilities for future R & D work.

EXPERIMENTAL

An AR1000N controlled stress rheometer from TA Instruments has been used for both flow and oscillatory measurements. Standard cone and plate geometry (4cm diameter/2 degrees angle) is used. The presence of thixotropy requires the standardization of a sample's history, prior to measurement. If this is not achieved, reproducibility is poor for repeat tests. Tests with the same ramps or profiles are compared to achieve steady state measurements via "equilibrium flow" and avoid variability.

Flow describes the relationship between the stress and the shear rate. A controlled shear stress σ is applied on the paste ink in order to cause a velocity gradient and shear the sample at a shear rate γ. The resistance of the sample to flow is the viscosity $\eta = \sigma/\gamma$.

The oscillation technique is a non-destructive test and measures both the viscous and elastic behavior of a sample simultaneously. The input (stress) is applied in a sinusoidal manner with a well defined amplitude and periodicity. The output (strain) also has well defined amplitude and periodicity. In general there is a phase angle difference between input/output (stress/strain) known as phase difference angle delta "δ", unless the sample responds as an ideal elastic medium (Hookean material). By definition the elastic modulus is $G'=(\tau_o/\gamma_o)\cos\delta$, the viscous modulus $G''=(\tau_o/\gamma_o)\sin\delta$, and tangent delta $\tan\delta=G''/G'$.

RESULTS AND DISCUSSION

One of the most important components of an ink formulation (pigment, resin, oils, and additives) is the resin (5). The resin's role is to disperse the pigment, transfer and adhere it to the substrate, impart gloss, rub and water resistance, and film flexibility. The polymers used, whether of acrylic (polyacrylate, polymethacrylate or polystyrene) or rosin, or even hybrid nature, must meet some criteria. They must balance the properties of the ink and print, namely cost, drying and setting speed, gloss and adhesion or resistance.

Two types of waterless inks have been made based on **different chemistries** and they are compared to conventional waterless **inks**: water based, offset paste inks A with lower gloss and inks B with high gloss.

Data are presented from continuous flow (static) and oscillatory (dynamic) experiments to examine the influence of ink rheology on the gloss of the prints. Gloss is a complex parameter and depends on other factors such as tack, formulation (vehicle, pigment, pigment concentration), printing density, press speed, drying conditions and type and roughness of the substrate (6,7). This work focuses solely on rheological effects on the gloss, an important aspect of printability.

I. Continuous Flow Characteristics:

Conventional Waterless inks

The flow curves of four process color inks (K, C, M and Y) used in conventional waterless lithographic printing are shown in **Figure 1**. By examining the viscosity curves (n versus γ) it may be concluded that all four inks (perhaps with the exception of the black) show a fairly Newtonian behavior between 0.01 and 10 S^{-1}, followed by a drop in their viscosities at higher shear rates (>10 S^{-1}). Otherwise there is shear thinning at rates between 10-1000 S^{-1} due to stretching of the resin vehicle of the offset ink and disentanglement of the polymer chains. The black ink (K) shows a drop in the n below 10 S^{-1}, which may be attributed to slightly poor pigment wetting by the resin (8).

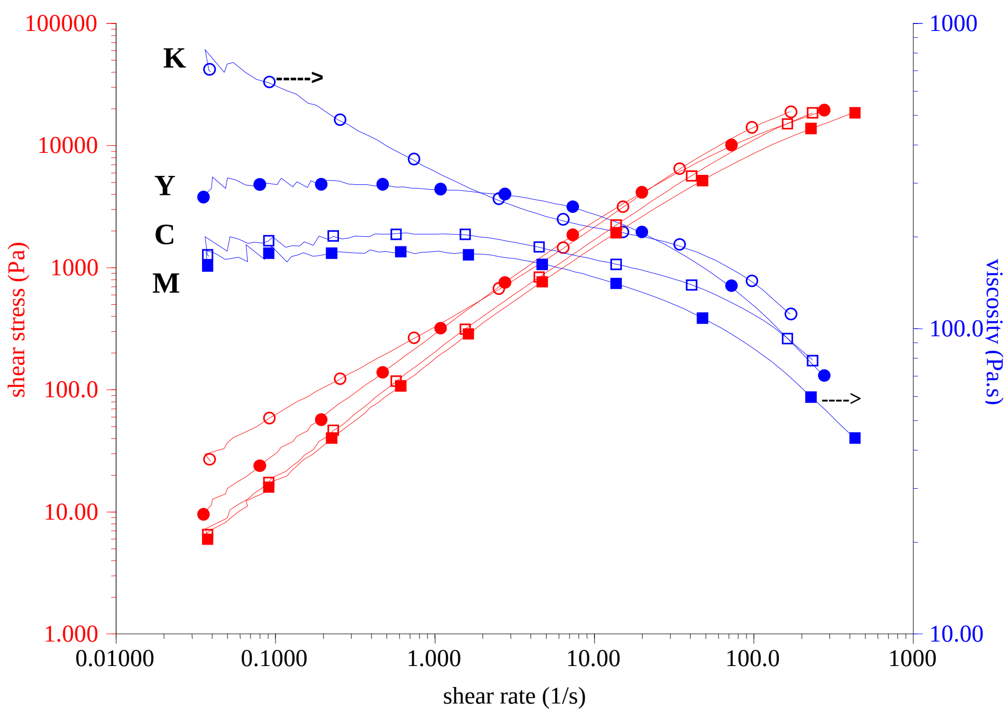

Figure 1. Flow curves of conventional waterless inks (K,C,M,Y).

The stress-rate curves look fairly linear in the region examined. Each curve can be fitted to the Herschel-Bulkley model $\sigma = \sigma_y + K\gamma^{\eta}$ where σ_y is the yield stress (minimal stress needed to observe flow), K is the viscosity coefficient and n the rate index. The σ_y values obtained from this model are listed on **Table I**. All σ_y are basically zero (x 10^{-12}) Pa. Therefore, there is no resistance to flow at very low shear rates. This is of vital importance once the ink is transferred onto the paper and leveling is initiated. The pigment particles are well dispersed, separated and wetted by the resin with no friction or resistance to smooth leveling (8). Only small stresses are created by this process on these inks (6).

Process color inks	**σ_y (x10^{-12} Pa) for conventional inks**	**σ_y (Pa) for type A inks (low gloss)**
K	17500	131
C	5.9	448
M	0.11	513
Y	5.2	785

Table I. Yield stress values from Herschel-Bulkley model: $\sigma = \sigma_y + K\gamma^{\eta}$.

Water based, water washable waterless inks with low gloss (type A)

Flow curves for the corresponding four colors (K, C, M and Y) of water washable, type A inks with lower gloss are shown in **Figure 2**. A comparison of their viscosity curves at shear rates of 0.01 - 10 S^{-1} vs. those of conventional waterless inks in Figure 1 shows that there is no Newtonian plateau. It is postulated that the absence of such a plateau may be due to poor pigment wettability by the selected resins which in turn suggests that new resin vehicles must be developed to improve pigment wettability and, therefore, good ink leveling and gloss of the prints. Higher shear rates (>10 S^{-1}) result in shear thinning as in the conventional waterless inks.

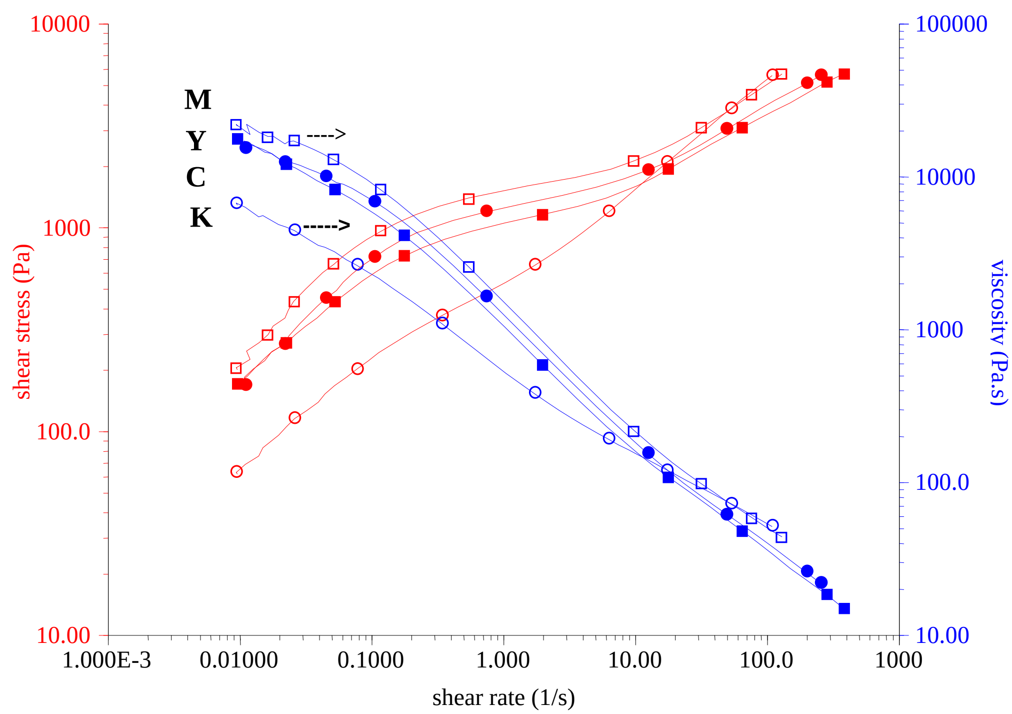

Figure 2. Flow curves of water washable waterless inks (K,C,M,Y).

The stress vs. shear rate curves, when fitted to Herschel-Bulkley model $\sigma = \sigma_y + K\gamma^n$, give substantial yield stresses (Table I) at low shear rates ranging from 131 Pa for K to 785 Pa for M. These yield stresses must be overcome to achieve smooth ink leveling on the prints. This affects not only the gloss of type A inks, but also their flow in the fountain roller of the press, as it has been observed during printing. In fact, M with the highest yield stress had the worst flow behavior in the ink fountain.

A 1:1 comparison of the flow curves of the same color ink (M) from type A and conventional inks is shown in **Figure 3**. At lower shear rates (<0.1 s^{-1}) there is a two order magnitude difference in their viscosities. Type A magenta has a much higher yield stress, very low flowability and no Newtonian plateau. At 100 s^{-1} both magentas have similar viscosities. The stress rate behavior indicates a 785 Pa yield stress for type A (lower gloss) magenta at low shear rate vs 0 Pa for conventional magenta. Pigment-pigment interactions must be ovecome at low shear rates to initiate flow or proceed to smooth leveling, following transfer of the ink onto the substrate (9). Eliminations of such interactions necessitates a new resin vehicle that wets the pigment better. This in turn would result in the formation of very uniform and stable pigment dispersions that provide excellent flow and help eliminate piling on the press rollers during long runs.

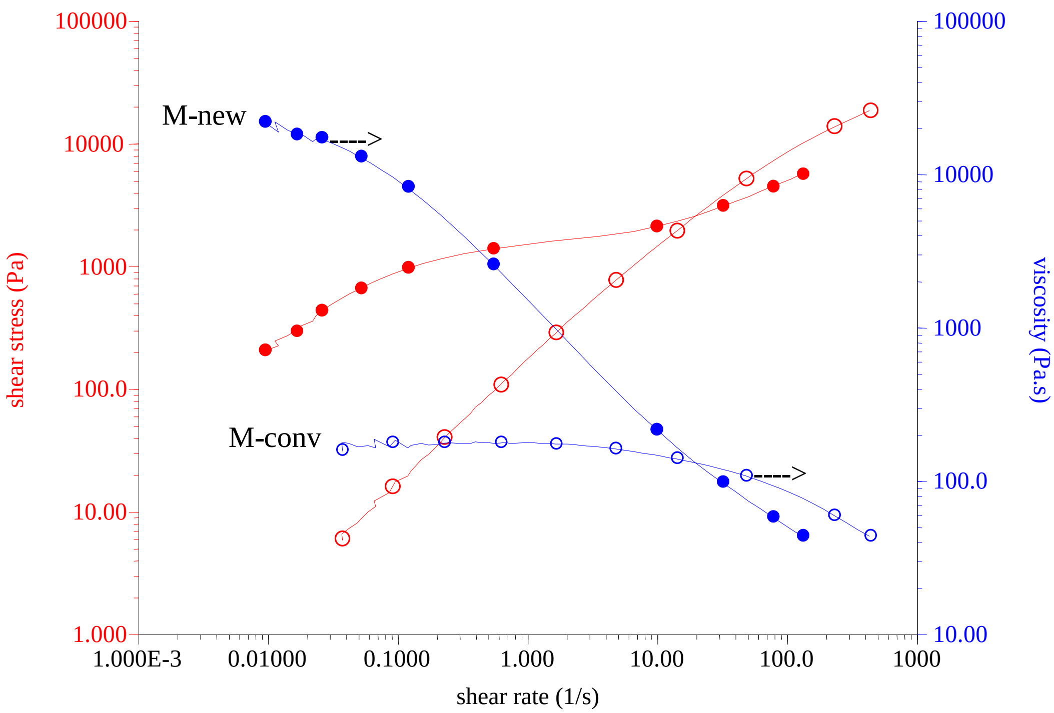

Figure 3. Flow curves of conventional and new waterless M (low gloss).

Water based, water washable waterless inks with high gloss (type B)

In order to meet the needs of the type A inks for higher gloss a second series of water washable, offset paste inks was developed, type B. Flow measurements were then used to compare it to conventional waterless inks. Viscosity-rate and stress-rate curves are shown in **Figure 4**. Both type B and conventional magenta show similar viscosities at 10^{-2} s^{-1} rates and small Newtonian plateau. Deviations from this plateau occur as the shear rate is increasing and to a larger degree for type B magenta ink. This is due to the different nature of the resin vehicle involved. The stress-rate curves show low yield stress and practically coincide. Gloss improvement via elimination of the yield stress at very low shear rates has been accomplished. Proper formulation of the resin vehicle improved pigment wetting and dispersion stability.

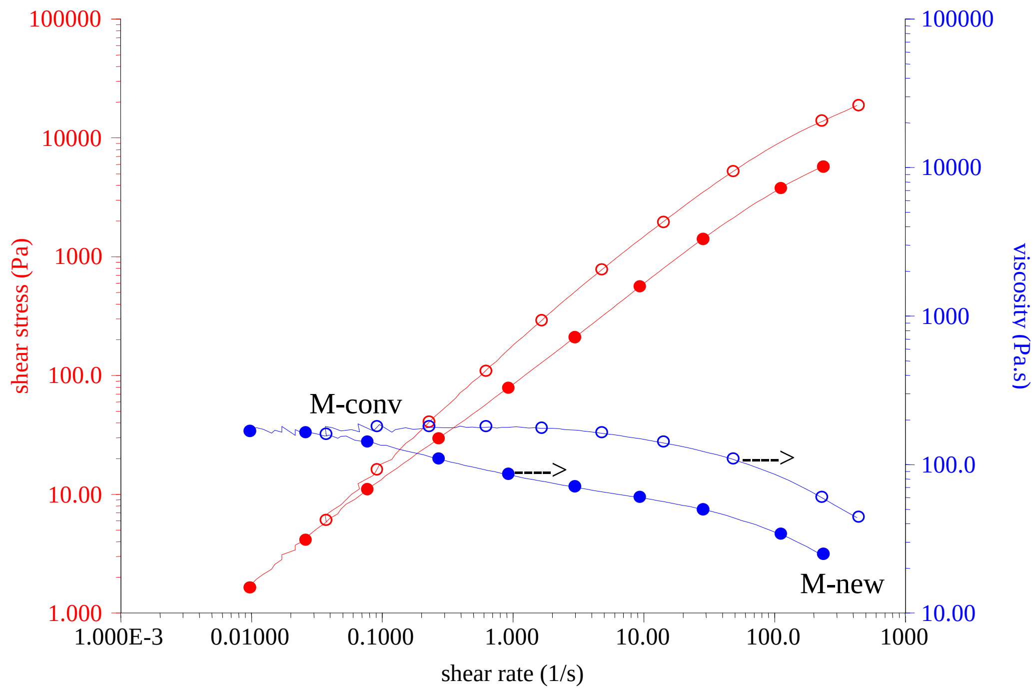

Figure 4. Flow curves of conventional and new waterless M (high gloss).

<u>II. Viscoelastic Characteristics</u>:

In an oscillatory measurement the elastic modulus is defined as $G' = (\tau_o/\gamma_o)\cos\delta$, the viscous modulus $G'' = (\tau_o/\gamma_o)\sin\delta$, and tangent delta $\tan\delta = G''/G'$. Tangent delta is a measure of viscous vs elastic flow of the offset paste ink and depends on the frequency of oscillation. High oscillation frequencies correspond to running press, pigment grinding conditions etc. and low frequencies to leveling and flow in containers.

The oscillation curves for conventional and type A magenta are shown in **Figure 5**. The elastic modulus G' and tanδ are plotted against frequency (Hz). At low frequencies (<0.1 Hz) the new magenta is more elastic vs the conventional magenta. As frequency is increasing both inks show similar G' and behave more elastically. Tangent delta curves indicate that type A magenta has tanδ <1 in the 0-100Hz regime vs tanδ in the range of 3-2 for conventional magenta. Absence of enough plastic flow (G") on type A magenta results in poor gloss development during the leveling process (G' for type A magenta is greater than G' for conventional magenta at 0.1 Hz). These results further support our conclusions from continuous flow measurements.

Oscillatory measurements for type B magenta (the highest gloss, water washable magenta) vs conventional magenta (**Figure 6**) indicate that the G' curves practically coincide over the entire frequency range. Tangent delta values of about 2 in the 10-100 Hz frequency regime (or higher than 1.5 in the entire frequency regime examined) for both inks, indicate similar rheological behavior and good gloss development characteristics.

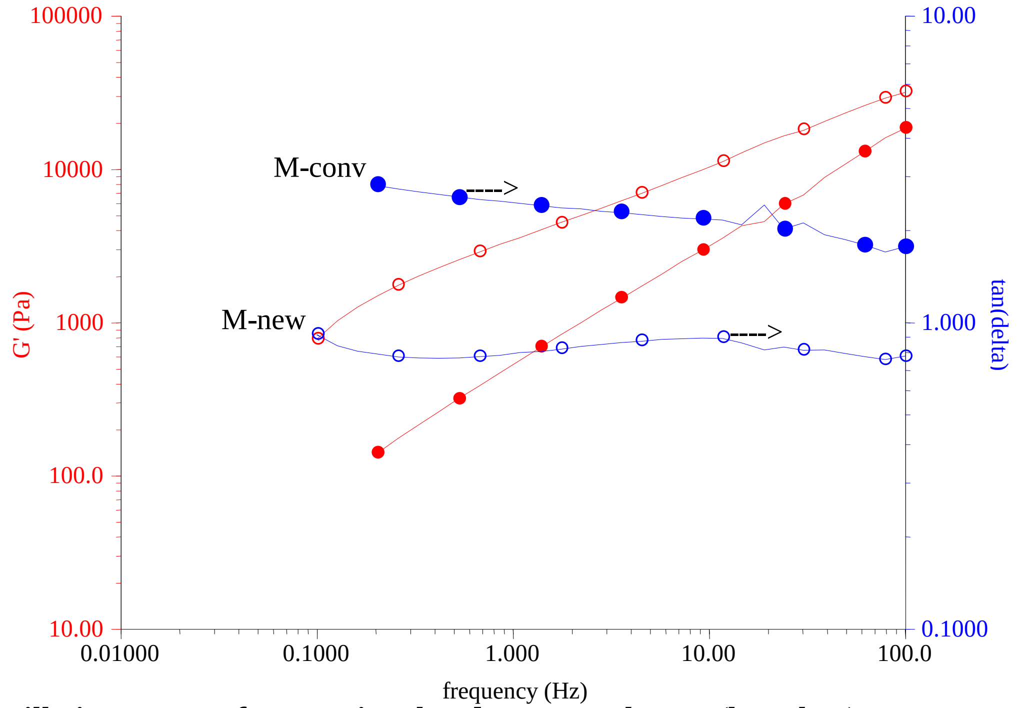

Figure 5. Oscillation curves of conventional and new waterless M (low gloss).

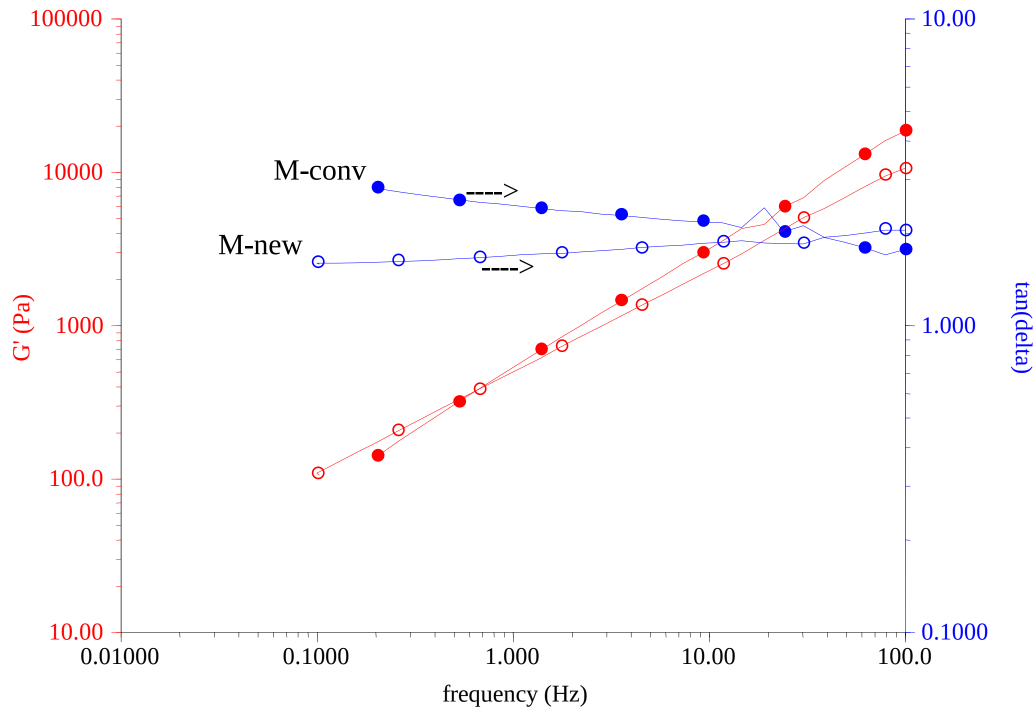

Figure 6. Oscillation curves of conventional and new waterless M (high gloss).

CONCLUSIONS

Two types of water based, water washable waterless inks with zero VOCs have been presented and introduced into the lithographic arena. This will enhance waterless's lithography share in the print on-demand color work with runs up to 5,000 or 10,000 copies per hour that is growing fast in view of the digital revolution.

The rheological parameters of new waterless inks were obtained. High gloss, a very important aspect of printability, has been linked to: 1) low yield stress at very low shear rates and newtonian plateau below 1 s^{-1} (flow measurements) and 2) tanδ values of about 2 at 0.1 Hz (oscillatory measurements). Low yield stress and Newtonian behavior at low shear rates also resulted in good flow and wetting in the ink fountain roller of the press.

The system with the best gloss had a ratio of viscous (G") to elastic modulus (G') similar to that of conventional paste inks. At low oscillation frequencies proper ink leveling and gloss development were observed. A more elastic behavior was observed at higher oscillation frequencies. Gloss development is a complex function and the significance of other factors such as tack is outside the scope of the present work.

The polymer chemistry employed, allows flexibility and variations in the offset ink formulations and determines their physicochemical and rheological characteristics.

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