VISCOELASTIC BEHAVIOR OF PRINTING INKS

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Abstract

Printing inks are best characterized as viscoelastic fluids. As more sophisticated and affordable instrumentation has become available, the ability to probe the elastic component has emerged. Several ink properties can be affected by these elastic features such as misting, ink dripping and flow behavior in a fountain, emulsified flow, recovery after shearing, and adhesion and release from waterless printing plates. The use of creep and oscillation methods provides a wide range of utility for assessing the elastic contribution to the printing phenomenon. Several case studies will be presented to exemplify the use of these measurements.

Introduction

The viscoelastic nature of printing inks has been recognized for some time. Its role in a variety of ink related phenomena (i.e. tack, transference, cohesion, drying, curing (UV)) has been acknowledged. Traditional viscometers are often inadequate for describing the viscoelastic character of inks. Ink flow behavior is governed by a variety of shear environments that it may encounter during handling and utilization. The intrinsic rheological nature of an ink can either be an asset or a liability to the processes involved (e.g. pumping, spraying, roll coating, etc.) Recent advances made in instrumentation have made the use of more sophisticated rheometers both technically and economically viable. Thus, viscoelastic measurements are becoming more commonplace for printing inks.

In particular, the techniques to monitor creep and oscillatory flow have been added to the arsenal of measurements available. Both techniques are suitable for probing flow properties at very low shear rates. These shear rates are

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more suitable for examining particle/particle and particle/vehicle interactions which contribute to the intrinsic fluid structure of the ink. Although the printing process, itself, involves many high shear interactions (e.g. printing nip), the low shear nature of the ink is still very much relevant to ink properties. Time is a key variable which is probed via the creep and oscillatory techniques. Time dependent properties, such as thixotropy, and the frequency dependent processes, can manifest themselves more easily via these methods.

Creep flow represents a measurement in which the sample is subject to a small constant applied stress, and the strain to maintain this stress is monitored over time. It is a technique which reveals details of fluid structure which are unlikely to be noted from typical flow curves (i.e. stress/rate curves). The creep technique is characterized by a long time scale which allows all the viscous and elastic contributions to be observed during the measurement.

In the oscillatory flow experiment, the response to frequency can prevent the viscous components from contributing during the time frame of the measurements. This variable (frequency) allows for the analysis of fluid structural components which have faster response times. For the actual experiment, a sinusodial low level stress is applied, and the resultant strain response is recorded. In order to exploit this technique, the response of the strain to stress must be linear in order to produce an interpretable output. The data obtained outside the linear region has no value to examining fluid structure.

For both creep and oscillatory techniques, the measurement process is meant to be "non-destructive" and thus allows for a unique characterization not normally available from simple flow experiments.

Experimental Section

Measurements were performed on a Carri-Med CSL-500 Rheometer (TA Instruments) using either a 2°, 4cm cone or a 200cm parallel plate. Temperature was maintained via a Peltier system. The oscillation experiments were normally first carried out manually at 1 Hertz at variable torque in order to determine the linear viscoelastic region for the samples. After determining the linear region, the time dependence of the response was examined to ensure stability existed (i.e. losses of solvent on drying were not affecting the observed behavior). The frequency sweep was then conducted over a range of 20 - 0.1 Hertz with typical strains less than 1%.

Creep flow curves were analyzed using software provided by TA Instruments which compares data using the Voight model.
The inks examined here were typical coldset products either commercially available or under laboratory development.

Results and Discussion

Viscoelastic Behavior and Press Equipment

Case I

Page packs are piston pumps used to provide column control of ink to the printed page. Ink feed keys are provided to regulate the amount of ink across a page via the stroke of the piston pump. In order to operate properly, the page packs must be able to establish a zero flow point. This must be accomplished by ink re-sponse, as the nozzle never closes. If the ink is not able to stop flowing after shear, then it may be difficult to zero the page pack and, thus, creates poor control of ink feed and a general press maintenance problem.

Figure 1 shows the viscosity/shear rate behavior for two black inks which had been used on a press with page pack controls, as noted above. Ink A was found to function properly on zeroing the page pack; whereas Ink B could not be ze-roed and would continue to flow to the ink rail. The simple flow comparison in Figure 1 does not offer distinction between these two inks. Figures 2 and 3 show the creep flow behavior for two different experimental conditions. Figure 2 shows the individual inks (A and B) as a function of whether they were presheared before the creep experiment was run. Figure 3 depicts the

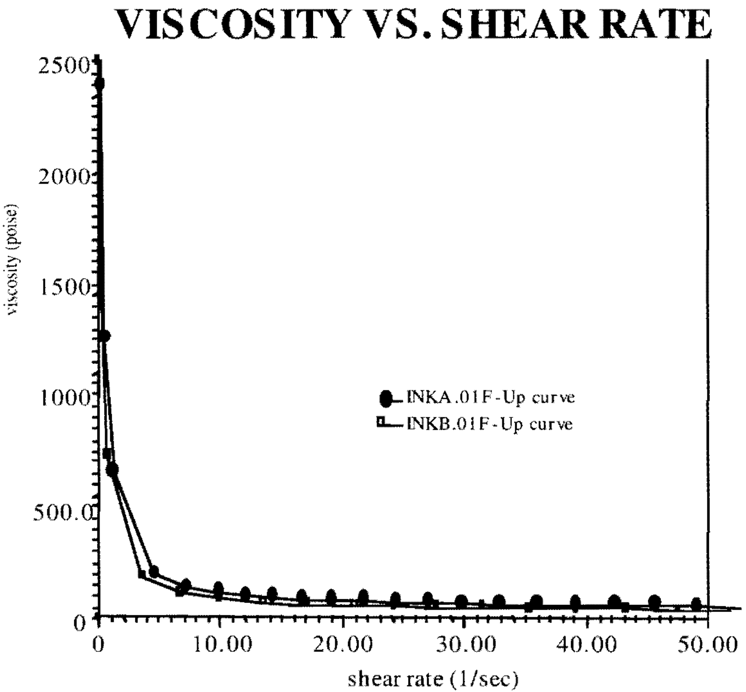

Fig. 1 - Viscosity vs. shear rate for Inks A and B on 4cm, 2° cone at 25°C.

comparison of the two inks (A and B) against each other, with and without pre-shearing.

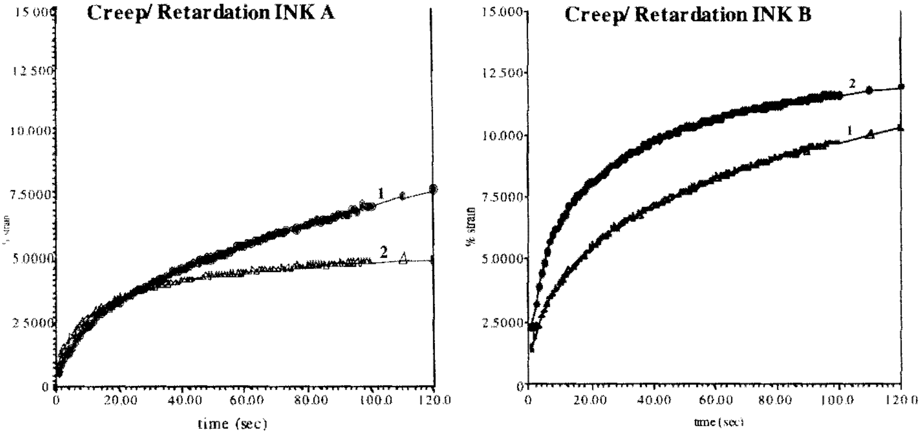

Fig. 2 - Creep for Inks A and B on 4cm, 2° cone at 25°C for Applied stress - 50 cynes/cm^2 (1 - without pre-shear; 2 - with pre-shear).

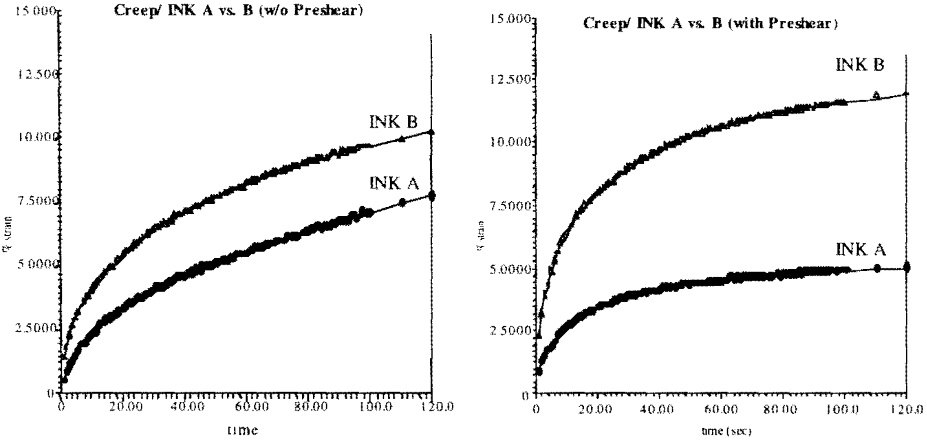

Fig. 3 - Creep for Inks A and B on 4cm, 2° cone at 25°C for Applied stress - 50 dynes/cm^2.

Table I offers a quantitative comparison by applying the Voight model to the creep data.

Table I - Model Parameters for Creep Data

	J_0 (%)	J_1(%)	η_1(Poises)
Ink A (w/o pre-shear)	0.24	2.35	49,500
(w/ pre-shear)	0.54	2.51	45,300
Ink B (w/o pre-shear)	0.96	5.75	18,700
(w/ pre-shear)	1.47	8.70	11,700

J_1, η_1 - corresponding % strain and viscosity for Voight Unit 1
J_0 - instantaneous % strain

It is clear that under creep conditions, Ink A appears to be much less structured without pre-shear and also much more sensitive to pre-shearing. Ink B maintains a great deal of structural integrity even when sheared. The lack of low shear structure for A and sensitivity to shearing could produce an inability to maintain zero flow for the page pack.

The origins of the ink structure should be associated with pigment/pigment and vehicle/pigment interactions in the manner previously described (Chou, 1991). Inks A and B were found to contain two different black pigments of very different oil absorption values. Further studies of how to control low shear flow with proper formulation corrected this problem.

Case 2

An oscillatory approach to examining the effects of shearing on ink structure is presented in Figure 4. A press maintenance problem existed for ink dripping excessively during a press run, after shearing, via the page packs. Three inks which had a known press history were examined for their ability to exhibit elastic recovery after shearing. A pre-shear stress of 5000 dynes/cm^2 was maintained for 1 minute and produced a shear rate of 100-150 sec^{-1}, which

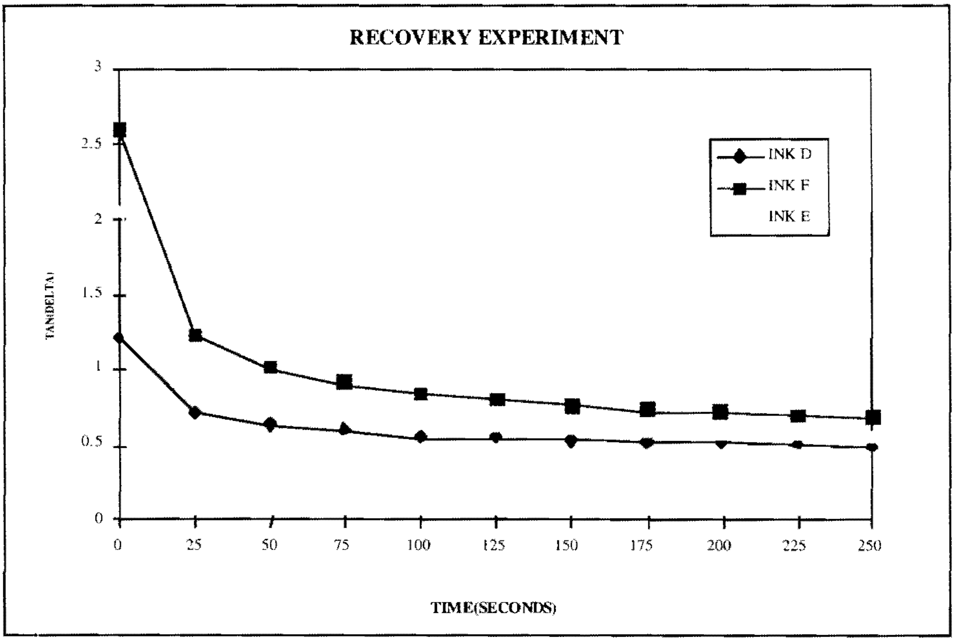

Fig. 4 - Recovery of tan (delta) over time for samples D, E, and F obtained on 4cm, 2° cone at 25°C with pre-shear stress - 5000 dynes/cm^2 and constant stress of 200 dynes/cm^2 after shearing.

would be typical for pumping ink. The tan (delta) was then monitored in oscillatory mode over time, within the linear viscoelastic region at 1 Hertz. The time to recover was very different between these inks. Ink D represented the best performance with respect to dripping; whereas Ink F was the worst. There appears to be a correlation with recovery phenomenon for this press maintenance problem. Once again, the exact reasons are dominated by the breakdown and recovery of specific pig-ment/vehicle structures. Similar examination of G' showed recovery to be better for Ink D.

Viscoelasticity and Pigment Dispersion

The low shear nature of creep and oscillatory flow methods make them ideal for characterizing interactions of collodial particles in dispersions. The specific interactions between dispersed particles and the vehicle are manifested in the low shear flow behavior, but it is often too complex to easily discern the exact nature of the interactions.

Figure 5 shows two dispersions of carbon black (26% by weight) prepared in mineral oil, where two different dispersing agents were substituted equally in the formulations. The dispersions were prepared via a pre-mixing step (conducted on a high speed mixer), followed by passing them through a horizontal media mill

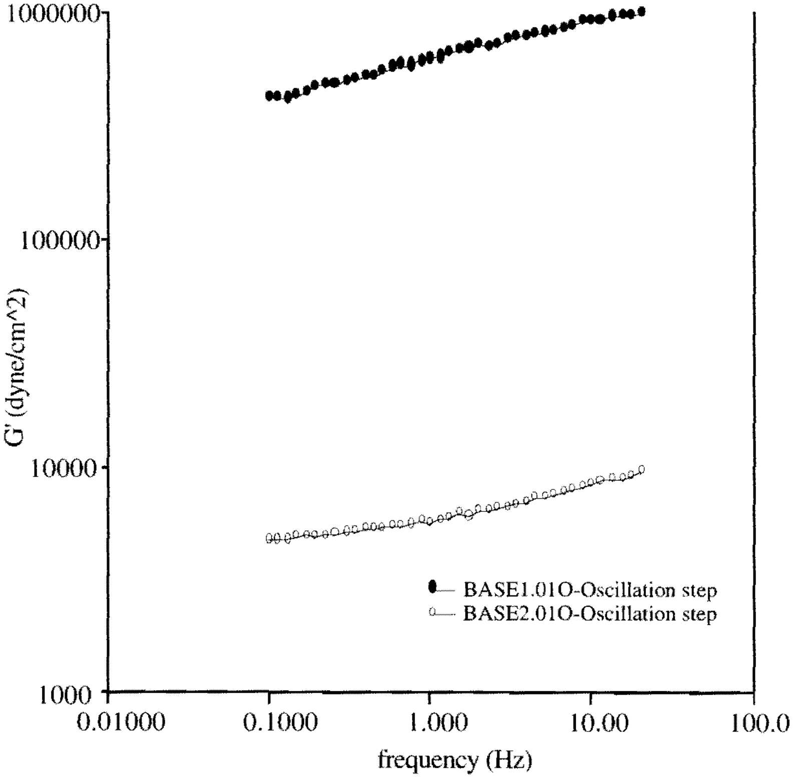

Fig. 5 - Elastic modulus (G') vs. frequency for two bases with 26% carbon black obtained on 2cm parallel plate with 200 micron gap at 25°C.

under the same conditions. Note that the elastic modulus shows an order of magnitude difference over the same frequency range. Base 1, with higher G', suggests a structure which is more rigid and elastic than Base 2. Such a large dispersity is very likely due to pigment wetting and stabilizing differences between the two dispersing agents investigated.

The practical consequences of the differences noted above can be subtle for the finished ink product. For the two dispersions, if they are both diluted to normal carbon black levels for ink, the typical physical properties measured (i.e. inkometer tack, Brookfield viscosity, Laray viscosity, grind, tint strength, etc.) are very similar and do not suggest that the inks are very different. The oscillatory flow of the diluted dispersions shows the structural character of the individual concentrates was maintained. A study of particle size distribution and press performance is currently underway for this particular example. Preliminary indications have been obtained that low shear properties can affect ink/fiber buildup on press. Studies of the type described here may also be particularly relevant in the future to addressing the effects of process scaleup on the quality of the dispersions obtained.

Viscoelasticity and Waterless Ink Release

Waterless lithography relies on the ability of the ink to release from the nonimage area in order to maintain clean printing. The mechanisms available for ink release are related to ink cohesion, elasticity, and weak fluid boundary considerations. The control of ink cohesion by way of viscosity has been the most common approach to insuring ink release. The weak fluid boundary approach is dificult to probe, and elastic characterization has not gotten as much attention relating to this process.

Figure 6 shows an interesting example of frequency and temperature sensitivity for a waterless ink. Note that the frequency dependence suggests that the elastic contributions can be monitored and possibly controlled. High speed web printing offers the variable of frequency for consideration in the process in a regime not available to the more established waterless sheetfed printing.

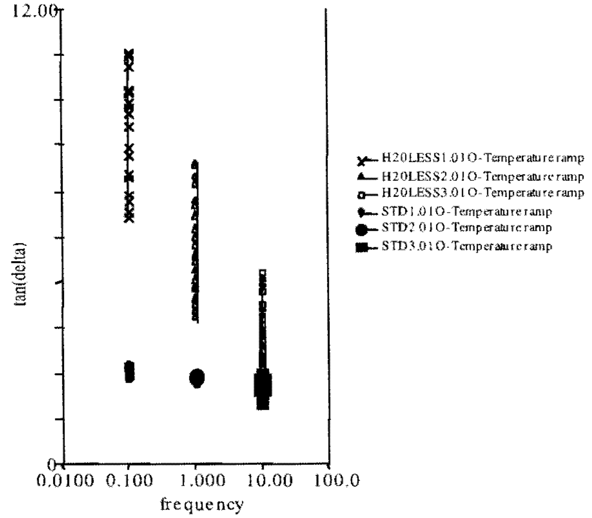

Fig. 6A - Tan (delta) vs. frequency for temperature ramp 17.5 - 32.5°C at 0.5°C/minute. (The width of vertical response always represents 15°C range of temperature. H_2O LESS = Waterless Ink; STD = Conventional Lithographic Ink).

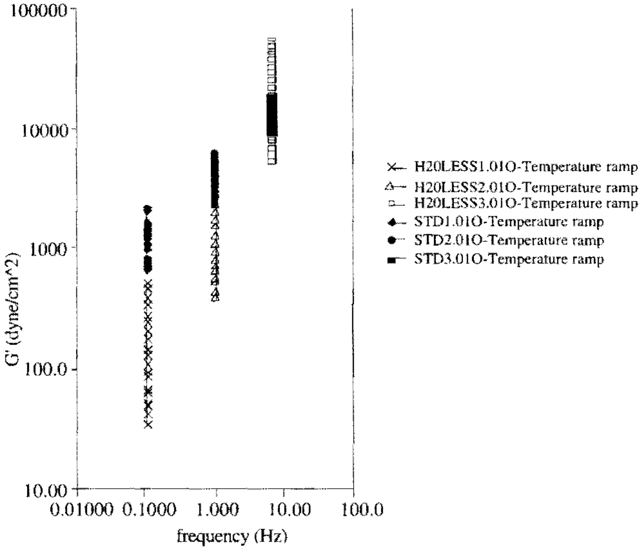

Fig. 6B - Elastic modulus for conditions in Fig. 6A.

In addition, as the waterless process is sensitive to temperature to ensure print quality, the extent to which it influences elasticity can also be useful to know. There is a marked dependence of G' and tan (delta) on temperature which can be exploited by the ink formulator. Note in the figure that a comparison of a waterless ink at 0.1, 1, and 10 Hertz - to a conventional lithographic ink, shows the waterless ink to exhibit a large temperature sensitivity. When combined with frequency dependence, there is a wider window of G" available. There is evidence for two temperature activated processes for the example shown here. Ultimately, understanding the nature of the ink elasticity and the ability to control this property can be used to reduce the reliance on a single ink release mechanism.

Viscoelasticity and Emulsions

It is well known that flow behavior of a lithographic ink can be altered when water is emulsified within it. The specific nature of water droplet size, distribution, and stability can have a major impact on flow, and has been usually monitored via stress/rate flow experiments (Durand and Wasilewski, 1993). The low shear details of the emulsified flow have not been extensively examined. The extent that viscoelastic properties of an emulsion impact on lithographic performance has been proposed (Bassemir and Krishnan, 1986). The use of oscillatory measurements to characterize emulsion behavior and ink performance has also been described, via a torque sweep (Rizk, Leary, Newton, 1994) and by frequency sweep for model inks (Hayashi, Morita, Amari, 1993). It is important to note that dynamic viscoelastic properties have not been found to correlate directly to apparent viscosity and yield value. Thus, these measurements offer additional insight into ink/water interactions.

Figure 7 shows the behavior for four keyless lithographic newspaper inks, des-ignated as: K1 - Cyan, K2 - Magenta A, K3 - Magenta B, K4 - Black.

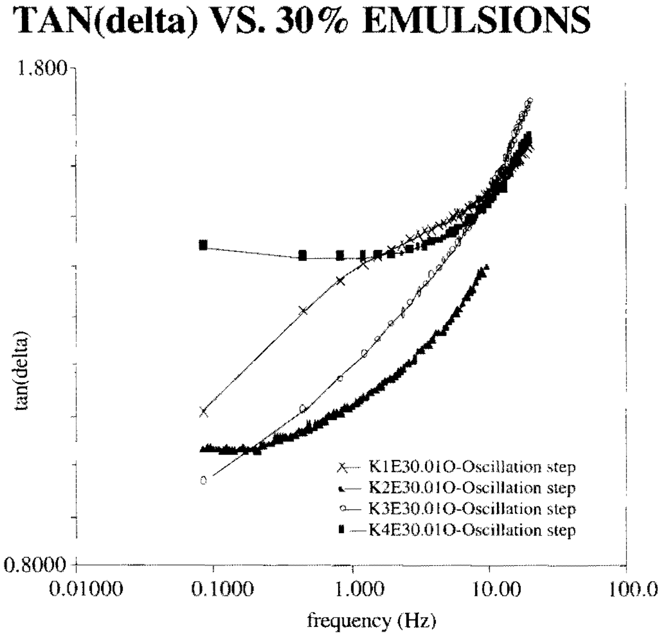

Fig. 7 - Tan (delta) vs. frequency (20 - 0.1 Hz) for 30% emulsions of four different keyless lithographic inks (K1, K2, K3, and K4). Conditions - 4cm, 2° cone at 25°C.

Inks K1, K3 and K4 were run on press and found to perform very well, with K4 being the best overall product. K2 represents a magenta formulation which was difficult to control on press and tended to become overemulsified and hard to clean. Ink K3 is the reformulation of K2, which greatly improved press performance. From the tan (delta) versus frequency response, ink K2 shows distinct contrast as a 30% emulsion. This high water content was chosen to emphasize stability properties. It has lower tan (delta) over the range of frequency tested here, reflecting that a greater relative elasticity is maintained. The other three inks exhibit a strong frequency dependence, which emphasizes the viscous component at high frequency as they all merge with each other. Ink K4, in fact, is inherently more viscous than elastic, even at low frequency. In general, black ink compositions are distinct from color inks in materials used and in actual production of the ink, itself. The implications of the data are that K2 exhibits an emulsified state which is more structured and probably more stable for this high volume of water. The greater contribution of elasticity for this ink can be counterproductive to print performance, as the action in the roller nip is a high frequency process (as well as high shear rate). It may actually indicate an excessive stability, as the keyless process requires the returned ink (via doctored blade) to resist carrying back too much water into the system.

Although the tan (delta) versus frequency relationship shows a clear trend, individual assessment of G', G" versus frequency shows that the actual magnitudes can vary for the inks (Figures 8 and 9). Ink K4 has an inherently higher G' and G" than the other inks, but similar tan (delta) at higher frequencies. K1 and K3 look virtually identical to each other, and K2 shows the most relative change in frequency dependence for G' and G". In order to fully characterize these oscillatory measurements, independent determination of emulsion character is necessary.

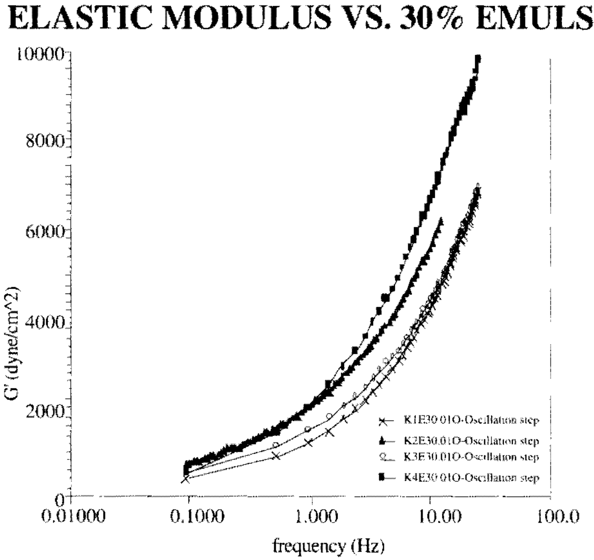

Fig. 8 - Elastic modulus for 30% emulsions as described in Fig. 7.

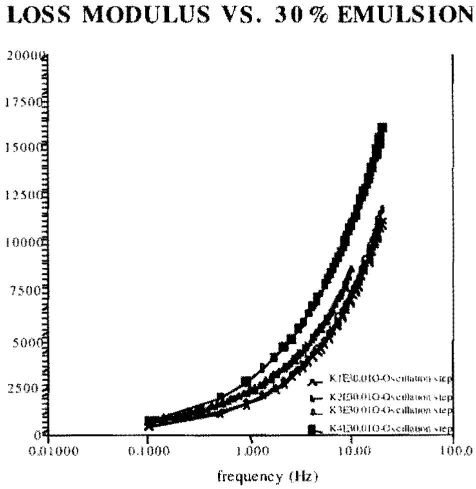

Fig. 9 - Loss modulus (G") for 30% emulsions as described in Fig. 8.

Figures 1012 show how ink K3 behaves at various weight fractions of emulsified water. Once again, a quite complex behavior is observed. Note that as the weight fraction of water increases G' generally increases, with the greatest change occurring from small increments (i.e. K3 E5). The loss modulus, however, shows that a transition occurs above 20% water to yield a G" (at 30%) close to the original neat ink. Tan (delta) versus frequency emphasizes the complex nature of the emulsions at different water contents. This type of information may be suitable to correlation to corresponding phase diagram for the emulsion. The oscillatory experiment, itself, offers a more discriminating means for examining emulsion rheology than would be available from simple flow experiments.

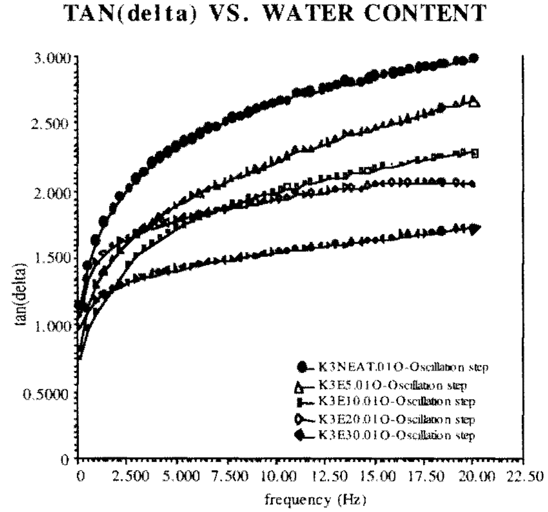

Fig. 10 - Tan (delta) vs. frequency (20 - 0.1 Hz) for a single keyless lithographic ink (K3) as a function of emulsified water content (0, 5, 10, 20, 30% by weight). Conditions - 4cm, 2° cone at 25°C.

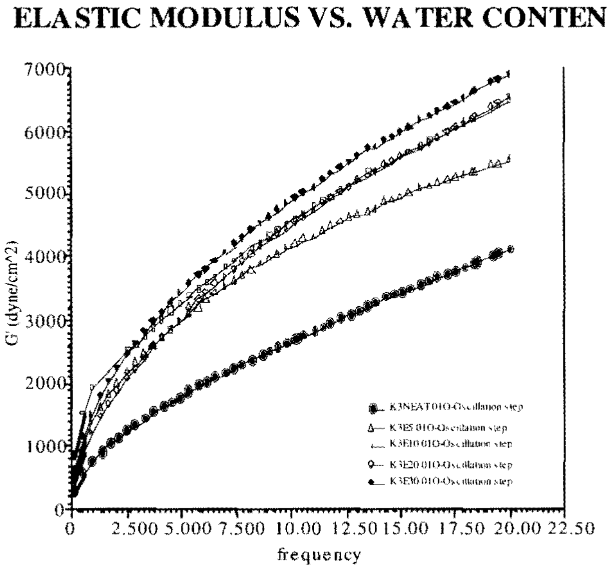

Fig. 11 - Corresponding Elastic modulus for Fig. 10.

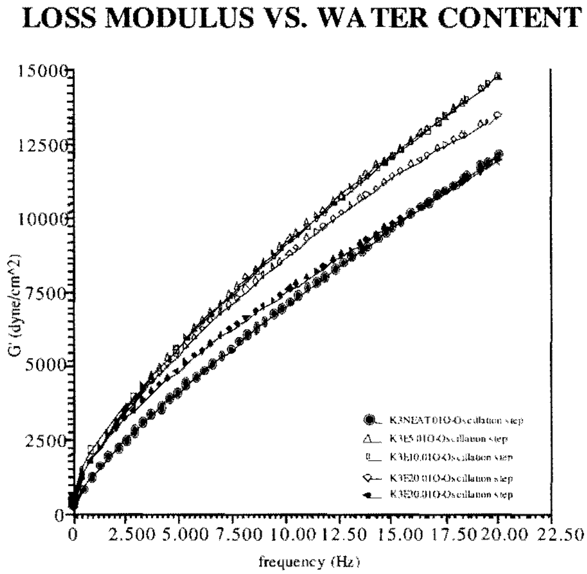

Fig. 12 - Corresponding Loss modulus for Figure 10.

Summary and Conclusions

There are certainly many other features of the printing process not discussed here which can be affected by viscoelasticity (e.g. misting, picking, transference, lubrication, tack). In addition, further improvements in instrument capabilities (e.g. higher frequency in order to approach nip behavior) will provide better correlation to ink behavior on press. As the knowledge base regarding the use of viscoelastic measurements increases, the significance of this type of measurement to the overall printing process will continue to emerge. We have offered several examples which show the diverse potential of this approach. As with any other measurement associated with the lithographic process, it is a complementary tool to improve our understanding of the multitude of variables present.

Selected Bibliography

Amari, T. and Watanabe, K.
1979 "Relaxation Modulus of Printing Ink at Various Magnitudes of Shear Strain", Progress in Polymer Physics in Japan, Vol. 22, pp. 105-109.

Amari, T. and Watanabe, K.
1979 "Strain Dependent Relaxation Modulus of Printing Ink", ACS Division of ORPL Papers 40, pp. 490-493.

Bassemir, R. and Krishnan, R.
1986 Presentation to GATF International Dampening Conference, Aug., 1986.

Cerny, R.
1993 "Rheological Evaluation of Heatset Inks", Graphic Arts Finland 22 No. 2, pp. 3-8.

Chou, S. M.
1991 "Study of Ink Structure by Creep Technique", TAGA Proceedings, pp. 351-369.

Chou, S. M.
1991 "Viscosity Measurement of Viscoelastic Inks at High Shear Rate", TAGA Proceedings, pp. 388-408.

Douglas, A. F.; Lewis, G. A. and Spaull, A. J. B.
1971 "The Investigation of the Dynamic Viscoelastic Functions of Printing Inks", Rheol. Acta 10, pp. 382-386.

Durand, Jr. R. R. and Wasilewski, O.
1993 "Characterization and Control of Lithographic Inks Emulsions", TAGA Proceedings, pp. 285-298.

Hartford, T. and Chasey, K.
1994 "Rheological Measurements of Printing Ink", American Ink Maker, Nov. 1994, pgs. 42-49.

Holland, D.
1993 "Characterizing Flow Regimes", European Coatings Journal, No. 5, pp. 360-364.

Hayashi, T.; Morita, K., and Amari, T.
1993 "Rheological Properties and Printabilities of Polybutadiene/Carbon Black Ink", J. Jpn. Soc. Colour Mater. 66, pp. 655-664.

Hsu, K. F.
1986 "Viscoelastic Properties of Thick Film Inks", American Ink Maker, Vol. 69, no. 8, pg. 30-42, 54, 60.

Lewis, G. A. and Spaull, A. J. B.
1975 "The Investigation of Dynamic Viscoelastic Functions of Printing Inks, Part II, Rheol. Acta 14, pp. 145-150.

Oittinen, P. J.; Kainulainen, J.; Mickets, J.
1992 "Rheological Properties, Setting and Smearing of Offset Inks", Graphic Arts in Finland 21 No. 2, pgs. 3-9.

Mewis, J. and Dobbels, F.
"Nip Flow and Printing Inks", Ind. Eng. Chem. Prod. Res. Dev. 20, pp. 515-519.

Rizk, J.; Leary, T. G.; Newton, J. A.
1994 "The Use of Rheometry to Predict Offset Ink Performance on Press", Technical Association of Graphic Arts, pp. 379-396.

Rohn, R.
1987 "Predicting the Application Behavior of Printing Inks from Dynamic Rheological Measurements", Technical Association of Graphic Arts, pp. 536-559.

Saunders, G.
1992 "The Rheological Evaluation of Inks", Ink and Print International, 10 No. 1, pp. 16-19.

Watanabe, K. and Amari, T.
1986 "Viscoelastic Behavior During Ink Drying", Prog. Polymer Physics in Japan, Vol. 24, pp. 125-132.

Watanabe, K. and Amari, T.
1986 "Rheological Properties of Coating During Drying Processes", J. Appl. Poly. Sci. 32, pp. 3435-3443.

Watson, T. N. and Young, F. R.
1975 "Correlation Between Viscoelastic Properties of Letterpress Printing Inks and Film Splitting Parameters", Rheol. Acta 14, pp. 1001-1011.