

# **Quantitative characterization of flocculation in UV-curable liquid inks by viscosity-temperature measurements**

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**ABSTRACT:** The ongoing need for UV-curable liquid inks with increased color strength has driven ink manufacturers into a never-ending pursuit for highly pigmented ink systems.

One of the major difficulties quickly encountered is the rapid drop in flow of ink as pigment load increases, generating numerous problems at all stages of ink lifetime, from manufacturing to final printing. Therefore, a need exists for a reliable method capable of quantitatively characterize flow (or lack thereof) in liquid inks.

Study of viscosity-temperature curve provides an accurate way of measuring the lack of flow in this type of systems. Viscosity-temperature behavior of highly pigmented inks can be divided in two regions:

At the lower temperatures, ink behaves typically like polymer melt. The Litt model, developed for the latter systems is applied and a universal relationship between the factors A and TC of the model is found.

At higher temperatures, viscosity substantially deviates from the model. Actual increase of viscosity with temperature is commonly observed in this region. A critical temperature (CT) can be defined, above which dramatic change in ink flow properties is observed. The term "puffy" is often used to describe the aspect of such dispersion. The created structure can be destroyed by moderate shearing at temperature below CT, fully restoring the original ink properties.

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These results are interpreted through pigment flocculation, leading to the creation of a physical network of associated pigments. Likewise physical gels, flocculated inks can be characterized by their lack of free flow. Examples of the use of the defined Critical Flocculation Temperature to identify manufacturing and printing problems are presented.

## INTRODUCTION

Conventional liquid inks (solvent-based or water-based) have typically low viscosity (less than 0.1 Pa.s) and contain about 10-15% pigment. Large amounts of ink must be laid down in order to achieve the desired color density after evaporation of the 40 to 60% solvent initially present. Radiation-curable liquid inks for the flexographic printing process are rather formulated at higher viscosity (0.5 to 1 Pa.s). Since 100% of the formula is reactive (no solvent evaporation), one of the commercial advantages claimed is that less ink could be laid down to achieve the same density (better mileage). This is made possible by the higher pigment content of the initial liquid composition.

Flow of such concentrated dispersions influences almost all the stages of the product use from manufacturing, handling (pouring, pumping), and printability (transfer), to properties of the finished print: density, gloss, dot gain and sharpness. For liquid dispersions such as UV-curable inks, the desired flow is defined as the ability of the system to exhibit uniform and homogeneous displacement upon application of a small stress, for instance its own weight. It is then called "free-flowing". For example, a system like Ketchup requiring some pre-shearing to flow is not considered free flowing. The flow obtained when pouring it out is uneven, time dependant, and the liquid flows in large lumps rather than in a continuous manner. For liquid inks, such behavior is commonly referred to as "puffy".

Rheological analysis of concentrated dispersions in general is the object of an abundant literature (1,2,3). Many studies focus on the more or less accurate description of the characteristic steady shear viscosity of such dispersions (4). Many papers describe the variation of shear flow (5) or dynamic properties (6) of dispersions with increasing particle contents. In these studies, it is found that above a certain volume fraction of solids, measurable dynamic moduli are observed. As volume fraction increases further, elastic modulus can become greater than plastic modulus, indicating that the system becomes more solid-like. Nevertheless, no reference to a correspondence with macroscopic flow is made.

Studies of colloidal systems exhibiting thixotropic behavior are numerous. The use of thixotropic loops is by far the least attractive method, since repeatability is extremely difficult to achieve and the actual results depend closely on the experimental conditions (7). Cross-field studies involving rheology and other techniques like microscopy (8) or light scattering (9) give interesting insight into the mechanisms behind particle-particle interactions. The concept of yield stress

is very popular, though it may sometimes be difficult to conciliate with the use of modern rheometers, where orders of magnitude of shear rates and stresses are visualized on logarithmic plots (10). On these plots, unless a strict horizontal line in the stress-rate curves is obtained at low shear rates, a non-null yield stress cannot be defined by extrapolation. Therefore, it is conceptually difficult to conciliate the measurements, showing never-ending displacement at the microscopic level, while it is clear that the system as a whole does not show concerted flow in a physically reasonable time.

In dynamic measurements performed on industrial liquid inks, significant elastic modulus is encountered, as well as rather low loss tangent on systems exhibiting free-flowing properties. This indicates that the sole presence of measurable dynamic properties is not a definite measurement of macroscopic flow.

It was observed that some inks designed to be free-flowing at ambient temperature showed some severe lack of flow during manufacturing at more elevated temperatures. In the mixing tub, the dispersion of the coarse pigment particles is initially fluid. As particle size is reduced during the grinding process, interaction between the pigment surface and the liquid media has an increasing impact on the dispersion properties. Eventually, progressive decrease of the flow is observed starting in the low shear regions by the tub walls. Often the entire mass gets "gelled", preventing any further fluid circulation and color development.

This observation, commonly made in the liquid ink industry suggested that the key to the accurate description of free flowing at macroscopic scale could be found in the behavior of the systems in temperature.

The approach presented in this paper is to characterize first the behavior of dispersions showing no apparent sign of flow reduction at high temperature. Modelization of these systems is made and used as a reference to study dispersions showing typical flow problems above a certain temperature. The formulations used are selected across colors and curing types.

#### EXPERIMENTAL

Two series of liquid dispersions were selected based on their behavior at elevated temperature. Series A was free flowing all along while series B could show lack of flow sometimes at room temperature. The formulations studied were commercially available flexographic or screen inks, or pigment bases for liquid inks. The systems chosen contained single or multiple mineral or organic pigments, pigment particle size was undetermined, and base chemistry could be cationic or free radical (11). The rationale is that any trend found across such different systems is likely to apply to any UV-curable liquid ink.

All samples were analyzed with a stress-controlled rheometer, model AR1000 from TA Instruments. The geometry used was a stainless steel 4 cm 2° cone featuring a polymer-made temperature stop at the base of the shaft to avoid

excessive dissipation of the heat in the geometry. The Peltier plate mounted on the AR1000 allowed rapid heating and cooling in the range  $-20^{\circ}\text{C}$  to  $180^{\circ}\text{C}$ . Two types of procedures were used interchangeably.

First, temperature ramps were carried out at constant shear rate. Since the AR1000 is a stress-controlled instrument, the actual shear rate during the ramp may depend on the experimental conditions and the sample properties. Therefore, it was monitored and recorder during runs and experimental values were discarded when the shear rate was off the desired value by more than 0.5%. Since all systems studied could exhibit thixotropic behavior to various degrees prior to their loading into the rheometer, a two-minute pre-shearing step at the desired shear rate was used in order to bring the repeatability of the measurement well within 1%.

Second, flow curves were recorded by a continuous sweep in stress-controlled mode. Here too, ink sample was preconditioned using a proprietary method, allowing reaching a repeatability of 1% or less across the entire shear rate range.

A chain of consecutive measurements was generally recorded in a row on the same sample. In order to avoid any influence of previous recordings on the nature of a sample, the initial curve was recorded again at the end of an experiment series. Any significant deviation from the original curve would discredit the entire set. Thus, in the samples studied and presented here no irreversible changes, such as polymerization, solvent evaporation or chemical changes occurred during any series of experiments.

Viscosity - temperature variations were fitted with Arrhenius and Litt (14) models using a curve fitting program (SlideWrite 4.0 from Advanced Graphics Software).

## METHODOLOGY

Two approaches were used in order to obtain the variation of viscosity with temperature and shear rate.

In the first type of experiments, a sweep in shear is made at constant temperature, and the operation is repeated at various temperatures, generating a family of curves, such as shown on Figure 3. In concentrated pigment dispersions, non-truly Newtonian behavior is always observed (12). At the typical pigment concentration encountered (up to 40 %wt. in this study), shear thinning is observed (see Figure 3).. Therefore, direct determination of the variations of viscosity with temperature demands that the measurements be made at constant shear rate. Extraction of temperature ramps at any shear rate in the range could be achieved by interpolation. The temperature ramp is described by as many points as there were flow curves (see for instance Figure 5).

In the second type of experiments, direct sweep in temperature is made at several shear rates. Because of the higher number of data points an accurate

determination of a model can be made on these curves and the variation of the model coefficients with shear rate can be attempted.

Since modelization is the objective of the study, several precautions should be taken when recording viscosity in temperature sweeps in order to improve measurement accuracy. Namely, shear rate must be stable, temperature homogeneous across the sample, and gap constant, as discussed next.

The rheometer used is stress-controlled. In such a device, the time necessary to reach a certain shear stress from initially zero is very short (less than 10 ms). Although using the rheometer in rate-controlled mode is made possible through software, the requested shear rate is indirectly obtained through a series of stress adjustment loops (13). In thixotropic systems, the variations of viscosity in the sample, which in turn drive the adjustments of the stress in the loop, closely depends on the initial state of the sample and is highly unrepeatable. Consequently the adjustment loops are never the same twice, and the exact amount of time required to reach a certain shear rate once the stress is established is not predictable. In typical UV flexographic inks observed at low shear rates, that duration was seen exceeding several minutes.

The first step in a rate-controlled temperature study on a stress-controlled rheometer (and vice-versa) is therefore to define the conditions in which the adjustment loop can be considered instantaneous. This happens when the reactions of the system are faster than the experiment sweep rate. In practice, constant monitoring was made of the shear rate and experimental values were discarded when the shear rate was off the requested value by more than 0.5%.

Another consideration when making a temperature sweep is the actual transmission of the heat from the lower plate across the thickness of the sample and its dissipation into the cone. The sweep rate must be kept low enough to avoid significant temperature gradients in the sample.

Finally, as temperature changes, both lower plate and upper geometry dilate or contract, accounting for slight differences in the gap between them. The AR1000 features an automatic gap correction, which adjust gap in real time depending on the temperature. In order to avoid large corrections the gap was initially zeroed at midpoint of the temperature range studied (50°C).

The absence of effect from the three points exposed above was verified experimentally. The first experiment exposed in Figure 1, shows the shear rate drifts from the requested value as temperature is changing due to the time-scale of the stress-adjusting loops. It was carried on the most viscous system: a highly pigmented (39 %wt.) base composed mainly of a low viscosity oligomer and a proprietary carbon black pigment. After two minutes pre-shearing at 500 s<sup>-1</sup> at the initial temperature, a temperature sweep was applied at 500 s<sup>-1</sup>. Two different sweep rates (10°C/min and 5°C/min) were used, and the starting temperature was either the high end (120°C) or the low end (20°C).

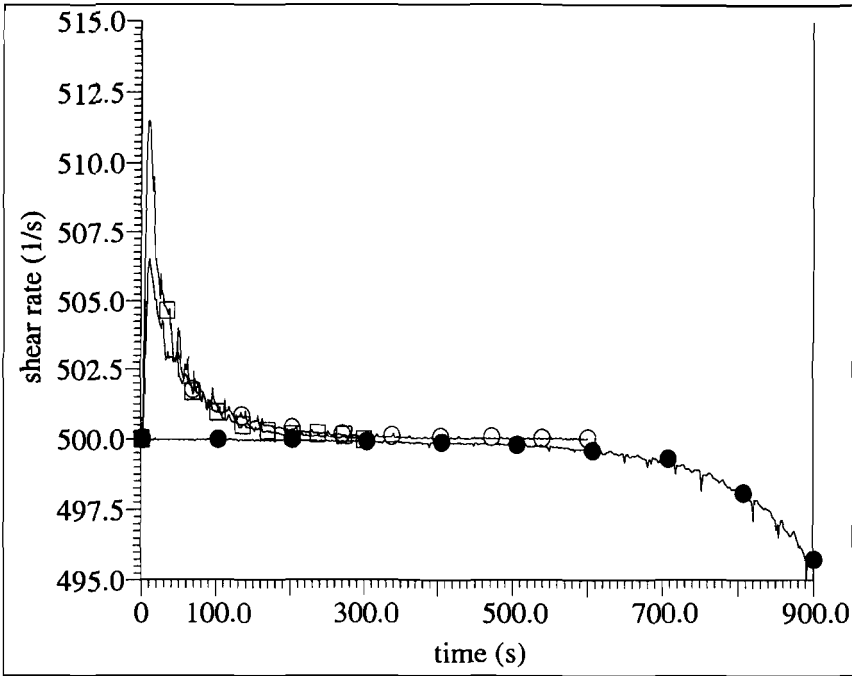


Figure 1: Actual shear rate during temperature ramps at "constant rate". Interval: 20 – 120°C; ●: downward ramp @ 6.7 °C/min; ○: upward ramp @ 10°C/min; □: upward ramp @ 20°C/min

Deviations up to 2% from the requested shear rates are observed in the initial portion of the upward sweep. It can be noted that deviations are less broad when the sweep rate is decreased. It is also clear that a lesser portion of the run is affected when the sweep is made upward (150 sec. worth of data lost vs. 250 sec. for the downward ramp).

In order to verify the presence of temperature gradients and gap effects described above, viscosity was recorded in manual mode. After temperature stabilization and manual gap adjustments, shearing at constant rate was applied until viscosity was stable. Viscosities at ten different temperatures were thus obtained.

On Figure 2, the automated (upwards and downwards) and the manual temperature ramps are superimposed in an Arrhenius plot. It is clear that despite all the possible sources of deviations considered, the curves are fairly close to each other, superimposed with the manual curve. Highest deviations are noted at the ends of the ramps.

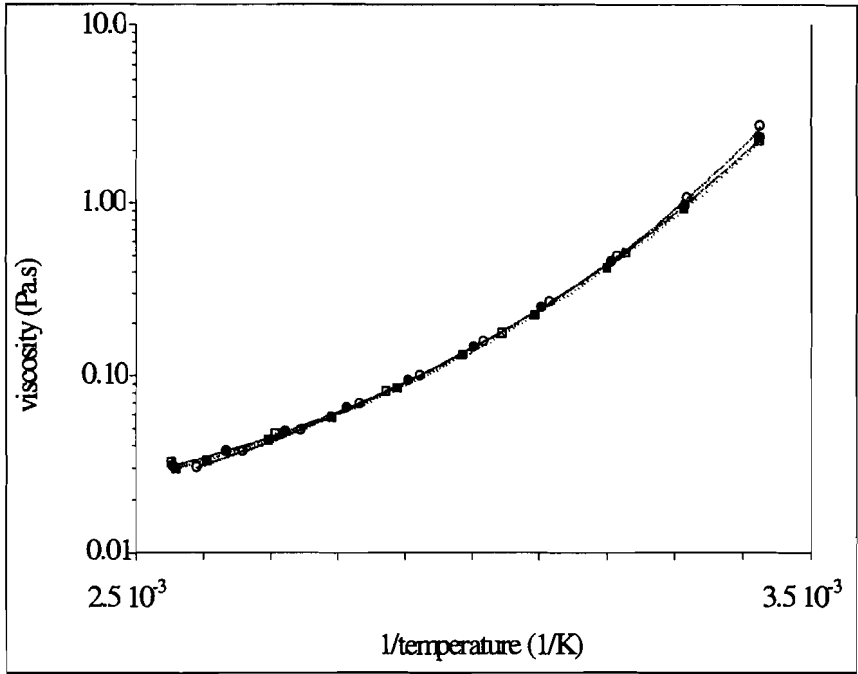


Figure 2: Variation of viscosity with temperature for various recording methods. ●: upward ramp @ 10°C/min; ■: upward ramp @ 20°C/min; ○: downward ramp @ 6.7°C/min; □: manual ramp (20 – 120°C, 10°C/min)

Curve fitting is intended for use to modelize the curves. In this type of analysis, end trends could have a profound effect on the obtained results. As shown on Figure 2, the ramp giving closest results to the fully manual, but time-consuming curve is the upward sweep at 10°C/min from 20°C on. Because of shear rate deviations, and for increased accuracy in the curve fitting, the data points in the first 10°C of the sweep are to be discarded before further analysis is conducted.

## RESULTS

### SERIES A: FREE-FLOWING INKS

The viscosity – temperature curves for these systems were obtained using the flow curve method described earlier. Extraction of a large number of temperature ramps at constant shear rates was possible by interpolation between consecutive data points.

Figure 3 represents the original flow curves obtained on a white screen ink system. This system is characterized by a rather low pigmentation. Above 80°C, the viscosity seems constant for all shear rates (all curves superimposed with each other).

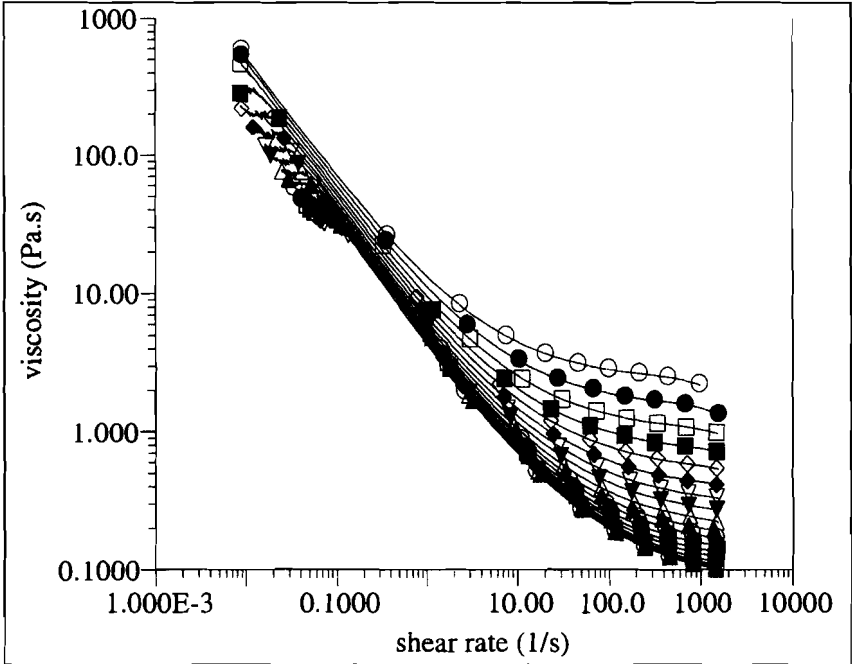


Figure 3: Flow curves at various temperatures on white silk-screen ink. 5°C interval from top curve (20°C) to bottom curve (120°C).



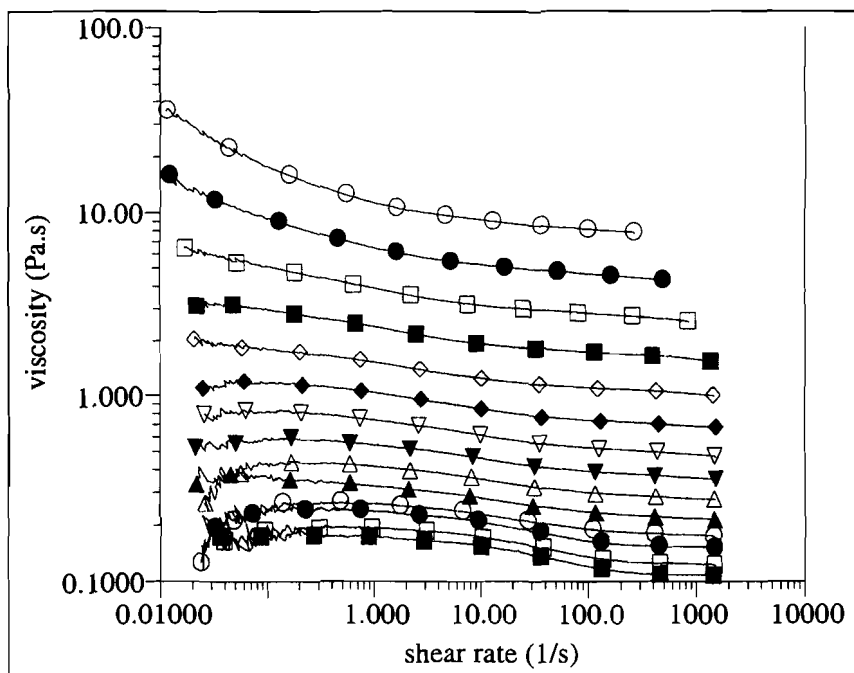


Figure 4: Flow curves at various temperatures on pigment base 44-39. 5°C interval from top curve (5°C) to bottom curve (70°C).

In the example presented on Figure 4 (obtained on a different ink system), viscosity decreases continuously with temperature, showing a much less pronounced leveling trend.

As shown on Figure 2, the variation of viscosity with temperature of free-flowing dispersions cannot be described by Arrhenius law even at the lowest temperatures. The same deviations are typically observed on all the dispersions studied.

In 1973, Litt (14) proposed a model based on "effective free-volume" considerations to describe polymer rheology in the melted state. The usual approach to viscosity changes with temperature is to consider "holes" (or free volume) created as temperature increases. Molecules can move into these holes. Therefore, movement is improved as temperature rises, and viscosity drops. Litt considered that in polydispersed polymeric systems, only the holes "big enough" could serve viscosity reduction. The higher molecular weight population could not fill the smaller holes, therefore were not participating in the viscosity reduction. Litt hence predicts in these systems a viscosity at a given temperature higher than Arrhenius does.

Based on these considerations, Litt proposed the following equation for molten polydisperse polymers:

$$\ln(\eta/\eta_0) = \left(\frac{T_C}{T}\right)^{3/2} / A \left(1 + \frac{T_C}{T}\right) \exp\left(\frac{T_C}{T}\right) \quad \text{eq. 1}$$

- where T is the temperature in K
- $\eta_0$  is the viscosity at infinite temperature in Pa.s
- $T_C$  is a characteristic temperature of the system in K
- A is a characteristic constant of the system

The Litt model predicts a finite viscosity at infinite temperature, as observed on Figure 3 and Figure 4). Application of the Litt model to concentrated pigment dispersions is surprisingly satisfactory as shown by the randomly scattered residuals on Figure 5.

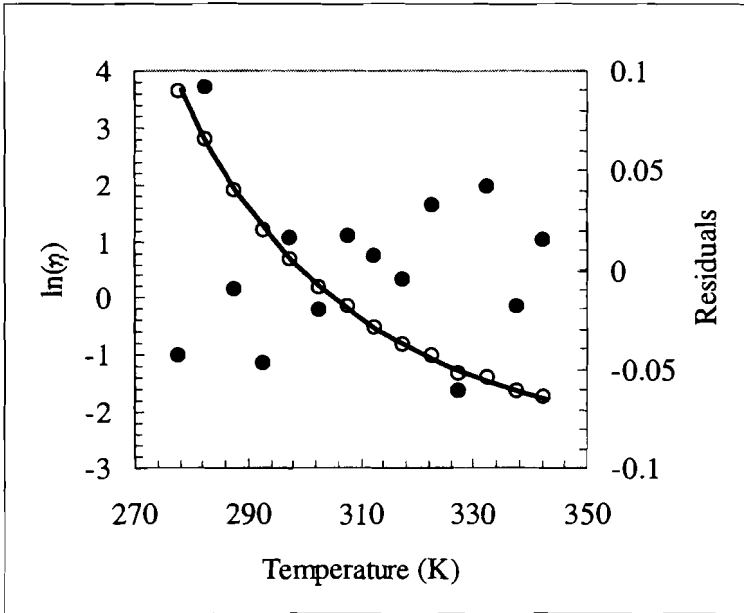


Figure 5: Typical fit of experimental data with Litt model. Data extracted at  $10 \text{ s}^{-1}$  from flow curves run at constant temperature on highly pigmented base shown on Figure 4. —: fit; ●: residuals; ○: experimental data

The Litt model parameters were thus collected for a variety of free-flowing dispersions at various shear rates.

Figure 6 shows the variation of  $\ln(A)$  with the critical temperature  $T_C$  for four different ink systems at multiple shear rates.

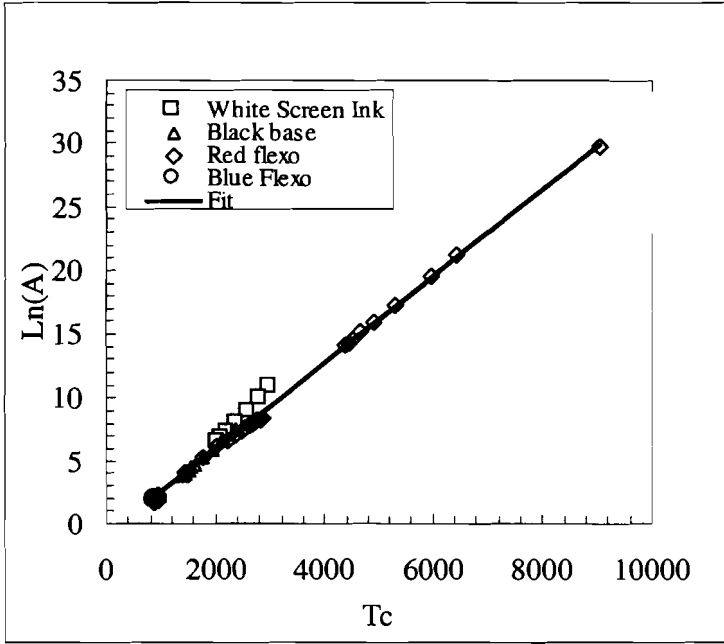


Figure 6 Correlation between characteristic temperature  $T_C$  and constant  $A$  of Litt model for free-flowing inks.

At all shear rates considered between  $0.1$  and  $1000\text{s}^{-1}$ , all ink studied fall on the same line over a wide range of  $T_C$  and  $A$ . In case of the studied screen ink, a slight difference was noted between the initial run and the same run applied at the end of the series. Other measurements showed that pigment settling occurred during the series of experiment. The series was nevertheless incorporated to Figure 6 to illustrate the effect that a not carefully controlled measuring process could have on the experimental results.

The equation of the correlation is found:

$$A = \frac{1}{B} \exp\left(\frac{T_C}{T_R}\right) \tag{eq. 2}$$

where  $T_R = 293.7 \pm 1.3$  and  $B = 2.47 \pm 0.12$

It appears that  $\eta_\infty$  does not correlate with  $T_C$ . It is therefore an independent variable.

It seems that stable ink systems could preferably be described by a new model derived from Litt. This new model would contain two universal constants instead of three: a reference temperature  $T_R = 293 \text{ K}$  ( $20^\circ\text{C}$ ) and a constant:  $B$  that could be equated to  $5/2$ .

Injecting eq. 2 into eq. 1 leads to the universal model:

$$\ln(\eta/\eta_\infty) = \frac{5}{2} \left( \frac{T_c}{T} \right)^{3/2} \left/ \left( 1 + \frac{T_c}{T} \right) \exp \left( T_c \left( \frac{1}{T} - \frac{1}{T_R} \right) \right) \right. \quad \text{eq. 3}$$

where  $T_R$  is the reference temperature =  $293 \text{ K}$   
 $T_c$  and  $\eta_\infty$  vary with shear rate

The above model was found applicable to most commercial free-flowing ink systems in a large shear rate range ( $0.01 \text{ s}^{-1} - 1000+ \text{ s}^{-1}$ ). It could be applied on data recorded in any temperature range. The identification of  $T_R$  with typical room temperature remains to be clarified.

#### SERIES B: INKS NOT FREE FLOWING AT ELEVATED TEMPERATURES

The proposed model described in the previous section could now be used to quantify the contribution of pigment flocculation to the viscosity-temperature profiles when it occurs. Since accurate application of a model by curve fitting requires numerous data points, temperature ramps were applied to the systems in this part of the study. The procedure consists in scanning a temperature domain wide enough to show a substantial section described by eq. 3. The model is then carefully extrapolated to higher temperatures and deviations of actual viscosity from the model are quantified.

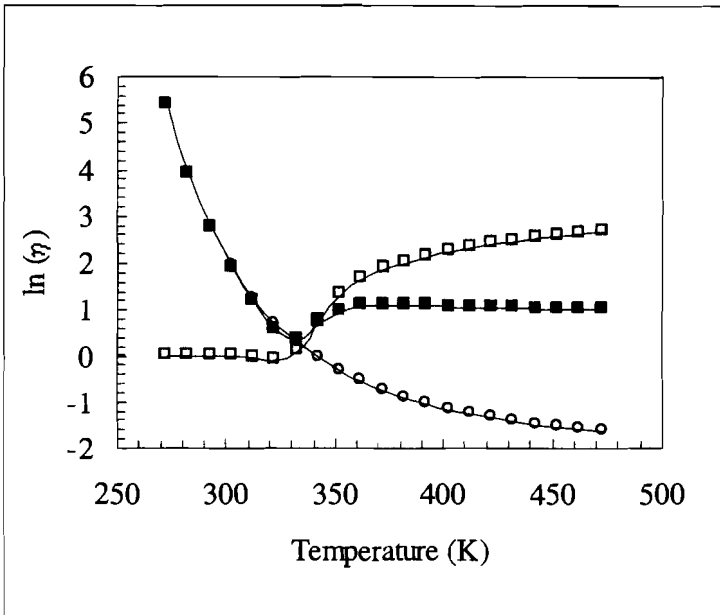
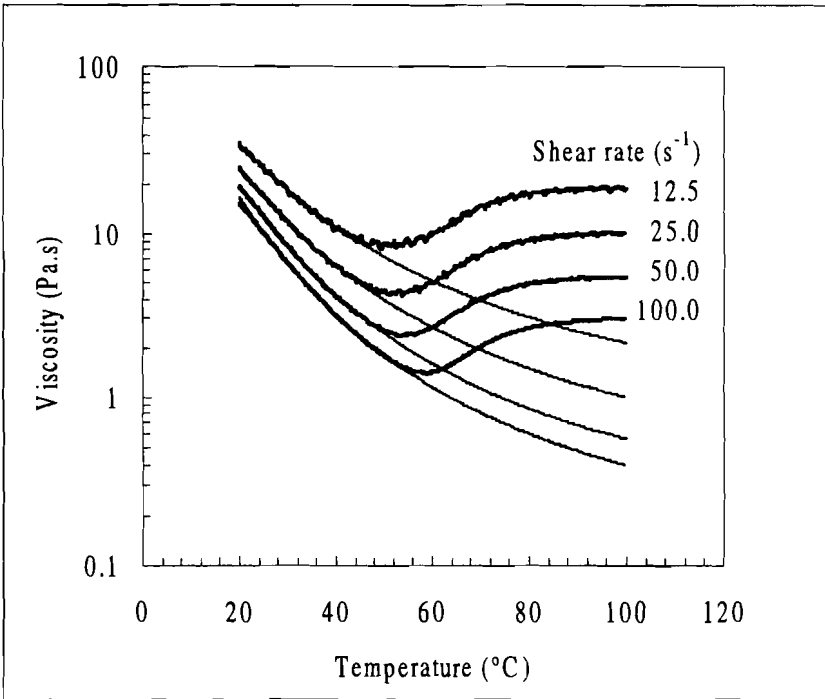


Figure 7: Typical observed data on non free-flowing dispersions. Ink: red flexo. ■: actual data; ○: model fitted to temperatures below 325K; □: residuals

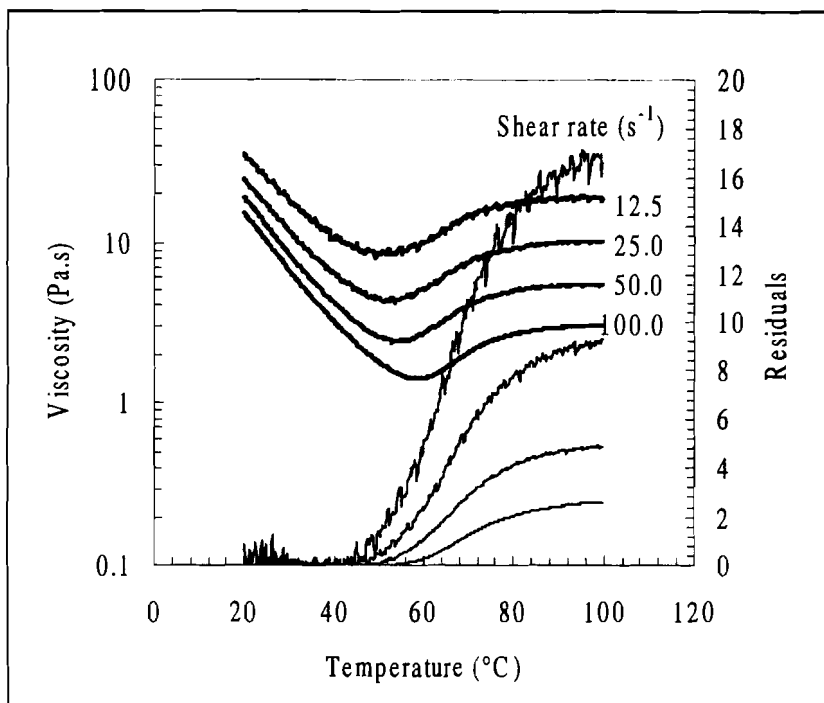
Figure 7 shows typical deviations observed from the model for inks showing lack of flow at elevated temperatures. A critical temperature (CT) can be defined from the residuals curve showed on Figure 7 (empty squares) by the temperature at which half the total jump in residual viscosity is observed. In the case displayed on Figure 7, the CT is 82°C. This technique is difficult to apply to systems having a CT below 10°C. The too brief region between -20°C (lower limit of the instrument) and CT may not allow accurate description by eq. 3 and therefore improper extrapolation.

#### VARIATION WITH SHEAR RATE OF THE DEVIATION FROM FREE-FLOWING SYSTEMS

A proprietary carbon black pigment (50%wt.) was ground in an epoxy-acrylate oligomer using a three-roller mill. No other chemical was used in the formula. Temperature ramps were recorded at various shear rates on this pigment base according to the procedure described previously. Figure 8 shows the observed variation of viscosity with temperature for this dispersion. It is visible on the figure that the curves become noisy at lower shear rate. Closer observation reveals that the “noise” is in fact the result of the stress adjustment loops the rheometer applies to maintain constant shear rate.



*Figure 8: Variation of the viscosity-temperature curves with shear rate. Example on black UV flexo base at 50%wt. pigment. Thin lines: modified Litt model describing viscosity drop without flocculation; thick lines: actual data.*



*Figure 9: Variation of the viscosity-temperature curves with shear rate. Example on black UV flexo base at 50%wt. pigment. Thin lines: residuals from the modified Litt model; thick lines: actual data.*

Fitting of eq. 3 onto the descending portion of the curve is made and displayed on Figure 8. Subtraction of that “normal” behavior from the actual experimental data is plotted on Figure 9. The same type of curves for a different ink system is plotted on Figure 10. In both cases, it seems that the CT is independent of shear rate.

Figure 9 shows that the amplitude of the viscosity jump decreases as shear rate increase. At the maximum, creative forces (temperature activated process) are balanced by the destructive effect of shear flow. The same shape of the deviation curves has been found in many systems. In multi-pigmented inks, deviations that are more complex may be observed, as shown on Figure 10. Since more than one pigment is present, it is conceivable that multiple structures with their own internal parameters could develop simultaneously and interactively.

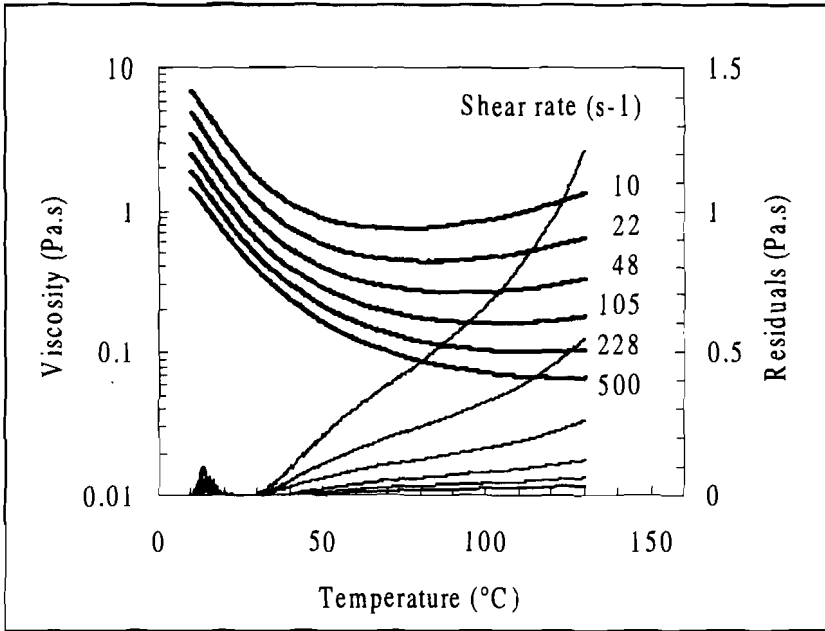


Figure 10: Variation of the viscosity-temperature curves with shear rate. Example on multi-pigmented red UV flexo base at 50%wt. pigment. Thin lines: residuals from the modified Lit model; thick lines: actual data.

Variation of the amplitude with shear rate for both systems at 100°C is plotted on Figure 11.



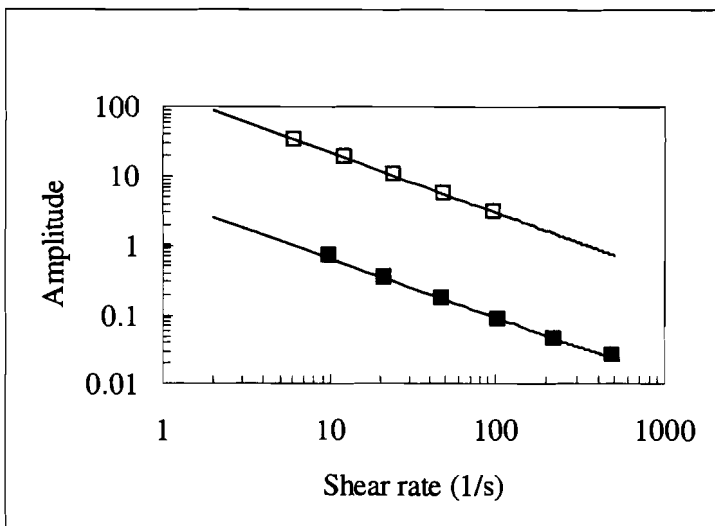


Figure 11: Variation of deviation amplitude at 100°C with shear rate. □: mono pigmented black base; ■: multi-pigmented red ink; solid lines: eq. 4

The amplitude seems to decrease following a power law in the domain of shear rates studied (see Eq. 4).

$$A = A_0 \dot{\gamma}^{-\alpha} \quad \text{eq. 4}$$

where  $A$  is the amplitude of the deviation  
 $A_0$  is the intercept of the straight line on log-log plot  
 $\alpha$  is the rate index (slope of the straight line on log-log plot)

The value of  $\alpha$  is 0.87 for the mono-pigmented black base and 0.85 for the multi pigmented red ink.

## DISCUSSION

The observed increase of the viscosity in a large shear rate range for a series of vastly different inks and bases above a certain temperature strongly suggests the existence of a non-specific phenomenon common to all the systems studied. The results obtained are consistent with some of the observations made by M. Fernandez *et al.* (15) on solvent-based inks. The authors noted an increase of viscosity with temperature. Limited temperature measurements lead the authors to use an Arrhenius-like model to describe the observed behavior. They noted also reverse behavior of the storage and loss moduli, which is consistent with the development of a network-like structure upon increase of temperature. They

relied upon pigment flocculation to interpret their results. In order to explain a greater extent of flocculation at higher temperatures, they used an additional argument of polymer phase separation. In the present systems, a similar behavior is observed in all flocculating inks, even in formulas containing a single liquid vehicle, thus excluding phase-separation considerations.

As described by Pignon (9), aggregated dispersions where a continuous network of aggregates is formed exhibit yield stresses, along with thixotropic behavior. The present models and theoretical approaches used to describe the rheological behavior of flocculated suspensions have been reviewed recently (16).

The very presence of such a physical gel of pigment created by flocculation can be related in the liquid inks studied here to the progressive loss of flow encountered in their manufacturing.

When flocculated, a concentrated dispersion exhibits no macroscopic phase separation or heterogeneity. Micrographs show that the dispersed phase has collapsed into flocs separated by spaces of lower pigment concentration (8). Depending on their fractal dimension, the flocs may be connected by a small number of weak pigment bridges. Application of a small stress results in the rupture of these bridges, which rapidly reform elsewhere. In the pouring process for instance, flocs can be separated along the high stress plans, resulting in the sliding of large lumps of sample. The flow is uneven and in practice, ink is not user-friendly if even printable.

Pigment-pigment attraction forces are non-hydrodynamic in nature (4). These interactions depend on electrical and chemical properties of the pigment particles and the pigment-vehicle interface, such as surface charge, surface potential or the presence of a surfactant layer (17). They are not influenced by the hydrodynamic forces applied on the particles by the stress in the fluid. The fact that the critical flocculation temperature observed in this study does not seem to vary with the applied shear rate (see Figure 9 and Figure 10) would indicate that the source of deviations from the model is indeed a pigment-build structure.

The dependency of the flocculation amplitude at constant temperature (or more accurately the amplitude of the effect that flocculation has on viscosity) to the shear rate is described by a power law (see Figure 11), where the exponent is close to  $-0.85$ . This value is in close agreement with the one found by Silbert *et al.* (18) in their study of the rheology of concentrated, aggregated solids using a more conventional approach. In this study, the authors determined that for dispersions with colloid volume fraction between 0.47 and 0.57, the viscosity decrease with shear rate scales with a shear-thinning index of  $0.84 \pm 0.01$ .

The amplitude of flocculation at constant temperature could be related either to the strength or to the extension (in terms of the number of pigment particles per unit volume involved) of the physical gel.

## CONCLUSION

A method to determine a critical flocculation temperature (CFT) in radiation-curable liquid inks is presented. The description of the variation of viscosity with temperature of non-flocculated dispersions has allowed the definition of a model that is specific to highly pigmented systems. Thanks to this model, flocculation effect on the viscosity-temperature variation has been extracted and quantified.

It was seen that the amplitude of flocculation decreases as shear rate increases. Moreover, the law of variation is in accordance with observations made on aggregated colloidal suspensions in the literature.

The independence of the CFT to shear rate is bringing strong evidence for the presence of a physical gel of pigment resulting from its flocculation. This structure is quantitatively responsible for the lack of macroscopic free flow observed in some liquid ink systems in manufacturing and other application conditions.

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