Rheological Properties of Highly Pigmented Inks: Consequence on the Color Printing Quality

Anne Blayo*, Alessandro Gandini* and Jean-François Le Nest*

Keywords: Ink, Offset, Pigment, Color, Rheology, Viscoelasticity

Abstract: In order to optimize color reproduction, especially in the context of four- six- or seven-color processes, ink makers formulate inks with unusually high pigment contents. The aim of this study is to examine the rheological characteristics of these pigment-rich inks, in order to get a better understanding of the ink tranfer, and thus of the color printing quality. These formulations give rise to peculiar rheological characteristics, such as shear-thinning behavior, yield behavior, thixotropy and viscoelasticity. Continuous flow and dynamic viscoelasticity results are analysed, with particular emphasis on the effect of temperature. The dependence of the rheological and viscoelastic properties with respect to frequency and temperature displayed interesting features which will be discussed together with the corresponding color reproduction results.

*Matériaux Polymères, Laboratoire de Génie des Procédés Papetiers,
Ecole Française de Papeterie et des Industries Graphiques, BP 65
38402 Saint-Martin-d'Hères, FRANCE.
E-mails: Anne.Blayo@efpg.inpg.fr
Alessandro.Gandini@efpg.inpg.fr
Jean-Francois.Lenest@efpg.inpg.fr

Introduction

Rheological and colorimetric properties are the main factors determining the upper limit of pigment concentration, hence throughput rate, in the manufacture of ink or paint concentrates. The ink formulator must find a compromise between the rheological properties and the color performance, particularly in the case of four-, six- and even seven-color printing. It is consequently important to characterize the rheological behavior of these dispersions, to get a better insight into their end-use properties. The purpose of the present investigation was to begin a study of the relationship between the rheological features related to highly pigmented inks and the ensuing color performances of their printed dried films.

I. General rheological characteristics of pigment dispersions

Dispersions are two-phase systems containing interactive (attractive or repulsive) colloidal solid particles suspended in a low molecular-weight medium. The rheological properties of dispersions have been the subject of much research for many years, mainly because these materials are of considerable industrial significance, for example in painting, papermaking, foods, cosmetics and printing inks. These rheological properties are much more complex than those of polymer solutions or melts. Printing inks are dispersions of non deformable particles (the pigment) in a non-newtonian, visco-elastic medium (the vehicle). Extensive studies have been conducted on the different parameters affecting the rheological behavior of model suspensions, namely volume fraction, shape, size and size distribution of the pigments, and interfacial interactions between the pigment and the dispersing medium [Coussot et al., 1993; McKay, 1993; Amari et al., 1983; Leonov, 1990; Quemada et al., 1985; Mani, 1996;]. Mani et al. [1996] pointed out that these studies have traditionally concentrated solely on the steady-shear flow behavior. More recently, such rheological investigations have begun to include linear viscoelastic measurements and the usefulness of this approach has been clearly demonstrated. However, most of these rheological studies probing interparticle interactions have concentrated on model systems consisting of spherical, monodisperse particles. What is lacking in the field of inks or paints is a systematic examination of the linear viscoelastic behavior of more complex, i.e. industrially relevant, dispersions typically containing polydisperse particles, which can

moreover aggregate due to strong interparticle attractions, and a viscous liquid matrix consisting of one or more polymers and solvents.
Because of interparticle interactions, dispersions can generate a particulate network which is usually ruptured in flow with the formation of flocs , but restored again once at rest [Coussot et al., 1993]. Flocculated suspensions are generally shear-thinning and thixotropic and can moreover exhibit a viscoelastic behavior. Elastic effects result from the attractive interparticle forces and the occurrence of flow arises because of floc rupture. In the particular case of concentrated dispersed systems in viscous media, the formation, rupture and restoration of flocs results in two macroscopic phenomena, viz. yield behavior and thixotropy, which are among the most complex problems encoutered in rheology.

A brief literature survey focused on printing inks

In an interesting study, McKay [1993] examined the rheology of inks under steady shear conditions and showed that the shape and surface properties of the pigment particles were determining factors in establishing flow properties. Experiments were made with PY 13-type and PR 57.1 pigments dispersed in litho ink media. The process of breakdown and buildup of the particle network is also a very important question treated for example by Pangalos et al. [1985]. Chou [1991] carried out an extensive analysis on the ink structure properties and thixotropic behavior by creep technique in order to gain a deeper knowledge of the nature of the pigment-vehicle interactions. Mani et al. [1996] described the linear viscoelastic behavior of copper phthalocyanine dispersions used in printing inks. The main conclusions of this study were: (i)the increase of the linear viscoelastic region in certain conditions, (ii) the behavior of the dispersions containing high pigment concentrations which was assimilated to this of a polymer near its gel-point. In this work, the existence of a plateau for G′ at low frequencies was also encountered. Another stimulating piece of research on printing dealt with very concentrated printing inks (intaglio type inks) which displayed a peculiar rheological behavior inks [Fernandez et al., 1998]. These authors placed particular emphasis on the effect of time and temperature on the formation of a pigment-based network structure and found that these inks exhibited a higher viscoelastic character at 40 °C than at 20°C. Such odd temperature inversion was not observed at the low pigment concentrations.
Kent and Lyne [1989] considered the consequences of the ink rheological properties on ink penetration into the paper. Offset lithographic inks

behave essentially as elastic materials at the shear rates encountered in printing and their elastic behavior tends to retard their migration. Emulsification of the fountain solution in offset inks may not influence pressure penetration, but it can have profound effects on post impression capillary penetration of inks into paper. At shear rates at least an order of magnitude lower than those encountered in printing, the ink predominantly stores and releases shear energy elastically, rather than dissipating it through viscous drag. In shear flow litho inks are observed to squeeze more slowly than inelastic fluids of corresponding viscosities. Consequently, the highly elastic behavior of litho inks retards significantly the rate of pressure penetration compared with that which would occur with an inelastic fluid of similar viscosity.
Finally, it is worth noting that some of these intrinsec rheological features may give rise to some technical problems. Several authors [Magnin et al., 1990; Gregory et al., 1993; Coussot et al., 1993] have pointed out the occurrence of experimental problems such as wall slip, fracture, crack propagation, long memory of the sample, etc., which made it difficult to obtain reliable quantitative results with these materials. Some of these problems can nevertheless be overcome, e.g. wall slip may be avoided by the use of rough surfaces, and standardization of the initial state may normalize the shear history of the different samples.

II. Experimental

II.1. Samples

The rheological properties of a series of offset inks used for six-color printing have been studied. The purpose of processes using more than four colors is to extend the color gamut beyond what can be achieved in the conventional four-ink process. Figure 1 present the gamut extension in the case of six-color and seven-color printing. This relatively recent technique leads to an appreciable improvement of the quality of color reproduction, based on two techniques: the use of more than four inks, and the stochastic screening, which enhances the reproduction of details (FM screening , instead of AM screening) and compensates the difficulties of the superposition of more than four screenings (no moire patterns, easier to register at the beginning of the run). This process requires therefore inks with specific characteristics, in order to limit dot gain and excessive superpositions,i.e. ink thicknesses. One way to avoid an excessive ink layer, while maintaining colorimetric requirements, is to increase the pigment content of inks.

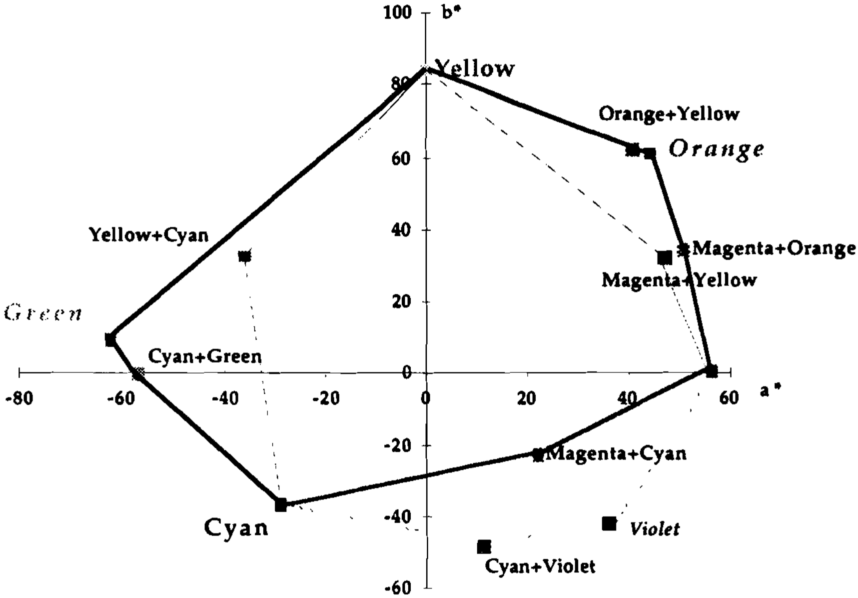

Fig. 1. Color gamut achieved in the four-color printing process (———), compared to that related with the six-color printing process (▬▬). For comparison, the gamut obtained in seven-color printing is also plotted (- - -).

In this study, inks had a pigment content about 20% above the typical pigment content in offset inks. They will be designed as Cyan, Yellow, Orange, Magenta, Green and Black, according to their color.

II.2. Measurements

II.2.a. Rheological characteristics

Steady shear and oscillatory flow experiments were conducted on a CSL^2500 controlled-stress rheometer, with the cone-plate geometry (diameter = 2 cm, top angle = 4°). In steady shear flow characterizations, increasing and decreasing shear stress scans were performed with a maximum shear of 1500 Pa, and temperatures varying between 20 and 32°C. Measuring time was 4 min for each run. Viscoelastic functions were obtained in frequency sweeps within

appropriate stress and frequency range, at temperature varying from 10 to 35 °C.
In addition to the dynamic measurements on the rheometer, viscoelastic properties of the inks were measured on a Metravib viscoanalyser. This equipment has been described in previous studies [Blayo et al, 1996]. In these experiments, the annular shearing mode was used, the temperature was allowed to vary from -20°C to 30°C, with steps of 5°C, and 7 frequencies were scanned with the logarithmic mode from 5Hz to 250Hz, at each temperature. Master curves of G', G'', η^* and tg δ were obtained from the use of the time-temperature superposition principle.
The tack of the inks was measured at different temperatures between 20 and 30 °C on a Tack-o-Scope.

II.2.b. Printing and colorimetric characteristics

Printing tests were made with these inks, with varying ink film thicknesses, and at different temperatures. The optimum ink densities were determined by preliminary laboratory transfer tests. Different substrates were printed at different temperatures between 20 and 35 °C, and at different densities. Spectrocolorimetric measurements were obtained from solids printed.

III. Results and discussion

III.1. Flow characteristics

The inks analysed presented a marked shear-thinning behavior in the range of shear rates applied. Figure 2 gives the rheograms obtained with Yellow at 20°C. For comparison, the corresponding tracing related to a conventional offset ink is also presented. The Herschel-Bulkley model gave a good description of this behavior, if the first part of the increasing curve is neglected. This shear-thinning characteristic is less pronounced for offset inks with a "normal" pigment content. At high shear rates (printing situation), the two types of inks show similar viscosities, but at low shear rates the "normal" ink displayed a higher fluidity than the pigment-rich counterpart.
The viscosity of the inks measured in the shear-thinning region at 1000 Pa, versus temperature followed an Arrhenius-like equation. Table 1 presents the values of the activation energy of flow obtained within the temperature range considered. These values are markedly higher than those we found in another study related to "normal" offset inks,

which ranged between 65 and 85 kJ/mol. [Blayo et al, 1993]. This is probably due to the strong interactions among pigment particles and/or among these and the vehicle. Also, the high E_a values found here imply a strong dependence of the viscosity on the temperature, at least in the range of shear stresses examined.

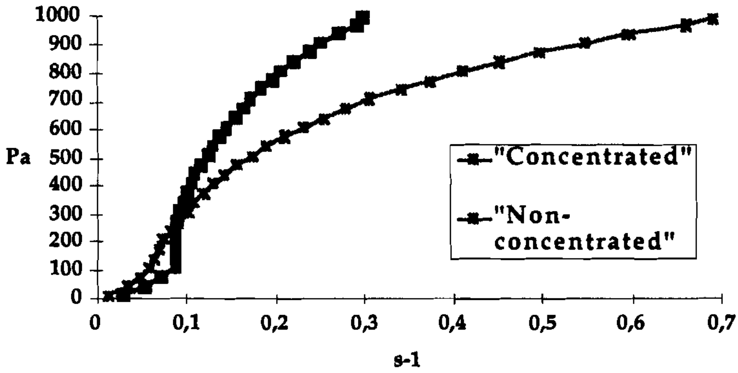

Fig. 2. Comparison of the rheograms of Yellow and a non-concentrated offset yellow ink, at 20°C.

Inks	E_a (kJ/mol)
Yellow	112
Orange	125
Green	105
Cyan	99
Black	146

Table 1. Values of the activation energy of flow

Additionally, Yellow and Orange displayed a very specific flow behavior, at the low shear stresses. These inks presented an inversion of the temperature effect on the viscosity measured at 150 Pa. The viscosity at low shear rates were found to increase with temperature between 20 and 25°C, which is unusual. This tendency was not observed for the other samples (see Fig3). Similar trends were reported by Fernandez et al. [1998], who concluded that a reinforcement of the cohesive interactions between components took place upon heating.

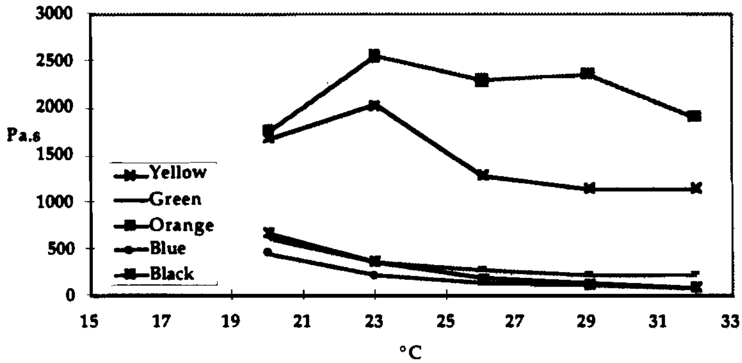

Fig.3. Viscosities of inks at 150 Pa vs. temperature

The flow experiment allowed to measure the extent of thixotropy of these inks. Figure 4 is an illustration of the hysteresis loops obtained with Orange and Yellow at 20 °C. As always encoutered with thixotropic materials, the structure was broken down during flow, and thereafter rebuilt progressively during the rest period. The comparison among the different inks, confirmed the stronger cohesive interactions occurring with Yellow and Orange. Moreover, this behavior was found to be strongly temperature dependent.

III.2. Viscoelastic characteristics

The coherence between rheometer and viscoanalyser data was verified with most of the systems examined. This is illustrated in Figure 5, which presents the variations of log G′ versus log ω, at 25°C for Cyan.

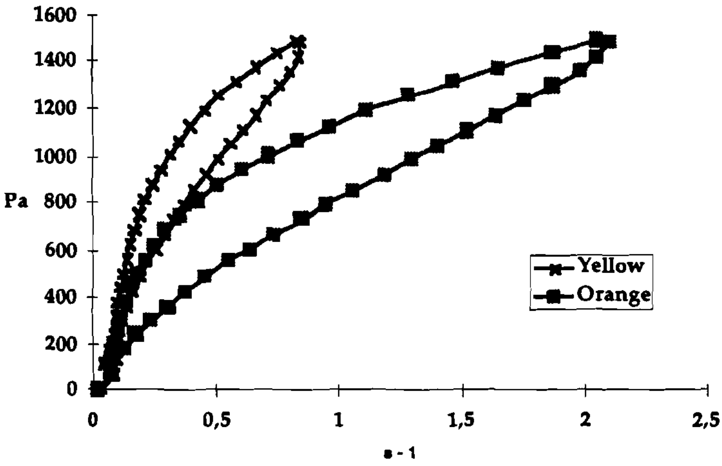

Fig.4 Thixotropy loop of Yellow(X) and Orange(■), at 20°C.

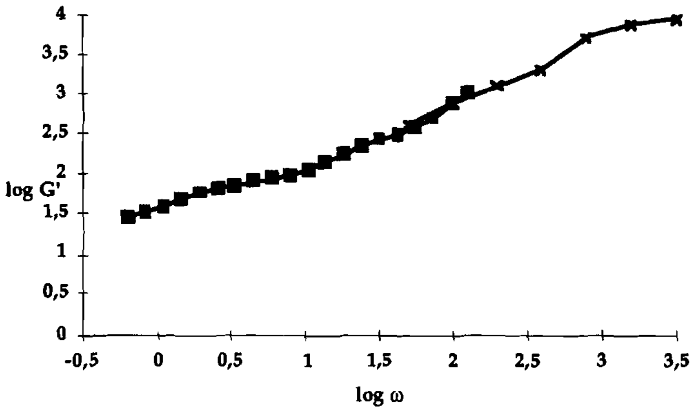

Fig. 5. Variations of log G′ vs. log ω at 25°C. Data obtained from the rheometer (■) and the viscoanalyser (X).

The variations of the storage modulus G′ as a function of frequency at different temperatures enabled to obtain the master curves as a function of the reduced variable $\omega.a_T$. The reference temperature was taken as 25°C. Figures 5 to 9 present these master curves.

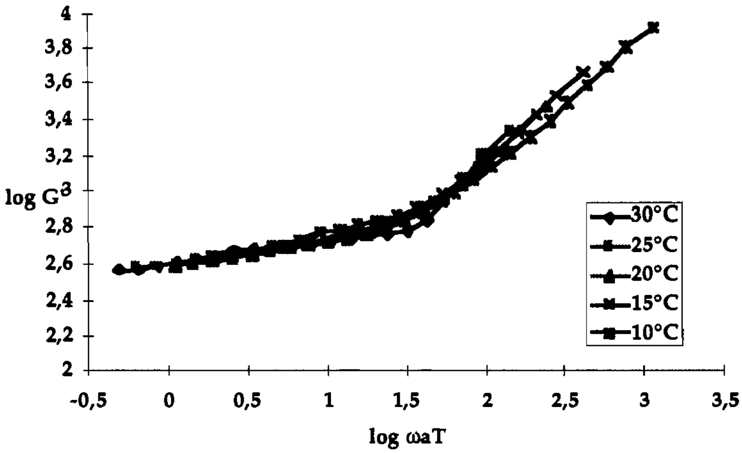

Fig. 6. Master curve of G'at 25°C, Yellow.

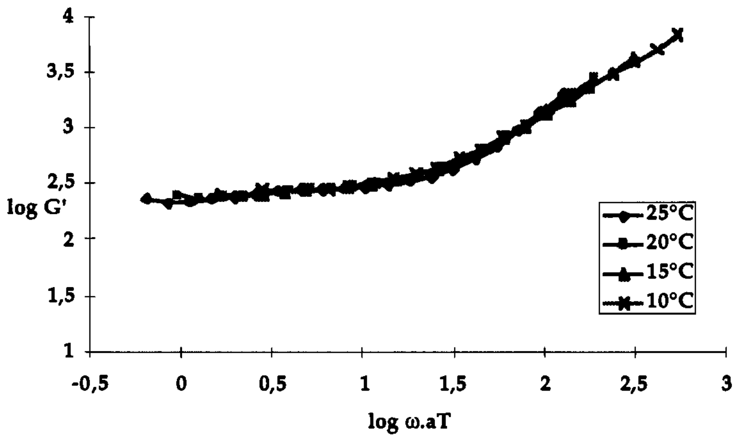

Fig. 7. Master curve of G'at 25°C, Orange.

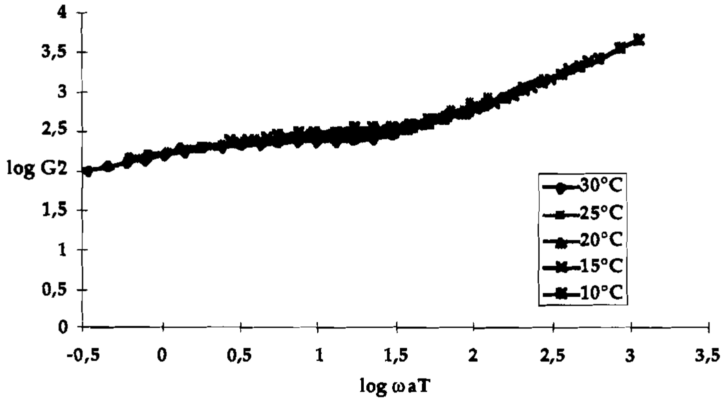

Fig. 8 Master curve of G'at 25°C, Green.

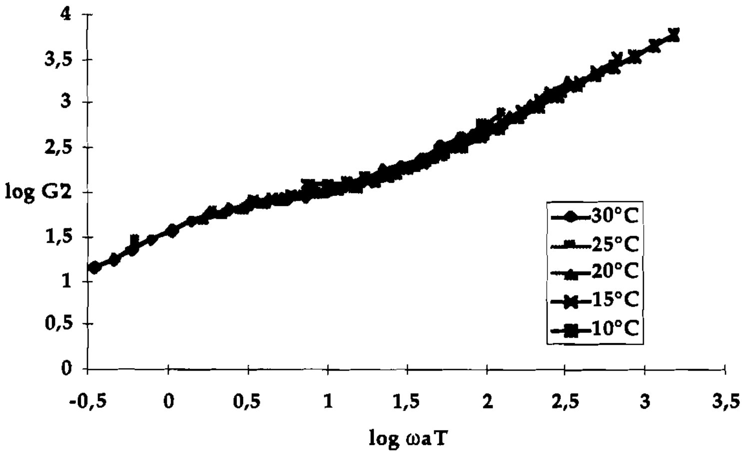

Fig. 9 Master curve of G'at 25°C, Cyan.

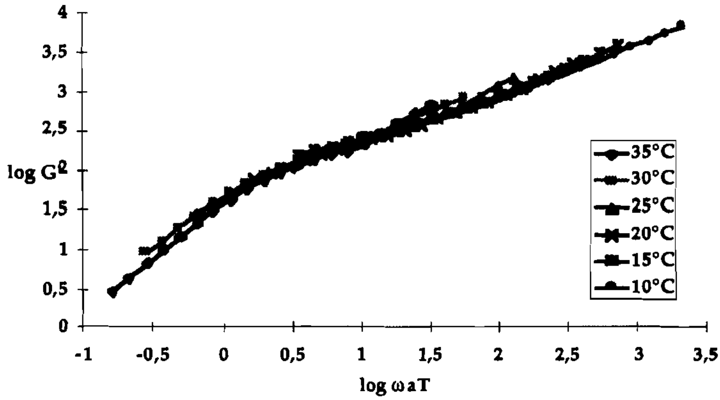

Fig. 10 Master curve of G'at 25°C, Black.

The master curves display similar shapes, viz. a flow zone at the lower frequency range, a viscoelastic plateau, a feature already detected previously by Onogi [1981], followed finally by a viscoelastic transition zone. The width of the plateau depended on the ink and more specifically on the physico-chemical nature and the concentration of its pigment. In other words, this feature was very sensitive to the extent of the interparticle and/or the particle-medium interactions. Moreover, this parameter also depended on the molecular weight of the polymers contained in the vehicle. This trend is analogous to that encountered on the rubbery plateau with entangled (resp. cross-linked) polymers, when the molecular weight (resp. the cross-linking density) is increased. Yellow and Orange displayed the widest plateaux, and consequently the flow region remained undetected within the frequency range inspected, contrary to its clear appearence with Cyan and Green. Finally, the behavior of Black was characterized by a narrower plateau within a well-defined master-curve.

In the high frequency range, log G' tended to increase linearly with log $\omega.a_T$. Normally, this trend is accompanied by the observation that the rheology of printing inks at high shear rates is controlled by the viscoelastic nature of the vehicle, whereas at low shear rates the rheological characteristics become controlled by the properties of the colloidal dispersion as a whole [e.g. Mani et al., 1996].

The values of the slope n of log G' vs. log $\omega.a_T$ are given in Table 2.

Sample	n (slope above 1Hz)
Yellow	0,77
Orange	0,94
Green	0,86
Cyan	1,2
Black	0,72
Polymers in the transition zone [Ferry, 1980]	0,5

Table 2 Values of the slope n of the linear high-frequency portion of the master curves.

With respect to the classical value 0.5 characteristic of neat polymers in the transition zone [Ferry, 1980], it was found that n was systematically higher with all inks tested. Moreover, there seems to be some correlation between the nature and the pigment concentration , on the one hand, and the relative increase in the value of n above 0.5, on the other hand. This feature clearly suggests that, contrary to expectation, in this frequency region, the suspended particles played a relevant role in determining the viscoelastic behavior of the ink.

III.3. Tack measurements

The tack of the inks displayed a good time stability over 10-15 min. Figure 11 shows the variations of the tack values, measured after one minute, with temperature. The tack of these inks varied linearly with temperature within 20-30°C. The tack values of Yellow and Orange were higher than those of Cyan and Green, and Black had the lowest tack. All these observations corroborate the previous conclusion, based on the behavior of the elastic modulus on the rubbery plateau, concerning the extent of interactions related to the presence of high pigment concentrations.

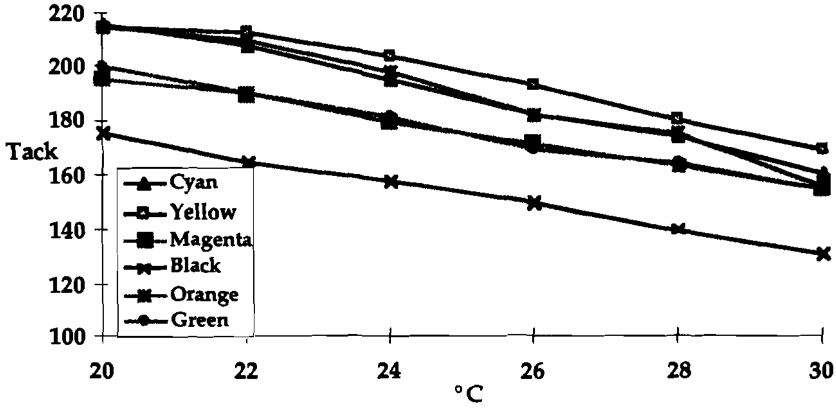

Fig. 11 Tack values (measured after 1 minute) vs. temperature

III.4. Colorimetric characterizations

Only some of the results concerning the printing tests are commented here. The measurements were conducted on a coated paper, characterized by a very low roughness.

	22°C		26°C		32°C	
	ΔC	Δh	ΔC	Δh	ΔC	Δh
Cyan	3.5	2.2	6.7	2.6	3.8	2.8
Yellow	14	1.4	24	1.5	19	1.4
Magenta	6	4.8	14.2	10.6	4.3	3.5

Table 3. ΔC and Δh* values for three inks, at different temperatures

For each color and at each printing temperature, the variations of a* and b*, were plotted on a [a*, b*] diagram as a function of the ink film thickness. Figures 12, 13 and 14 give examples of results for Cyan, Yellow and Orange, which clearly show that the spread of the relevant points were wider at 26°C in each case. Table 3 contains some of the corresponding ΔC values ($\Delta C = (\Delta a^{*2} + \Delta b^{*2})^{1/2}$ = Chroma

Difference, where $\Delta a^* = a^*_{max} - a^*_{min}$, and $\Delta b^* = b^*_{max} - b^*_{min}$) as well as the Δh ($\Delta h = h_{max} - h_{min}$ = Hue Difference, where h = Arctg b^*/a^*) values which also went through a maximum at 26°C.

The existence of a critical temperature in the context of color reproduction is an interesting feature which we believe to be related to some relevant change(s) in the rheological properties. Surprisingly, a similar trend was not observed in the measurement of viscosity and viscoelasticity and this suggests that either the changes were too modest to be detected by our experimental techniques, or that another rheological property was affected. Whatever the explanation, this unusual behavior must again be attributed to the higher pigment concentration.

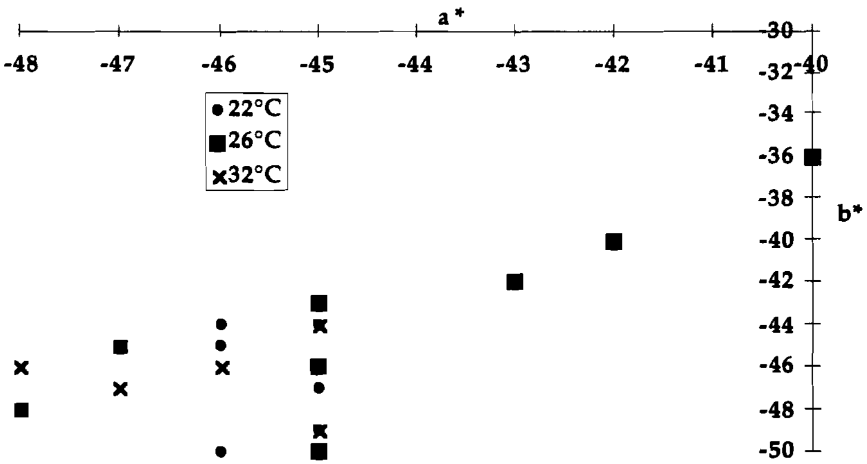

Fig. 12 a* and b* values, at various ink film thicknesses. Cyan

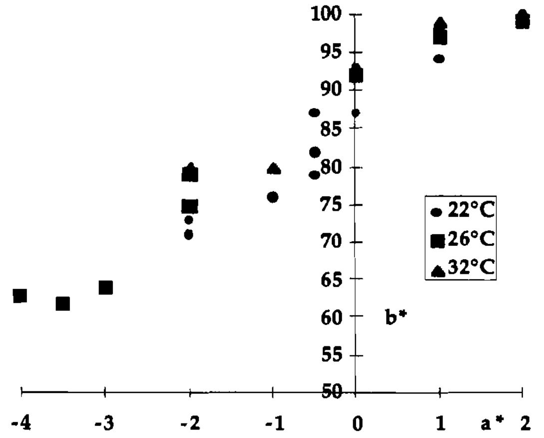

Fig. 13 a* and b* values, at various ink film thicknesses. Yellow

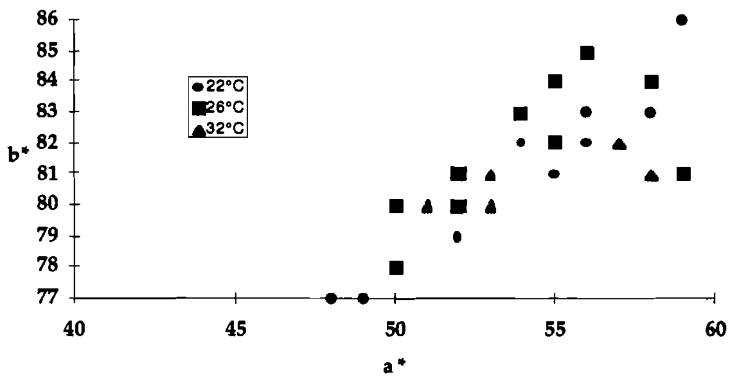

Fig. 14 a* and b* values, at various ink film thicknesses. Orange

Conclusion

The analysis of the rheological and viscoelastic characteristics of offset inks for the six-color process led to a better insight into their end-use properties. These concentrated suspensions displayed a shear-thinning together with a thixotropic behavior. The master curves of G′ presented a flow zone at the lower frequency range, followed by a viscoelastic plateau and a viscoelastic transition zone. The width of the plateau and the variations of log G′ vs. log(ωa_T) in the transition zone were characteristic of the surface properties and the concentration of the pigments.

Color measurements were carried out on the dried films. A peculiar feature, found at one printing temperature, suggested that further work on the rheological properties of inks is now necessary to confirm and enrich this observation.

Literature cited

Amari T. and K. Wanatabe
1983 "Rheological properties of dispersed systems of pigment", Polymer Engineering Reviews, vol. 3, n. 2-4, pp. 277-321.

Blayo A., A.Gandini and J.F. Le Nest
1996 "Rheological properties of heatset inks"
TAGA Proceedings pp 406-425.

Blayo A., N. Noel, A. Gandini and J.F. Le Nest
1993 "A comparative rheological study of waterless and conventional offset inks"
Surface Coatings International, vol.76, n.4, pp 164-171.

Chou S. M.
1991 "Study of ink structure by creep analysis"
TAGA Proceedings pp 351-369

Coussot P., A.I. Leonov and J.M. Piau
1993 "Rheology of concentrated dispersed systems in a low molecular weight matrix", Journal of Non-Newtonian Fluid Mechanics, vol. 46, pp. 179-217.

Fernandez M., M.E. Munoz, A. Santamaria, R. Azaldegui, R. Diez and M. Pelaz
1998 "Rheological analysis of highly pigmented inks: flocculation at high temperatures", Journal of Rheology, vol. 42, n.2.

Ferry F.D.
1980 "Viscoelastic properties of polymers", 3rd ed., Wiley, New York

Gregory T. and S. Mayers
1993 "A note on slippage during the syudy of the rheological behaviour of paste inks", JOCCA, n.2, pp. 82-86.

Kent H. J. and M. B. Lyne
1989 "On the penetration of printing ink into paper", Nordic Pulp and Paper Research Journal, n. 2, pp. 141-145.

Leonov A.I.
1990 "On the rheology of filled polymers", Journal of Rheology, vol. 34, n.7, pp. 1039-1068.

McKay R.B.
1993 "Crystal morpholgy of organic pigments and rheology of dispersions in ink and paint media", Progress in Organic Coating, vol. 22, pp. 211-229.

Magnin A. and J.M. Piau
1990 "Cone-and-plate rheometry of yield stress fluids. Study of an aqueous gel.", Journal of Non-Newtonian Fluid Mechanics, vol. 36, pp. 85-108.

Mani S., Grover G.S. and S.G. Bike
1996 « Linear viscoelastic behavior of copper phthalocyanine dispersions used in printing inks », Rheologica Acta, vol. 35, pp. 329-336.

Onogi S. and T. Matsumoto
1981 "Rheological properties of polymer solutions and melts containing suspended particles", Polymer Engineering Reviews, n. 1, pp. 45-87.

Pangalos G., J.M. Dealy and M.B. Lyne
1985 "Rheological properties of news inks", Journal of Rheology, vol.29, pp 471-491.

Quemada D., P.Flaud and P.H. Jezequel
1985 "Rheological properties and flow of concentrated disperse media", Chem. Eng. Commun., vol. 32, pp. 61-83.