

RHEOLOGICAL PROPERTIES OF HEATSET INKS

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Abstract : Viscoelastic and flow measurements were conducted on different heatset varnishes in order to clarify some of their peculiar rheological characteristics. A succinct characterization of the industrial varnishes studied, followed by the rheological measurements carried on, are described. These measurements were conducted on a cone-plate rheometer, on a visco-analyser and on a tackmeter. The influence of temperature on the rheological properties of liquids is examined. The frequency-temperature superposition principle, applied with the appropriate conditions, allowed the simulation of the working mode at high frequency. Correlations between viscoelastic properties, and more specifically values of $\text{tg}\delta$, and tack measurements are presented.

Introduction

Heatset printing has known quite important mutations over the last two decades : the main trend of these evolutions is the increasing press productivity. Nowadays, maximum press speeds have increased from 2,000 ft./min. to 3,000 ft./min. (ie : 15 m/s) (Loebbert, 1995; Hutchinson, 1994). The consequences of these higher speeds are multiple in the printing industry background. Among other things, printers and suppliers have to adapt presses and materials to these new conditions.. Particularly, heatset inks must be formulated to fulfill the requirements of the highest press speeds, the fast drying implied, together with an acceptable printability on stocks of various quality (including papers with a relatively low pick resistance). In this context, their rheological properties are crucial. With such conditions, the simulation in laboratories of the real situation on the press is always a challenge.

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To predict the press performances of an ink on the basis of rheological measurements remains difficult, despite the indisputable efforts made by the printing ink industry. For example, accompanying the relatively recent increase of press speeds, the need of studies on the dynamic properties of inks arose. Thus, examination of the viscoelastic characteristics is becoming an indispensable routine for printing inks.

In this work, rheological properties of heatset varnishes are investigated, with the aim to describe some peculiar characteristics of heatset ink components. This article is mapped out as follows : first, the specificities of an offset heatset ink are recalled, with a special emphasis on their rheological properties in relation with the process, the high speed and the fast drying. Second, a state-of-the art on viscoelasticity of offset inks is presented. The influence of temperature on the rheological properties of liquids is examined. Then, the choice of the studied products is argued. A succinct characterization of the industrial varnishes studied, followed by the rheological measurements carried on, are described. Finally, the results are presented with special emphasis on (i) flow behavior, (ii) viscoelastic properties and (iii) tack measurements. Correlations between the viscoelastic properties and tack values are investigated.

Specific characteristics of heatset inks

Heatset inks have generally the following indicative formulation (Leach et al, 1993; Cerny 1993; Korhonen, 1993) :

Pigments : they are introduced into the ink in their dry form, or, more often in heatset inks, in the form of flush (concentrated dispersion). Pigment content is about 15-20% in heatset inks.

Vehicle : this liquid of high viscosity is a mixture of different varnishes. Varnishes contain the binders dispersed in the solvents. Binders are polymers and/or oligomers of various chemical nature : hard resins (solid polymers at room temperature) are generally rosin-modified phenolic, maleic and hydrocarbon resins, while liquid resins are alkyd resins, modified with vegetable oils. Phenolic resins are available in low or high molecular weight modifications and with different solubilities in solvent commonly used in offset ink manufacture. Solvents are petroleum distillates with boiling ranges currently comprised between 260 and 290°C or 240 and 270°C. Heatset inks contain 30-40 % mineral oil-based solvent, of which 70-90% will evaporate in a hot-air dryer .

Additives : these products of diverse nature enhance peculiar properties of the ink, in its liquid or dried state. Micronized PTFE (polytetrafluoroethylene) or PE (polyethylene) waxes are currently added in heatset compositions in order to optimize the rub resistance and slipping properties indispensable in high speed finishing of printing. One of the difficulties of a good formulation is to find a balance between the tack and the viscosity. As a matter of fact, the possibility of misting, picking and other problems connected with high level of tack are

are increased at the higher speeds of rotation. To minimize the tack by the addition of vegetable or mineral oils would have the undesirable effect of the fall down of the viscosity, which might lead to bad emulsification, poor ink distribution and transfer. A correct viscosity together with a moderate tack is achieved by the use of gelified resins in the varnish. Gelation techniques are not new, but their use has recently become systematic in the manufacture of this type of inks. A crosslinked structure is obtained by the reaction of gelling agents (aluminium chelate type) with terminal carboxyl and hydroxyl groups of resin molecules. In the past several years, new developments in resin technology have led to an extended use of high molecular structured viscoelastic resins in offset inks. "Structure » can be defined as a fraction of molecules with a very high molecular weight (10,000 to 100,000). This new trend permits to avoid the step of gelation in the varnish manufacture (Baarends, 1995). As a result, the newly developed vehicles may be described as suspensions or matrix systems in which a less-soluble high-molecular-weight resin is dissolved or dispersed in a more soluble resin. These recent advances have several consequences on the technical and scientific approach of the suppliers towards rheological properties of their products. Today, more and more of them use the techniques of oscillation rheometry to obtain information on the rheological properties of inks under the high shear rates of fast running presses. This involves measuring resins, vehicles and ink structures in the viscoelastic domain. Besides, so-called higher viscoelastic type resins were found to confer improvements in gloss, flow, transfer, dot sharpness, and litho behavior, while the high molecular weight contributes to faster setting and better hold out on coated papers (Scarlati, 1993; Baldassare, 1995). It might be noticed that the use of gelified resins as well as high molecular weight polymers in the varnishes leads also to a certain degree of thixotropy of the varnish and the resulting ink.

Recent tendencies of rheological studies on inks

The relevance of rheological measurements has been of increasing interest to varnish and ink makers for the past 20 years, with the help of the technological progresses in instrumentation (development of controlled-stress rheometers for example). However, it has become clear that flow measurements alone are not sufficient any longer to characterize the new generations of varnishes and inks, especially in the field of heatset inks. As pointed out before, viscoelasticity plays a key role in the runnability and printability of heatset inks. In earlier years, several authors had already investigated viscoelastic properties of inks, in order to interpret the splitting of ink films and tack phenomena (Voet and Geffken, 1951; Sjobahl, 1951; Oittinen, 1976; Dobbels and Mewis, 1978). The recent infatuation for viscoelasticity aims more especially at a better knowledge of the ink components, together with the prediction of the new ink behavior on a press (Chou 1992; Rohn, 1987). Many recent studies concern the evaluation of different vehicles or inks in term of viscoelastic

parameters. More and more, in technical information, the useful dynamic parameters are defined and discussed on the basis of oscillatory measurements (Loebbert, 1995). Cerny (1993) reviewed the different methods available for measuring the rheological properties of inks. Viscometric flow, oscillatory shear, relaxation tests and normal stress measurements are the main techniques commonly used today. Linear viscoelasticity is generally adopted to interpret the results, especially to appreciate the extent of gelled varnishes. For example, Reuvers (1995) has analyzed the "structure" of varnishes by measuring the elastic modulus G' at low shear stresses ($<10 \text{ Pa.s}$) and low frequencies ($<0.1 \text{ s}^{-1}$). Studies were performed on model systems in order to clarify the role of the different components (Aspler, 1992; Hayashi et al. 1993). The influence of different parameters, like solubility or molecular weight, are also investigated. Some authors (Amari et al. (1979), Patel et al.(1987); Pangalos et al.1985) however examined critically the relevance of these measurements, considering that the production environment does not provide the adequate conditions of application, and thus invalidates the predictions made in laboratories. Indeed, deformation of the printing inks between rollers is much larger than the deformation on the rheometer. Extensional viscosity and non-linear viscoelasticity may become alternative methods, but linear viscoelastic characteristics still provide useful information on the properties of inks and their constituents. In many cases, $tg\delta$ is adopted as a reference measure of the elasticity.

Temperature-viscosity relationships

During a printing process, the variations of the viscosity and other rheological characteristics with the temperature may disturb the quality of the production. These variations are of great impact : for example, the viscosity of an offset ink may lose 10% of its value when the temperature rises by 1°C . The impact of this loss of viscosity is multiple : changes in emulsification with fountain solution, excessive dot gain, variations of ink setting, etc. In the following, two different approaches of the variations of the viscosity with temperature are presented. The first concerns the activation energy of flow. It correctly fits to the low-DP polymers (Eyring, 1935). In our context, it can be exploited in a relatively narrow, but suitable, range of temperatures, typically from 15°C to 50°C , viz. a plausible domain during a printing process. The second approach deals with the free volume theory (Williams, Landel and Ferry, 1955). This theory is applicable preferably to high-DP polymers. Heatset varnishes may be concerned since they contain a proportion of high polymers, or "gelified" resins.

a. Activation theory, Eyring equation

The elementary process of flow of a viscous liquid is described by Eyring as the overcoming of an energetic barrier by the elementary unit of the liquid. This transition is favoured by an elevation of temperature. This

leads to an expression of the viscosity as a function of temperature indicated by equation (1) :

$$\eta = A \cdot \exp(E_a/RT) \quad (1)$$

where A is a constant which depends on the frequency of intermolecular vibration and E_a is the activation energy of, expressed in kJ/mole, T is the temperature, expressed in K.

Generally speaking, E_a depends on (i) the cohesive energy of the liquid and (ii) its molecular size. In addition, in the case of a non-newtonian liquid, variations of the viscosity with the shear rate must be taken in account, and then E_a is a shear rate function.

b. Free-volume theory, equation W.L.F. (Williams-Landel-Ferry)

According to this theory, the fluidity of liquids is due to the presence of a free volume in them. The temperature dependence of free volume had been suggested by Williams, Landel and Ferry (1955), who derived the following equation :

$$\log(\eta/\eta_0) = - C_{1,0}(T - T_0) / (C_{2,0} + (T - T_0)) \quad (2)$$

where T_0 is the reference temperature (in K)

and η_0 is the viscosity at T_0 .

At $T_0 = T_g$, the constantes $C_{1,0}$ and $C_{2,0}$ of the WLF equation are:

$C_{1,g} = 17,4$ and $C_{2,g} = 51,6K$.

Experimental

1. Systems examined in this study

In this study, we chose to work with commercial varnishes, which are used in offset heatset ink formulations. Their exact compositions are unknown. The aim is to present some of their peculiar rheological and viscoelastic characteristics. Four industrial varnishes were examined, which will be designed as A, B, C and D. They are formulated on the basis of modified phenolic and hydrocarbon resins, alkyd resins and petroleum distillates. Some of their characteristics are presented in Table1.

IR spectroscopy analyses were carried on the dried varnishes (see Figures 1,2,3 and 4). The assignments of the main peaks are:

- around 3.500 cm^{-1} : absorption due to the -OH functions,
- around 2900 cm^{-1} : absorption due to the >CH-, -CH₂- and -CH₃ groups,
- at $1732\text{-}1735 \text{ cm}^{-1}$: peak of the carbonyl functions
- around 1610 cm^{-1} : peaks corresponding to the absorption of the C=C of aromatic rings,

- around 1464 cm^{-1} and 1380 cm^{-1} : absorptions corresponding to the harmonics around 2900 cm^{-1} ,
- between 1100 and 1300 cm^{-1} : peaks characterizing the C-O-C moieties of the ester functions, present in the phenolic modified and in the alkyd resins.

	Solvent content	Role in the corresponding heatset ink	Type of substrate recommended
Varnish A	47 %	Used as the main vehicle	LWC stock
Varnish B	47 %	Used in combination with varnish C	Poor picking resistance papers
Varnish C	51 %	Used in combination with varnish B	Poor picking resistance papers
Varnish D	34 %	Used as the main vehicle	News paper type

Table 1 : Information about the varnishes used in this work.

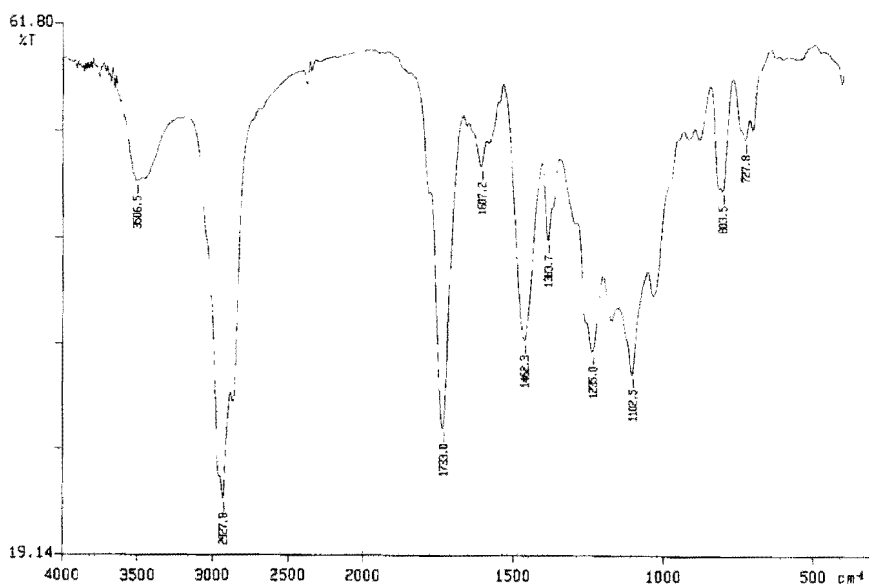


Fig.1 : IR spectrum of the varnish A, after solvent evaporation.

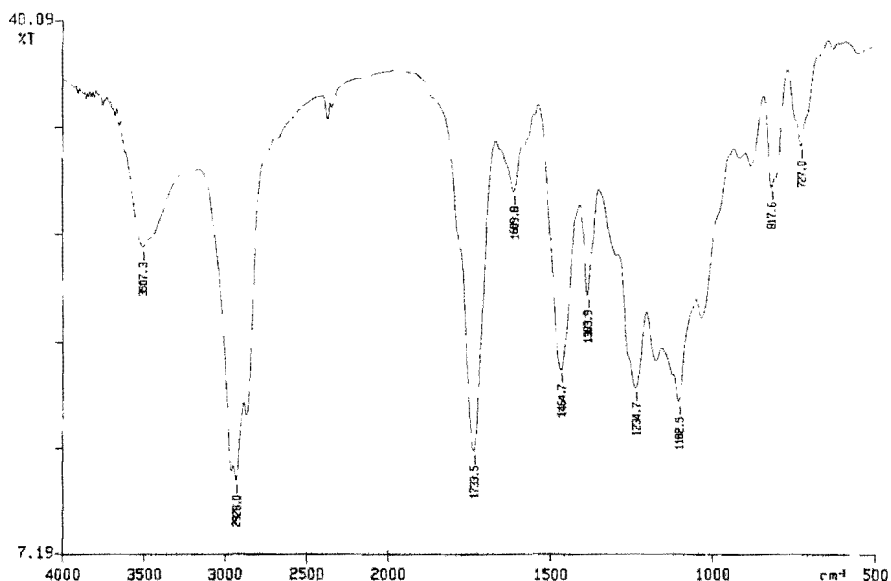


Fig.2 : IR spectrum of the varnish B, after solvent evaporation.

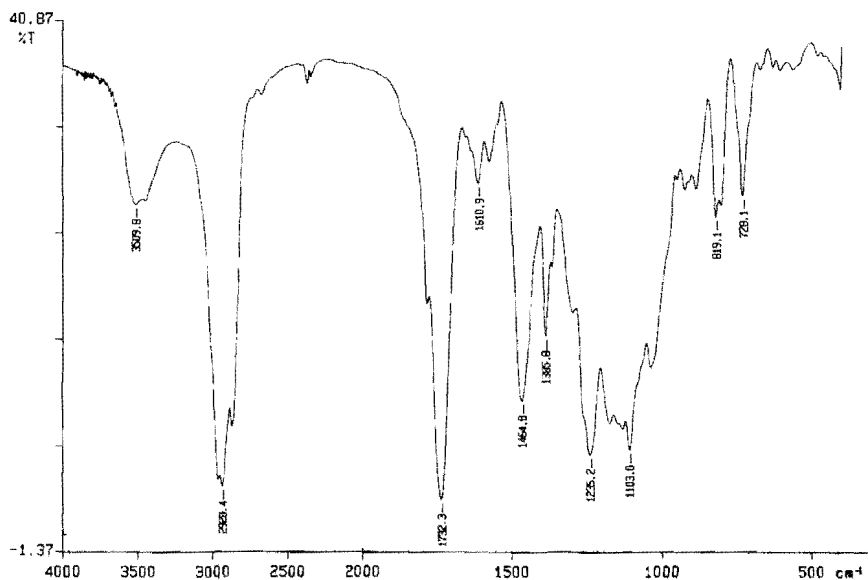


Fig.3 : IR spectrum of the varnish C, after solvent evaporation.

Varnishes A and B have very similar IR spectra, which let suppose very close formulations. Varnish C presents a relative strong absorption at 1732 cm^{-1} , compared that at 2900 cm^{-1} , i.e. this varnish contains more

carbonyl functions. As for varnish D, its spectrum displays an important absorption corresponding to the -OH functions.

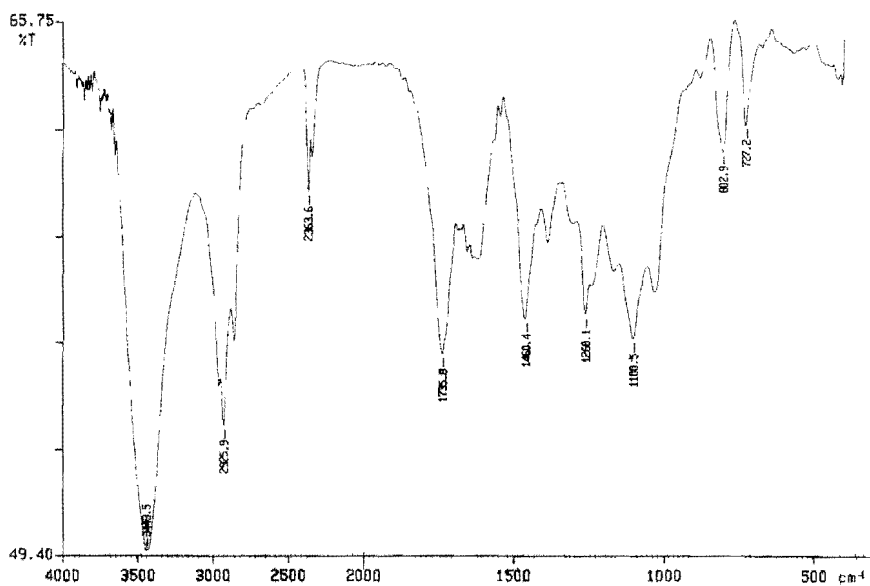


Fig.4 : IR spectrum of the varnish D, after solvent evaporation.

For the sake of comparison, we also studied an alkyd resin. We chose a specific composition characterized by a relatively low drying oil content, compared with previously-examined alkyd (Blayo, 1994).

2. Rheological measurements

Rheological characterizations were conducted on a Carrimed controlled-stress rheometer, with the cone-plate geometry (diameter=2 cm, top angle=4°). Steady shear and oscillatory flow experiments were conducted within appropriate stress and frequency ranges.

In addition to the dynamic measurements on the Carrimed rheometer, viscoelastic properties of the varnishes were measured on a Metravig viscoanalyser. This equipment permits the determination of dynamic characteristics of various polymeric materials, with solid, pasty or liquid consistency. It measures the complex rigidity modulus and the loss angle of a sample submitted to a sinusoidal strain, whose frequency and amplitude are known. Four parameters can vary : the frequency (from 5 to 1000 Hz), the temperature (from -80°C to 200°C), the stress or the strain. All the experiments were performed in the annular shearing mode. The temperature was allowed to vary from -40 to 30°C with steps of 10°C, and 20 frequencies were swept, from 5 to 500 Hz, at each temperature. With these measurements and the use of the time-temperature superposition principle, master curves were obtained, which

enlarged the range of frequencies towards higher levels. The modalities of this operation are explained in the appendix.

The tack of the varnishes was evaluated with a Tack-o-Scope. Experiments were carried on with 0.6 cm³ samples at 30°C, using rotating speeds from 50 to 350 m/min.

3. Results and discussion

3.1. Flow measurement

For the varnishes studied, rheo-thickening was observed at low shear rates (<0.1-0.2 s⁻¹, at 20°C), before the establishment of the classical rheo-thinning behavior. This anomaly could be attributed to a micro-sliding at the interface between the liquid and the measuring, at the beginning of the rotation.

Beyond this deviation, varnishes A, B and C presented a similar behavior in the range of shear rates and temperatures considered, viz. a shear-thinning profile up to the point of shear fracture. This phenomenon has been observed for printing ink with elastic properties (Chou, 1992; Cerny, 1995). It is caused by the effect referred to as « the Weissenberg effect », which is typical of viscoelastic fluids (Barnes et al, 1989): when the shear rate reaches a certain value, the varnish sample begins to accumulate on the rotating cone and consequently does not fulfill the measurement requirements. In our cases, the shear fracture began to appear at relatively low shear rates, even at about 10 s⁻¹ for varnish A, despite the small cone geometry used, and this limited dramatically the range of shear rates which could be applied.

The Cross model (Cross, 1965) gave good results to describe the shear-thinning behavior of varnishes A, B and C. This model expresses the variations of the viscosity η with the shear rate $\dot{\gamma}$ by equation (3):

$$(\eta_0 - \eta) / (\eta - \eta_{inf}) = (K \cdot \dot{\gamma})^m \quad (3)$$

where η_0 and η_{inf} are the asymptotic values of the viscosity at low shear rates and high shear rates, respectively,

K is a relaxation time and m is an adimensional constant.

The results obtained at 20°C are summarized in Table 2.

	η_0 (Pa.s)	η_{inf} (Pa.s)	K	m	Regression coefficient
Varnish A	1843	40	0.71	0.59	0.99
Varnish B	18410	110	6.4	0.72	0.99
Varnish C	15090	346	2.5	0.75	0.99

Table 2 : Parameters of the Cross model, obtained for varnishes A, B, and C from flow experiments at 20°C.

Very high values of η_0 were obtained for varnishes B and C. The implication of this result is that the two varnishes present a characteristic known as « yield value ». As for varnish D, the flow experiments were more difficult to interpret because of a strong elasticity, manifested by the Weissenberg effect mentioned before.

3.2. Calculation of E_a ; influence of the temperature on the viscosity

For ink vehicles, the activation energy E_a provides useful information, complementary to the viscosity, since it gives a quantitative parameter of the dependency of the viscosity of the vehicle with temperature. The activation energy of flow of a couple of vehicles may be compared : the higher E_a , the more dependent of temperature is the viscosity of the liquid, around a given temperature.

E_a values for the varnishes were calculated from viscosity values obtained from the Cross model. E_a was obtained from the slope of the graph $\ln \eta$ vs. $1/T$. The determination coefficient fits quite well, that confirms the validity range of activation energy of flow theory. The results are given in Table 3 and are compared (Table 4) to those obtained in the context of a previous study on various components of printing inks (Blayo, 1994).

	E_a (kJ/mole)
Alkyd resin	78
Heatset varnish A	96
Heatset varnish B	92
Heatset varnish C	88
Heatset varnish D	98

Table 3 : Activation energies of flow of the alkyd resin and heatset varnishes A,B,C and D.

		E_a (kJ/mole)
<i>Vegetable oils</i>	Linseed oil	25
	Tung oil	41
	Soyabean oil	28
	Rapeseed oil	30
<i>Petroleum distillates*</i>	3/6 distillate	18
	6/9 distillate	17
	4/7 distillate	19
	28/31 distillate	20
<i>Standolies (linseed oil)</i>	3 Pa.s at 20°C	50
	6 Pa.s at 20°C	54
	30 Pa.S at 20°C	60
<i>Alkyd resins</i>	Linseed alkyd (150 Pa.S at 20°C, Mw = 4000)	82

	Linseed alkyd (150 Pa.S at 20°C, Mw = 4500)	73
	Soyabean alkyd (60 Pa.S at 20°C, Mw = 5000)	72

Table 4 : Activation energies of flow of various components of ink vehicles.

* For comparison, the energy of activation of flow for a linear hydrocarbon consisting of about thirty carbon atoms is 25 to 29 kJ/mole (Vinogradov and Malkin, 1980).

The E_a value for the alkyd resin studied is of the same order of magnitude (72 to 82 kJ/mole) as those measured for the alkyd resins of the previous investigation. This activation energy of flow is much higher than those of vegetable oils, or petroleum distillates. It is also higher than the E_a of the standolies. This is due to the molecular weight and the branching degree of the alkyd resin that are more important than those of standolies. (A standoly is a prepolymer obtained from drying vegetable oils cooked during a variable and controlled time in an inert atmosphere. This leads to products of various molecular weights, depending on the reaction conditions.)

The activation energy of the varnishes is higher than that of alkyd resins, which implies a stronger dependence of their viscosity with temperature.

3.3. Oscillatory shear

Oscillatory shear measurements were performed on the cone-plate rheometer at 20°C, with the objective of comparing the results with those obtained under steady-shear flow, at the same temperature. Using the Cox-Merz rule (1958), it is theoretically possible to determine the viscosity of liquids at higher shear rates than those reached in the steady-shear experiments. According to this empirical rule, a correspondence exists between the variations of $\eta(\dot{\gamma})$ and the modulus of $\eta^*(\omega)$, compared at equal values of $\dot{\gamma}$ and ω , viz. :

$$\eta(\dot{\gamma}) = \eta^*(\omega) / \omega = \dot{\gamma} \quad (5)$$

Figures 5 to 9 present the comparative variations of $\eta(\dot{\gamma})$ (steady shear) and $\eta^*(\omega)$ (oscillatory shear) for varnishes A, B, C and D and the alkyd resin analysed.

This type of experiment gives the opportunity to determine the tendencies at elevated shear rates, without the sample being « squeezed out » by the Weissenberg effect. For example, the measurements on varnish D were

extended to at least 250 s^{-1} thanks to the oscillatory shear, whereas the steady shear experiments had to be stopped before 50 s^{-1} .

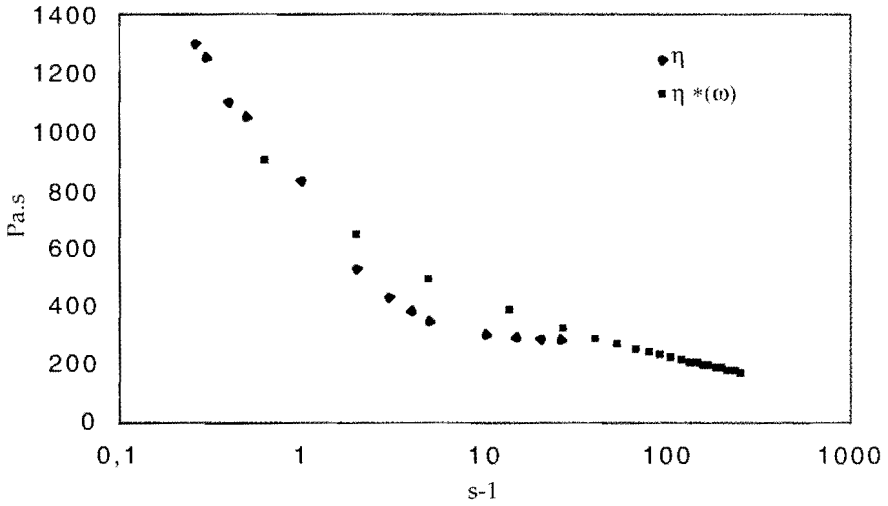


Fig.5: Comparison of the variations of $\eta(\gamma)$ and $|\eta^*(\omega)|$ at $\omega = \gamma$. Varnish A.

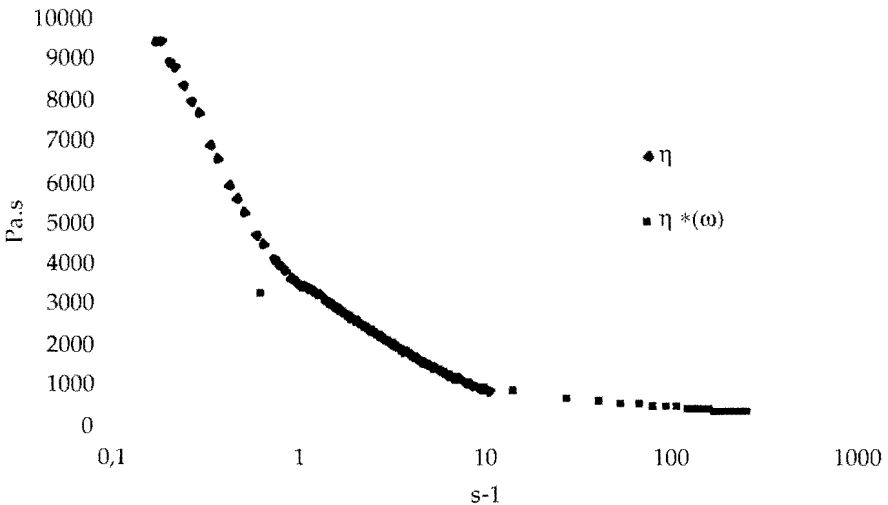


Fig.6: Comparison of the variations of $\eta(\gamma)$ and $|\eta^*(\omega)|$ at $\omega = \gamma$. Varnish B.

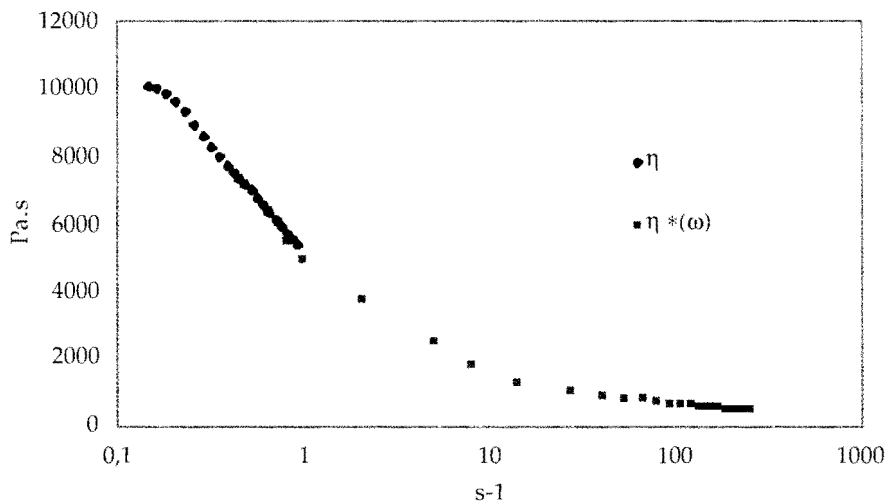


Fig.7: Comparison of the variations of $\eta(\gamma)$ and $|\eta^*(\omega)|$ at $\omega = \gamma$. Varnish C.

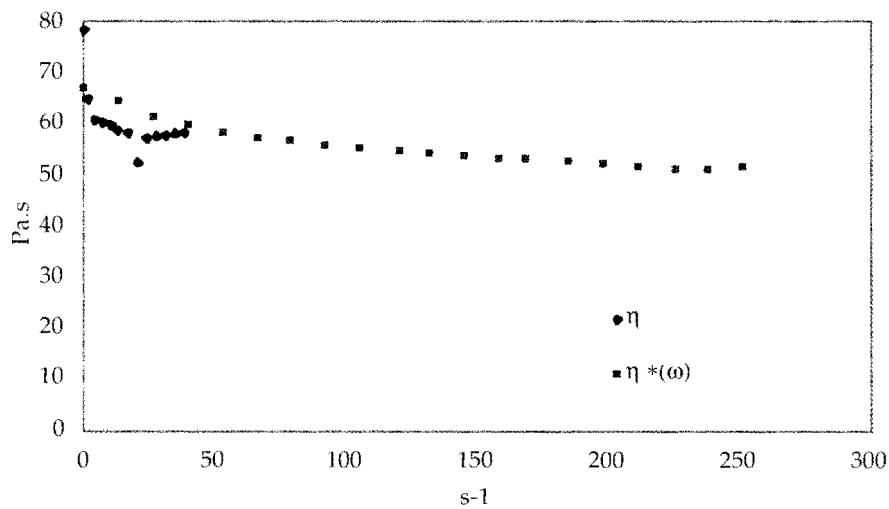


Fig.8: Comparison of the variations of $\eta(\gamma)$ and $|\eta^*(\omega)|$ at $\omega = \gamma$. Varnish D.

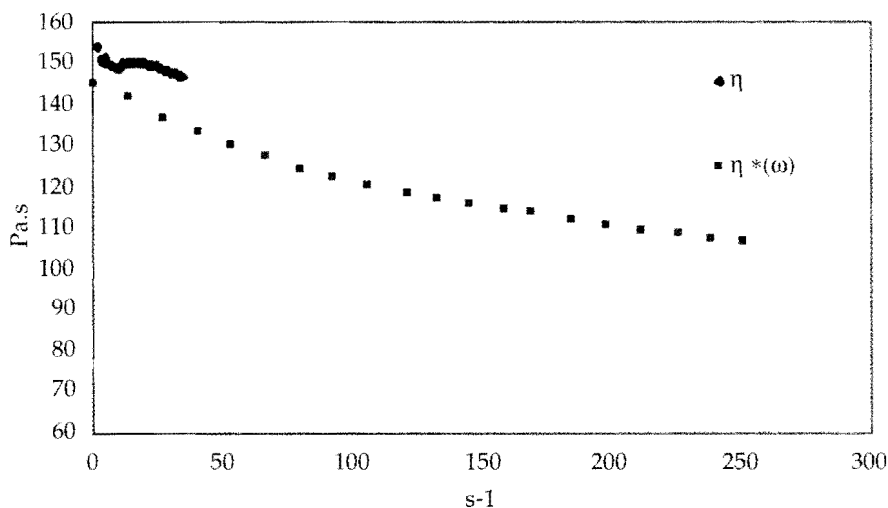


Fig.9: Comparison of the variations of $\eta(\dot{\gamma})$ and $\eta^*(\omega)$ at $\omega = \dot{\gamma}$. Alkyd resin.

3.4. Viscoelastic measurements on a larger range of frequencies, master curves

Measurements on the viscoanalyser were performed on varnishes A, B, C and D and on the alkyd resin. The variations of the storage modulus G' as a function of the frequency at different temperatures allow to obtain the master curves of G' , G'' , η' and $\text{tg}\delta$, as a function of $\omega \cdot a_T$, at reference temperatures close to room temperature. The evolutions of $\text{tg}\delta$ with the frequency are particularly interesting in our context, as they give an indication of the extent of the elasticity of the varnishes. The master curves of $\text{tg}\delta$ of our materials are presented on the Figures 10 to 14.

The interest of these master curves is the fact that the rheological behavior of the varnishes is considerably enlarged, thanks to the frequency-temperature superposition principle, and this enables to evaluate tendencies at high shear rates.

Varnishes A and B present similar variations of $\text{tg}\delta$ with $\omega \cdot a_T$. $\text{tg}\delta$ falls from 1.8 to 0.4 for varnish A and from 2 to 0.6 for varnish B, when the frequency increases. These variations are not very important in absolute values, but prove that varnish A presents an elastic character which is slightly more important than that of varnish B.

The variations of $\text{tg}\delta$ with frequency for varnish C are not very large, despite the extended range of frequencies explored.

The $\text{tg}\delta$ of varnish D and the alkyd resin present a similar behavior, viz. important variations in the range of frequencies swept, together with a strong elasticity at the higher values of $\omega \cdot a_T$.

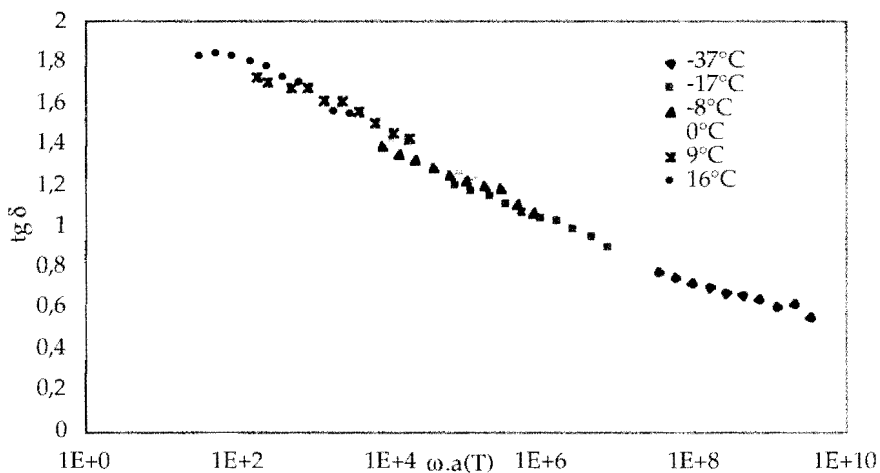


Fig.10 : Master curve of $\text{tg}\delta = f(\omega \cdot a_T)$, at 16°C , varnish A

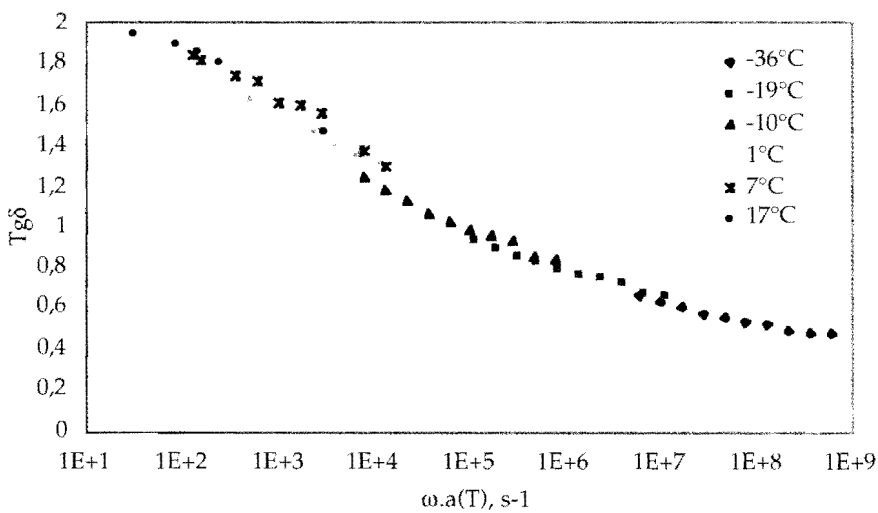


Fig.11 : Master curve of $\text{tg}\delta = f(\omega \cdot a_T)$, at 17°C , varnish B

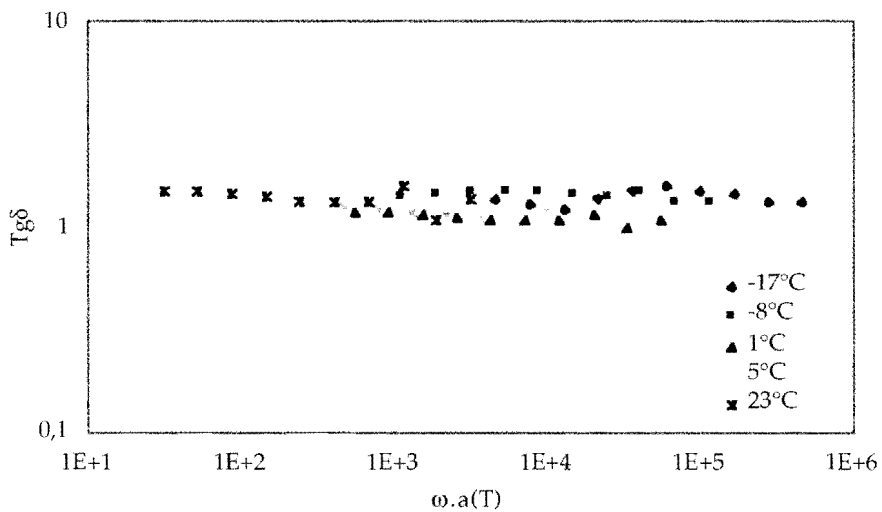


Fig.12 : Master curve of $\text{tg}\delta = f(\omega \cdot a_T)$, at 23°C, varnish C

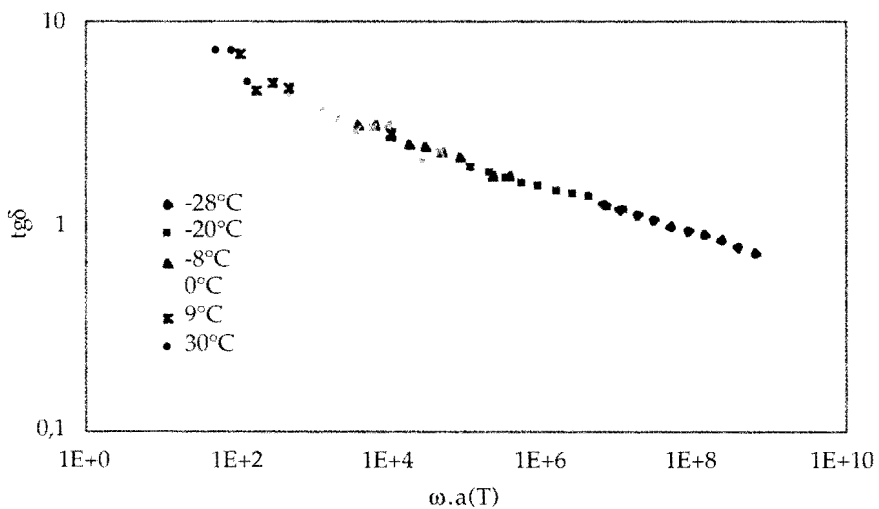


Fig.13 : Master curve of $\text{tg}\delta = f(\omega \cdot a_T)$, at 30°C, varnish D

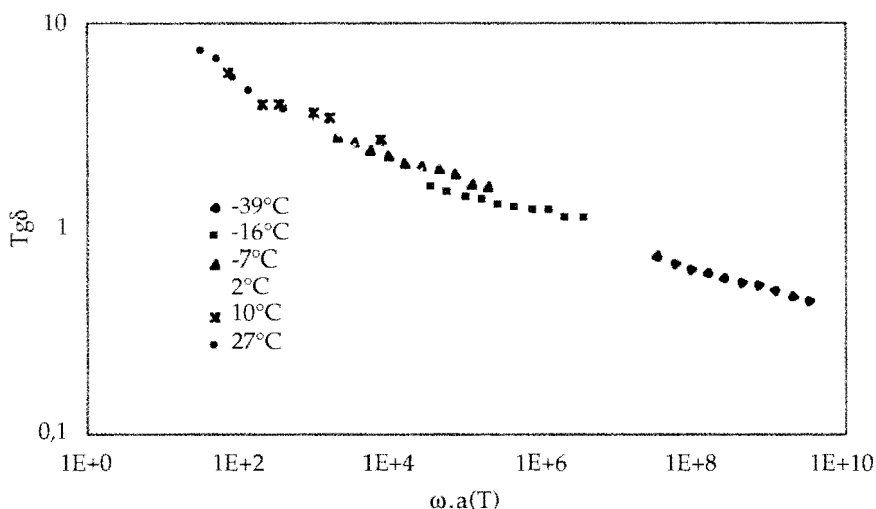


Fig.14 : Master curve of $tg\delta = f(\omega.a_T)$, at 27°C, alkyd resin

4.4. Tack results

Tack measurements were carried out on the four varnishes and the alkyd resin. The main results are summarized in Table 5.

	50 m/min	100 m/min	150 m/min	200 m/min	250 m/min	300 m/min	350 m/min
A	140	160	175	180	185	180	173
B	110		120		122		105
C	32			30			27
D	208	218	254	310	326	307	313
Alkyd resin	115	230	305	355	410	440	510

Table 5 : Initial tack measurements at 30°C, on 0.6 cm³ samples of ink vehicles, at different rotation speeds

The tack of varnishes A and B presents similar variations : an increase of the tack with the increasing tackmeter speed, followed by a decrease at the highest speeds. This may be explained by the gelled structure of these varnishes, which guarantees a high viscosity, together with a relatively moderate tack, compared to the tack of varnish D, or of the alkyd resin, for example. The slightly lower tack of varnish B helps the runnability and the printability of the corresponding ink, which is recommended for poor picking resistance stocks (see Table 1). It is also coherent with the

differences in the elastic character exhibited by the variations of $\text{tg}\delta$ (Figures 10 and 11).

The tack values of varnish C are quite low, compared to those of the other varnishes. This may be explained by the relatively high solvent content of this varnish. Also, the stability of this low tack value is consistent with the stability of the values of $\text{tg}\delta$ in the range of frequency considered.

The alkyd resin and varnish D both present very high levels of tack. They are also the vehicles presenting the higher elastic character, and the largest variations of $\text{tg}\delta$ values with frequency.

Conclusions

In this work, we examined some peculiar rheological characteristics of four industrial heatset varnishes and one alkyd resin. The dependence of their viscosity on temperature has been quantified with the calculation of activation energies of flow. Another objective of this study was to find ways to simulate the high shear rates reached in the heatset printing process. In the context of flow measurements, the Cox-Merz rule allowed the comparison of steady and oscillatory shear viscosities, on an enlarged range of shear rates, and the frequency-temperature superposition principle to simulate much higher shear rates, on the basis of measurements carried out at low temperatures. These results were compared to the classical tack measurements. The elastic characteristics observed with the viscoanalyser were corroborated by the behavior of the varnishes on the rotating rollers of the tackmeter. Experiments on the corresponding inks are in progress.

Appendix : Frequency-temperature superposition principle

It is possible to describe all the viscoelastic parameters of polymeric materials as a function of temperature, by the use of the frequency-temperature superposition principle (Ferry, 1950). The effect of an elevation of temperature on the viscoelastic properties of a polymeric material is equivalent to the effect due to a decrease of frequency. In a plot of $\log G'$ vs. $\log \omega$, it is possible to superpose all the representative curves of G' in a master curve, at a reference temperature T_0 , by two translations : a vertical translation of $\log(\rho_0 T_0 / \rho T)$ and a horizontal translation of $\log a_T$, with

$$G'(\omega_0, T_0) = G'(\omega, T). (\rho_0 T_0 / \rho T) \text{ and } \omega_0 = \omega a_T$$

where $\rho_0 T_0 / \rho T$ is the term that takes into account the variation of volume with the temperature, and a_T , designed as the "shift factor", is a function of the temperatures T_0 and T . a_T equals the ratio of the relaxation times at T and T_0 :

$$\log a_T = \log(\eta / \eta_0) = - C_{1,0}(T - T_0) / (C_{2,0} + (T - T_0))$$

where $C_{1,0}$ and $C_{2,0}$ are the constants defined in equation (2). Experimentally, the range of frequencies is often restricted. By the use of this principle, the frequency range is then extended towards respectively higher and lower values, thanks to measurements made at low and high temperatures, respectively. The empirical use of the frequency-temperature superposition principle had preceded chronologically the microscopic theories which justify its validity.

Literature Cited

- Amari T. and K.Wanatabe
1979 "Relaxation modulus of printing ink ", ACS Div. of ORLP Papers., vol.40, pp. 490-493.
- Aspler J.S.
1992 "NMR spectroscopy, Polymer Motion and « Tack » of model printing inks", Pol. Ing. Sci., vol.32, no. 18, pp. 1379-1385.
- Baarends J.
1995 "Resin Technology Shifts Gears ", Ink World, July/Aug. 1995, pp. 46-47.
- Baldassare J.
1995 "Performance Comparisons of Heatset Ink Formulations", Am.Ink Maker, vol. 75, no. 6, pp. 50-54.
- Blayo A.
1994 "Rheological properties of printing inks", Ph.D. Thesis, National Polytechnic Institute of Grenoble, France.
- Cerny J.
1993 "Rheological Evaluation of Heatset Inks ", Graphic Arts in Finland, vol. 22, no. 2, pp. 3-8
- Chou S.M.
1992 « Viscosity Measurement of Viscoelastic Inks at High Shear Rates », TAGA Proceedings, pp.388-408.
- Cox W.P. and E.H. Merz
1958 "Correlation of Dynamic and Steady Flow Viscosities ", J. Polym. Sci., vol. 28, pp. 619-622.
- Cross M.M.,
1965 "Rheology of non-newtonian Fluids : a new Equation for Pseudo-plastic Systems", J. Colloid Sci., vol. 20, pp. 417-437.
- Dobbels F. and J.Mewis
1978 "Analysis of Nip Flow Operations Involving a Viscoelastic Roller", Chem. Eng. Sc., vol.33, pp. 493-500.
- Eyring H.
1935. J. Chem. Phys. vol.3, p.107.
- Ferry J.D.
1950 J. of Am.Chem. Soc., vol. 72, p. 3746.

- Korhonen J.
1993 "The Effect of Paper and Ink on Heatset Drying ", *Graphic Arts in Finland*, vol. 22, no. 2, pp. 16-22.
- Hayashi T., K. Morita, T. Amari
1993 "Rheological Properties and Printabilities of Polybutadiene/Carbon Black Ink", *J. of Japan Soc. Col.Mat.*, vol. 66, no. 11, pp. 655-664.
- Hutchinson G.
1994 "Progress in the Technology and application of Lithographic Inks", *Essentials of Ink Technology Conference*, 13-14 sept.
- Leach R.H., R.J.Pierce, E.P.Hickman, M.J.Mackenzie and H.G.Smith,
1993 "The Printing Ink Manual " (Blueprint, London), 5th ed.
- Loebbert G.
1995 "Web Offset Heatset: Challenges at Higher Press Speeds", *Ink World*, May/June 1995, pp. 32-39.
- Oittinen P.
1976 "Fundamental Rheological Properties and Tack of Printing Inks and their Influence on Ink Behavior in a Printing Nip" , Ph.D. Thesis, Helsinki University of Technology.
- Pangalos G., J.M. Dealy and M.B. Lyne
1985 "Rheological Properties of News Inks ", *Jour. of Rheol.*, vol.29, no.4, pp. 471-491.
- Reuvers A.J.
1995 "Hard Resins in Mineral Distillates ", *Am.Ink Maker*, vol. 75, no. 3, pp. 46-52.
- Rohn C.L.
1987 "Predicting the Application Behavior of Printing Inks from Dynamic Rheological Measurements ", *TAGA Proceedings*, pp. 536-559.
- Scarlatti, A.N.
1993 "The effect of Resin Properties on Lithographic Ink Vehicle Construction ", *Am.Ink Maker.*, vol. 71, no. 10, pp. 28-34,44.
- Sjodahl L.H.
1951 "Ink Flow on Rotating Rollers", *Am.Ink Maker*, vol.29, no.3, pp. 31-57.
- Voet A. and C.F. Geffken
1951 "The Nature of Tack ", *Ind. Eng. Chem.*, vol. 43, no. 7, pp. 1614-1624.
- Vinogradov G.V. and A.Y. Malkin
1980 "Rheology of Polymers"(Mir Publishers, Moscow).
- Williams M.L., R.F. Landel and J.D. Ferry
1955 *J. Am.Chem. Soc.*, vol. 77, p.3701.