ELABORATION AND CHARACTERIZATION OF WATERLESS INKS CONTAINING VEGETABLE DERIVATIVES

Véronique Lanet*, Anne Blayo* and Alessandro Gandini*

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Abstract : The aim of this work was to prepare sheet-fed waterless inks in which the petroleum diluent would be replaced by rapeseed methyl ester and to determine the viability of such formulations. Rheological and printability tests were carried out on these new inks and showed that the vegetable diluent gives rise to blends with higher tack and lower viscosity and elasticity than their mineral counterpart. Moreover, a higher degree of elasticity was needed for inks containing the vegetable diluent in order to obtain reliable toning capacities.

Introduction

After the petroleum crisis of 1973 and the ensuing rise in distillates' prices, the United States saught substitution products for the printing ink compositions. Between 1981 and 1983, ANPA (American Newspaper Publishers Association) tested 2000 different combinations of natural products in order to try to find alternatives to petroleum derivatives.

* Polymeric Materials, Laboratoire Génie des Procédés Papetiers
Ecole Française de Papeterie et des Industries Graphiques
BP 65, F-38402 Saint Martin d'Hères Cedex, France
e-mail : lanet@efpg.inpg.fr, blayo@efpg.inpg.fr, gandini@efpg.inpg.fr

A black letterpress formulation based on a blend of "gilsonite" and tall-oil fatty acids (paper-making by-products) was proposed (Moyhihan, 1983), but this approach was not satisfactory because of its cost and the difficulty in developing a stable ink. The avaibility and low cost of soya oil imposed eventually this renewable raw material as the base of a newspaper ink comprising alkali-refined soybean oil, a hydrocarbon resin and a carbon black pigment (Moyhinan, 1985a, 1985b).

The development of inks containing renewable triglycerides was encouraged by (i) the Hazard Communication Standard in 1985 which required ink manufacturers to label their products as carcinogenic if they contained more than 0.1% of aromatic mineral oil and (ii) the Clean Air Act in 1990 which regulated the emission of VOC (Volatile Organic Compounds) contained in mineral distillates.

Workers at USDA (United States Department of Agriculture) tested 150 varnishes containing 100% vegetable oils, as opposed to the above ANPA formulation, especially soybean oil, polymerized at very high temperatures (Erhan, 1991, 1992). Their properties during printing proved correct.

Despite their higher price (especially for black ones), soya-based inks widely spread in the USA from the first test in practice carried out in 1987. Today, 90% of the newspapers in the USA are printed with vegetable inks (IFRA, 1995) as well as 25% of the country's commercial prints (Watson, 1994). In Europe, the use of soybean inks is much more modest and only a manufacturer in Belgium (Trénal) specialized in vegetable inks as from 1987.

A number of advantages have been pointed out for these inks, namely :

- they are easier to clean with cleaners containing less VOC (Raines, 1995)
- they are more biodegradable (Erhan, 1993, Raines, 1995)
- they decrease the rub-off (Patterson, 1995, IFRA, 1995)
- they increase the print contrast (Patterson, 1995)

Concerning their aptitude to deinkability, the opinions are divided. Watson (1995), Patterson (1995) and Erhan and Bagby (1995) state, without concrete results, that soy ink is easy to remove from the paper surface, whereas an IFRA Special Report (1995) gives proof that soybean oil based inks produce poor deinking properties and results obtained in Finland showed the same tendencies (Hartus, 1995). When other oils like rapeseed are added to soja, results are much more favorable.

The NAPIM (National Association of Printing Ink Manufacturers) (1993) is rather sceptic about the decrease in the VOC emission arising from the use of vegetable inks.

The market of waterless lithography has not yet been touched by the use of vegetable inks. From an environmental point of view it could be an interesting opportunity to ally the elimination of the mineral distillates containing VOC with that of isopropyl alcohol.

The aim of our investigation is to prepare waterless inks in which the petroleum distillate is replaced by a vegetable derivative and to verify the viability of the formulations through rheological and physico-chemical properties and printability tests.

The vegetable derivatives employed stem from rapeseed oil, a European crop for which the agricultural world is trying to find new non-food utilizations, in order to avoid limitations by the European Community policies.

Experimental

Elaboration of varnishes and inks

The ink and varnish formulations which were at the root of our work are commercial ones. The varnish contained the following main components :

- a hard resin
- a polymerized linseed oil (standoly with a given viscosity)
- a petroleum distillate

Two other derivatives of linseed oil and a gelling agent were also present in much lower proportions.

The varnish was obtained by cooking all the components at 180°C while stirring in a nitrogen atmosphere for 2 hours.

Two kinds of hard resins and two types of diluents were used.

The two hard resins used were :

(i) a phenolic modified hydrocarbon resin reported as having a high molecular weight and bringing a high viscosity, a high structure and a low tack to the resulting solution

(ii) a phenolic modified rosin ester also reported as having a high molecular weight and providing a high degree of gel structure in solution, a high viscosity and excellent solubility in oil-based ink vehicles.

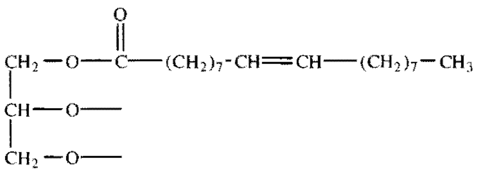
These two hard resins will be called respectively "*H*" and "*R*".

Two kinds of varnishes were made with each hard resin, namely :

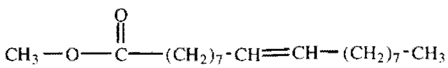
(i) those containing the petroleum distillate provided for the base formulation

(ii) those in which this distillate was replaced by a methyl ester derived from rapeseed oil.

The rapeseed oil was not used as such because of its excessive viscosity related to the fatty acid triglycerides it contains. By reaction with methanol, the corresponding methyl esters with molecular weight three times lower were obtained whose viscosities were closer to those of petroleum distillates. Examples of a triglyceride and of the ensuing methyl ester are shown below, taking oleic acid, i.e. the most important fatty acid in rapeseed oil, as reference.



Oleic acid triglyceride



Oleic acid methyl ester

The viscosity values of the petroleum distillate and the rapeseed methyl ester used in this work were 4.5 and 8 mPa.s, respectively.

Inks were prepared with a flushed pigment, a home-made varnish and additives (wax, drying agents and solvent). They were first dispersed with a Dispermat during about 10 minutes at 3000 rpm and then homogenized with a three-roller mill (low pressure).

Rheological measurements

- A CSL[2] 500 controlled-stress cone/plate rheometer was used to obtain the rheograms related to the inks studied. Measurements were carried out at temperatures varying from 10 up 50°C with a 2 cm 4° cone.

- Tack measurements were carried out with a Tack-O-Scope at 30 and 40°C applying a speed of 200 m/min.

- A Metravib viscoanalyser was used to assess the viscoelastic behavior of the inks. The storage (elastic) modulus (G'), the loss (viscous) modulus (G") and the loss tangent were determined at temperatures varying from 25°C to 50°C in the 5-250 Hz frequency range. The linear viscosity domain of each sample was preliminary determined and the amplitude of the applied strain was chosen accordingly, which varied from 8 to 12 μm, depending of the sample.

Printability tests

- The first printability test carried out was the determination of the "toning speed". This test, which is used at SunChemical France's control lab, uses an Inkometer. A test plate placed on the upper roller of the device is inked at different speeds, the apparatus is then stopped and a coated paper is applied on the plate. The speed at which there is no more toning on the printed paper is determined visually. This speed must be lower than 240 rpm in order to have an ink with a good resistance to toning.

- The inks prepared were tested on a two-color sheet-fed Man Roland press on which the dampening unit was deactivated. The test plate comprised four pictures and halftone areas of various coverages (10 to 100 %). Half of the elements had 150 dpi screen ruling and the other half 200 dpi. The printing speed was 5000 rph.

Results and discussion

The five inks for which results are presented in this paper contained magenta flushed pigments. The summary of their composition follows :

- a commercial ink called "*Com*" (its base formula was not the same as ours)

- one made with the hydrocarbon hard resin H and the petroleum distillate, called "*H dist.*"
- one made with the hydrocarbon hard resin H and the rapeseed methyl ester, called "*H est.*"
- one made with the rosin based hard resin R and the petroleum distillate, called "*R dist.*"
- one made with the rosin based hard resin R and the rapeseed methyl ester, called "*R est.*"

Rheological measurements

The rheograms obtained with the five inks at 30°C are given in Figure 1.

We observed a difference in behavior between the inks made with the hard resin H and those made with the hard resin R, the former giving rise to blends with a higher viscosity. Blends with the hard resin R and the commercial ink had similar viscosities. The second main observation concerned the influence of the replacement of petroleum distillate by the methyl ester which entails a decrease in the viscosity of the blends.

On the contrary, concerning the tack values at the same temperature (Figure 2), the new diluent brought an increase compared to blends containing the distillate. In the same way, the hard resin H gave rise to blends with tack lower than those containing R which moreover differed sharply from the commercial ink.

The same tendencies concerning tack and viscosity were observed when studying varnishes alone. The difference in viscosity between varnishes containing the mineral diluent and those with the vegetable one was certainly due to the difference in compatibility between each diluent and the hard resin. Indeed, trouble point measurements, carried out previously, demonstrated that the methyl ester showed a much higher compatibility with both hard resins than its mineral counterpart because of enhanced molecular interactions with the polar groups of the resins. This produces a corresponding increase in the solubility of the resin. These additional interactions found in blends containing the vegetable ester increase their internal cohesion and consequently their tack values.

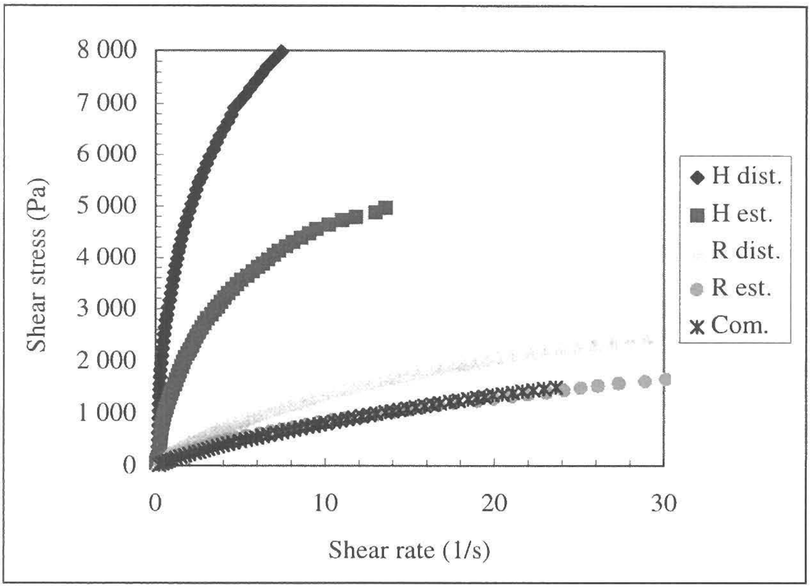


Figure 1 : Rheograms of the inks at 30°C

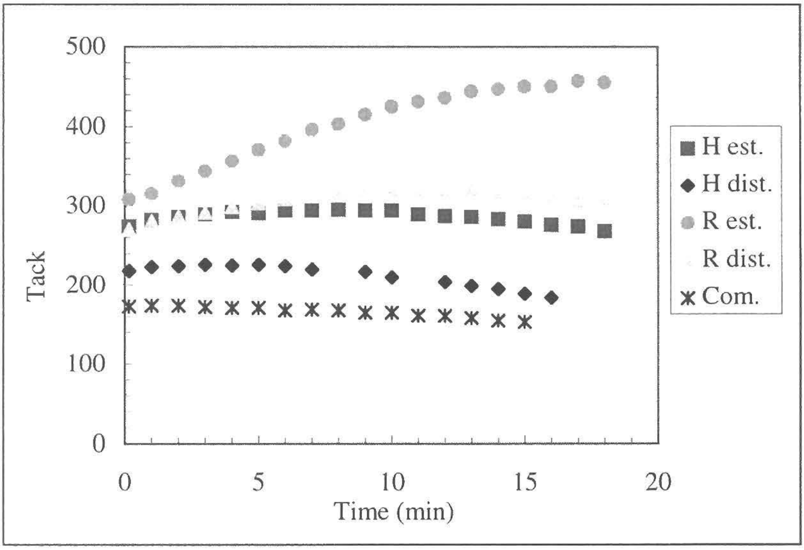


Figure 2 : Tack evolution of the inks at 30°C and 200 m/min

The rheograms obtained for each ink at different temperatures (10 to 50°C) allowed to determine the corresponding viscosity values and the plot of its evolution as a function of temperature (see Appendix) gave the activation energies E_a reported in Table 1.

All the inks prepared in this study had activation energies lower than that of the commercial sample. Moreover, inks containing the vegetable diluent had activation energies equal to (hard resin H) or lower (hard resin R) than those of the same blends made with the petroleum distillate. This result is very interesting since the evolution of the rheological properties with temperature is a very crucial point for waterless lithography where the cooling of the rollers by the fountain solution does not occur.

Ink	E_a (kJ/mol)
Commercial	71
R ester	45
R distillate	68
H ester	60
H distillate	60

Table 1 : Activation energy values of the inks

The viscoelastic behavior of the inks at room temperature is presented in Figures 3 and 4 which give the elastic modulus (G') and the loss tangent, respectively. These results indicated that the elastic character was more marked for blends with the hard resin H which also had a more important "structure", in accordance with their low tack and high viscosity. The commercial ink had the lowest elastic behavior, similar to that of inks containing the hard resin R. The loss tangent of blends containing the methyl ester were slighly higher than those of the corresponding blends with the mineral diluent. This observation implies that the relative viscous/elastic ratio was higher for the vegetable diluent, as already shown by the somewhat lower viscosity (see Figure 1).

All the inks displayed the same relative rheological behavior, whatever the test temperature.

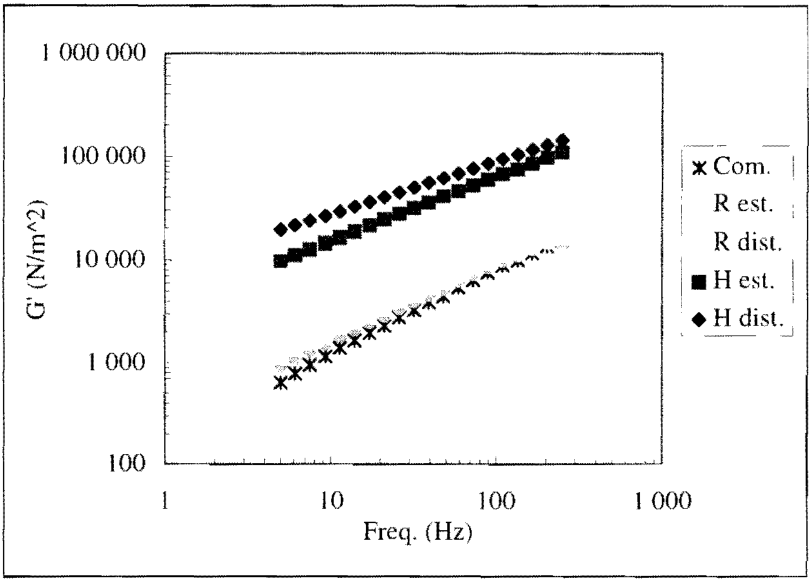


Figure 3 : Elastic modulus of the inks at 24°C

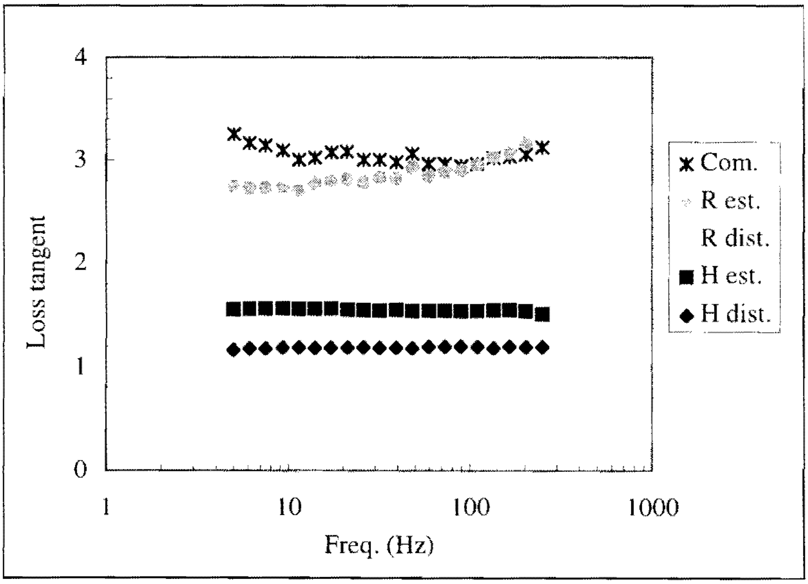


Figure 4 : Loss tangent for the inks at 24°C

The above results can be summarized as follows :

- The hard resin H gives rise to inks with low tack, but high viscosity and elasticity.

- The hard resin R gives rise to inks with high tack, but low viscosity and elasticity.

- The replacement of the petroleum distillate by the vegetable diluent gives rise to blends with higher tack and lower viscosity.

Printability test

- Toning speed

This parameter is the speed corresponding to the disappearance of toning for each ink on the test plate on the Inkometer.

The main property which governs this measurement is the elasticity of the ink. The higher the rollers' speed, the higher the frequency at which the ink is sheared and consequently the higher the elasticity of the ink.

A certain degree of elasticity is needed during the splitting of the ink in the nip so that the normal forces transmitted through the ink exceed the adhesive force at the ink/silicone interface. If the ink elasticity is loo low, the splitting will not occur at the ink/silicone interface any longer, but within the ink film and the ink will not be released from the substrate. This phenomenon appears at speeds lower than the "toning speed" or when the ink properties change as a consequence of an increase in temperature. Therefore, the "toning speed" can be linked to the tendency that an ink will show to tone when the temperature is increased. The lower the "toning speed", the lower the tendency of an ink to tone.

The "toning speeds" determined for our inks are given in Table 2. Only one of them was out of the tolerated limits, namely *R est.* This ink had nevertheless the same elasticity as the commercial ink and the other blend containing the hard resin R, both showing acceptable toning values. It can therefore be concluded that a parameter other than elasticity intervenes in this particular case and this might be the "Weak Fluid Boundary Layer" (WFBL) proposed by Gaudioso et al. in 1975 in the context of driography. This approach attributes the non-adhesion of the ink on the silicone surfaces to the diffusion of the low viscous diluent contained in the ink within the silicone network. This liquid would create a film with poor cohesive properties at the ink/substrate interface causing its splitting in the nip. Thus, the presence of a WFBL would allow the complete release of the ink from the silicone areas. In the case of our ink, the diluent is a relatively polar methyl ester with a viscosity a little higher than that of classical diluents, which displays therefore less affinity for the non-polar silicone surface than traditional petroleum distillates. If the diffusion in the silicone layer is insufficient to form a WFBL, the ink will continue to adhere to the silicone. A degree of elasticity higher than that normally acceptable is required in that case in order to obtain the ink release. This behavior was indeed observed with the highly elastic *Hest.* ink which, despite its vegetable diluent, gave an acceptable "toning speed".

Ink	Toning speed (rpm)
Commercial	230
R ester	> 260
R distillate	230
H ester	200
H distillate	230

Table 2 : Toning speed related to the various inks

- Printing tests

The five inks were tested on a two-color press in order to observe their performance in real printing conditions. With the speed used for the test, no ink toned, not even *R est.* which had a non-acceptable "toning speed" because the conditions chosen stayed within its non-problematic elasticity domain. Tests with each ink were limited in time to about ½ hour, which minimized the influence of a sharp increase in the temperature of the rollers.

The only real problem observed during printing came from an excessive tack of the blends with the hard resin R. This resulted in a bad detachment of paper sheets from the blanket at the top of the printing areas as noticed by the lack of ink in these parts of the resulting printing sheets.

In conclusion, the main problem of the formulation containing the hard resin R and the methyl ester, which had a correct viscosity, was the lack of elasticity and too high a tack. Therefore, we decided to make varnishes by mixing the two hard resins in order to increase the elasticity and to decrease the tack with respect to the previous blend. This work is in progress.

Physico-chemical considerations

In this paper we did not present any result concerning the physico-chemical characterization of the different varnishes and inks, but are of course aware that this aspect is very important for the waterless process. The use of different methods like contact angle measurements, Inverse Gas Chromatography is in progress. Preliminary results indicate that there are no sharp differences between blends with the mineral non-polar diluent and those with the more polar vegetable counterpart, probably because the difference in their polarity is blurred by the presence of all the other components.

Conclusion

The major conclusion that can be drawn from this investigation is the necessity for an ink containing vegetable ester to have an elasticity higher than that normally sufficient to counterbalance the lack of diluent diffusion into the silicone layer (WFBL model) and to achieve a complete release of the ink even when the temperature is increased. Even if some adjustements concerning tack are necessary in the case of our formulations, this work demonstrated that vegetable sheet-fed inks for waterless lithography seem to be a realistic proposition. This conclusion is corroborated by the fact that the evolution of the rheological properties of the inks containing the vegetable diluent with temperature was quite satisfactory, indeed better than that found with mineral diluents.

Acknowledgements

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Appendix

Temperature influence on viscosity

We used Eyring's theory to study the variations of the ink viscosity with temperature.

In 1935, Eyring described the flow process of a viscous liquid as the clearing of an energy barrier by an elementary unit of the material. This activated transition is therefore favoured by an increase in temperature.

Eyring's law gives an expression of the variation of the viscosity (η) as a function of temperature (T) which is similar to Arrhenius equation, viz. :

$$\eta = A\exp\left(\frac{E_a}{RT}\right) \tag{1}$$

where,

A : constant related to molecular oscillation frequency

E_a : activation energy for viscous flow

R : gas constant

The slope of the plot of ln η vs. 1/T gives E_a which is the quantitative parameter of the thermal sensitivity of the viscous response of a liquid.