Studies related to the Weak Fluid Boundary Layer model in waterless lithography

Véronique Lanet* and Alessandro Gandini*

Abstract :   This article deals with some experiments which were carried out in order to tend to verify if the model based on a Weak Fluid Boundary Layer proposed by Gaudioso et al. in 1975 for the ink release from the non-image area of a driographic plate could apply to the current waterless process. After the characterization of the silicone layer of a positive Toray plate before and after exposition, we carried out some experiments to show the possibility for two standard waterless ink diluents to diffuse into the exposed non-image area of this plate. Comparisons will be made with polydimethylsiloxane (PDMS) samples.
We established that the silicone used for the waterless plates is a PDMS with reactive chains. The diluent diffusion in this layer does indeed take place.

Introduction

The waterless lithographic plate used today was introduced at DRUPA in 1977 by Toray Industries. Nevertheless, the idea to make a lithographic plate which would allow to eliminate the use of water and thereby the primordial problem of ink/water balance in the lithographic process, is older. The first system developped and brought to the market was the "Driographic plate" of the 3M

* Polymeric Materials, Laboratoire Génie des Procédés Papetiers, URA 1100 CNRS
Ecole Française de Papeterie et des Industries Graphiques,
INPG, BP 65, 38402 Saint Martin d'Hères, France
        e-mail : lanet@efpg.grenet.fr, gandini@efpg.grenet.fr

577

Company in 1970 (Curtin, 1970). In the four following years, a number of other companies like Scott Paper Company (Gipe, 1973), Itek Corporation (Gracia et al., 1974) and Eastman Kodak Company (Yoerger et al., 1975) registered patents for this kind of plates using different ink-repellent materials for the non-image area.

The 3M plate was pre-sensitized and composed of several layers coated on an aluminium base. A silicone elastomer of low surface energy (composed mainly of high molecular weight cured polydimethylsiloxane) constituted the non-image area, the image area being the support itself, i.e. the uncoated aluminium base. This plate had a short life. The reasons for its failure were essentially its poor durability and the inks which were not yet suitable for this new form of process (O'Rourke, 1992).

In 1972, Toray Industries, a Japanese company specialized in synthetic materials development, purchased the 3M patent for the driographic plate. Five years of research were required to develop the present Toray waterless plate.
It is at the time of the 3M plate that the first research work concerning the mechanism of the waterless process was carried out.

Mechanisms proposed for ink release in waterless lithography

In 1975, Gaudioso et al. tried to explain the ink release from the silicone non-image areas of driographic plates. They reviewed the different models which could explain this phenomenon, namely :

- a model entirely based on surface energies

In 1969, Padday explained the phenomena of ink release and ink adhesion in conventional lithography in terms of a thermodynamic surface energy model. This model implies the following criteria : if the work of cohesion within the ink exceeds the work of adhesion between ink and substrate, the ink will release, whereas if the work of adhesion is larger, the ink will adhere.
Gaudioso et al. considered that these conditions were valid only under the assumption of thermodynamic equilibrium and could not be applied to the dynamic conditions of printing processes. They demonstrated this fact by taking a low surface energy surface roller (Teflon) and a high surface energy model ink. At high roller speed, the ink adhered to the Teflon because it had no time to retract. Moreover, during the waterless process there is always an initial period (quite short) during which the ink adheres to the silicone. Then, it cleans up. So, for these authors, a model based uniquely on surface energy was not sufficient to explain these two features.
Nevertheless, later, Ström (1988) took up again this idea and defined a model based on the surface chemistry for the two lithographic processes with and without water. It used Padday's criteria on the splitting process, but added the dependence of the splitting energy on the viscoelastic properties of the

liquids, considering that the splitting takes place in the weakest layer at the detachment zone of the roller nip.

- elastic release model

Typical lithographic inks are viscoelastic materials which exibit a viscous flow behavior in the inking nip. An ink with an elastic character high enough to be mainly elastic in this zone would be released only because of this property. But, in this case, other printing difficulties will appear i.e. incomplete image fill-in, excessive paper picking and poor transfer.

- the Weak Fluid Boundary Layer (WFBL) model

This model is considered by Gaudioso et al. as the most appropriate to explain the ink release of the silicone zones of the waterless plates. It was taken from the adhesion field and had been developped by Bikerman (1961) in the case of polyethylene surface impurities which weaken its adhesion to a given substrate in peeling tests.

Gaudioso et al. assumed that a low viscosity layer appears between the ink and the silicone so that splitting occurs in this weak layer rather than *within* the ink film at the nip exit. This layer originates from the diluents contained in inks which prediffuse at the interface ink/substrate. Therefore, inks must contain solvents with diffusion coefficient allowing them to form the WFBL.
This theory was supported by some tests with model inks and masters of different compositions showing the swelling of the silicone or the printing without toning with highly diffusible solvents.

For Gaudioso et al., this model also provides an alternative model for ink release in conventional lithography where water is the low-viscosity boundary layer. In the same vein, Ström (1988) assumed that the non-image area consisted of a layer of bound water below a layer of free water which acted as a WFBL during printing.

Gaudioso et al. stated in their paper that a certain degree of elasticity is all the same necessary for inks to satisfy the diffusion requirements related to a complete release.

To our knowledge, since the work of Gaudioso et al., very few authors have published studies on the waterless theory although several papers accepted its basic aspects. Even if this theory referred to a plate different from those used at present, the non-image areas of the two types of plates are probably similar (viz. silicone-based polymers), the image area being a photopolymer with Toray's plate.
These two reasons incite us to think that the features associated with this model could intervene in today's waterless process. Therefore, in the present work, we wished to verify its validity by carrying out different tests in order to check the ability for the ink diluents to diffuse into the silicone layer.
In a preliminary study, we tried to obtain more information about the composition of this layer.

Characterization of the silicone layer

The precise composition of the silicone layer of a Toray waterless plate, the silicone moities used to make the elastomer and its cross-linking density are unknown. The patent describing the composition of this plate is secret. Nevertheless, we can think that, as with the 3M driographic plate, polydimethylsiloxane (PDMS) is its main constituent.

At the present time, no company has succeeded in making a silicone sufficiently hard so that the resulting plates have a good durability. In order to have more information about this surface, we carried out the following tests:

- FTIR spectra
- differential scanning calorimetry test
- nuclear relaxation dynamics

FTIR characterization

Two methods were used to take an IR spectrum of the silicone surface :
- a specular reflexion spectrum of the layer as it sits on the plate
- a transmission spectrum of a pellet made with particles of the scraped layer

With the later method, we plunged pieces of a plate in dichloromethane in order to detach parts of the silicone layer. The specular reflexion spectrum was made with a special device on which a piece of the plate could readily be placed. The analyzing beam penetrated ca 1-2 μm of the layer. This thickness corresponds to that of the silicone layer coated on the plate.

The two spectra thus obtained were entirely similar and Figure 2 shows the one for the pellet. This was compared with spectrum of a silicone oil composed of 50 siloxane units (Figure 1). In the plate layer, we can find all the characteristic peaks of polydimethylsiloxane, namely the $Si-CH_3$ bonds (at about 1260 cm^{-1}), the $Si-O-Si$ bonds (between 1100 and 1000 cm^{-1}) and the $Si-(CH_3)_2$ bonds around 800 cm^{-1}.

Some differences were however detected, particularly in the 1760-1460 cm^{-1} region, with notably a carbonyl peak at 1735 cm^{-1}. Peaks at about 1630 cm^{-1} are characteristic of carbon-carbon double bonds and the shouder just above 3000cm^{-1} represents a C-H bond linked to a C=C unsaturation.
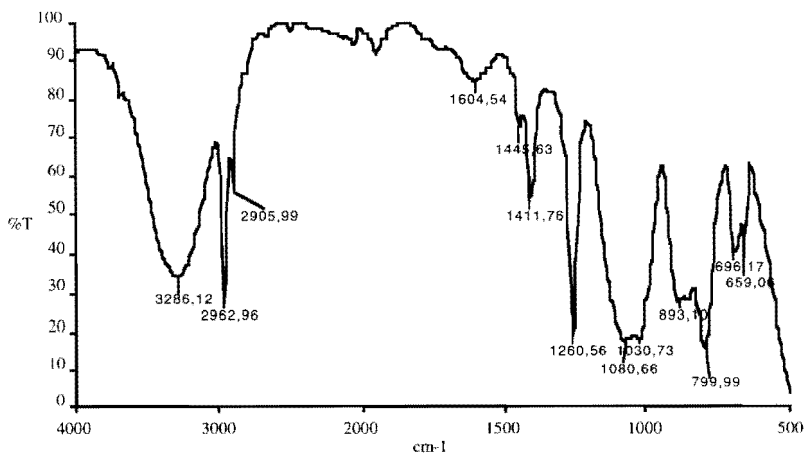
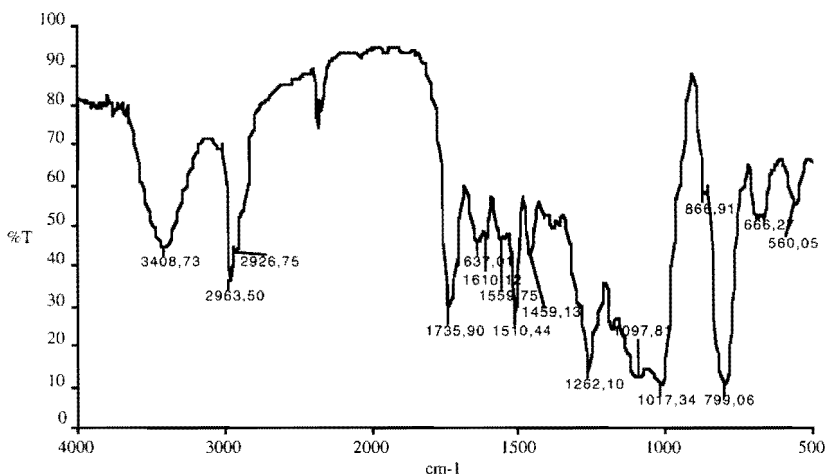Figure 1. IR spectrum of a silicone oil (50 PDMS units)

Figure 2. IR spectrum of a pellet of exposed silicone non-image area

The PDMS is not reactive as such towards excited species, so that in order to link with the excited photopolymer during the exposition of the plate, it must bear some reactive groups along its chains. These might be allylic groups or other unsaturated groups, Si-H bonds or more specific moieties. There is no peak around 2100 cm^{-1} corresponding to Si-H bonds in our spectrum. Nevertheless, we can think that the unsaturations observed could belong to allylic groups, unless they were part of the photopolymer collected with the

silicone, since we can find them also in the photopolymer spectrum. Further investigation will allow us to conclude.

Characterization by Differential Scanning Calorimetry (DSC)

Experiments were carried out with a SETARAM DSC 92 calorimeter.
Its principle is based on the heat quantity absorbed or emitted by a material when it undergoes a change in physical state or when it reacts chemically. The setup determines the enthalpies of these processes by measuring the differencial heat flow necessary for maintaining the sample and an inert reference (an empty capsule) at the same temperature. Thermograms obtained essentially show thermal transitions, solvent departure...

We tested a weakly crosslinked PDMS and samples of exposed and non-exposed silicone which were all quenched. The thermograms obtained during warming at a rate of 10°C per minute were similar and showed a glass transition temperature at about -120°C, a crystallization peak at -100°C and a melting peak at -45°C. These results are in accordance with the litterature (Helmer, 1969).
In view of the similarity of the three thermograms, both for the general aspect and the characteristic temperatures, we can conclude that all these products have the same structure.

Characterization by nuclear relaxation dynamics

This experiment is based on the Nuclear Magnetic Relaxation of the proton spins on a polymeric chain. These NMR observations are analyzed by assuming that a polymeric gel is a giant molecule which can be described as an ensemble of network chain segments. The presence of cross-links corresponds to constraints applied to both ends of each network chain segment. These constraints prevent monomeric units from rotating freely in space. There exists a permanent nonzero average of dipole-dipole interactions between protons. The residual dipole-dipole interactions is stong enough to govern the transverse magnetic relaxation process and to screen the dynamics of monomeric rotations.

For our sample of exposed silicone, the signal obtained in this experiment showed a drastic decrease in intensity during the first 100 µs. Then, the decrease was attenuated. These observations mean that our gel is highly reticulated (sharp decrease) but with pendant chains responsible for the second feature of the signal.
These chains could be the reactive groups on the silicone network.

It may be tentatively concluded that the silicone layer could be made up of a tight network with pendant reactive chains e.g. bearing allylic functions.

Swelling of PDMS samples

In order to examine if an ink diluent could swell PDMS samples, we dipped some of them into two commercial waterless ink diluents (called diluent 1 and diluent 2 hereafter) and measured their increase in weight vs. time.
Figure 3 shows that this increase is indeed quite important since it can reach 50 or 60 % of the initial weight. A saturation typical of thermodynamic swelling equilibrium is observed after 4 hours contact.
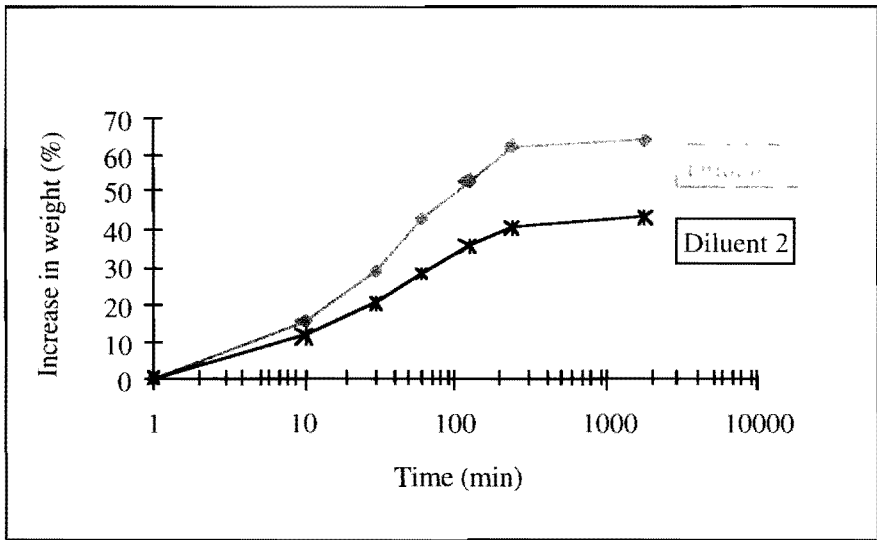Clearly, diluent 1 has a higher affinity for PDMS than its counterpart.

Figure 3. Increase in weight of PDMS samples in different diluents

Selective diffusion in the exposed silicone layer

This test was carried out from a blend of each ink diluent (5 ml) with a more polar material, i.e. ethyl phthalate (0.1 ml), which was put in contact with a Toray plate in order to see if the selective diffusion of one product rather than the other would take place in the silicone layer.
These tests simulated the real printing situation in that the phthalate represents an alkyd resin and the diluent is the non-polar "solvent" in an ink.
We ran FTIR spectra of the blends before and after 5 hours' contact with the plate. Figures 4 and 5 show the results obtained for the blend with diluent 2.
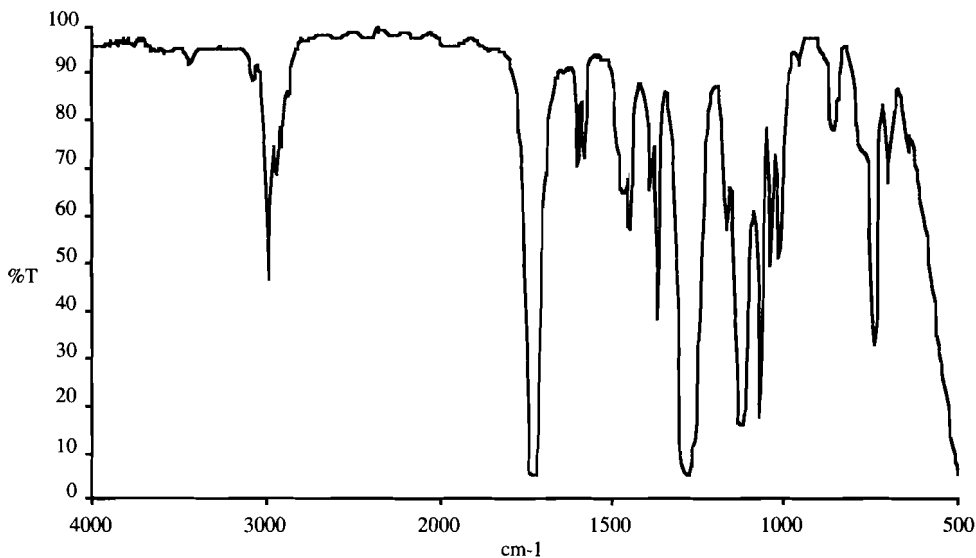
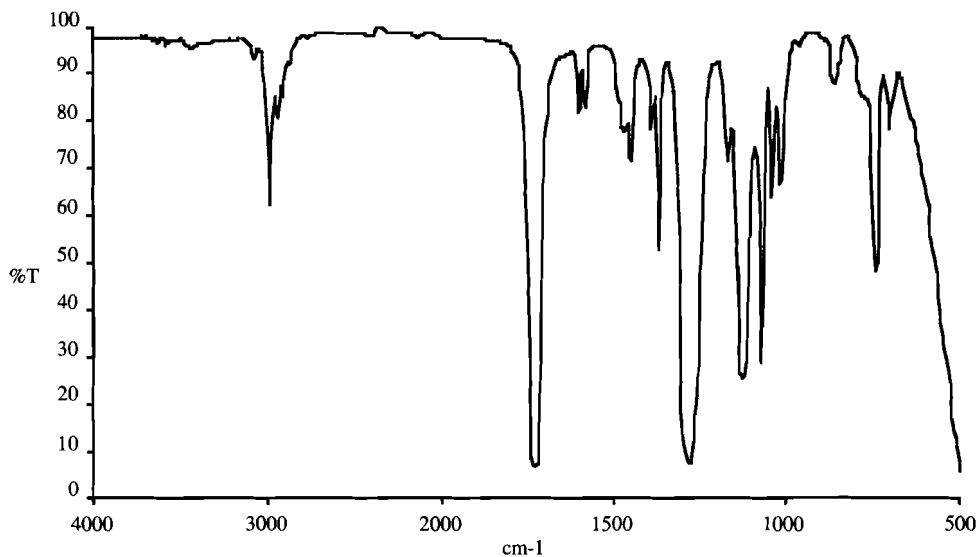Figure 4. IR spectrum of the blend before the contact with the silicone

Figure 5. IR spectrum of the blend after 5h contact with the silicone

The best comparison was that between the aliphatic peak (just below 3000 cm^{-1}), coming mostly from the diluent which is an hydrocarbon product, and the carboxylic peak (at about 1730 cm^{-1}), coming only from the phthalate. After 5 hours, the intensity of the aliphatic peak decreased compared with that of the carboxylic one, with both diluents. The ratio of the area of the aliphatic

peak to that of the carboxylic one before and after contact with the silicone layer are given in Table 1.

	Before contact	After 5h contact
Diluent 1	0.44	0.34
Diluent 2	0.45	0.31

Table 1. Ratio of areas of aliphatic and carboxylic peaks

These results clearly indicate that a preferential migration of the diluent in the silicone had taken place.

Kinetics of adsorption of a diluent drop

A video analysis system was used to follow the changes of the contact angle θ (and consequently adsorption) of a diluent drop on an exposed silicone non-image area. These contact angles were measured with a CCD camera and processed by an image analysis video card which calculated θ using the following equation :

$$\tan \frac{\theta}{2} = \frac{2h}{D}$$

with,
h : height of the drop
D : diameter of the drop

The deposited drops had an average volume of no more than 3 μl, in order to assimilate them to a spherical shape and to avoid problems arising from gravity.

This test was carried out with the two-liquids method because the angle of a diluent drop on the silicone layer in air is too low to give reliable values. Our plate was therefore put in a receptacle full of water. The diluent drop was then placed on the silicone part of the plate in this water environment.
We followed the evolution of the contact angle at short and longer times.
Figure 6 shows one example of an experiment with diluent 2 lasting 10 minutes. We can clearly see two phases for the contact angle evolution on a logarithmic scale. The first corresponds to a spreading of the drop, by expelling the water film present under it, when it is placed on the silicone layer. This is over within ca 1 minute. Then, the line obtained has a smaller slope. The same slope is obtained for longer experiments (5h) like the one shown in Figure 7 for the same diluent. This part of the graph corresponds to the adsorption of the diluent in the elastomer layer which stabilizes after a certain time, as we have already remarked in the PDMS swelling experiments.
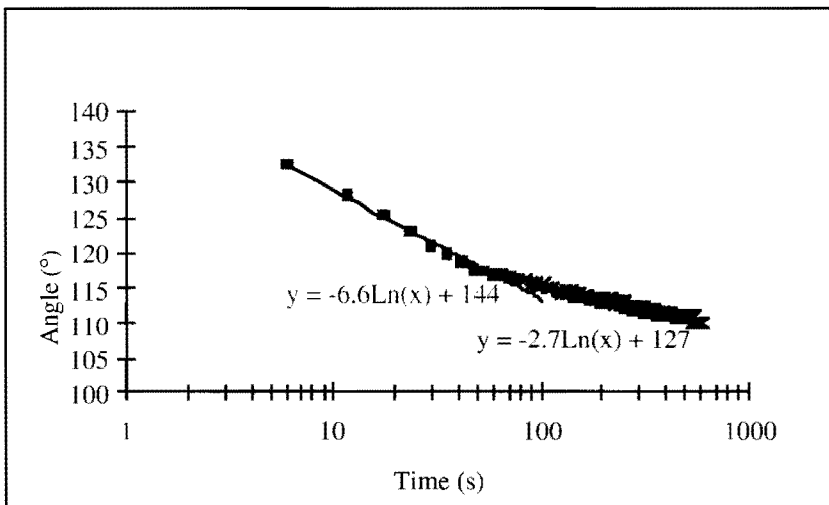
Figure 6. Contact angle vs. short time for a drop of diluent 2 on the silicone layer
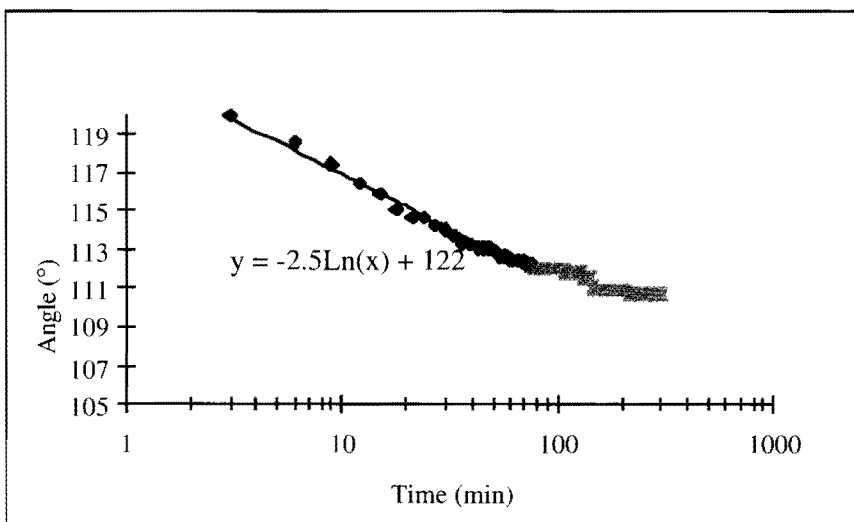

Figure 7. Contact angle vs. long time for a drop of diluent 2 on the silicone layer

If we compare the slopes of the adsorption behavior for the two diluents 1 and 2 (see Figure 8), we can observe that diluent 1, which swelled PDMS more efficiently, gave also the higher slope, i.e. the strongest adsorption.
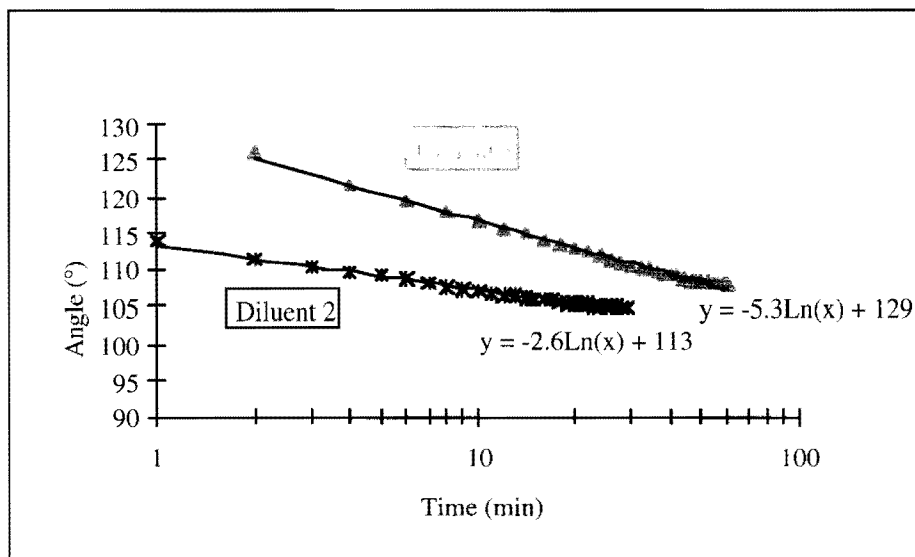
Figure 8. Contact angle in water of diluent drops on silicone layer

The chart shows:
- y = -5.3Ln(x) + 129
- y = -2.6Ln(x) + 113
- Diluent 2
- Y-axis: Angle (°), from 90 to 130
- X-axis: Time (min), from 1 to 100

Conclusion

We have shown in this investigation that the main constituent of the silicone layer of the Toray waterless plates is PDMS with pendant reactive chains which could bear allylic groups.

Moreover, the diluents contained in typical waterless inks can readily diffuse into the non-image area of the plate. Therefore, the model described by Gaudioso et al. in 1975 seems applicable to the actual waterless process and certainly explains part of the ink release phenomenology.

It remains to be seen whether these features also occur when dynamics and pressure conditions, like those encountered on a press, are applied.

Acknowledgements

587

Literature Cited

Bikerman, J. J.
      1961.   "Effects of impurities on polyethylene adhesion"
              J. Appl. Chem., vol. 11, pp 81-85

Curtin, J. L.
      1970.   U.S. Patent 3,511,178 (May 12, 1970)

Gaudioso, S. L., Becker, J. H. and Sypula, D. S.
      1975.   "Macanisms of ink release in waterless lithography"
              TAGA Proceedings, pp 177-194

Gipe, H. F.
      1973.   U.S. Patent 3,728,123 (April 17, 1973)

Gracia, R.F., Laughrey, R. A. and Tuohey, P. F.
      1974.   U.S. Patent 3,835,780 (September 17, 1974)

Helmer, J. D. and Polmanteer, K. E.
      1969.   "Supercooling of Polydimethylsiloxane"
              J. Appl. Polym. Sc., vol. 13, pp 2113-2118

O'Rourke, J. L.
      1992.   "The waterless printing process : U.S. market. Considerations and applications"
              TAPPI Proceedings, pp 305-313

Padday, J. F.
      1969.   "Surface Chemistry of Lithography"
              Printing Technology, vol. 13, pp 23-31

Ström, G.
      1988.   "Wetting studies related to offset printing"
              Ph. D. Thesis, Institute of Surface Chemistry, Stockholm University

Yoerger, W. E., Mc Cabe, J. M. and Wright, J. F.
      1975.   U.S. Patent 3,859,090 (January 7, 1975)