

INTERACTIONS BETWEEN PRINTING INK BINDERS, PRINTING INK OIL AND FOUNTAIN SOLUTIONS

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Abstract: This paper reports the effect of alkyd resin and surface active additives in fountain solution on the interfacial tension between the aqueous solution and a heat-set oil as well as on the emulsification of the aqueous solution into the oil. Data on the dynamic surface tensions of the aqueous solutions are also presented.

Isopropyl alcohol, non-ionic surfactant and alkyd resin all had a strong influence on the interfacial tension, and the alkyd resin had a strong influence on emulsification and drop size. The lowest interfacial tension as well as the smallest water drop size were obtained with the most polar alkyd resin. This suggests that as the polarity of the alkyd increases the surfactant behaviour of the alkyd also increases and the polymer orients in the interface with polar groups in the water and apolar segments in the oil. The alkyd resin then acts as an emulsifier and stabilises the emulsion.

Introduction

The lithographic offset printing process of today requires that paper and board accept oil-based ink and water-based fountain solution when these are applied rapidly up to eight times in succession without refusal to allow transfer. Increasing speeds also put higher demands on fountain solution-ink interactions to obtain proper emulsification during the short times that are available.

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Interactions between inks and fountain solutions basically depend on molecular interactions between the different components in the fountain solution and the ink. These are surface active additives to the fountain solution such as isopropyl alcohol and non-ionic surfactants as well as components within the ink where the alkyd resin plays an important role. The work presented in this paper therefore concentrates upon the effect of these compounds.

The properties of the fountain solution are of course important for the water balance and the water-ink interactions. Bassemir and Krishnan (1987, 1988) have pointed out that the relevant physical property when designing the fountain solution is the dynamic surface tension rather than the static surface tension. They found that, as the dynamic surface tension is decreased, the water balance improves and the press can be run at lower water feeds.

Several studies concerning emulsion stability and rheology have been reported (Chou et al. 1987, Tasker et al. 1983, Bassemir and Krishnan 1987, 1988, Karttunen et al. 1985, Larsson and Trollsås 1985). Most of the work concentrates on the properties of the fountain solutions, and commercial inks of unfortunately unknown composition have most often been used. The effects of ink properties are fairly unknown, although it has been shown, as in the work by Larsson and Trollsås (1985), that polar inks are able to emulsify a higher amount of fountain solutions.

The work presented in this paper aims at a further understanding of the effect of alkyd resin on ink-fountain solution interactions. Alkyd resins are an important component of printing inks. They are used as binders because of their good binding capacity, wetting potential and low cost. They affect the balance between the amount of ink and fountain solution (Elliott 1993) and are involved in the drying process, due to the content of drying oils. Alkyd resins also interact with components of the paper surface e.g. cellulose, clay and calcium carbonate (Wickman and Johansson 1992, Wickman et al. 1994).

Alkyd resins are chemically classified as polyesters. The ones used in printing inks are formed by dibasic acids, polyols and fatty acids (Owen 1990). Ester linkages are prevalent in alkyd resins and these resins are characterised by good solubility in ink solvents and good vehicle compatibility.

Experimental

Materials

The alkyd resins used were kindly supplied by Bergvik Kemi AB, Sweden, SOAB, Sweden and Veitsiluoto Oy, Finland. Properties of the alkyd resins used are given in table 1. They were all of technical quality and were used without further purification. The content of free carboxyl groups (acidic value) and of

hydroxyl groups (hydroxylic value) was determined. The molecular mass distribution was determined by size exclusion chromatography (SEC). The contents of fatty acid residues (oil length) are according to the suppliers.

Table 1. Properties of alkyd resins used

Alkyd resin	Hydroxylic value (mg KOH/g)	Acidic value (mg KOH/g)	Molecular mass (M_w)	Oil length
A	71	3	26000	76*
B	69	2	25000	62*
C	88	12	10000	62*
D	43	8	7000	82*
E	70*	9*	5800*	78*
F	46*	11*	5600*	78*
G	47*	14*	4400*	78*
H	44	16	3000	84*
I	48	10	3000	72*

*) Values according to supplier

The printing ink oil used was a heat-set mineral oil. This heat-set oil is a mixture of paraffinic, naphthenic and aromatic hydrocarbons, mainly C16-C18, manufactured by Haltermann, Sweden (commercial product name PKWF 28/31).

The fountain solution used was a commercial fountain solution containing a non-ionic surfactant (commercial product name Aqualith NCD PR 9600), manufactured by Casco Nobel Inks, Sweden, diluted to 2 % (v/v) with de-ionised water.

The isopropyl alcohol was of p.a. quality and obtained from Merck. The non-ionic surfactant was based on a straight primary alcohol with a HLB number of 11.8, and is manufactured by Akzo Nobel Surface Chemistry AB, Sweden (commercial product name Berol 160).

The water used was de-ionised and distilled.

Methods used

Surface tension

The static surface tension of all solutions used was determined by the du Noüy ring method using a Sigma 70 surface tension meter (KSV Instruments Ltd, Finland) at low ring speed.

Dynamic surface tension was measured using the maximum bubble pressure method (Sensa Dyne surface tensiometer 6000, Chem.-Dyne Research Corp., USA).

Interfacial tension

The interfacial tension was measured at 20° C by determining the shape of a pendant drop. Our in-house designed instrument uses a video image from which the interfacial tension, γ , is calculated from the expression:

$$\gamma = \frac{\Delta\rho \times g \times R^2}{\beta} \quad (1)$$

where

- $\Delta\rho$: mass density difference between the drop and the surrounding medium
- g : acceleration due to gravity
- R : radius of the curvature at the drop apex
- β : shape factor. The shape factor is a function of the droplet shape, and values are tabulated (Adamson 1976).

A pendant drop of fountain solution or water was formed at the tip of the needle of a Hamilton syringe, while the needle was kept inside a quartz cuvette filled with a mixture of alkyd resin and oil. The interfacial tension was measured over a period of 40 minutes, or until the interfacial tension maintained a constant value. The experiments were repeated for at least three triplets.

Droplet size

Emulsions were formed by emulsifying 15 % (v/v) water solution into the oil phase, using a colloidal mill, Ultra Turrax (Janke & Kunkel GmbH, Germany). The dispersing tool used has a diameter of 10 mm and the gap between the stator and rotor is 0.35 mm. The samples were stirred at 1000 rpm.

The initial size of the water droplets formed was measured with a laser diffraction instrument, Mastersizer (Malvern instruments, England) with pure heat-set oil as the continuous phase. The instrument uses an approximation of the Mie scattering theory, which utilises the refraction index of the dispersed phase and its adsorption. The droplet size is expressed as D(0.5) which is the volume-weighted median diameter.

Results and discussion

Surface tension

Dynamic surface tension measurements were performed on aqueous solutions containing isopropyl alcohol, fountain solution or a non-ionic surfactant. The static surface tensions for the aqueous solutions used were all approximately 40 mJ/m², as can be seen in Table 2.

Table 2. Static surface tension

Sample	Surface tension (mJ/m ²)
Water	72.8
Isopropyl alcohol (10 %)	41.5
Fountain solution (2 %)	39
Non-ionic surfactant (0.072 g/l)	39
Non-ionic surfactant (0.36 g/l)	28
Heat-set mineral oil	32

The aqueous solutions containing isopropyl alcohol, fountain solution and non-ionic surfactant respectively showed different dynamic surface tensions, as shown in Figure 1. Isopropyl alcohol solution reached its static value already at the first measuring point, whereas both the non-ionic surfactant and the fountain solution showed a decrease in surface tension with time. The molar mass of isopropyl alcohol is much lower than that of the non-ionic surfactant. This results in a much higher rate of diffusion of the isopropyl alcohol molecules and thus a faster appearance of equilibrium.

The curve of the fountain solution is parallel to that of the non-ionic surfactant solution. This is quite reasonable since the fountain solution contains non-ionic surfactant. The type and concentration are unfortunately not known. The extensive decrease in surface tension from the value of water to 60 mJ/m² suggests that the commercial fountain solution also contains some alcohol. The data on dynamic surface tension agree fairly well with the literature data (Defay and P  tr   1971, Karttunen et al. 1985).

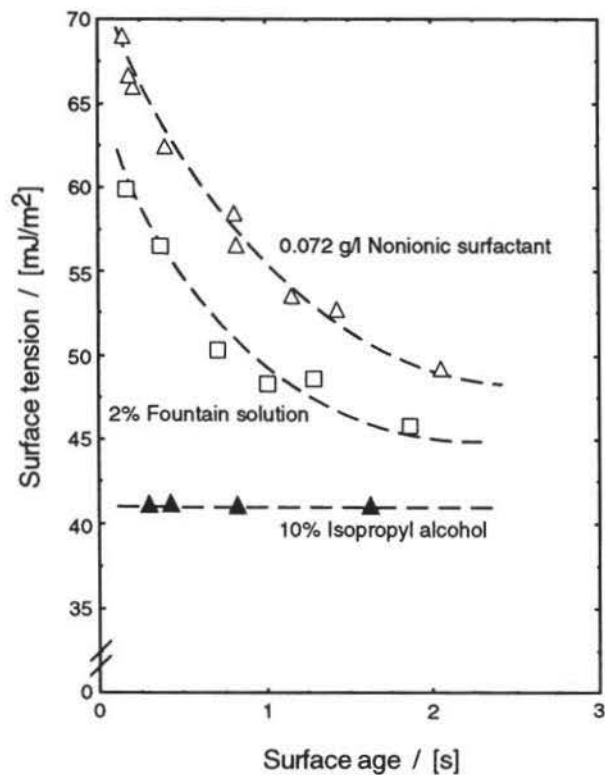


Figure 1. Dynamic surface tension for aqueous solutions containing isopropyl alcohol, fountain solution and non-ionic surfactant, respectively. Isopropyl alcohol solution shows a constant surface tension as a function of time, while the fountain solution and the non-ionic surfactant solution show a decrease in surface tension.

Interfacial tension

The pendant drop instrument is suited to measure surface tension and interfacial tension for systems which reaches equilibrium slowly, e.g. polymer solutions. In Figure 2, the dynamic interfacial tension between pure heat-set oil and aqueous solutions is shown. Although the time scale is much longer for the interfacial tensions than for the surface tensions, it is clear that equilibrium is established much faster in the solution containing isopropyl alcohol than in solutions containing non-ionic surfactant or fountain solution.

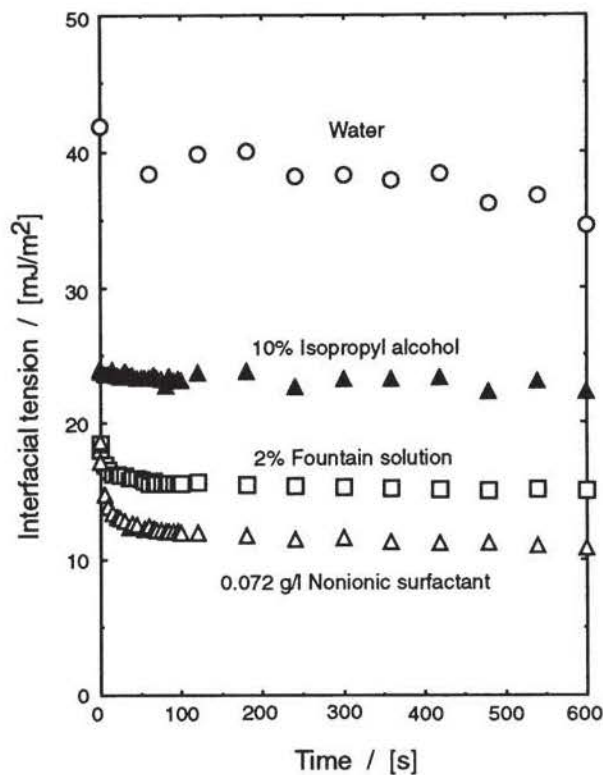


Figure 2. Interfacial tension between pure heat-set oil and aqueous solutions. The interfacial tension between the oil phase and the water phase is decreased when the static surface tension is decreased by the addition of surfactants or isopropyl alcohol. However, the decrease in interfacial tension differs, despite the fact that the static surface tension is approximately the same for the aqueous solutions used.

As expected, the interfacial tension between the oil phase and the water phase was decreased when a surfactant or isopropyl alcohol was added to the water. The reduction was however quite different even though the static surface tensions of the aqueous solutions were approximately the same. The interfacial tension was 22 mJ/m^2 with the isopropyl alcohol solution and 11 mJ/m^2 with the non-ionic surfactant solution. The difference is probably due to the solubility of the additive in the oil, i. e. isopropyl alcohol is more soluble in oil than the non-

ionic surfactant, and thus less additive remains at the interface. The interfacial tension value obtained using the fountain solution is intermediate between those of non ionic surfactant and isopropyl alcohol solutions, which again indicates that some alcohol is present in the fountain solution.

When 10 % (w/w) alkyd resin was added to the heat-set oil, the interfacial tension between oil phase and aqueous phase was reduced, as shown in Figure 3. The effect of the alkyd resin addition was stronger than the effect of adding fountain solution to the aqueous phase. The lowest interfacial tension was obtained when alkyd resin was present in the oil phase, and the surface tension of water was decreased by the addition of fountain solution.

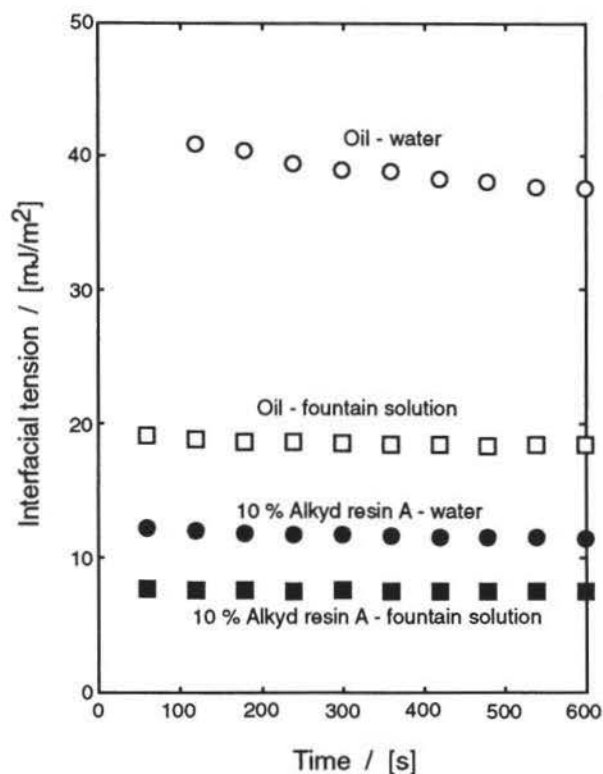


Figure 3. Interfacial tension between oil phase and water phase. The lowest interfacial tension is obtained when both alkyd resin was present in the oil phase and the surface tension of water was decreased by addition of fountain solution.

The value of the interfacial tension depends on the properties of the alkyd resin as well as on the aqueous phase composition. In Figure 4, the interfacial tension

between oil, containing 10 % (w/w) alkyd resin and the aqueous phase is shown as a function of alkyd resin hydroxylic value. The results show that the higher the hydroxylic value the lower is the interfacial tension. This behaviour was observed both with water and with water containing non-ionic surfactant. The polarity of the alkyd increases with increasing hydroxylic value and the polymer becomes more water-soluble and less soluble in hydrocarbons. Polar alkyd resins thus concentrate within the water-oil interface which results in a low interfacial tension, whereas alkyd resins with low polarity (low hydroxylic value) remain to a higher extent in the oil phase.

These results are in agreement with the work of Karttunen et al. (1985). They used inks dissolved in xylene and centrifuged the mixtures in order to remove the pigments. Using the spinning drop method, they showed that inks with high relative polarity gave lower interfacial tension towards fountain solutions.

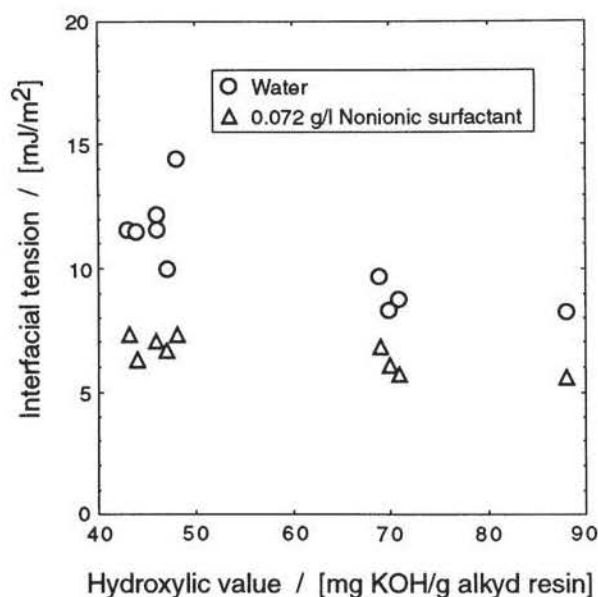


Figure 4. Interfacial tension between oil phase and aqueous phase as a function of alkyd resin hydroxylic value. Alkyd resins with high hydroxylic values show the lowest interfacial tension. These alkyd resins are less soluble in the oil and are likely to orient towards the water-oil interface.

Carlick (1984) examined the physico-chemical properties of the major solvent-soluble ink resins. He showed that nearly all resins based on drying oils and

rosin compounds have a surfactant potential. Linseed alkyd resins are suggested to fall into the non-ionic surfactant class with the hydrocarbon tail of the fatty acids as the hydrophobic part and polyol esters with carboxyl and hydroxyl end groups as the hydrophilic part. Located in an oil-water interface, the polar groups of the polymer tend to concentrate in the aqueous phase while the apolar segments project into the oil phase. Today we regard these type of compounds as surface active polymers.

Surfactants are characterised by the presence of a polar part and an apolar part of hydrophobic nature (Rosen 1978). The polar part of the molecule has a high affinity for water and other hydrophilic compounds but low affinity for hydrocarbons. The apolar part has the opposite properties, i.e. low affinity for water and high affinity for hydrophilic materials. Although surfactants are very efficient agents to reduce surface and interfacial tensions, this is also achieved by surface active amphiphilic polymers (Fleer et al. 1993). They differ from surfactants in having many polar groups interspaced by segments of hydrophobic material. Given their structure and physical-chemical behaviour polar alkyd resins can be considered as one class of amphiphilic surface active polymers.

Our results show that the decrease of interfacial tension between oil and water depends on both the surface active material present in the fountain solution and the polarity of the alkyd resin used. The presence of alkyd resin clearly has an impact on the interfacial tension between oil phase and water phase.

Droplet size

An emulsion comprises three components, oil, water and emulsifier. The emulsion is formed during a process in which the water phase is dispersed into small droplets by the use of energy. As the emulsification proceeds, the size of the droplet decreases and the tendency to sedimentation and coalescence is reduced. The emulsifier supports this action first by decreasing the interfacial tension, and then by protecting the droplets from flocculation and coalescence by creating a repulsive barrier around them. In order to obtain very stable emulsions, the interfacial tension should be small but positive (Ruckenstein and Krishnan 1980). Emulsions with small droplets are normally more stable than emulsions with large drops.

Figure 5 shows the initial droplet size as a function of interfacial tension. The emulsions were formed by emulsifying 15 % water phase containing 0.072 g non-ionic surfactant/l water into heat-set oil to which 10 % (w/w) alkyd resin had been added. The different alkyds used gave different interfacial tensions, as shown in Figure 4. It is quite clear that low interfacial tension gives a low drop

size. Thus the choice of alkyd strongly affects the emulsification of fountain solution.

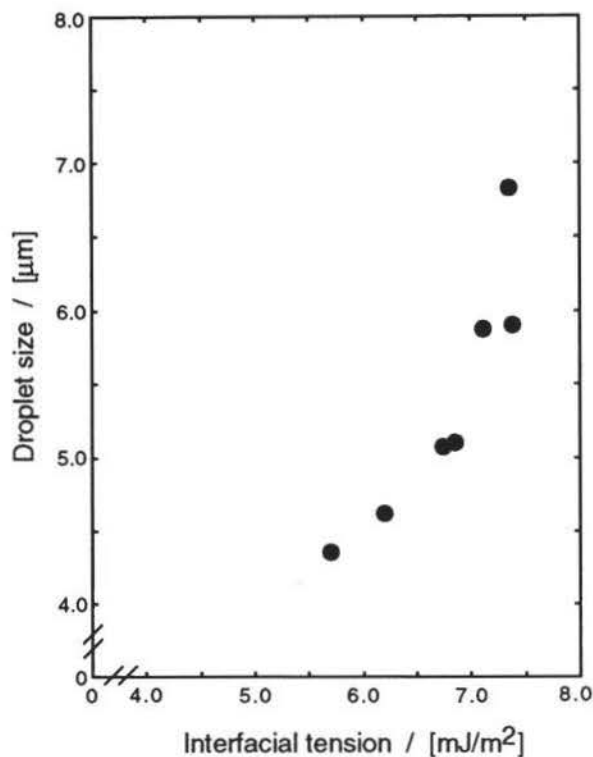


Figure 5. Initial droplet size as a function of interfacial tension after 300 s agitation. Alkyd resins giving a low interfacial tension form emulsions with small water droplets.

The emulsification of fountain solution, isopropyl alcohol solution or non-ionic surfactant solution in heat-set oil containing no alkyd was extremely poor. The drop diameter of the aqueous phase became 100 μm or larger. The emulsions were extremely unstable and total coalescence occurred within a few seconds.

Although the drop size is strongly dependent on the type of alkyd dissolved in the oil, it is interesting to note that the concentration of non-ionic surfactant in the aqueous phase did not influence the drop size when an alkyd was present in the oil. This is evident in Figure 6 where drop sizes are given as a function of agitation time. The aqueous phase was either water or a solution of non ionic surfactant. Even when the concentration of non-ionic surfactant was increased

above the critical micelle concentration (0.36 g/l), the concentration had no impact on the droplet size. Addition of isopropyl alcohol to the aqueous phase resulted in a slightly lower droplet size.

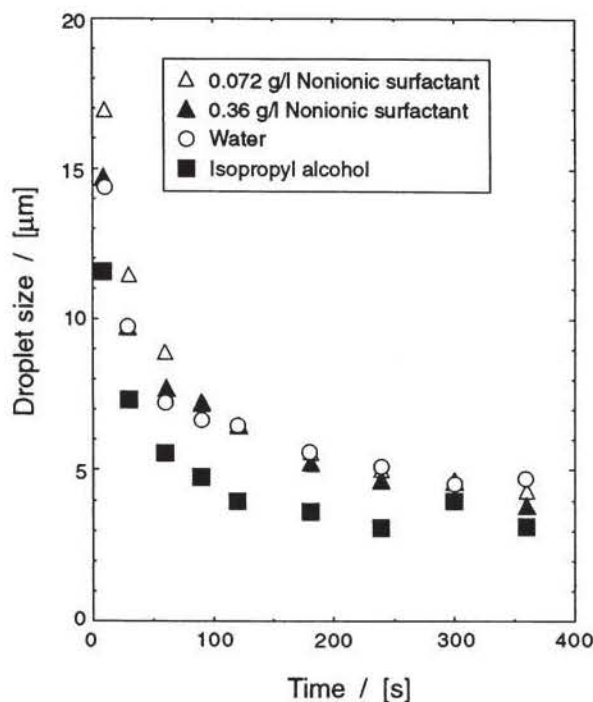


Figure 6. Initial droplet size as a function of agitation time. The droplet size was approximately the same if pure water was used as when non-ionic surfactant was added to the aqueous phase. Addition of isopropyl alcohol resulted in a slightly lower droplet size.

Chou et al. (1987) showed that the physico-chemical nature of the emulsifiers and the quantities of these present in both ink and fountain solution must be affecting the emulsification behaviour. However, our results show that the droplet size was independent of the non-ionic surfactant present in the water phase but strongly affected by the properties of the alkyd resins present in the oil phase, Figures 5 and 6.

Our results clearly show that alkyd resins act as emulsifiers and stabilise the emulsions, in fact much more efficiently than isopropyl alcohol or a non-ionic

surfactant. Alkyd resins with a high solubility in heat-set oil, on the other hand, are likely to remain within the oil phase. The water droplets can then easily coagulate into larger ones.

Conclusions

The interfacial tension between fountain solution and solutions of printing ink oil and alkyd resins are affected by the composition of the fountain solution as well as by the polarity of the alkyd resins. The lowest interfacial tension between oil phase and fountain solution was observed with alkyd resins showing a low solubility in printing ink oils.

However, when emulsions are formed, the surface tension of the water phase does not affect the droplet size during the formation of emulsions. The droplet size depends upon the properties of the alkyd resins. Alkyd resins giving a low interfacial tension between oil phase and aqueous phase also form stable emulsions with small water droplets. This clearly shows that alkyd resins act as emulsifiers and stabilise water in oil emulsions formed during offset printing.

In order to obtain stable lithographic emulsions, alkyd resins with a low solubility in printing ink oil are recommended. These alkyd resins act as emulsifiers and stabilise the emulsions.

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Literature cited

- Adamson, A.W.
1976. "Physical chemistry of surfaces" (Published by Wiley-Interscience, New York, USA), 3rd ed.
- Bassemir, R. and Krishnan, R.
1987. "Optimizing lithographic performance - a physical-chemical approach" TAGA Proceedings, p. 560-573.

- Bassemir, R. and Krishnan, R.
 1988. "A study of lithographic performance, mechanical vs. thermodynamic considerations" TAGA Proceedings, p. 339-353.
- Carlick, D. J.
 1984. "Physical-chemical similarities among typical printing ink resins" Am Ink Maker, p 27-31, 34-35, 54-62.
- Chou, S.M., Fadner, T.A. and Bain, L.J.
 1987 "Analyzing Surland's emulsification test in terms of HLB theory" TAGA Proceedings, p. 371-396.
- Defay, R. and Pétré, G.
 1971. "Dynamic surface tension" Surf. Colloid Sci, Vol. 3, p. 27.
- Elliott, W.T.
 1993. "Alkyd resins" in Surface Coatings Vol. 1: "Raw materials and their usage". Prepared by the Oil and Colour Chemist's Association, Australia (Published by Tafe Books, New South Wales University Press Limited, Australia)
- Fleer, G.J., Cohen Stuart, M.A., Scheutjens, J.M.H.M. and Cosgroove, T.
 1993. "Polymers at interfaces" (Published by Chapman & Hall, London, UK)
- Karttunen, A., Virtanen, J. and Lindqvist, U.
 1985. "Measurement of ink and water compatibility in litho offset lithography" Adv. Printing Sci., p 241-263.
- Larsson, L.-O., and Trollsås, P.-O.
 1985. "Emulsification of fountain solution in newsprint offset inks as related to ink chemistry" (in Swedish). TFL rapport 5:25 (Published by Swedish Newsprint Research Centre)
- Owen, D.J.
 1990. "Printing inks for lithography" (Published by SITA Technology, London, UK)
- Rosen, M. J.
 1978. "Surfactants and interfacial phenomena" (Published by J. Wiley & Sons Inc., New York, USA), Chapter 8, p. 224-50.

- Ruckenstein, E. and Krishnan, R.J.
1980. "Effect of electrolytes and mixtures of surfactants on the oil-water interfacial tension and their role in formation of microemulsions" *Colloid and Interface Sci.*, Vol. 76, p. 201-211.
- Tasker, W., Cygan, L., Fang, W., Lachcik, K. and Nakamura, U.
1983. "Water pick-up test for lithographic inks" *TAGA Proceedings*, p. 176-190.
- Wickman, M. and Johansson, K.
1992. "Adsorption of ink binders on paper surfaces" *Proceedings, International Printing and Graphic Arts Conference*, p. 93-101. (TAPPI Press 1992).
- Wickman, M., Beadle, A., Sebring, T., Gurrera I Magrané, L., and Larsson, A.
1994. "The effect of alkyd resin composition on the adsorption on calcium carbonate" *Nordic Pulp Paper Res. J.*, Vol. 9, No 2, p. 94-100.