Pollution-preventing anionic lithographic inks

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Abstract

Lithographic printing presses use aliphatic and aromatic solvents for cleaning various surfaces, which are coated with the ink. The conventional printing inks also contain volatile solvents. During printing and cleaning operations, volatile organic compounds (VOCs) present in the inks and cleaning solvents are lost to the atmosphere by evaporation and these losses are quantifiable and alarmingly high. A new type of ink based on castor oil, which completely eliminates emissions of VOCs, has been developed. Synthesis of resins and the kinetics of washing of the ink, similar to the recently announced pollution-preventing ink [development of a VOC-free lithographic printing system. TAGA Proc., 324], with water at a slightly elevated pH are studied. A correlation between the mass-transfer coefficient characterizing the washing of ink and the experimental process variables is confirmed. New data are also reported on flake-formation dynamics.

Keywords: Lithographic inks; Pollution prevention; Washing kinetics; Diffusion; Mass-transfer coefficient; Cleaning solvents; Printing

1. Introduction

Printing is an inevitable human activity, but it causes pollution too. The pollution mainly comes from the ink and cleaning of the presses which removes the ink that is coated on various surfaces. The ink may contain an aliphatic solvent. Mixtures of aliphatic and aromatic solvents are normally used for cleaning the solvent-based inks. Emissions of volatile organic compounds (VOCs) from these solvents and their discharge in the waste streams are quantifiable [11] and account for as much as 47-50% of all conventionally printed materials in USA [1]. For example, a typical medium size coldset web plant uses 40,000 kg per year of ink, of which 6000 kg is lost as emissions. The plant uses over 10,000 kg per year of cleaning solutions all of which is lost [3]. A typical US newspaper
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$a$</td>
<td>surface area of the ink per volume of wash solution (m$^{-1}$)</td>
</tr>
<tr>
<td>$k$</td>
<td>overall mass-transfer coefficient (m s$^{-1}$)</td>
</tr>
<tr>
<td>$[\text{OH}^-]$</td>
<td>concentration of hydroxide in aqueous phase (kmol m$^{-3}$)</td>
</tr>
<tr>
<td>$[\text{resin}]$</td>
<td>concentration of resin in ink (kmol m$^{-3}$)</td>
</tr>
<tr>
<td>$t$</td>
<td>time (s$^{-1}$)</td>
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Greek letters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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</thead>
<tbody>
<tr>
<td>$\eta$</td>
<td>soap-layer viscosity (kgm$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$\omega$</td>
<td>stirring speed (s$^{-1}$)</td>
</tr>
</tbody>
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Subscripts

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<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
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<tr>
<td>$0$</td>
<td>initial</td>
</tr>
<tr>
<td>$\infty$</td>
<td>at infinite time</td>
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Uses over 100,000 kg per year of ink and emits over 8000 kg of volatile solvents [11]. In USA alone, about 130,000 tons of VOCs are emitted into the atmosphere annually by the printing ink, while in European Union (EU), the printing industries emit approximately 187,000 tons of VOCs per annum (Trenal Ltd., http://www.Trenal.be/).

To overcome the problems of emissions due to solvent-based inks and cleaning of presses, a new type of ink based on vegetable oil has been developed which is biodegradable and environment-friendly. The new ink avoids pollution by eliminating these volatile solvents [3,10,12,14]. It does not contain aliphatic solvents, and hence its use produces virtually no emissions during printing. Also, this ink contains vegetable oil (castor-oil)-based alkyd resins, which are biodegradable and generate no waste-water threat of a secondary pollution during washing of presses. The resin in the ink becomes a good emulsifying agent when it is brought in contact with an aqueous basic wash solution. Because the new printing ink involves no volatile solvent and the presses are cleaned by washing with water at slightly elevated pH, the solvent emissions during printing as well as cleaning cycles are completely eliminated.

An oil, a resin, and other ingredients including pigments/dyes are the main components of the ink. The oil and the resin are the most important components. The oil is a drying oil, a natural product containing triglycerides of fatty acids with unsaturated double bonds. These triglycerides react in the presence of light with oxygen in the air to crosslink, making the ink permanent on paper. The alkyd resin is a non-volatile, synthetic, low molecular weight polyester with pendant aliphatic and carboxylic acid groups. It is similar to the resins made for use in paints. In its acid form, it is hydrophobic. As a sodium salt, however, it is sufficiently hydrophilic to act as an emulsifier. Thus, during printing, the resin is hydrophobic, but during clean-up, it makes the ink emulsifiable in the mildly alkaline aqueous wash solution.

The washing of ink resembles "spontaneous emulsification" in the older sense [6] and leads to formation of flakes. The clues to the new ink's value are not only its strong performance in printing, but also its kinetics of washing. The latter is quantified by measuring...
the rate of neutralisation of the wash solution and thereby obtaining the mass-transfer coefficient as dependent on process variables. Qualitative feel of washing kinetics is obtained by observing the dynamics of flake formation, which may be measured in the sense of an average as discussed later.

In this paper, the synthesis of resins and washing kinetics of the new ink system are discussed. A correlation between the mass-transfer coefficient and the process variables given by Bhaskarwar and Cussler [3] is further validated over wider ranges of process variables and formulations including the synthesis parameters. Experimental data have also been generated for quantifying the dynamics of flake formation.

2. Theory

The new ink exhibits slow spontaneous-emulsification characteristics. The ink turns white gradually when placed in an aqueous base. It retains a smooth surface while only the colour changes. The surface of the ink, however, slowly becomes rough, and then starts breaking into flakes, which are sheared away by the wash solution. The size of these flakes depends upon the composition of the wash solution. The size of the flakes decreases with time, and the detached flakes do not seem to contain any unreacted acidic resin.

Acid-base kinetics are very fast. Washing rates will vary with factors like diffusion coefficients, stirring rates, interfacial areas, and concentrations. It is expected that these rates will be largely independent of the acid-base constants.

The following assumptions seem reasonable:

(a) The detached flakes do not contain any acidic resin.
(b) Ink washing follows three steps:
   (i) Initially, acidic resin in ink reacts with hydroxide, producing soap,
   (ii) Later, the resin or hydroxide diffuses across this soap layer to react further, producing a thicker layer,
   (iii) When the soap layer reaches a critical thickness, it is peeled away by shear.
(c) The time scale of individual flake formation is small compared to the total time of washing.
(d) The overall kinetics are a function of coupled diffusion and chemical reaction.
(e) For low shear used here, the shear stress should be proportional to the first power of the flow.
(f) Reaction is instantaneous and irreversible at the reaction front.
(g) Base and acidic resin never coexist in a differential volume.

The washing rate in terms of mass-transfer coefficient for hydroxide can be given by

\[
\text{d}H^+_{\text{net}} = -k_f c_f (\text{OH}^-) - \text{d} \text{OH}^-/\text{dt}
\]

or

\[
ka = \frac{1}{[\text{OH}^-]_0} \frac{\text{d} \text{OH}^-}{\text{dt}}
\]
where \([\text{OH}^-]_0\) is the hydroxide concentration at time 0, \([\text{OH}^-]\) the hydroxide concentration at time \(t\), \([\text{OH}^-]_\infty\) the hydroxide concentration at infinite time, and \(k_a\) the volumetric mass-transfer coefficient.

More specifically, \(k\) is the mass-transfer coefficient and \(a\) the ink surface area per volume of wash solution (constant in our experiments).

The first important limit for washing of ink occurs when the hydroxide is the limiting reagent, so that \([\text{OH}^-]_\infty\) in Eq. (1) is 0.

In this limit, it is assumed that the reaction between hydroxide and resin occurs at the interface between the soap and the aqueous base [3] and the concentration profiles of resin and base are illustrated in Fig. 1.

In this special case, the growth of the soap layer is controlled by diffusion of resin across the soap layer. Thus,

\[
\text{[Moles acidic resin consumed]} = \text{[resin diffusion]}
\]

For the first limit of excess resin, Bhaskarwar and Cussler [3] have shown that

\[
k_a \approx \frac{[\text{resin}]}{\omega} [\text{OH}^-]_0
\]

where \(\omega\) is the stirring speed, \(\mu\) the soap-layer viscosity, and \([\text{resin}]_0\) the initial concentration of resin in ink.

The second important limit is the converse of the first, assuming that hydroxide is now present in excess, and that resin is the limiting reagent. This is shown in Fig. 2. In this case, \([\text{OH}^-]_\infty\) is not 0. Here, the hydroxide first dissolves in the soap and then diffuses across it to meet the unreacted resin at the soap-ink interface. We have,

\[
\text{[Mole acidic resin consumed]} = \text{[hydroxide diffusion]}
\]
This, for the second limit of excess base, leads to

\[
\frac{k_{\text{ac}}}{k_{\text{resin}}} \left[\text{OH}^-\right]_0
\]

Eqs. (2) and (3) are checked experimentally.

3. Experimental approach

3.1. Synthesis

3.1.1. Materials

Three different types of alkyd resins were synthesised in the laboratory by fatty acid-oil method for developing the no-VOC inks. The materials used for synthesis of resins include castor oil of LR grade, glycerol (glycerine) about 98% purified (E. Merck India Limited), acetic anhydride (E. Merck India Limited), phthalic anhydride of LR grade (Ranbaxy Laboratories Limited, India), and oleic acid (extra pure, LOBA CHEMIE Private Limited, India). The chemical composition and physico-chemical properties of alkyd resins synthesised are reported in Table 1.

3.1.2. Procedure of synthesis of alkyd resins

Alkyd resins were synthesised under controlled conditions in a reaction kettle (temperature: 150-280 °C) with stirring. The chemical compositions of initial batch were: fatty acid oil (25 ml) + polyhydric alcohol (25 ml) + dibasic or monobasic acid (50 ml by volume or 50 g by weight).
Table 1 Properties of alkyd resins synthesised

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Composition for alkyd synthesis</th>
<th>Acid number</th>
<th>Specific gravity (cP)</th>
<th>Viscosity (cP)</th>
<th>Average molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oleic acid + acetic anhydride + glycerol + castor oil</td>
<td>48</td>
<td>0.95</td>
<td>213.74</td>
<td>273.74</td>
</tr>
<tr>
<td>2</td>
<td>Castor oil + glycerol + phthalic anhydride</td>
<td>47</td>
<td>1.14</td>
<td>5701.53</td>
<td>5701.53</td>
</tr>
<tr>
<td>3</td>
<td>Castor oil + glycerol + phthalic anhydride</td>
<td>68</td>
<td>1.31</td>
<td>7333.45</td>
<td>7333.45</td>
</tr>
<tr>
<td>4</td>
<td>Castor oil + glycerol + phthalic anhydride</td>
<td>66</td>
<td>1.31</td>
<td>5826.60</td>
<td>5826.60</td>
</tr>
<tr>
<td>5</td>
<td>Castor oil + glycerol + phthalic anhydride</td>
<td>64</td>
<td>1.31</td>
<td>2397.04</td>
<td>2397.04</td>
</tr>
<tr>
<td>(a)</td>
<td>Oleic acid + glycerol + castor oil</td>
<td>23</td>
<td>0.98</td>
<td>3313.83</td>
<td>3313.83</td>
</tr>
<tr>
<td>(b)</td>
<td>Oleic acid + acetic anhydride + glycerol + castor oil</td>
<td>50</td>
<td>1.09</td>
<td>1382.93</td>
<td>1382.93</td>
</tr>
</tbody>
</table>

V: volume of NaOH Solution; N: normality of NaOH solution = 0.1 N; W: weight of resin in grams.

The reactants were mixed together and heated in the reaction kettle for different times. Reactions were carried out to meet the desired parameters such as acid numbers, specific gravities and viscosities [9].

Different samples of the ink were formulated by dissolving different alkyds, reported in Table 1, in castor oil. Of these, three samples were chosen for a detailed investigation on washability of the new type of ink.

3.2. Washability studies

3.2.1. Experimental set-up

The experimental set-up for carrying out the studies on washability and washing kinetics of alkyd resins, and the ink samples based on their solutions in castor oil are shown in Fig. 3.

The apparatus consists of a 500 ml beaker, a watch glass of 5.6 cm diameter weighing 11.993 g, a magnetic stirrer and a pH electrode attached to a pH meter [3].

3.2.2. Procedure

A weighed quantity of ink (56 mg) was coated at the centre of a dry watch glass over a fixed area of 1.2 cm². The ink contained only a mixture of castor oil and resin without any pigment. The watch glass with liquid-inl coating was placed eccentrically on the magnetic stir bar rotating, in a beaker containing 300 ml of aqueous sodium-hydroxide wash solution.

The magnetic stir bar, imparted a wobbling rotation to the watch glass. pH of wash solution changed because of the reaction between resin and hydroxide and was recorded against time with a pH meter model L1 120 of ELICO (India) make. The beaker was kept in a sealed condition throughout the course of pH measurement, to avoid errors from CO2 absorption from air. This simple apparatus provided low-shear conditions for washing to elucidate the governing diffusional and physico-chemical phenomena.

In the experiments, the variables studied were ink composition (varied from 10 to 100% resin), stirring speed (varied from 10 to 25 rpm), and pH of wash solution (varied from...
Fig. 3. Experimental set-up for washability and washing kinetics of alkyd resin-based inks under low-shear conditions (watch glass).

7.7-13). The temperature of the wash solution in contact with the ink was recorded over a period ranging from 5 to 60 min. The pH was recorded at 1-min interval for the first 5-10 min, and thereafter at 2.5- and 10-min intervals.

The first and complete flakes formation times were also recorded. The time of appearance of the first visible flake in the wash solution after being sheared from the ink should be a measure of the ease of washing of ink. The complete flakes formation time corresponds to the completion of washing of ink from the watch glass and may be important in practice.

4. Results and discussion

Alkyd resins were synthesised under controlled conditions by adopting fatty acid-oil method. Reactions were carried out to meet the desired parameters such as acid numbers, specific gravities, viscosities and molecular weights. Miscibility studies of these resins in various oils were also carried out. It is found that the resins synthesised in the laboratory are quite stable with respect to their properties over the period of 3-4 years. Even the miscibility study showed the same properties of the resin-oil solutions over the period of time.

The advantages of these resins synthesised in the laboratory over commercially available resins are that they do not change their physico-chemical properties and no gelation occurs over the keeping period. The basic problem with the commercially available resins was that
alkyd resins of the same manufacturer, of same composition, but from different batches showed different physico-chemical properties and also changed their properties over time, i.e. the commercially available resins were not stable. Three different resin samples, out of the eight samples synthesised in the laboratory, were chosen for the washing kinetics experiments. These resins were chosen based on their acid numbers, specific gravities, viscosities and chemical compositions, i.e. the chemistry of resins, so as to cover the widest ranges of parameters possible and to entail a generality for the findings.

The pH-time data obtained from the above experiments are converted into concentration-time data. The logarithms of dimensionless concentrations are plotted against time to obtain the mass-transfer coefficient, i.e. by fitting Eq. (1) to the data. The washing kinetics of the new ink systems discussed here and earlier by Bhaskarwar and Cussler [3] are notoriously difficult to describe. The conventional methods of correlating the mass-transfer coefficients to the fundamental physical properties of the system, as represented for example, by the correlation by Calderbank and Moo-Young [15], fail to account for the dependency of the mass-transfer coefficient on the process variables.

The mass-transfer coefficients, $ka$, for the washing of the new type of volatile solvent-free lithographic ink are plotted against a group of process variables in Figs. 4-7, depicting linear correlations with regression coefficients of 0.6048, 0.8127, 0.2217 and 0.8926, respectively. The regression coefficient of 0.2217 is too low but the experimental data do show a linear correlation. This is perhaps because the chemistry of this resin (i.e. sample no. 6, Table 1) is different from that of the other two resin samples where "anhydride" is present in the raw material. These figures strongly support the correlation suggested by Eq. (2). Fig. 4 presents together all the data obtained for the ink samples based on resins numbered 6, 7 and 8 and the data from the earlier research [3,7]. Bhaskarwar and Cussler [3] had used three types of resins, namely McWhorter Technologies’ alkyd with an acid number of 63, the phenolic resin (Filtrez 681, 80,000 Da, AKZO with an acid number of 30), and the fumaric resin (Unirez 8100, Union Camp, with an acid number of 98) commercially available in USA. Nair and Bhaskarwar [10] had used alkyd resin (Dura Chemicals, Mumbai) with an acid number of 14, commercially available in Indian market. The Figs. 5-7 illustrate separately the data for ink samples based on individual resins numbered 8, 6 and 7, respectively.

These correlations confirm the hypotheses that the diffusion varies inversely with the viscosity, and that the soap removal varies directly with shear. Resin diffusion across the growing soap layer is the key to the kinetics of washing with a dilute base. These results (Fig. 4) support the assumption that the process is limited by diffusion of acidic resin.

Thus, the predictions of Eq. (2) are verified by experiments done for the excess of the three different types of resin (Figs. 5-7). For excess resin, the mass-transfer coefficient increases with [resin]/[OH~]. These results are characteristic of mass-transfer with an instantaneous chemical reaction [2,3,7].

The new ink avoids the need for VOC-based solvents by using a resin, which has pendant carboxylic acid groups. These acid groups mean that in the basic form, the resin acts like a high molecular weight soap. The kinetics of emulsification given in this paper are limited by diffusion in this soap layer. At a slightly elevated pH, the diffusion is of the unreacted resin through a layer of soap. Washing can therefore be effected simply through the use of mildly alkaline aqueous solutions.
Fig. 4. Testing of Eq. (2) for a resin-based ink (resins numbered 6, 7 and 8 in Table 1).
Fig. 5. Testing of Eq. (2) for a resin-based ink (resin numbered 8 in Table 1).
The resin’s function is not basically an altered solubility. An altered solubility would result in a stable homogeneous solution and would depend on solubilisation in micelles and other nanometre-sized aggregates. Although some micelles may exist, their equilibrium thermodynamic properties are not responsible for the ink’s improved performance. The emulsification kinetics and not the thermodynamics of solubilisation is important here.

The experiments on kinetics above suggest how the ink’s performance might be improved through the diffusion coefficient. The diffusion coefficient should be inversely proportional to the viscosity under normal conditions. Such an inverse relation was assumed in developing the successful correlation [3]. Diffusion depends on the short-range molecular order in the ink, perhaps over the size of a few molecules. Viscosity often depends on a much longer range order. Thus, diffusion and viscosity are not always closely related [3,4]. It might be possible to obtain a larger diffusivity without adversely affecting the viscosity, the flow and surface properties of the ink.

Fig. 8 shows the experimental data corresponding to inks based on resins numbered 6, 7 and 8. It shows a decrease in log(ka) with an increase in log{[r_e sin(θ_e)]/[OH−_o]}.

The data of Bhaskarwar and Cussler [3] for oleic acid show just the reverse trend. ka is directly proportional to ([&gt;OH−_o]/[x(resin)_o])^a, where a = -0.0951 for inks based on
The resins synthesised in the present investigation reveal a much smaller negative power ($a = -0.0951$) than for the excess-base situation. An increase in the initial concentration of hydroxide ions hinders the washing process. The reaction in this case takes place at the soap-resin interface and the hydroxide ions have to diffuse through the soap layer to react with the resin. This indicates that a very high hydroxide-ions’ concentration in excess-base situation offers no real advantage in washing, but rather the disadvantage of more severe corrosive conditions. In the oleic acid model system of Bhaskarwar and Cussler [3], with much lower viscosities, the oleic acid lenses do not hold layers of sodium oleate, which could offer a high resistance like the resins which we have synthesised here. The surface resistance is thus minimal in the oleic acid system. This factor together with the higher hydroxide solubility in the oleate soap compared with that in the polymeric soap, resulting from the synthesised resins, might account for the different findings from these two investigations.

The experimental data on variation of the first-flake formation and complete-flakes formation times with resin concentration in the ink were recorded. These have not been reported by any researcher so far. These flake-formation times’ data are plotted in Figs. 9-11 for constant stirring speed and initial pH of the wash solution. Each point in these figures corresponds to an average of four to six measurements of the flake formation times.
Fig. 8. Testing of Eq. (3) for a resin-based ink (resins numbered 6, 7 and 8 in Table 1).
Fig. 9. Flake-formation time as a function of resin concentration in ink (resin numbered 8 in Table 1).
Fig. 10. Flake-formation time as a function of resin concentration in ink (resin numbered 6 in Table 1).

Figs. 9-11 illustrate that both first-flake and complete-flakes formation times show oscillations with resin concentration. Furthermore, the minima in both of these times occur at identical concentrations of the resin in the ink, i.e. at 30, 55 and 70% for resin numbered 8 (2856 cP) and at 30, 45 and 80% for resin numbered 7 (159 cP). At concentration of 30% for resin numbered 6 (332 cP), the times required for both first-flake formation and complete-flakes formation are minimum.

The first-flake formation times corresponding to the minima for resin numbered 8 at concentrations of 30, 55, and 70% are 0.77, 0.5 and 0.73 min, respectively, and the minima for complete-flakes formation times at concentrations of 55 and 70% are 2.56 and 3.05 min, respectively. Similarly, for resin numbered 7 at concentrations of 30,45 and 80%, the corresponding minimum first-flake formation times are 0.067,0.092 and 0.092 min, respectively, and the corresponding complete-flakes formation times are 0.40, 0.227 and 0.202 min, respectively. For resin numbered 6, the corresponding minimum first-flake formation times for resin concentrations of 30, 55 and 70% are 0.05, 0.12 and 0.10 min, respectively. The corresponding complete-flakes formation times are 0.17, 5.29 and 3.7 min, respectively.

The agreement in the resin concentrations corresponding to the minima in the two kinds of flake-formation times appears to be too good to be fortuitous.

Similar trends are thus seen in Figs. 9 and 11, for inks based on resins of higher acid numbers (44 and 58). Fig. 10, for an ink containing a lower acid number (23) resin, however,
shows a somewhat different behaviour. The resin concentrations for minima in first-flake formation times and complete-flakes formation times nevertheless always match, for a given resin.

Apparently small differences in times of flake formation may be still very important in printing applications involving repetitive cleaning, like in printing of personalised cheques. The first-flake formation time and the complete-flakes formation time may be of help in establishing the optimum resin concentration in ink, and perhaps also in developing a better combination of ink-wash compositions.

Theoretical predictions of the flake-formation dynamics may also pose interesting challenges for further work.

5. Conclusions

Emissions of volatile organic compounds during printing and cleaning of the printing presses, cause significant air pollution. The conventional ink may contain an aliphatic solvent. Mixtures of aliphatic and aromatic solvents are commonly used for cleaning the conventional inks. The new type of ink discussed in this paper avoids pollution by eliminating these volatile solvents. It becomes a good emulsifying agent when brought in contact
with an aqueous basic wash solution at slightly elevated pH. The new ink system contains no volatile organic compounds, hence the solvent emissions during the printing/cleaning cycles are completely eliminated. The correlation between the mass-transfer coefficient characterizing the washing and the process variables is confirmed. The variations of the first-flake formation and complete-flakes formation times with resin concentration in the ink have also been reported. This investigation would be useful in arriving at the optimum resin concentration in ink, and also in developing better ink-wash compositions.

For further reading

The following references may also be of interest to the readers: [5,8,13].

References