

# THE DRYING MECHANISMS OF WATER-BORNE PRINTING INKS

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**Abstract:** The aim of the study was to gain a deeper understanding of the drying mechanism of water-borne printing inks. The study was divided into two parts. In the first part, the evaporation of water from resin emulsions was investigated. The second part of the study concentrated on the absorption and spreading of resin and water in an uncoated paper structure. It was found that the molecular weight and composition of the resin had an impact on the drying rate. It was also found that confocal microscopy offers a potential to understand more about the drying mechanisms within the paper.

## Introduction:

### The Ink System

A printing ink consists of at least four components: pigments, resin, solvent and additives. The objective of the pigments is to provide the colour of the ink. The resin aims to bind the pigment onto the substrate. The solvent lowers the viscosity of the ink system in order to facilitate ink transfer. The additives are added in order to improve certain properties of the ink for example light stability, drying rate, and film flexibility.

A pigment consists of an organic or inorganic insoluble substance which has a particle size of approximately 0.1  $\mu\text{m}$ . Carbon black has particle sizes down to 0.02  $\mu\text{m}$ . In water-borne printing inks, the resin consists mainly of water-insoluble styrene- or acrylate-based polymers. Since the resin is not water-soluble, a aqueous emulsion is produced where the polymers are emulsified with an emulsification agent. The resin particle sizes are larger than 1  $\mu\text{m}$ . The pigment is dispersed in the aqueous phase. Co-solvents can be present in the resin phase in order to reduce the viscosity and the softening point of the polymers. The ink system is illustrated in fig.1.

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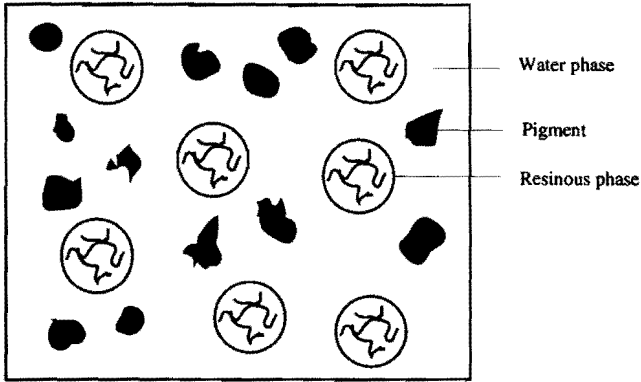


Fig.1. The water-borne printing ink system.

### A Model for the Drying Mechanism

The primary feature of the drying process in these water-borne inks is a removal of water. The evaporation of water starts during the ink transfer process. After the ink is printed on the substrate, further evaporation occurs. The resin stays on the surface of the paper, but the water departs from the film by two mechanisms, either by evaporation to the surroundings or by absorption into the substrate. The water absorbs in the pores as well as diffuses into the fibers and causes them swell. This swelling causes dimensional changes in the paper (*Bristow, 1971*). With time, the absorbed part of the water evaporates to the surroundings. It is hard to determine when the film is completely dried. Water can be encapsulated in the film due to vitrification of the polymer and the film can be dry on the film surface but not inside the film. The course of events is illustrated in fig.2

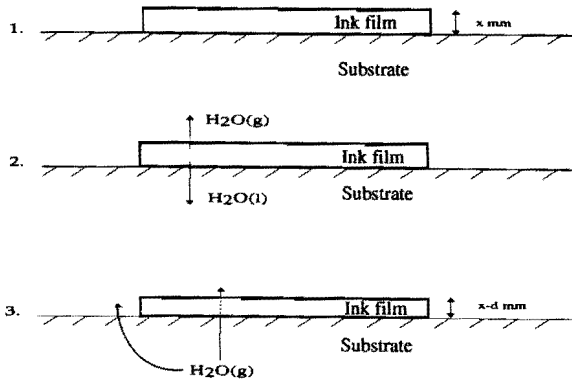


Fig.2. A model for the drying mechanism.

The efficiency and speed of the evaporation process in step 2 is determined by three factors (*Williams, 1992*). The first factor is the rate of evaporation of the solvent. The second factor is the chemical and physical interaction between the solvent and the other three components in the ink affecting the solvent release. The third factor is the rate of removal of the evaporated solvent from the surface of the film. The drying of the film is also affected by the absorption properties of the substrate (*Aspler et al., 1992*).

During and after drying, it is mainly the resin particles and the pigments which remain on the surface of the substrate. The pigments are at first completely wetted by the resin, and the resin and the pigments then form a continuous film. Film formation starts when the fraction of the solids in the ink starts to increase. The surface tension and the aqueous capillary forces tend to minimise the surface area of the system. The space between the resin particles decreases and finally interparticle contact occurs. The film formation is completed when the particles have coalesced (*Miller, 1968*). The film formation is divided into three stages: 1) evaporation of water; 2) coalescence of resin particles and wetting of pigments; and 3) interdiffusion of resin molecules (*Vanderhoff, 1992*). The process is illustrated in fig.3. The penetration of resin into the fiber structure is very small. Due to the cohesive forces, the resin particles stick together and dry in a close-packed hexagonal cell system. The pattern is shown in fig.3

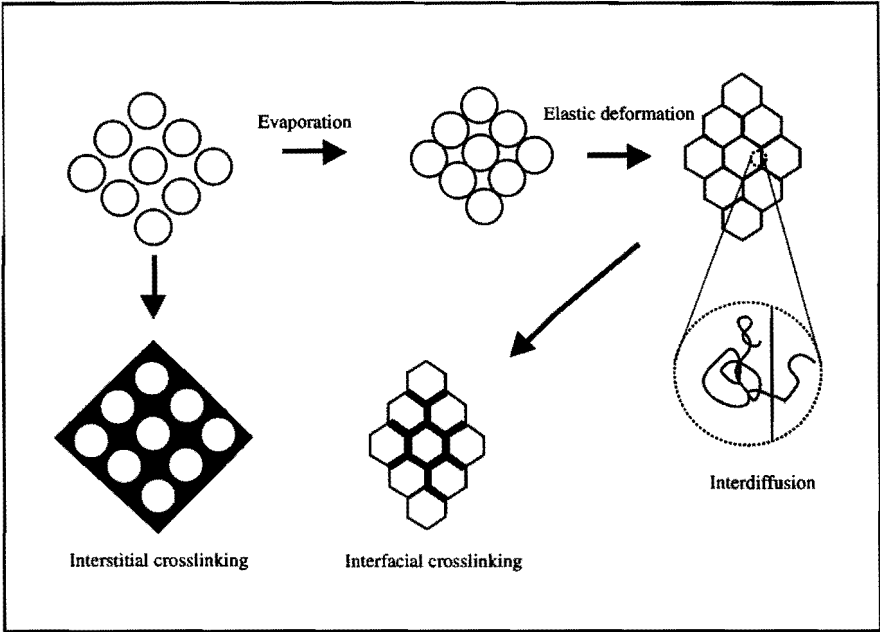


Fig.3. The different stages in film formation of water-borne resins (*Vanderhoff, 1992*)

## Aim of the Study

The first aim of the study was to distinguish between the amount of water evaporated to air and the water initially absorbed by the paper. The second aim was to study the spreading of water in uncoated paper

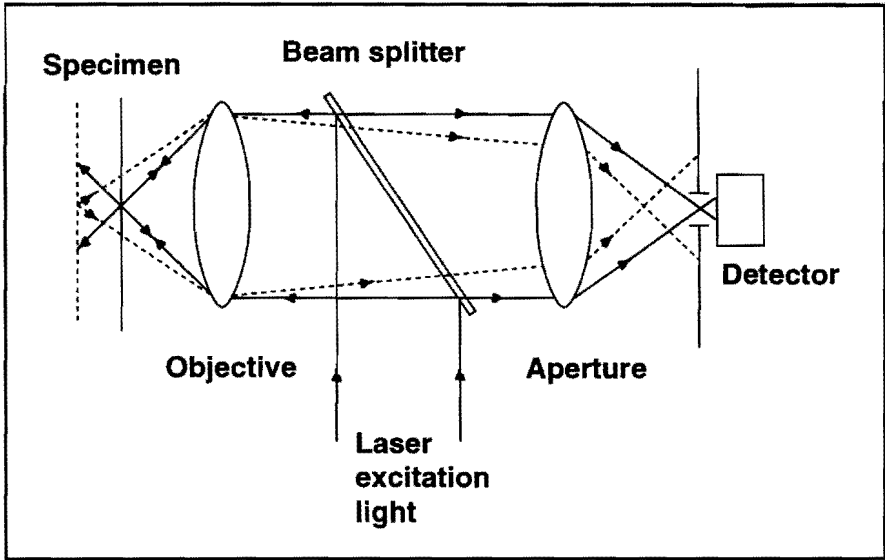
## Materials and Method:

Four different water-borne resins commonly used in the formulation of flexographic inks were chosen. Instead of choosing a complete ink, only the emulsions were studied in order to reduce the number of interfering factors. A solvent-based resin was chosen as a reference. The resins were obtained from Casco Nobel Inks. The resin compositions were characterised by infrared spectroscopy. The continuous phase in the emulsion was analysed in a head-space gas chromatograph connected to a mass spectrometer. The resin droplet size in the emulsion was determined in a Master Sizer. The dry weight was determined in a thermogravimetric analyser, at a scanning rate of 10°C /min from 40°C to 200°C. The shear viscosity was determined in a Contraves Reomat 115, device no MS-0 115, at different shear rates at 23 °C. The shear stress was measured and the viscosity was calculated.

The drying of the resin emulsions was studied using a digital balance. 0.04g of the resin emulsion was evenly spread out on a glass plate measuring 26×76 mm. The mass corresponds approximately to a wet film thickness of 20µm. The glass plate was placed in the balance and the weight was recorded in a computer 5 times per second over a period 1000 seconds. The experiment was carried out at 23°C. The balance had closed doors and no circulation of air was allowed. In a second experiment, a paper was placed on the glass plate, with the same dimensions, and 0.04g resin emulsion was allowed to dry on the paper under the same conditions as in the first experiment. The paper chosen was a Multi Fine uncoated copy paper from STORA Papyrus. The paper had PCC as a filler and had a pH of 9.4.

The spreading of water in paper structures was studied using confocal fluorescence microscopy. In this technique, a focussed laser beam is used to excite fluorescent molecules in the paper structure. The beam is scanned across the specimen and the emitted fluorescence is recorded using the confocal technique. Since the technique has pronounced depth discrimination it is possible to record thin optical sections without physically cutting it (*Hedlund et al., 1994*). The discrimination in the Z-direction is the main advantage of confocal microscopy over conventional microscopy (*Mangin et al., 1993*). Fig.4 shows a schematic diagram of the ray path in a confocal microscope. The water-phase in the resin emulsion was doped with rhodamine dye. Half-tone areas were printed with the doped emulsion on Multi Fine paper using an IGT Reprint AIC2-5 Printability Tester equipped with a flexographic device. The diameter of the screen dots on the printing form measured 0.3 mm. The samples were

scanned at a laser beam wavelength of 488nm. The scanned areas were  $1 \times 1$  mm and  $400 \times 400$   $\mu\text{m}$ .



**Fig.4.** Schematic diagram of the ray path in a confocal laser microscope. The detector strongly discriminates light from out-of-focus specimen regimes (*Carlsson et al., 1991*).

**Table 1. Table of properties of the resin and the emulsion**

<b>Resin emulsion</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Composition	styrene	styrene/ ester	styrene	styrene/ amine
Molecular weight of resin				
Mn [g/mole]	36,000	76,000	34,000	38,000
Mw [g/mole]	73,000	204,000	123,000	86,000
Diameter [ $\mu\text{m}$ ]				
d(0.1)	0.18	0.23	1.45	0.17
d(0.5)	0.37	7.09	18.15	0.33
d(0.9)	17	17.19	73.19	3.04
Density( $\text{g}/\text{cm}^3$ ) of emulsion	1.04	1.03	1.04	1.03
weight% resin in emulsion	45.55	46.66	45.50	50.52
Viscosity (mPas)				
Shear rate ( $\text{s}^{-1}$ )				
24.2	-	796	-	-
34.7	-	-	331	-
49.6	218	734	-	-
71.0	-	716	-	-
101.7	205	-	295	286
145.5	-	-	-	260
209.0	187	-	260	233
pH	7.5	7.5	7.5	7.5
Tg [ $^{\circ}\text{C}$ ]	110	-	100	11

## Results and Discussion:

### Drying rates of resin emulsions

The samples were put on the pan of an analytical balance and the weight loss was determined. The amount of solid phase was determined by TGA. The measurements were made over a period of 1000 s. After application of the emulsion to the slide, a period of about 3s elapsed during which the slide was placed in the balance and before measurement could be made, see fig.5. This time was however considered to be negligible in relation to the total evaporation time and the time when it was possible to begin measurement was taken as the zero point on the time scale.

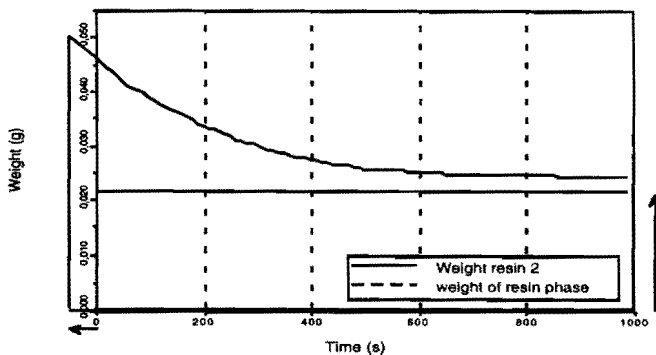


Fig. 5. The curve represents the weight loss of resin 2 dried on a glass surface. The arrow to the left represents the elapsed time before measurement started. The arrow to the right shows the weight of the solid phase.

From a knowledge of the weight of the solid phase, it was possible to calculate the weight of the water phase in the sample and this was used to normalise the curves to show the proportion of the total water evaporated and thus permit a direct comparison of the curves obtained.

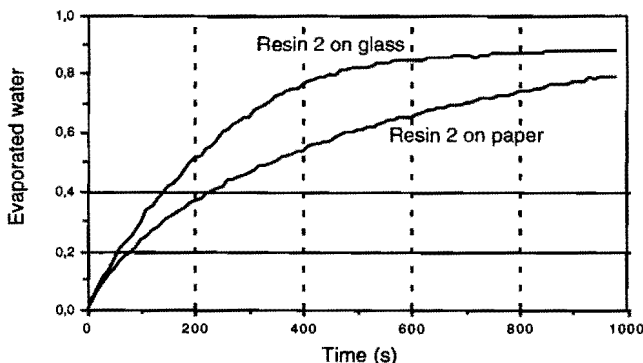


Fig.6. The graph shows resin emulsion 2 drying on glass and on paper.

In fig. 6, the difference in the amount lost by evaporation during drying on an absorbing and non-absorbing substrate is seen. However, the weight measured during drying on a paper substrate is composed of two components, namely the water left in the film and the water absorbed by the paper. This assumption is therefore here made that the difference between the two curves represents the water absorbed by the paper. Fig. 7, shows the curves representing the evaporation of water to air and the absorption to paper during the drying on paper.

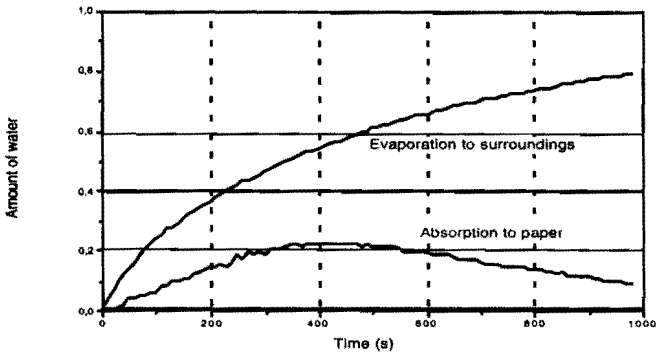


Fig. 7. The plot shows evaporation to air and the absorption to paper at every moment.

It is interesting to see how this treatment of the data leads to a curve which indicates that the water is absorbed into the paper and then released by evaporation. In fig. 8, the drying speeds for a quick drying resin 1 and resin 4 used to provide high gloss on the printed matter are compared. The evaporation to the surroundings is approximately the same for both. However, when dried on paper, the evaporation rates and the behaviour attributed to sorption into the paper differ remarkably. Since the measurements have been made on the same paper and under the same conditions, the difference must lie in the interaction between the resin and the paper, and in the degree to which the resin restrains sorption into the paper.

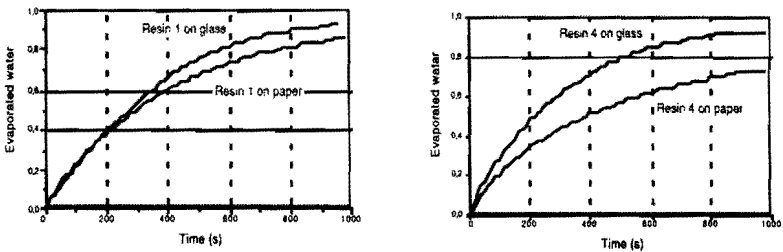


Fig. 8 (a) and (b). Plot of evaporated water versus time for resin 1 and 4.

The amount of water present in the paper at each moment is much less for resin 1 than for resin 4, as seen in fig. 9. Within the scope of this preliminary survey it has not been possible to study all the contributing factors, but the difference in behaviour of resin 1 and resin 4 on the same paper indicates the potential of this simple approach to reveal essential differences in the behaviour of different resins.



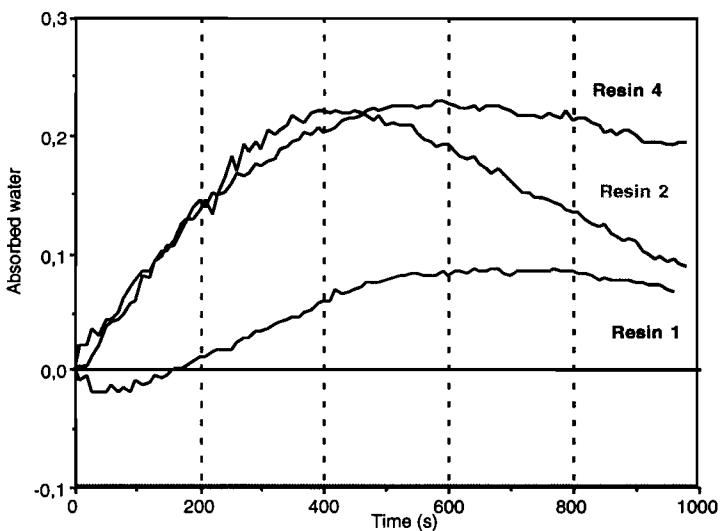


Fig. 9. A comparison of the amount of absorbed water for resins 1, 2 and 4

Factors such as the resin composition and the molecular weight apparently have a tremendous importance for the way the emulsion dries. The softening point of the polymers presumably has an impact especially on the film formation. Here it is seen that resin 4, that forms a film easily since the  $T_g$  is 11 °C, allows the water to be absorbed but later prevents it from being evaporated, whereas resin 1, that has the property of quick drying, allows both easy absorption and easy evaporation allows the water to evaporate, but hinders its absorption and little water is absorbed.

No differences in drying speeds on absorbing and non-absorbing substrates are seen in the case of solvent-based resins, as shown in fig.10. The tendency for solvent to be absorbed by the paper is apparently very small since the evaporation predominates over the absorption mechanism in both cases.

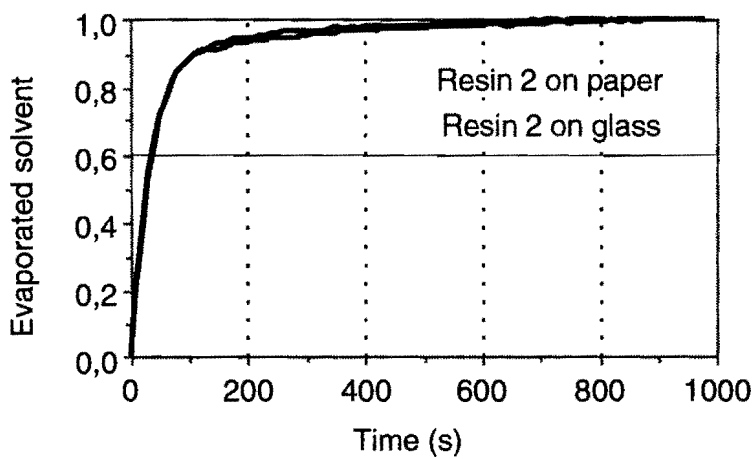


Fig.10. Evaporation of solvent from the solvent-based resin as a function of time

## Studies in confocal fluorescence scanning microscope

It was seen in the confocal microscope that the tendency of the water to diffuse in the xy-plane of the paper was much less than the tendency to spread in the z-direction. However this statement must be handled with caution since the tendency of the fluoresceine and rhodamine to spread in the same manner as the water has not been fully clarified. By simply dipping a sheet of paper vertically in a beaker with fluorescent substance dissolved in water it was evident that the absorption of water in the x-direction was quicker than for both fluoresceine and rhodamine.

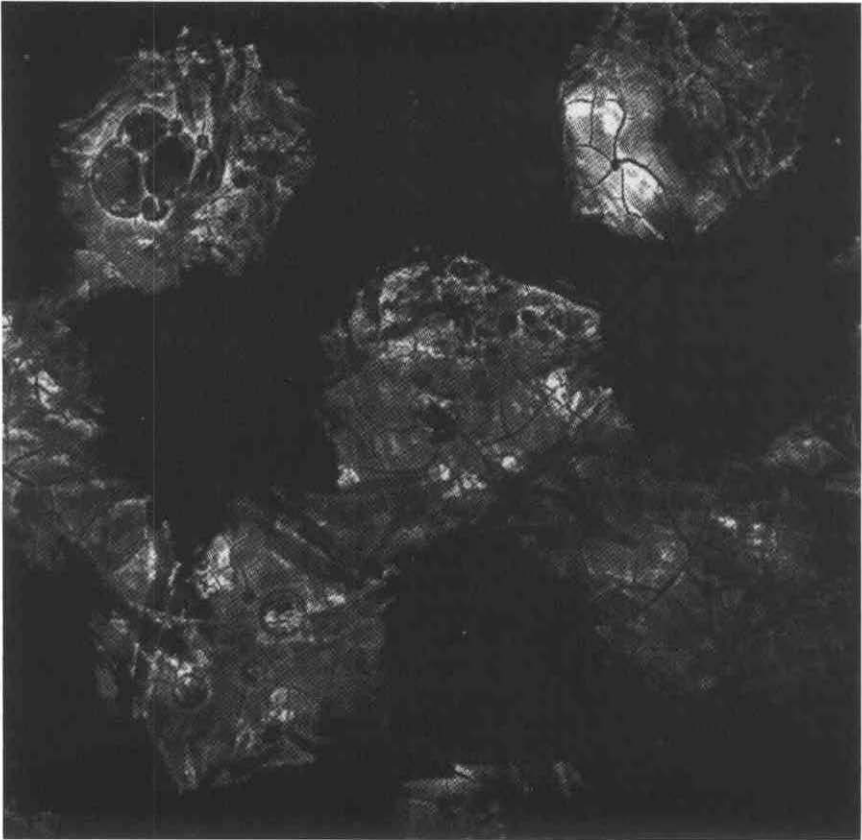


Fig. 11. Screen dots of approximately 300 microns in diameter. The circular areas at the top left corner are most probably air bubbles separated by a water film.

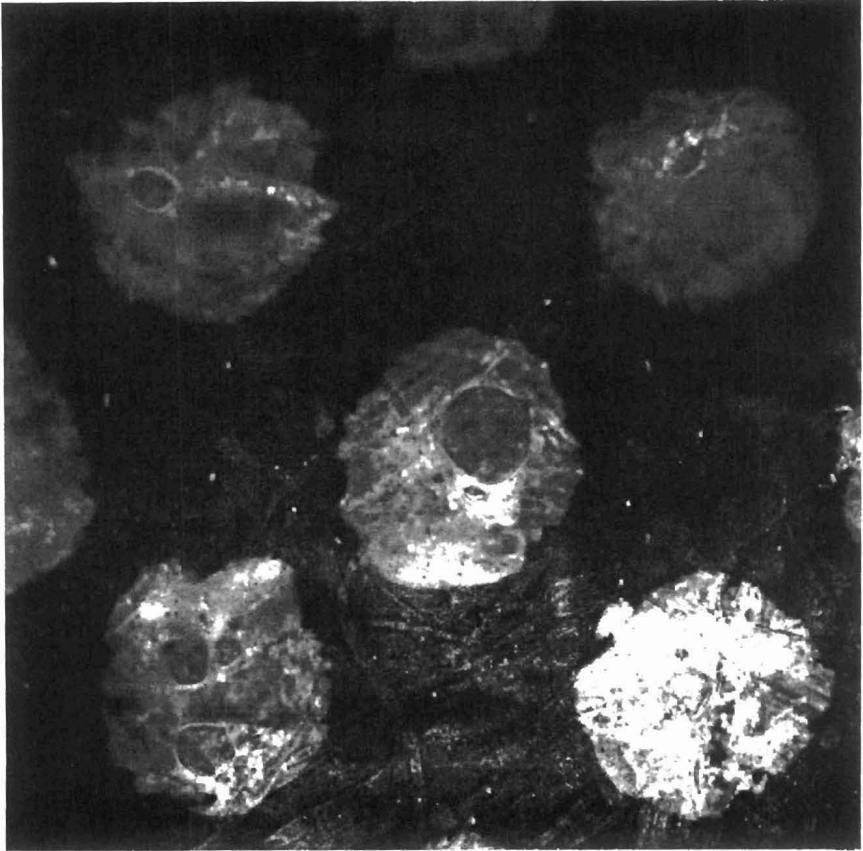


Fig. 12. Image showing five screen dots. The resin emulsion was mixed with a small amount of blue water-borne flexo ink. The high intensity white areas indicate high concentration of fluorescent molecules.

A tendency for the water to follow the fiber orientation was observed. The fibers had some autofluorescence at the scanned wavelength, as can be seen in fig.12, where the fibers around the printed dots are seen clearly.

In fig.13, one screen dot shows five dark circular areas from which cracks are initiated or terminated. These areas can be of two kinds. Either they are composed of large resin particles or they are air bubbles. This particular resin emulsion has the property of quick-drying. The film has problems in forming a continuous layer probably since the shrinkage is large during drying and the cohesive forces are not strong enough to keep the film together. The evaporation to air was relatively rapid and the film formed could perhaps not adjust to the dimensional changes in the paper during the absorption of water.

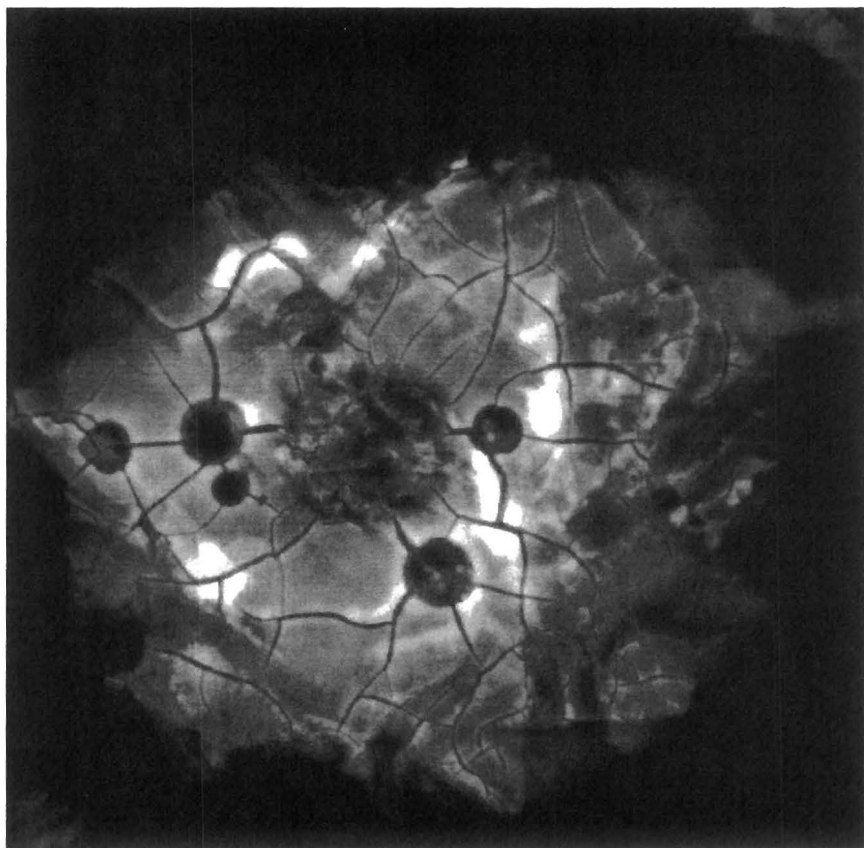


Fig.13. Image of a printed screen dot. Real size is  $400 \times 400 \mu\text{m}$ . The image is composed of 80 images scanned through the paper in the z-direction

### **Conclusion:**

This paper has dealt with the drying mechanisms of water-borne printing inks. The method used has been shown to have a potential in revealing essential differences in the behaviour of different resins. Both the composition and the molecular weight distribution seem to have an impact on the drying rate of emulsions containing water-borne resins. It has also been shown that confocal fluorescence microscopy offers a possibility of obtaining further information relating to the drying mechanisms within the paper structure.

## Commentary for future work

In order to understand the drying mechanisms of this type of printing inks more thoroughly, the next step is to investigate the contribution of pigments, fillers and additives during drying.

It would also be of interest to use a well-defined porous substrate instead of paper to be able to study more clearly the absorption and penetration mechanisms of water from a water-borne printing ink. Other model substrates with, for example, defined fiber orientation and surface energies are also of interest.

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