THE NATURE OF INK/SUBSTRATE INTERACTIONS USING CRYOFRACTURING AND SCANNING ELECTRON MICROSCOPY

Robert W. Bassemir* and Mark A. Featherstone*

Abstract

Direct observation of ink/substrate interaction has always been extremely difficult due to the thin ink films and the thermoplastic nature of them. This gave rise to smearing and artifacts when microtome cross sections were attempted. A technique using quick freezing and cryogenic fracturing has been devised which produces clean sections of many different types of ink and substrates. The sections can even be made on undried inks by holding the specimen at -200°C while in the chamber of an SEM. This allows direct observation of ink film thickness, composition, and penetration into the substrate.

Introduction

For many years printing ink scientists have wanted to view actual printed ink films in order to directly observe the uniformity, thickness and any interactions with the substrate on which the films are printed. The only practical way to do this in the past has been by making a microtome section of prints. However, inevitably smearing of the ink film and distortion of the substrate tended to occur unless the print was embedded in some material which would hold the substrate and film rigid. Even then, some smearing of the film usually was present, preventing good observations of ink film details. In addition, the embedding medium could distort either the ink film or the substrate due to swelling or partial solution of the ink film in the medium. This was particularly true with inks which were formulated with polymers

* SunChemical Corporation

that were relatively low in molecular weight and more prone to such effects.

The advent of widespread use of cryogenic microtome sectioning in the biological and medical sciences provided a methodology which could be readily adapted to this long existing problem of the ink scientist. The use of the fracturing technique obviates the need for embedment and provides a relatively artifact free specimen for direct observation in the scanning electron microscope, which also reveals a 3 dimensional aspect of the film that sectioning cannot.

Discussion

As an example of the problems encountered with microtome sectioning, Figures 1 and 2 illustrate sections that have been done using microtomy and cryofracturing. It is evident that the true nature and thickness of the coating film has been obscured by smearing due to the knife blade.

Prints on Paper and Board:

The technique that is used for sectioning prints on flexible, porous substrates such as paper is slightly unusual in that it involves the use of a volatile organic solvent to impregnate the paper before the specimen is frozen. The choice of this solvent is critical since it must not dissolve or swell either the ink film or the substrate and yet must be sufficiently volatile so that it is easily evaporated without the use of excessive heat. In addition, this solvent must form a friable solid at temperatures produced with liquid nitrogen (LN2). The use of this technique is essential if one is to obtain clean fractures in fibrous substrates which tend to remain flexible, even at -200°C. We have found that pure Pentane liquid is a suitable penetrant for most printed samples. Low boiling polar solvents may be useful for some news inks, where the ink oil may tend to dissolve in pentane.

Another critical factor is the rate at which the solvent saturated specimen is frozen. As is well known, if macrocrystallization occurs during a slow freezing process, a distending effect can be

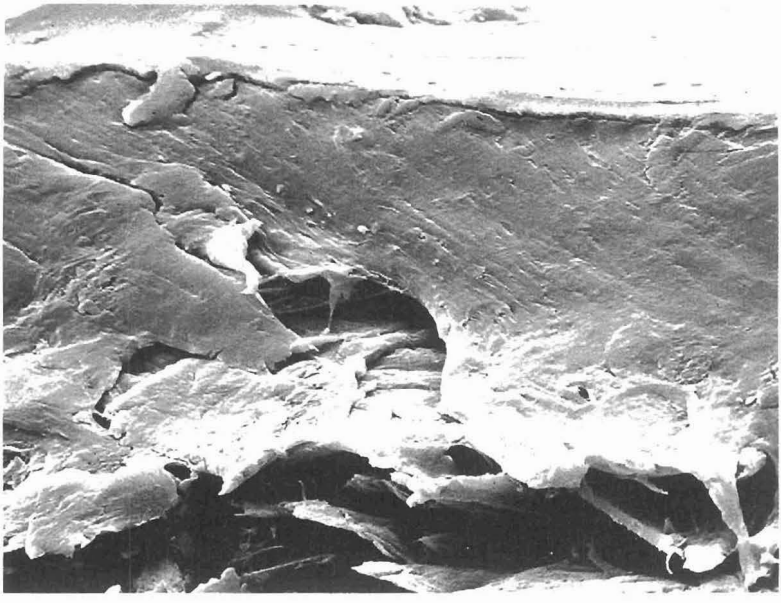


FIG. 1 - EXTRUDED POLY ON PAPER BOARD
MICROTOME SECTION - 10K X

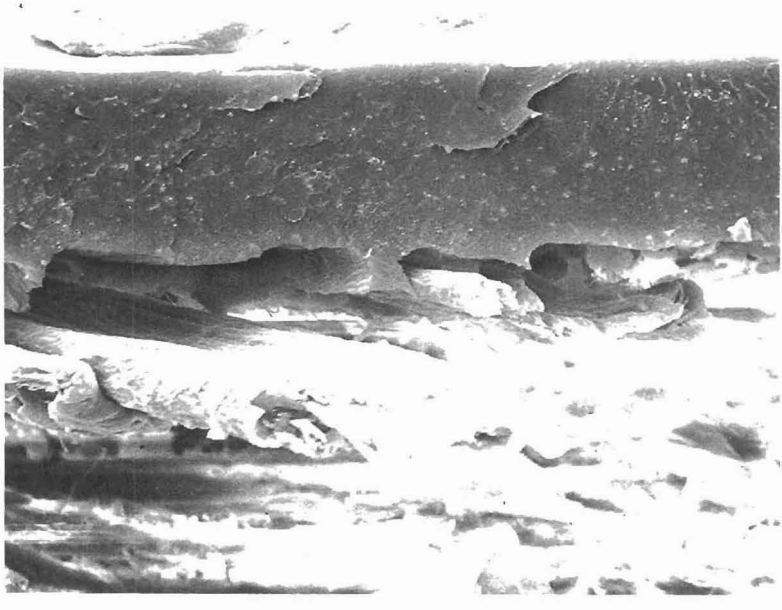
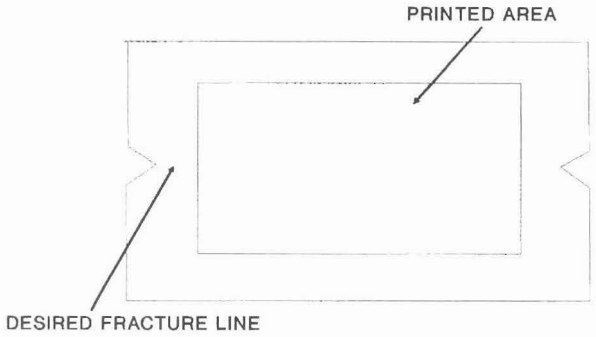


FIG. 2 - EXTRUDED POLY ON PAPER BOARD
CRYOFRACTURE - 10K X

produced which will distort the structure of the porous substrate and produce possible artifacts. A way of accomplishing extremely rapid freezing is by the use of LN2 slush. This mixture of liquid and solid nitrogen is produced by evaporating a portion of the LN2 in a Dewar flask by application of a vacuum to it for a short period of time. This causes the LN2 to boil (boiling point = -195.8 °C) and the heat thus removed cools it to the freezing point (-210°C). Thus some of the liquid is converted to solid and the mass takes on a slushy texture. When a specimen is plunged quickly into this slush, the solid phase will absorb heat from the specimen and be converted to a liquid rather than the liquid absorbing heat and being converted to a vapor. Thus, the utilization of the latent heat of fusion of the solid nitrogen phase precludes vapor formation which would slow down heat transfer from the specimen enormously, leading to macrocrystal formation.

Print samples are best prepared by cutting out a section of the area desired and cutting two small "V" shaped notches on both sides of the chosen line of fracture. This gives a weak starting point so that the fracture will occur in the desired location. A schematic of such a specimen is shown in Figure 3.

FIG.3 TYPICAL PRINT FRACTURE SPECIMEN



In practice the specimen is grasped on either side of one end of the fracture line with pressure locking forceps, such as the hemostats used in

surgical procedures, is then plunged quickly into a pool of LN2 slush and held beneath the surface for several seconds until it reaches equilibrium. The forceps are then pulled apart quickly to produce the fracture while still immersed. The fractured specimen is removed from the LN2 and allowed to reach room temperature by itself. During this period the pentane will evaporate. If humidity is high, this step should be carried out in a desiccator. The sample can then be mounted in a vertical clamping stage, coated with gold and viewed in a SEM in the normal manner.

Liquid Specimens:

In the case of inks and emulsions, an auxiliary piece of equipment which is attached to the SEM is required. See Fig. 4. This is necessary in order to keep the sample frozen at all times, even while examining it in the microscope chamber. The technique used here is to freeze the liquid sample inside a miniature hollow rivet which is stacked in two sections. After freezing in LN2 slush, the

FIG. 4 - SEM EQUIPPED WITH CRYOFRACTURE ATTACHMENT FOR LIQUID SAMPLES

rivet is transferred through a vacuum lock into the cold chamber where the top section of the rivet is broken off producing the fractured surface of the frozen fluid. It then can be coated with gold while at -190 to -200°C and transferred through a second vacuum lock into the actual microscope specimen chamber. The stage of the SEM is also cooled to -190 to -200°C using LN2 vapor so that the sample remains solid while being examined and photographed. This cryoscopic attachment [1] allows handling of both aqueous and non-aqueous liquids at these very low temperatures with a minimum of difficulty.

Applications

Some interesting applications of this technique are the examination of emulsions of fountain solution in lithographic ink to determine the quality and particle size of the dispersed phase. Figures 5 through 8 show freeze fractured litho ink emulsions. The difference in sizes of the droplets of water in the internal phase is obvious in comparing Figure 5 with Figure 6. The poor emulsion has much larger droplets and the distribution of the sizes is much wider than in the good emulsion of Figure 6. These photos also illustrate a technique for identifying the presence of water by subliming the water from the fractured interface. This is done by warming the stage electrically to -90°C and watching the water leave the film. This produces the round voids which are present in the photographs. In Figures 7 and 8, the sublimation technique was not used and here one can see some droplets of water which remained with the fractured half, while other holes are noticed where the droplets of water were in the upper part of the fracture which was discarded. The question of whether the droplet of internal phase will remain with one side of the fractured specimen or the other, depends on the relative adhesion of the droplets and in most fractures you will see a division of the droplets between both pieces of the fractured specimen. Another use is the examination of how well pigments are dispersed in the vehicle of an ink and whether or not over sized aggregates may be present.

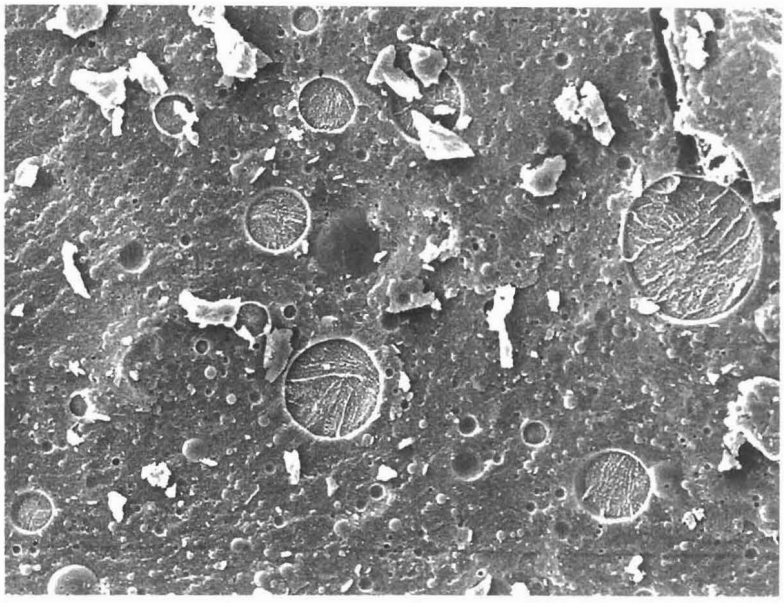


FIG. 5 - CRYOFRACTURED & SUBLIMED LITHO INK - 370 X OF POOR EMULSION

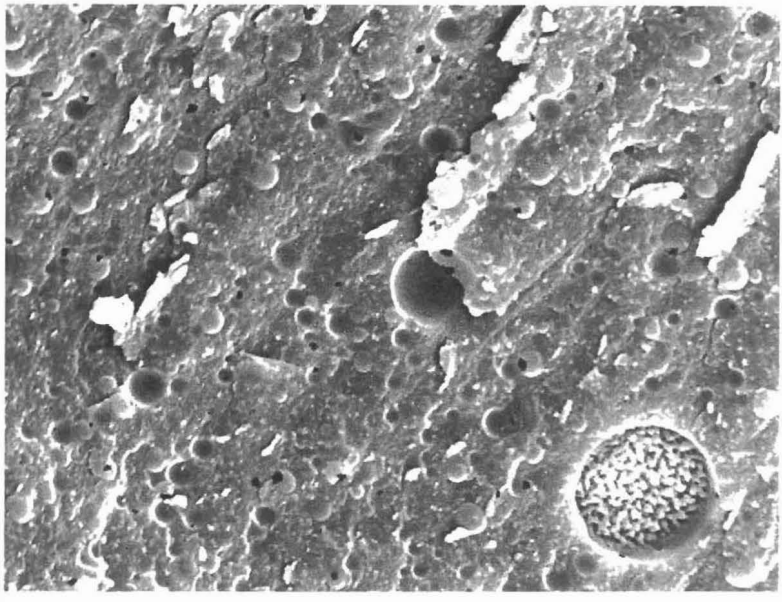


FIG. 6 - CRYOFRACTURED & SUBLIMED LITHO INK - 2500 X OF GOOD EMULSION

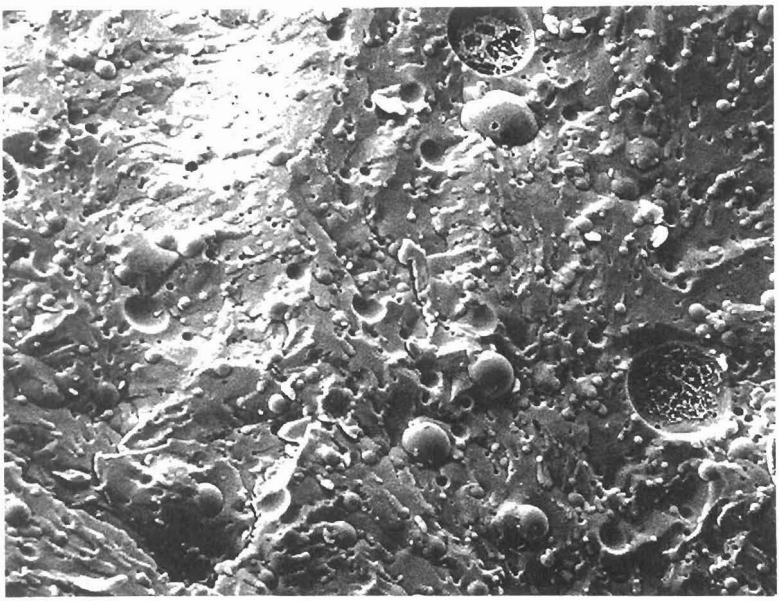


FIG. 7 - UNSTABLE LITHO EMULSION 1.5K X
- NOTE LARGE WATER DROPS & CRATERS

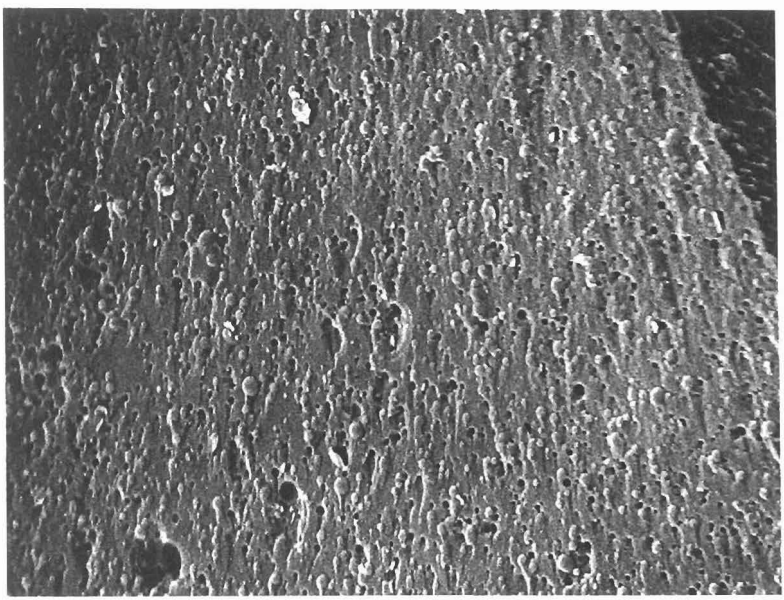


FIG. 8 - STABLE LITHO INK EMULSION 1.5K X
- NOTE SMALL UNIFORM DROPLETS

In the case of pigments that are sufficiently large to be easily observed, the distribution of pigments and other dispersed phases such as waxes and fillers is also possible. For example, Figure 9 shows a flexo print on polyethylene film where a base print of white ink is overprinted with a blue ink. The Titanium Dioxide pigment in the white is very apparent, since the particle size is generally between 0.2 and 0.3 micrometers. The demarcation between the blue and white ink is thus readily apparent since the blue pigment is much smaller in particle size (>0.10 micrometers). In this case the blue ink was printed on a dried white ink as is the usual case in flexographic printing, where interstage drying is normally used.

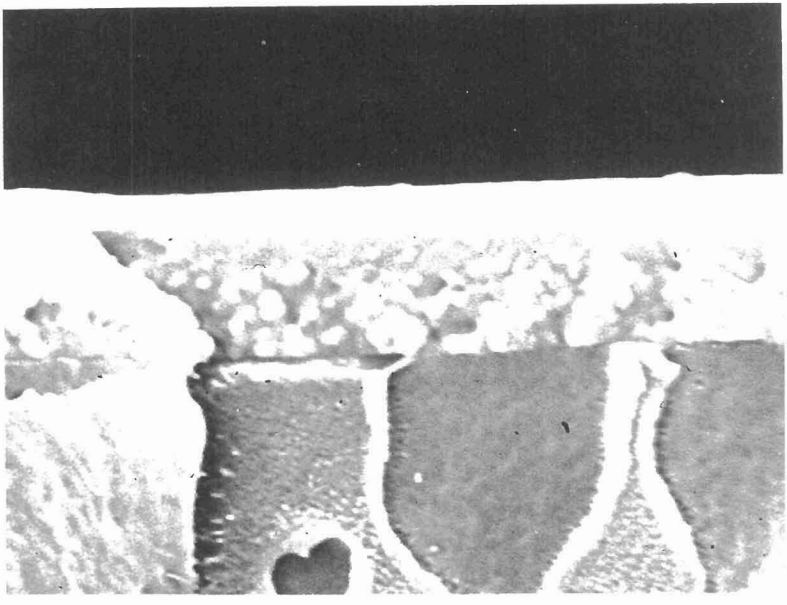


FIG. 9 - BLUE OVER WHITE FLEXO INKS ON POLY FILM - 10K X

One of the major applications of cryofracturing is to help elucidate interactions between ink and substrate, in particular when ink is printed on various types of papers. It is often possible to directly observe penetration of inks and/or vehicles into the upper layers of the paper. For example, Figure 10 shows a freeze fractured web offset print on coated paper. Here the penetration

of the 1 micrometer offset film into the clay tablets of the paper coating is quite evident, since the ink obscures the sharp edges of the clay plates. This photograph, although at very high magnification does not reveal any pigmentation in the actual ink film since it is a carbon black ink and the pigment is extremely fine in particle size.

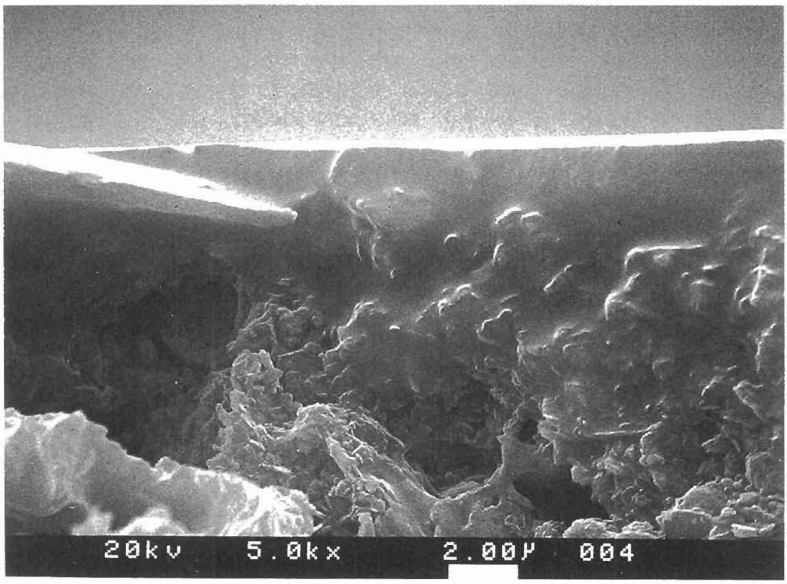


FIG. 10 - WEB OFFSET HEATSET PRINT ON CLAY COATED STOCK - 5K X

One of the common comparisons usually made is that of the efficiency of gravure printing vs web offset. Many printers have the capability of using either process and the choice of which is more efficient and economical is an important consideration in deciding how a job is to be printed. Some examples of this type of comparison were made using signatures with identical copy and printed by both gravure and web offset on a similar type of coated stock. In Figures 11 and 12, different magnifications of freeze fractured gravure prints are shown and may be compared with Figures 13 and 14 for web offset prints of an identical area. Using Energy Dispersive X-Ray Analysis (EDX) it is also possible to probe the specimen at various locations and depths to

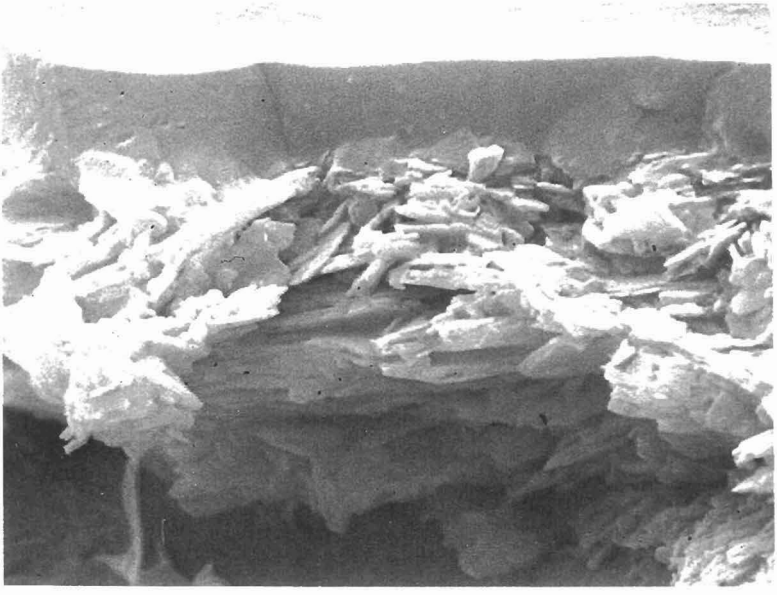


FIG. 11 - PUBLICATION GRAVURE SOLVENT INK ON COATED PAPER - 10K X

FIG. 12 - PUBLICATION GRAVURE SOLVENT INK ON COATED PAPER - 20K X

FIG. 13 - WEB OFFSET HEATSET PRINTS ON COATED PAPER - 5K X

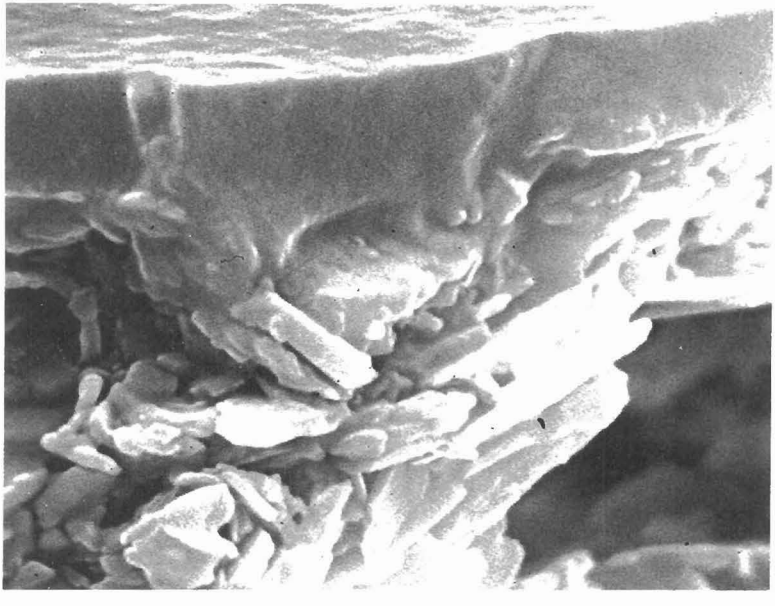


FIG. 14 - WEB OFFSET HEATSET PRINTS ON COATED PAPER - 15K X

determine elements which can be used to identify pigments and/or vehicles.

In the case of gravure inks, there is a convenient tracer element in the common metal resinate binders used in such inks. Most of these contain either calcium or zinc as part of the binder molecule and can be easily detected. In the case of Figure 12, the ink films appear not to have penetrated to any great degree into the paper. However, since gravure inks are low viscosity and contain an aromatic hydrocarbon solvent, the total vehicle is more likely to penetrate into the coating than a relatively high viscosity web offset vehicle. However, the low concentration of resin and low viscosity may prevent the clay particles of the coating from showing any loss of sharpness of their edges under the microscope, because the resin is distributed over a large area. This loss of sharpness as an indicator of vehicle penetration is obvious in the web offset prints in Figure 14.

The EDX analysis of the paper coating under the gravure ink film did show the presence of large quantities of Zinc which could only have come from the vehicle of the ink and clearly indicates high penetration of the hydrocarbon solution through the entire paper coating in Figure 12.

Both of the areas shown for gravure and web offset are solids, mainly of black ink.

Intaglio Ink

Figures 15 and 16 show views of an Intaglio engraving ink printed on an uncoated security stock. In this case, the printing consisted of a grid of fine lines about 0.5 mils width. The fracture penetrated one of the grid lines as can be seen in Figure 15, which has been further magnified in Figure 16 to show the relatively thick ink film applied by this method of printing. Intaglio prints can be as thick as 50 um, but in this case, the grid lines are only about 12 um. Also noticeable are the large amount of fillers and other inorganic pigments commonly used in this type of security ink to facilitate wiping from the non-image area of the plate.

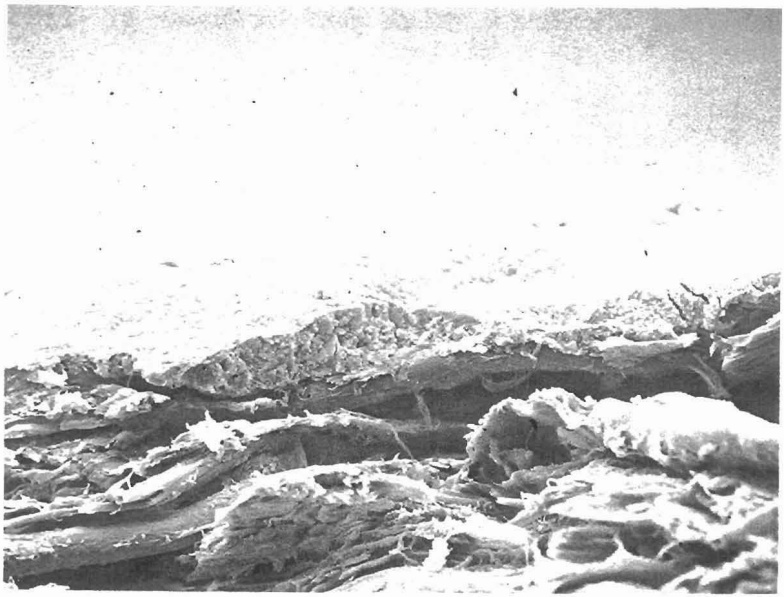


FIG. 15 - CRYOFRACTURED INTAGLIO INK ON UNCOATED STOCK - 1200 X

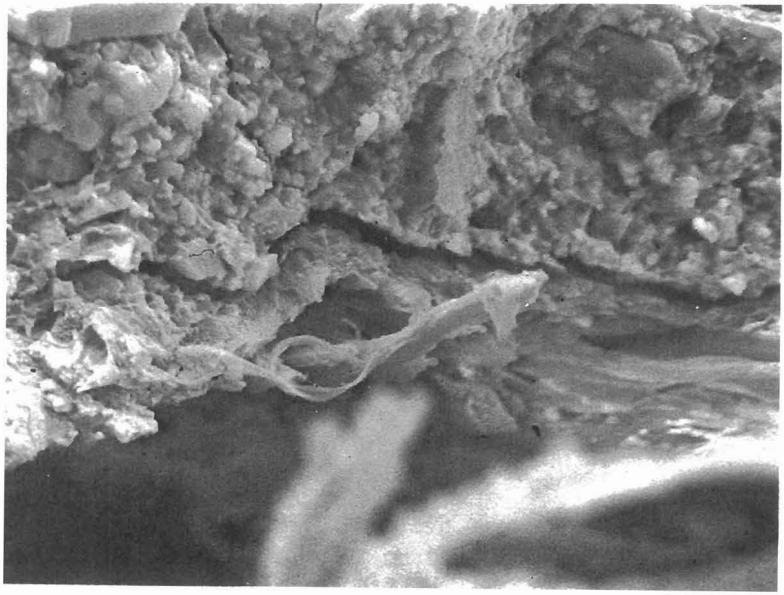


FIG. 16 - CRYOFRACTURED INTAGLIO INK ON UNCOATED STOCK - 7000 X

Overcoating of Printed Films

A common process employed today in order to enhance gloss and improve print resistance is overcoating of a previously dried print with a clear material. Two methods are commonly used in this process. One uses a water based overcoating which is dried by air flow and mild heating. The second is the use of radiation cured coatings such as ultraviolet

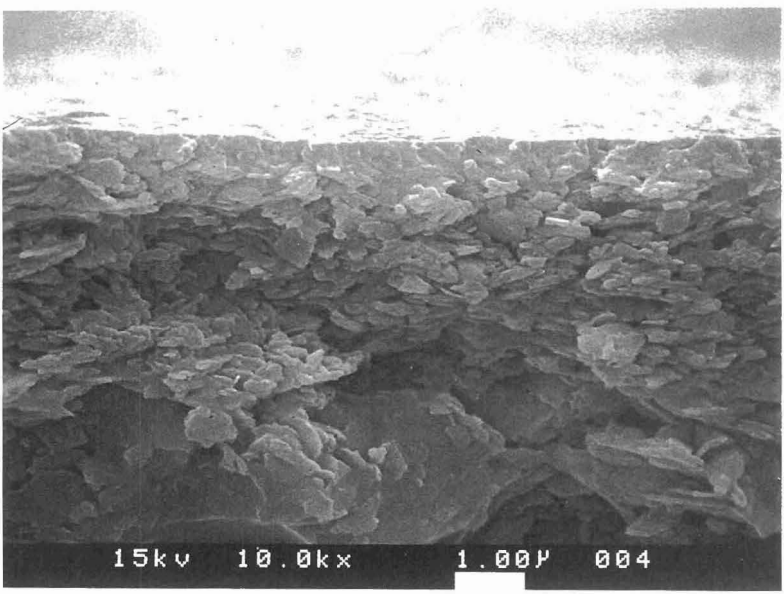


FIG. 17 - BLACK PRINTED PAPER BOARD FOR OVERCOATING - 10K X

clears. Fig.18 shows a water based coating over a black litho ink printed on clay coated board. Fig.17 shows the uncoated printed board. It is evident that the overcoating is quite heavy and appears to be in the order of 5 micrometers. A UV cured clear overcoat is shown in Figure 19 and here it is difficult to see the interface between the coating and ink which is so readily evident in the case of the water based overcoating. This is probably due to the interaction of the UV coating materials with the dried litho ink causing a partial fusion of the two layers and producing excellent adhesion.

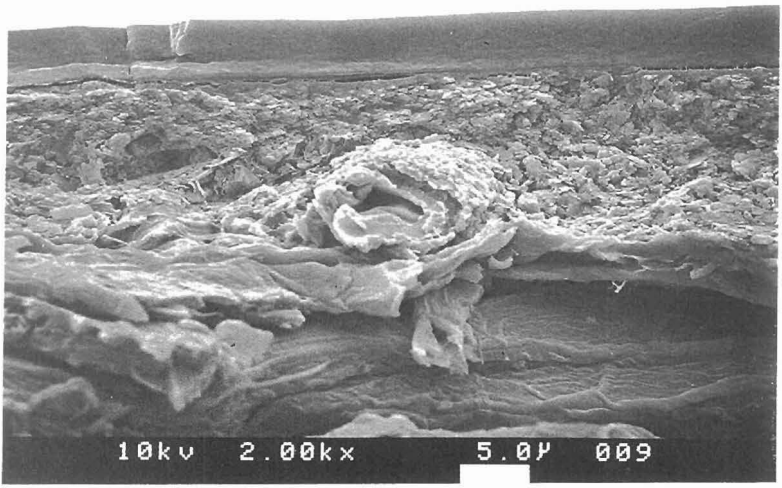


FIG. 18 - WATER BASED OVERCOATING OF PRINTED BOARD - 2000 X

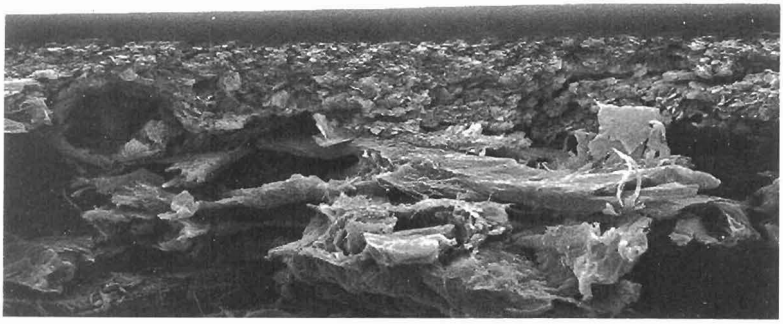


FIG. 19 - ULTRAVIOLET OVERCOATING OF PRINTED BOARD - 1500 X

Liquid Ink Printing

Figures 20 and 21 show a water and solvent based gravure ink on a clay coated paper. Here it is clear that the microstructure of the water based ink is much more heterogeneous than the solvent based ink film. Possibly the use of emulsion polymers, which are common in water based systems, is one of the reasons for this grainy appearance. Here the interaction with the clay platelets is also apparent. Figure 22 is a particularly interesting fracture of a solvent based gravure ink on coated paper where the penetration of the film into the clay coating is evident.

Figure 23 shows a unique photograph where the fracture was able to differentiate between three trapped gravure ink films of different colors. Since gravure inks are dried between printing stations the three layers did not show much intermingling. The different coefficient of expansion of the different colored inks produced a sufficiently different surface fracture to make all layers visible.

Complex packaging ink structures can also be investigated using the freeze fracture technique. For example, Figure 24 shows a part of a laminate structure where a white ink is printed over a colored ink which was printed on oriented polypropylene which in turn was coated on the reverse side with a clear polymer. All of the components of this structure are readily visible in the fracture, even the orientation of the plastic film. The white ink layer is again readily apparent because of the relatively large TiO_2 pigment particles.

Figure 25 shows an ultraviolet cured clear coating over a U.V. cured ink.The separation of the two films can clearly be seen. The surface also shows ripples, which usually occur as a result of shrinkage during curing.

Figures 26 and 27 show two white flexo inks having widely different pigment to binder ratios. Figure

FIG. 20 - WATER BASED PUBLICATION GRAVURE INK ON COATED PAPER - 12K X

FIG. 21 - SOLVENT BASED PUBLICATION GRAVURE INK ON COATED PAPER - 12K X

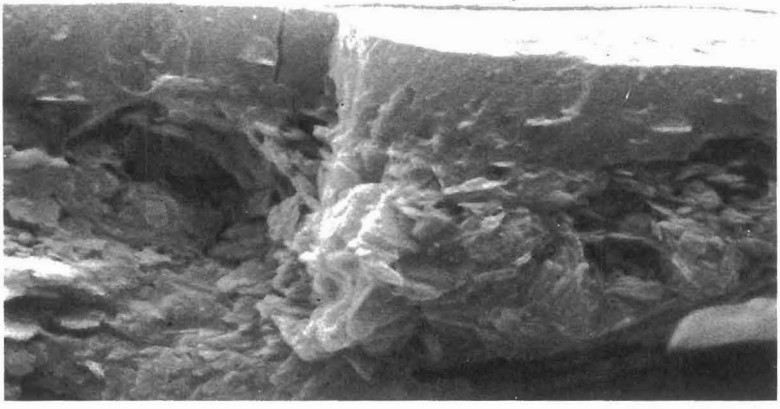


FIG. 22 - SOLVENT BASED GRAVURE INK PENETRATED INTO COATED PAPER-5K X

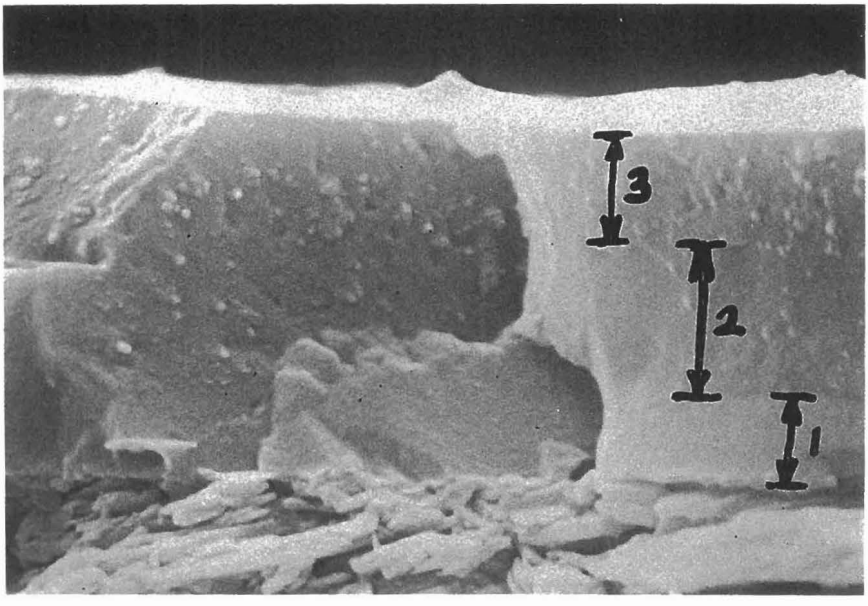


FIG. 23 - 3 COLOR SOLVENT GRAVURE TRAP ON COATED PAPER - 15K X

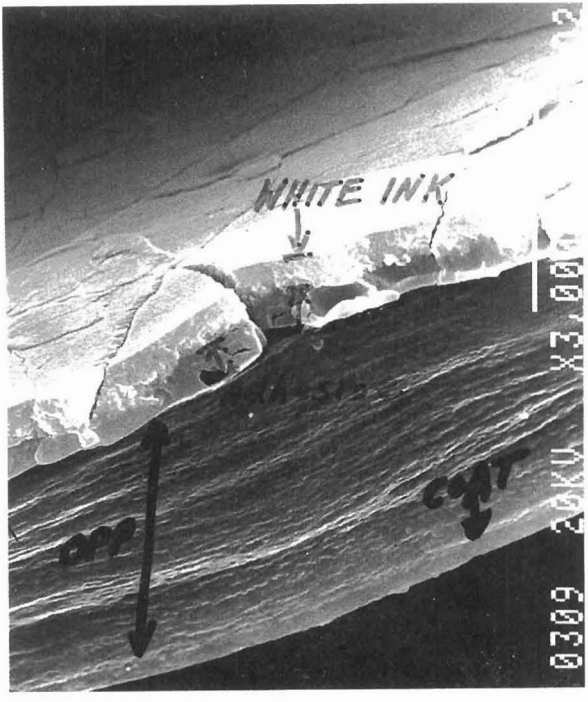


FIG. 24 - WHITE OVER COLORED FLEXO INK ON REVERSE COATED POLYPROPYLENE-3K X

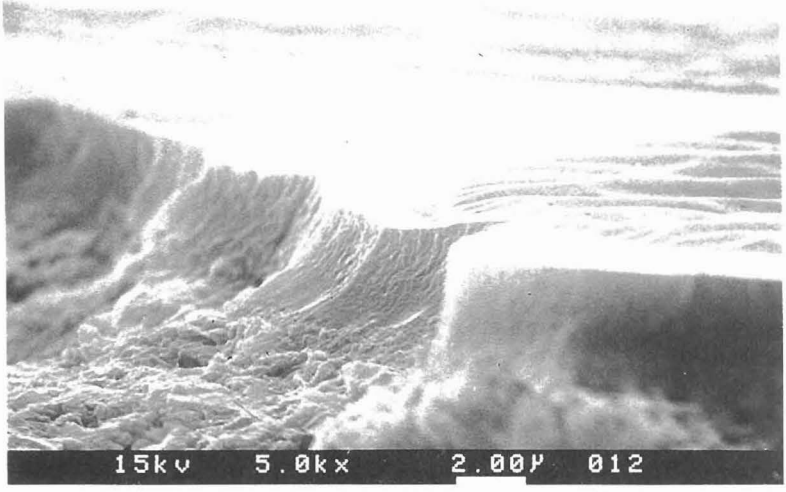


FIG. 25 - CLEAR ULTRAVIOLET COATING OVER DRIED UV INK ON BOARD - 5K X

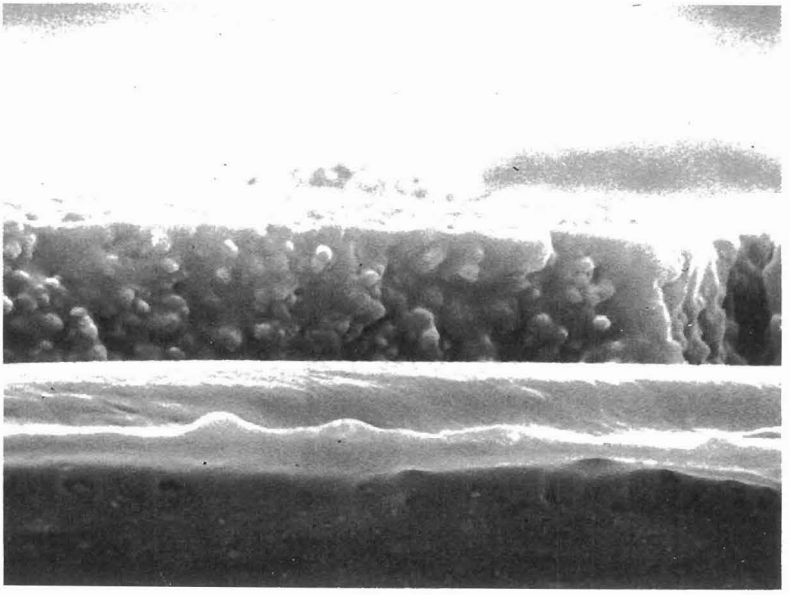


FIG. 26 - WHITE FLEXO INK WITH 1.5:1 PIGMENT:BINDER RATIO - 10K X

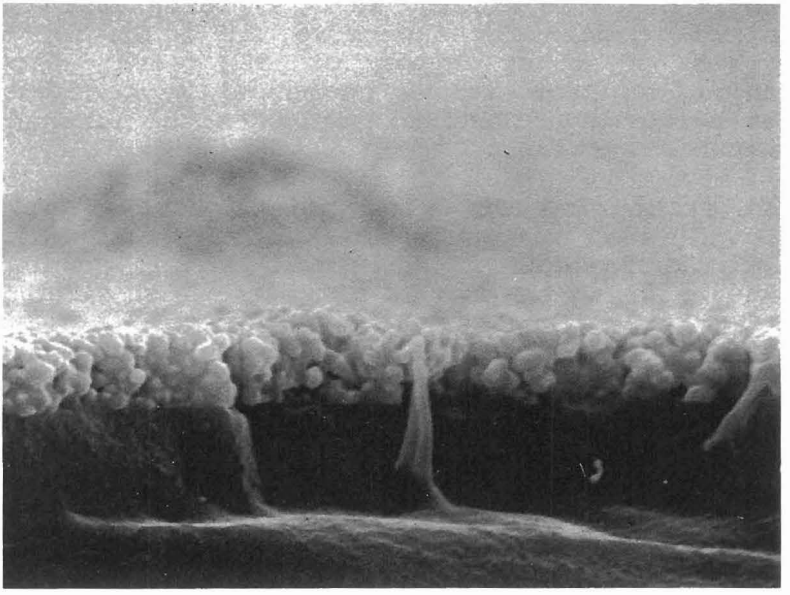


FIG. 27 - WHITE INK BASE WITH 4:1 PIGMENT:BINDER RATIO - 10K X

26 has a ratio of about 1.5 pigment:1.0 binder. Figure 27 is about 4.0 pigment: 1.0 binder. In this case, the relative amount of polymeric binder is readily apparent in the appearance of the fractured ink films, especially when printed on an impervious substrate such as polyethylene.

Conclusions

In this paper we have described a new technique for examining printing inks and coatings in their native liquid state as well as printed films of these materials on a wide variety of substrates. The ability to image them using an SEM at high magnification opens up many applications for observing the microstructure of the ink films themselves as well as the interactions with the substrates upon which they are printed. The use of Energy Dispersive X-Ray Probes (a common SEM accessory) also permits the following the depth of penetration of vehicles.

The use of this technique with liquid samples requires some accessory equipment for an ordinary SEM in order to examine it in a frozen state. While this is moderately expensive, it is useful for a number of other types of SEM work, such as minimizing beam damage to sensitive samples, and retarding any physical or chemical changes in unstable systems.

The fracturing of dried prints however, can be accomplished with a minimal amount of additional equipment, excepting for a small vacuum chamber for manufacturing the liquid nitrogen slush required.

It is hoped that other researchers will utilize this technique and share their findings about ink films and their interactions with various printing substrates with the Graphic Arts Industry.

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W&G Estate, East Challow, Wantage
Oxfordshire, UK OX12 9TF

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Bedford, MA 01730

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