THE APPLICATION OF PLASMA ETCHING TECHNIQUES FOR THE PRINTING AND PACKAGING INDUSTRIES

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1. Abstract

Although the principles of radio frequency generation of chemically active gas atoms have long been known (since 1884 [1]) it is only in recent years that commercial equipment has become available.

Commercially low temperature ashers, frequently described as "plasma generators", generally require only an electrical connection, a source of oxygen and vacuum pump to be ready for operation.

The application of the plasma etching technique is new not only to the printing and packaging industries, but also to a large range of laboratory and industrial applications.

This technique shows advantages over the conventional wet chemical etch methods and is finding many applications that range from the preparation of biological material for atomic absorption spectroscopy and electron microscopy to its use as a standard production tool in microelectronics manufacture.

Plasma chemistry is a dry chemical technique employing various gases which become highly reactive when ionised by radio frequency power applied to a reduced pressure reaction chamber. The spectral composition of the resulting plasma is a characteristic of the gas used. The choice of gas controls the type of reaction; typical gases are oxygen, hydrogen and fluorinated and chlorinated hydrocarbons. Reaction products are removed in the gas stream.

However, oxygen is used for the removal of an organic film such as a photoresist, it is also used for etching

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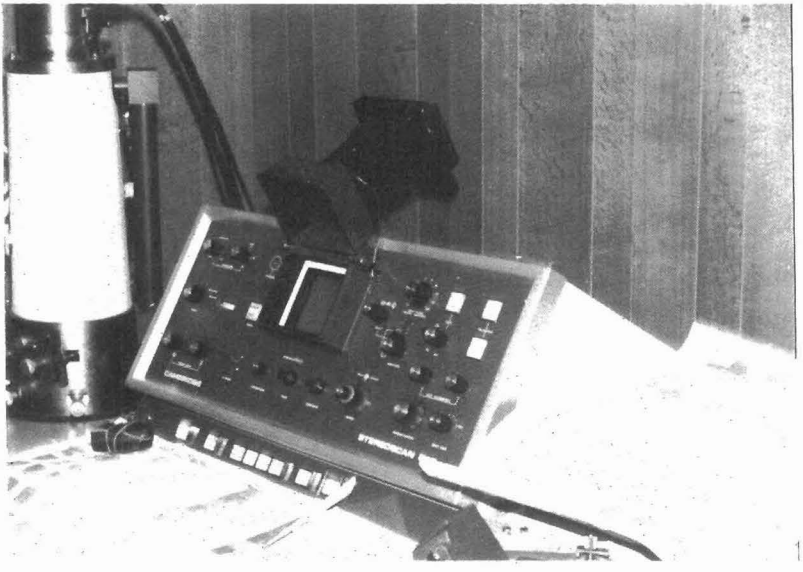
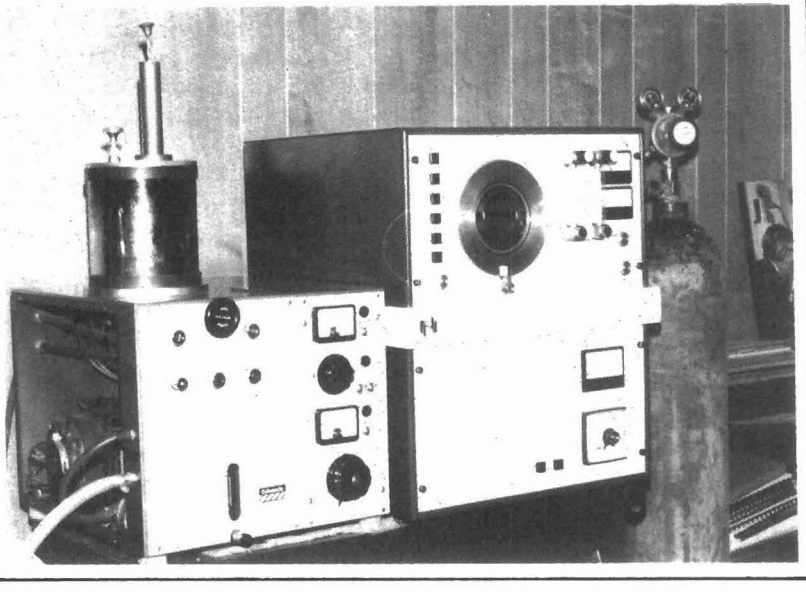


Figure 1 Electron Microscope and Cambridge Stereoscan 600

Figure 2 Sputter Coater and Plasma Chemistry Unit P300



organic material for subsequent examination together with the treatment of plastics prior to the application of various coatings.

2. Apparatus and Procedure

Low temperature ashing was carried out in the apparatus shown in Fig 2.

Basically, the apparatus consists of a source of oxygen, a radio-frequency generator and antenna, a sample chamber, and a vacuum pump. The apparatus is also equipped with a means of measuring gas flow and a pressure gauge.

The radio frequency generator operates on the scientific and medial frequency of 13.56 MHz so that only minimum shielding is required. The plasma unit P300 has a stationary sample chamber with oxygen as the treating gas, figure 2.

Since plasma oxidation takes place at a low temperature, it can be used to ash organic samples for trace metal analysis. Materials containing such elements as arsenic, selenium, tin, etc usually can be ashed without the loss of these relatively volatile elements [2].

3. Sample Preparation

3.i Samples Preparation for LTA and SEM

1. The samples were cut from the printed sheet representing single colour and overprint colours, printed on Silver Star paper. They were mounted on glass slides using an inorganic adhesive such as the sodium silicate on an aluminium carrier.

2. The samples were etched for a short time (3-9 mins) which is long enough to remove surface organics but not long enough to remove organics more deeply buried in the sample.

3. So far the samples of "paper and pigments" are not suitable to be investigated using Scanning Electron Microscopy. This is due to the absence of electrical conductivity which is an essential requirement for SEM.

The samples were rendered conductive by the vacuum evaporation of a thin layer of metal onto their surface

using the Edward's equipment seen in Fig 2.

3.ii Preparation technique for the scanning of samples by the electron microscope (SEM)

Upon finishing the Plasma Etching Stage, the specimen had to be prepared for the electron-microscope.

These samples needed to be coated with a conducting medium e.g. gold, silver, aluminium or carbon (aluminium was used for this work). Otherwise without continuity of the conducting surface a charge could have built up in the electron beam which could have lead to degradation and breakdown of the specimen image.

It is worth mentioning in this case, that paper as a printing substrate is considered a difficult specimen, due to the entrant areas not always accessible to the evaporant.

An Edwards Sputter Coater was used. This was equipped with a rotating planetary workholder which aligned the sample at many angles of incidence to the evaporation source. This allowed the mounted specimens to receive a complete all-over thin layer of coating of the conducting material. A pressure of 10^{-4} torr was used.

It should be noted that, under the examination of the printed surface, the organic spray powder particle was not destroyed or altered by this sample preparation.

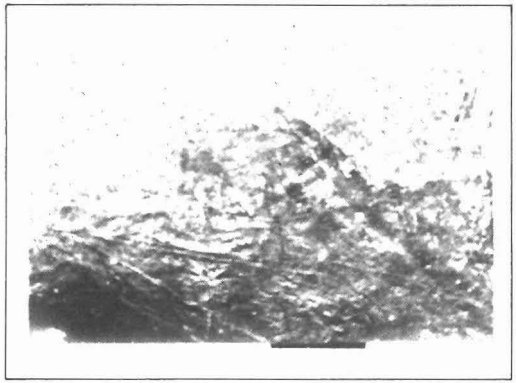
It is also worth mentioning that the clay surface was not damaged by stripping the absorbed water from the clay.

4. Results and discussion of plasma etching

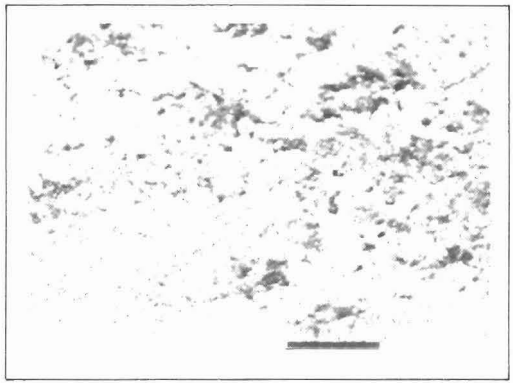
4.i Cyan-etched

The plasma etching process utilises low pressure oxygen which has been activated by radio frequency energy into a highly reactive condition where it is capable of oxidising (burning) organic matter at room temperature with complete removal of carbon compounds as carbon dioxide.

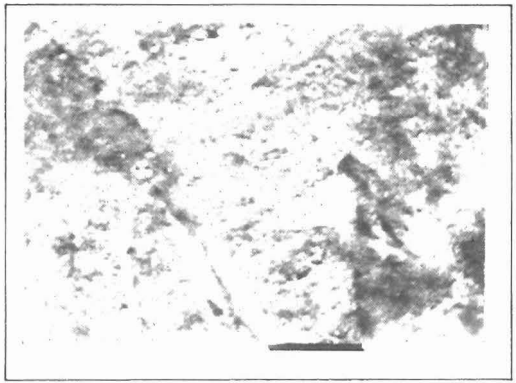
In Figure 3 the cyan ink polymer vehicle has been 'burned' away together with polymer binder used in the clay base paper coating. This under high magnification (photograph C an D) shows the outline of the compacted clay platelets more clearly than is normally observed in unetched



A 140X



C 2800X



B 700X

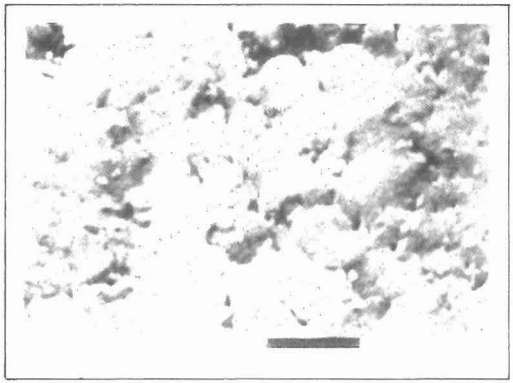


Figure 3 A.B.C.D 100% Cyan (ETCHED)
D 14000X

specimens. It also shows fine particulate materials of about 0.2 micron diameter which are presumably derived from components in the ink which will either not oxidise or will produce a non volatile oxide. These are probably the copper residues from the phthalacyanine pigment of the cyan ink. At lower magnification the removal of the polymer ink vehicle and binder show the surface fibre structure more prominantly (as in photographs A and B).

4.ii Cyan unetched

Photograph A in Figure 4 shows features very often seen in light-weight coated papers. Because of the roughness of the surface of the fibre matte which forms the paper base, and the presence of prominent surface fibres there are depressed areas and areas protected by fibres which will receive some coating but will not be compacted during a subsequent calendering process. The details of one such uncompacted area are shown in photographs B to E inclusive, where photograph E shows individual clay platelets and evidence of fibre near to the surface. Photograph F is of a different area which has been flattened and compacted by calendering and also carries an ink film. The ink film is continuous and only shows surface features at high magnification. These are small particles of <0.2 micron - presumably ink pigments within the polymer vehicle.

4.iii Yellow etched

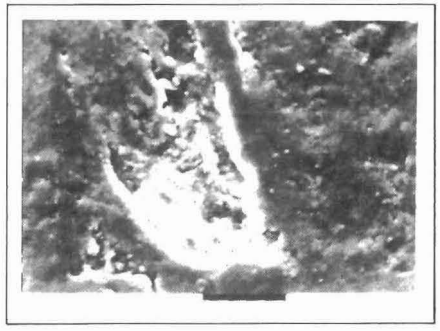
As with the cyan, the yellow ink polymer vehicle and the paper coating binder have been 'burned' away. As the yellow pigment was also wholly organic, this also would have gone, leaving on the surface, above the clay platelets, which can been seen in Figure 5 a generous distribution of Barium Sulphate particles, some aggregated, together with other residues form the ink.

4.iv Yellow unetched

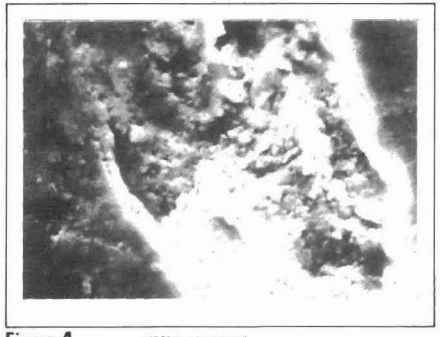
Figure 6 shows a smooth paper surface covered with an ink film in which light coloured particles are present. These range in size from approx 1/4 micron to 3 microns. Some of the larger spherical particles are aggregated (photograph C). These particles are believed to be the barium sulphate which has been added to the yellow ink as detectable element by x-ray measurement [3-5] for the IFT. The larger spherical particles are aggregates of the primary particles which are 0.2 - 0.3

A 280X

B 7000X

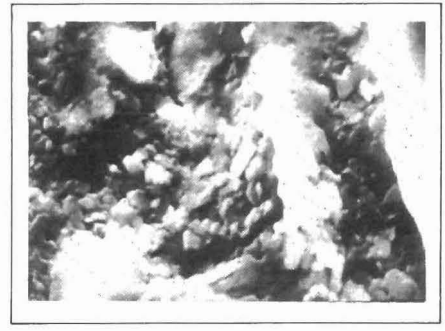


C 1400X

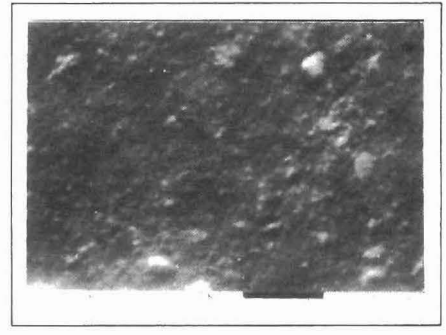


D 2800X

Figure 4 100% Cyan (UNETCHED)



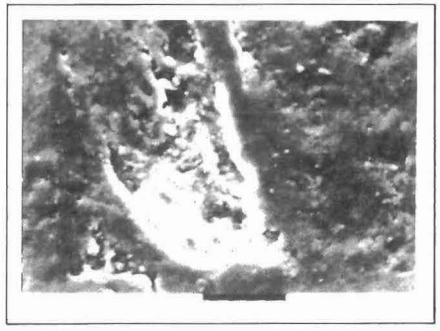
E 7000X



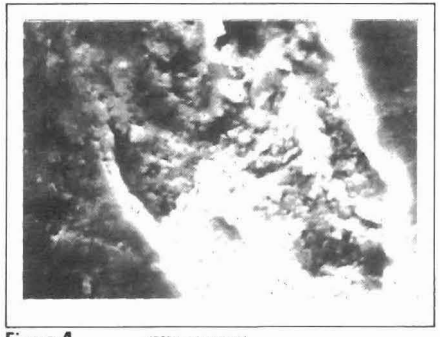
F 14000X

A 280X

B 7000X

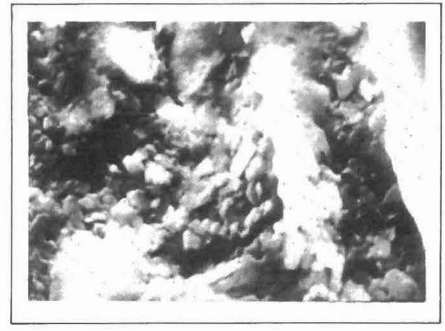


C 1400X

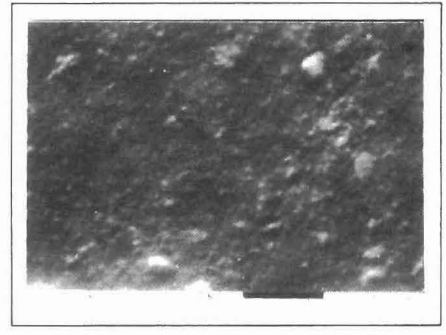


D 2800X

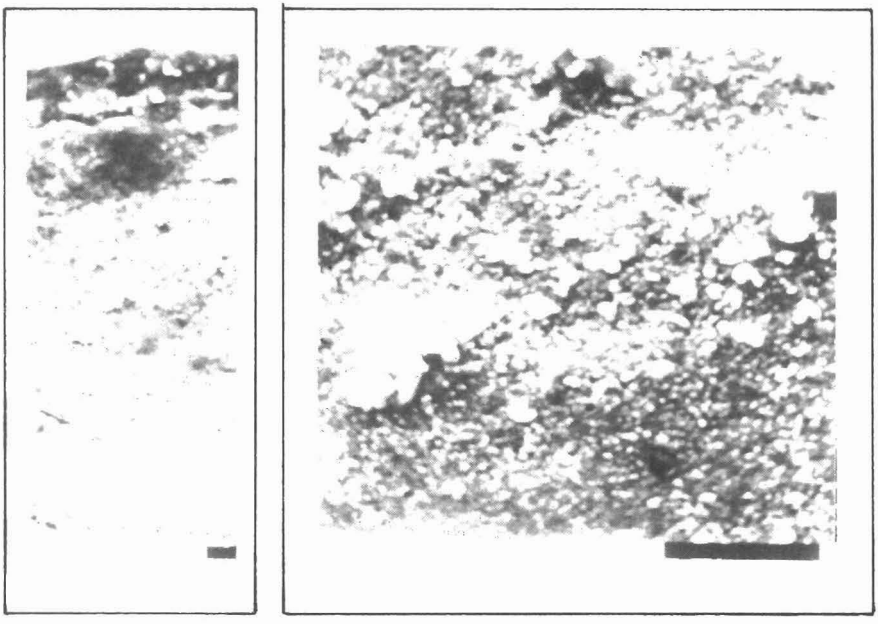
Figure 4 100% Cyan (UNETCHED)



E 7000X



F 14000X



A 700X B 2800X

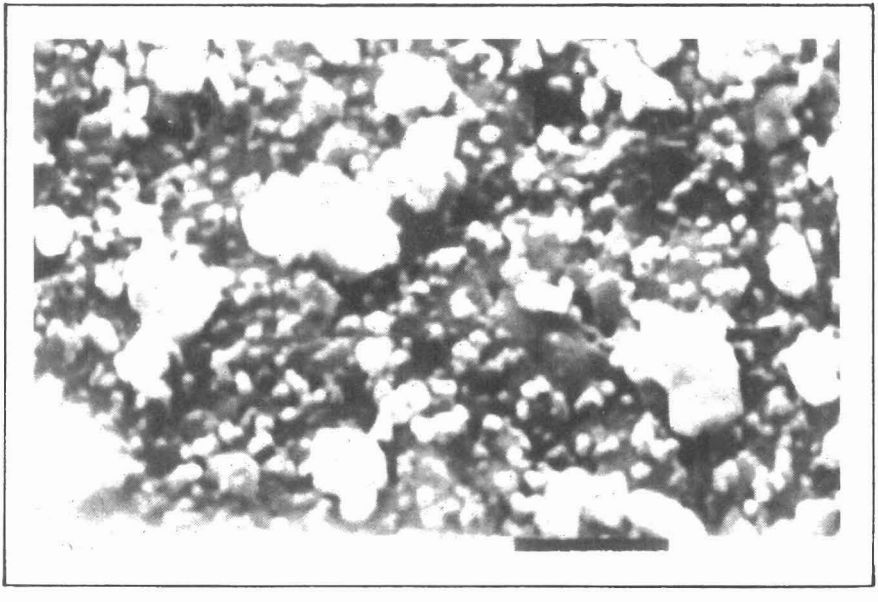
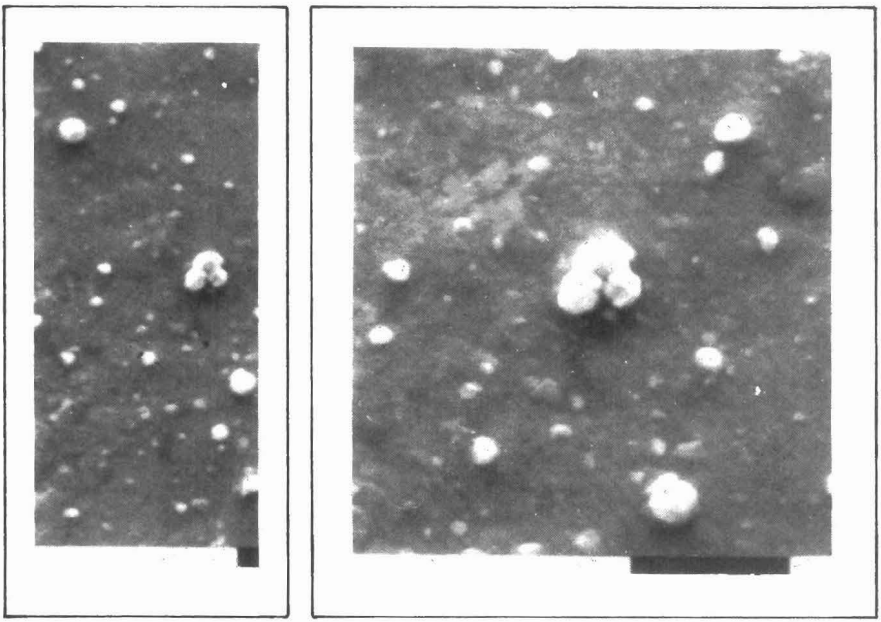


Figure 5 100% Yellow (ETCHED)

D 14000X



A 1000X B 2000X

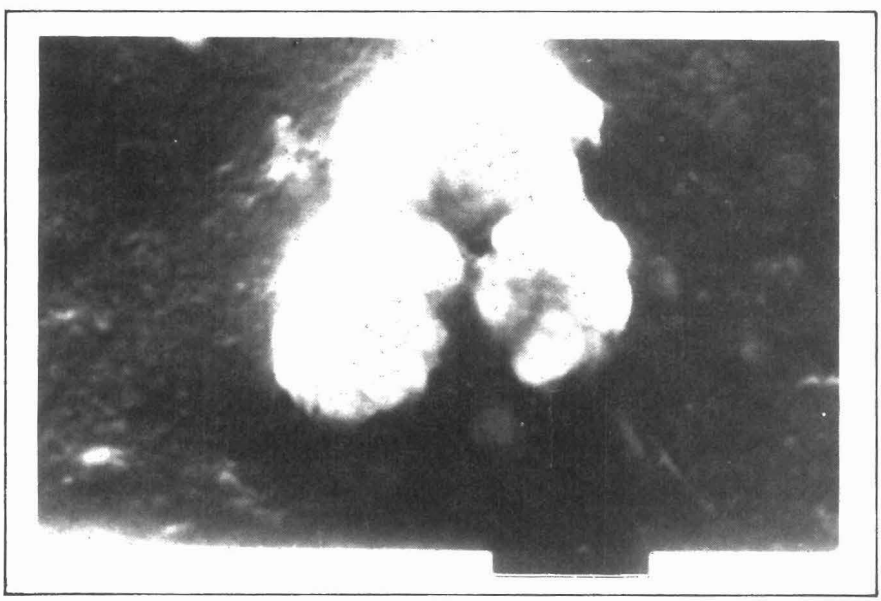


Figure 6 100% Yellow (UNETCHED)

C 10000X

micron in diameter. The heavy metal in the pigment (barium) ensures a high secondary x-ray emission in the SEM and produces the lighter "whiter" colour in the photograph.

5. The application of the plasma etching technique in comparing the two inks used in this work

Samples taken from solid yellow (Ba) - [photograph A Figure 7] and solid cyan (Cu) [photograph B Figure 7] were both etched and enlarged 10000X. Photograph A shows the $BaSO_4$ as the white particles and photograph B shows inorganic residues after plasma etching of the printed surface, presumably Cu compounds.

It is worth noticing that the rough appearance in photograph A compared to photograph B, is in fact due to the effect of Cu phathalocyanine in B, to purely organic yellow in A, which is the basic difference between the two inks, upon which, the trapping and the penetration of inks depend.

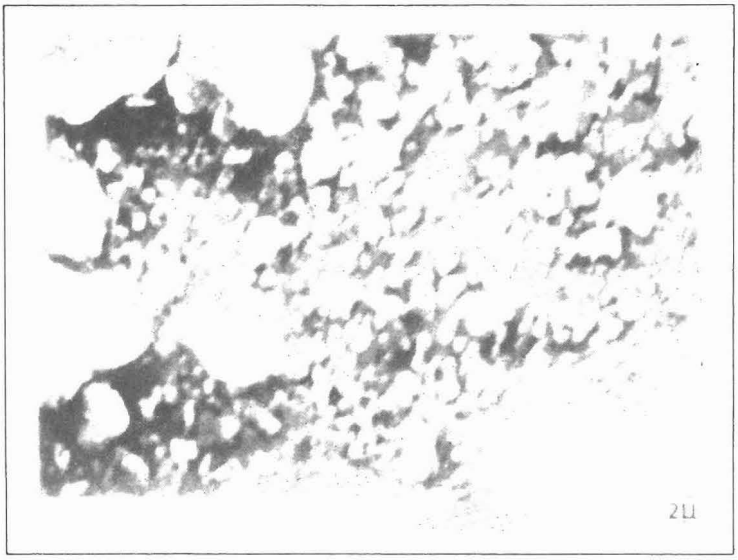
6. Conclusion - Plasma investigation

6.i Low temperature ashing (LTA) provides a useful tool in the Microscopy of coated and filled papers. Low temperature ashing treatment is a very selective "etching" process and organics such as adhesives can be removed from a pigmented surface so that the underlying particles can be examined.

6.ii The plasma etching technique is a good way of achieving greater contrast for investigations involving microscopy since it is possible to distinguish between the yellow ink, which leaves barium sulphate as residue, and the cyan ink, which leave copper compounds.

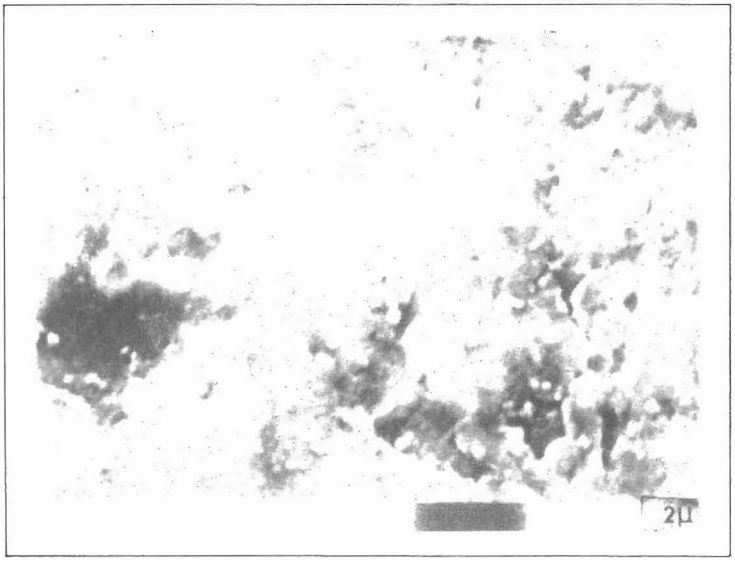
6.iii By using the dry plasma etching technique, all the essential stages applied in the wet-chemical process are eliminated. This, together with the reduction of chemical costs and the easier dispensing of spent reagents are important environmental considerations for the introduction of the plasma etching technique to our industry.

6.iv With the use of plasma etching it is possible to etch small geometries with minimal undercutting, resulting in finer resolution that the chemical etching process.



A Solid yellow ink surface

10000X



B Solid cyan ink surface

10000X

FIGURE 7

The application of low temperature plasma etching in comparing two ink

6.v Finally, extension of the plasma etching technique could yield useful quantitative information on the distribution of ink over a paper surface. Plasma etching offers exciting possibilities for the future; further research is required to realise its potential.

7. Acknowledgements

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1) Heidelberg Graphics Ltd, Brentford, London, UK, particularly Messrs A.J.A. Wood, D. Durham, W.J. Gorth and J. Knight
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8. References

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