Printing of micro-fine Structures

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Abstract:

For technical applications such as the production of etch resist masks for printed circuits the generation of micro-fine structures on substrates having particular electric properties, of interest. Although offset printing regarding detail resolution and generation of ink areas with higher optical density and evenness is very efficient, difficulties arise beyond the usual visibility conditions. The printed areas are not pore-free, the outlines are slightly blurred, the printed ink layers sometimes do not adhere sufficiently on the substrate. According to practical test results the practicability of pore-free printing and good adhesion will be shown.

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Introduction

The representation of visual information is the classic task of the printing technology. For that on the printing substrate visible structures are created by partially coating with printing ink. These structures can be, for instance, characters or lines.

A basically different application of the printing technology is to create structures with special electric properties [3] on a flat substrate in order to generate circuit boards for electronics, for example. Here, the lines have the function of strip conductors. Generally, they are copper strips on a dielectrics, which means on a synthetic foil or plate.

Such a structure, a conductive pattern, can be produced on a carrier substance by means of the printing technology.

The production of conductive patterns out of electrically conducting paste on synthetic substrate is known from screen printing. Despite the low conductivity of these pastes compared with copper the demanded electric functionality is achieved due to a thick ink layer and broad conductor tracks and therefore larger conductor cross-sections. The described application of conducting structures on a non-conducting substrate is called positive technology.

In contrast to this positive technology the proceeding of the negative technology is to laminate a thin copper foil solidly onto a synthetic carrier layer. The conductive pattern to be produced is applied on the copper surface by means of an etch resist lacquer. The lacquer-free copper areas are completely removed by the etching. Thereby the copper remains everywhere where it is covered with a layer of etch resist lacquer. With it the conductor plate is completely structured [1].

The application of the lacquer film is done by, for instance, screen printing, but mostly photolithographically. For this the copper surface is completely coated with a photopolymer etch resist lacquer. After attaching the film carrying the conductive pattern it is exposed with actinic light. The non-exposed areas are washed subsequently. So the etch resist structure is completed and can be etched.
In both procedures the lacquer films are several 10μm thick. This guarantees a safe etching resistance.

The resolution limit of the des screen printing process for this application is reached at a line width of several 100μm. Due to the structure of the screen thinner lines can not reliably be printed uninterruptedly.

In the meantime, the demands of the electronic industry have gone to significantly finer structure parameters for circuit boards. Line and gap widths have already fallen below 150 μm, the trend is beyond 100 μm structures towards 50 μm structures. Structure widths of 25 μm for circuit boards have already been prognosticated in the multi-layer technology, for instance. These are excessive demands for screen printing. Furthermore, considering the growing needs a more productive printing technology is appropriate.

The photolithographic procedure has a poor productivity, it uses relatively large amounts of etch resist lacquer and damages the environment by sewages from the washing process.
The need for a productive, high-resolution and qualitative structuring process is apparent.

Selection of Procedures and Pretests

Animated by an inquiry of an association of representatives from circuit board industry and university and research institutes the basic applicability of other printing procedures that distinguish themselves by a high resolution, high productivity and stable quality parameters was discussed.

The reason for offset printing was at first the high resolution; dots with a diameter of 5 μm on the plate are printable on art paper.

In addition, the printing formes that can be produced quickly at low cost and the clean and evenly opaque output that, compared with gravure printing, shows a perfect edge definition are further arguments in favor of offset printing regarding the problem to be solved in the circuit board production.

Flexographic printing because of its poorer resolution and gravure printing because of its costlier production of printing formes, rough outlines and feathering, were left out of further consideration of the present case of application.

In first pretests at the Institute for Print and Media Technology of the Technical University Chemnitz on a small-format sheetfed offset press a UGRA offset control wedge was printed on a flexible copper-polyamide lamination with black sheetfed offset ink. Directly before the printing the surface of the copper was carefully cleaned mechanically. The print shows a good representation of details (fig. 1).

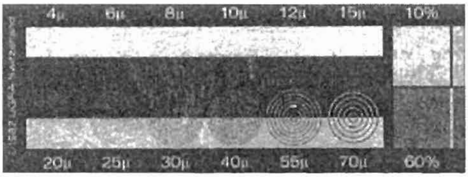


Fig. 1: Offset printing of a UGRA offset control wedge on copper substrate

The non-absorbing printing substrate makes special demands on the drying of the printing ink. A rise in temperature up to 200°C or 100°C resulted in a quick drying; without this rise in temperature the printing ink had not been rub-proof for another three days.

In later applications the oxidatively drying ink will be replaced by a UV hardening ink or lacquer system in order to achieve an immediate drying.

After the etching with $FeCl_3$ a visible result was only provided by those samples that were dried without thermal treatment (fig. 1). The ink layer of the samples dried under a risen temperature did not have sufficient etch resistance.

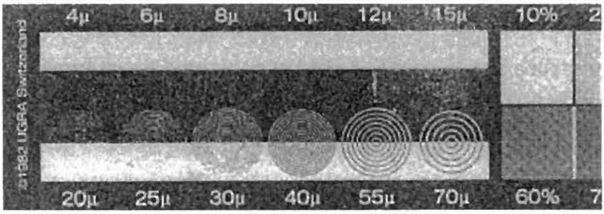


Fig. 2: Etching result of the printing according to fig. 1

Die macroscopic consideration of the etching result shows a good detail resolution up to a line width of 40 μm. The expected change of the line width was not measured in this figure.

Pores in the Ink Layer

Under the microscope, however, the structure being visible was clearly porous and heavily riddled with holes (fig. 3).

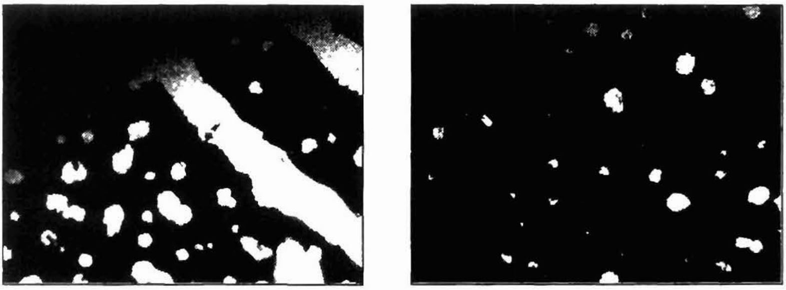


Fig. 3: Microscopic picture of a detail of the etching according to fig.2 (40 µm line and solid tone)

The ink layer did not provide a coherent etch resistance. With it the effects in the generation of conductive patterns described in literature [1] have been confirmed.

Also from printing of full tone areas on even the smoothest paper in quality offset printing every offset printer knows that within the ink area small unprinted areas can almost not be avoided. For the visual impression concerning optical density and brilliance of the printing this is redundant, but a look through the linen tester makes the these pores visible (fig. 4).

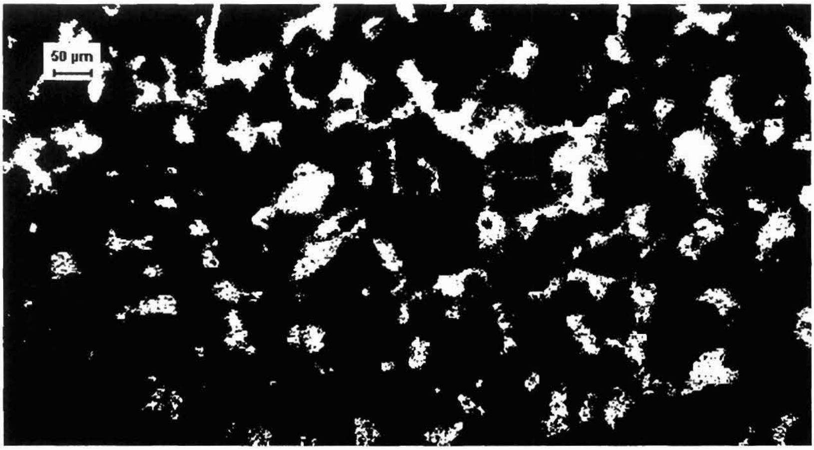


Fig. 4: Enlargement of a solid tone area in quality offset.

Pores within the etch resist layer are success-related quality faults. Even the smallest pores lead to unusable results because the etch medium penetrates through these pores. One of the basic demands on printing micro-fine structures is to avoid pores within the etch resist layer.
Causes for the resulting pores consist of inhomogeneities within the ink film and untidy surfaces of the printing substrate:

- Inclusions of fountain solution - fountain solution emulsified in the ink which in small drops is embedded in the ink and, on the one hand, spoils the regularityof the ink splitting [2], but also, on the other hand, locally reduces the etch resistance of the ink layer because of its watery composition.

- Pigment particles – these are deposited in the binding agent and are not needed in the function of the ink layer as etch resistance. Therefore, for the benefit of an improved homogeneity of the ink these can be left aside.

- Dust on the surface of the printing substrate - these are also partially included in the ink film. In both forms they contribute to the formation of pores.

Concluding from this for all further tests were used:

- Waterless offset printing (to avoid inclusions of fountain solution),
- Pigment-free inks and lacquers (to get a homogenous, specially etch resist layer),
- UV hardening ink and lacquer systems (to delete the drying time).

Although printing tests with UV inks and lacquers for waterless offset showed on the fore-mentioned copper lamination as printing substrate a perfectly hardened layer, the faulty part of the printing result was the strikingly porous and badly outlined structure (fig. 5).

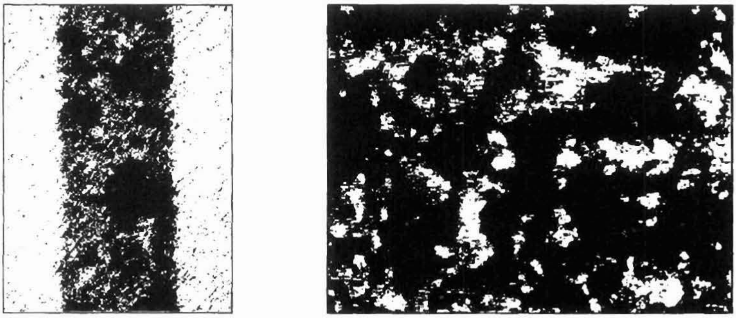


Fig. 5: UV color print on copper substrate shows large faulty areas

Additionally, in the etching bath the ink layer got off the copper substrate extensively so that no etching result was achieved. Even at an extremely thick ink application with a doctor blade, which proved to result in a pore-free lacquer film, the hardened layer got off in the etching bath. A clear correlation between the layer's adherence, proven by the Tesa-Test, and the degree of the tendency to get off in the etching bath.

Adhesion on the Substrate

Solutions providing a well adhesive printing ink layer on a copper substrate had to be found.
The general proceeding in foil printing, the solid pre-printing of a primer as adhesive agent, was not applicable in this case since this adhesive agent works as an etch resist itself.

Just as well the natural thought not pre-print the primer as a solid area but as a complete conductive pattern true to register had to be condemned with regard to the intended fineness of the structure. Register printing does not guarantee the needed exactness.

Comparative test printings with special foil and metal inks for offset printing did not lead to better results regarding adhesion.

Only the etch resist lacquer commonly used in the circuit board industry showed an excellent adhesion on the copper substrate.
In the production of circuit boards this lacquer is used for the total coating. It is not suited to being used in waterless offset printing.

In order to use this lacquer in waterless offset, the manufacturer modified it with regard to viscosity and composition. The result was the following:

- after a certain run clean phase the lacquer differentiates on the waterless offset printing plate,
- the printed image shows in comparison with standard UV inks for waterless offset printing as well as in comparison with foil printing inks clearly better outlines on the copper substrate,
- the adhesion of the lacquer film on the copper substrate was very good, as was proven by the Tesa-Test,
- the lacquer film immediately hardened perfectly in the UV dryer, however
- the thickness of the achievable in an offset press was very low, it ranged from 0.1 to 0.2 μm, and even at a modest increase of ink application in the offset press toning started on the plate,
- the lacquer film on the substrate showed large and numerous pores in full tone areas as well as in the lines,
- the etching results were uncertain and faulty because, on the one hand, the pores lead to faulty areas and, on the other hand, the very thin lacquer film offered only an insufficient etch resistance.

Figure 6 shows a detail of an image printed with one of these modified lacquers.

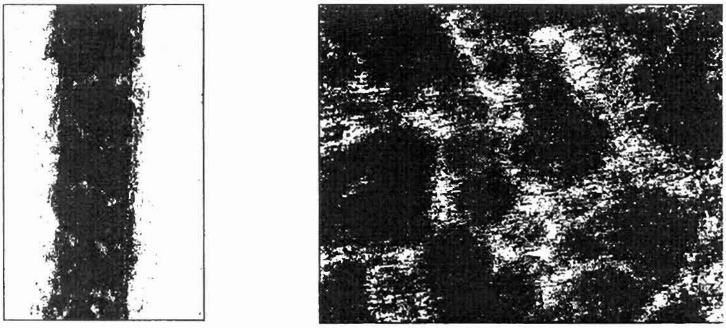


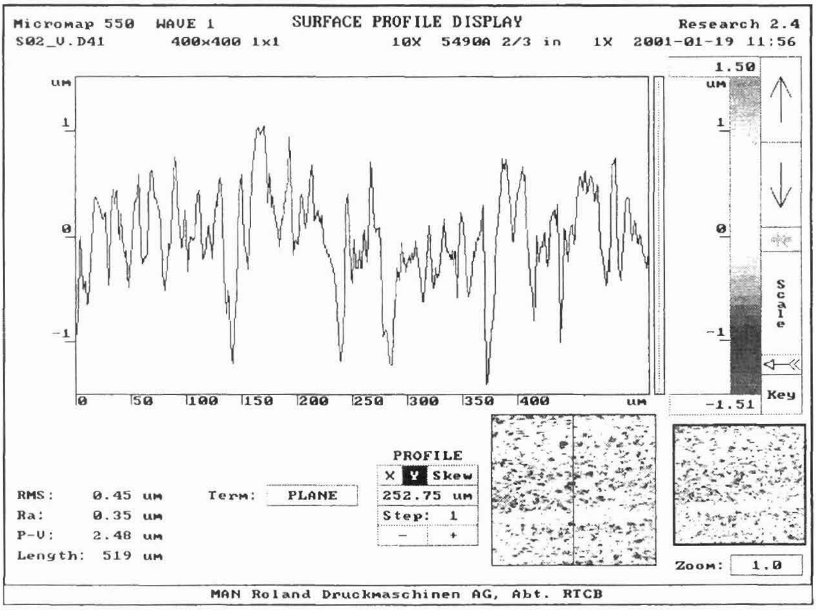
Fig. 6: Print result with modified etch resist lacquer

Thickness of Lacquer Film and Roughness of Substrate

For the improvement of the printing results two questions had to be settled:

1. What is the optimal thickness of this particular lacquer film on the chosen substrate to generate a coherent pore-free film (if in offset printing pore-free is possible at all), and
2. What is the correlation between the thickness of the lacquer film and the roughness of the surface of the printing substrate?

The surface roughness of the copper substrate was measured by means of a white light interferometer. This substrate is e-copper which is commonly used in the circuit board industry. The measured result is shown in figure 7.



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MAN Roland Druckmaschinen AG, Abt. RTCB
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Fig. 7: Surface profile of e-copper, measured with white light interferometer (Picture: MAN Roland, Augsburg)

It becomes immediately clear that the height differences in profile ranging from R_z = 2.5 to 3 μm are not very likely to be covered uninterruptedly by the lacquer film which is thinner by the factor of 10. The surface tension of the lacquer and the interfacial tension of the system copper-lacquer are responsible for the fact that the lacquer gathers mainly in lower areas by building a minimal surface and the risen profile parts have to remain uncovered. In coating technology this appearance is known as the edge coverage phenomenon.

It is to be expected that on a more even substrate a pore-free lacquer film is already achieved at a reduced thickness of the lacquer film than on a rougher substrate. Examinations confirmed this.

Copper foils with a significantly smoother roughness of the surface than e-copper are available as super-finished sheet copper. Figure 8 shows the measuring of a super-finished sheet copper foil with the white light interferometer.

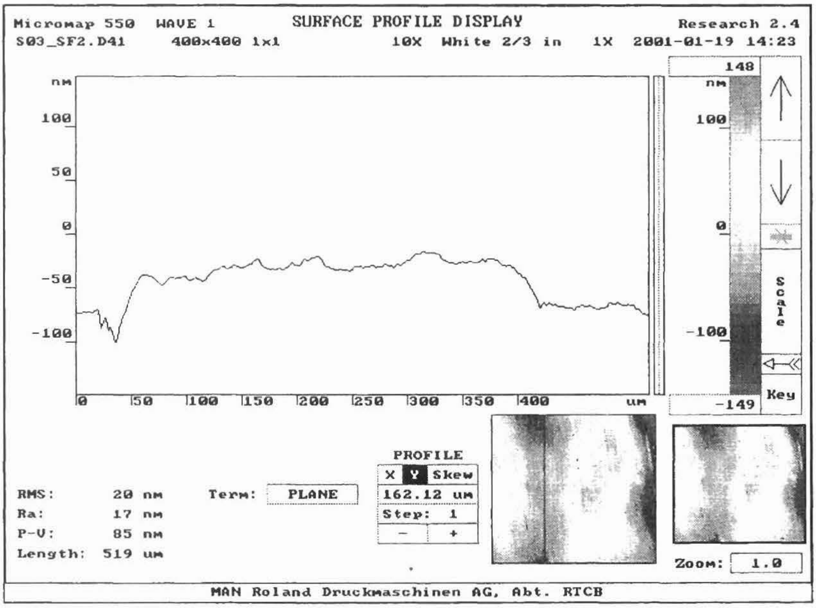

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Fig. 8: Surface profile of super-finished sheet copper substrate (Picture: MAN Roland, Augsburg)

The R_z value of this substrate is 0.2 μm.

In special series of tests on a test printing device (fig. 9) the correlation among the thickness of the film, the pore-free film and the roughness of the surface was determined.

The test printing device allows the production of full tone areas with a thickness of the layer in a wide variation range.

In the test printing device the lacquer is applied on the printing substrate by rollers under an adjustable printing pressure.
Insofar the printing conditions are similar to those in an offset printing press; at least regarding the ink transfer principle which in both cases is based on ink splitting.
By means of the test printing device printing tests proved that actual pore-free full tone areas can be produced by printing according to the ink splitting principle.

The deciding parameter hereby is the thickness of the layer. With an increase of the thickness the number and size of the pores decreased until eventually no pores were detectable anymore.
The most reliable proof of pores was made possible by a halftone electron microscope. Figure 9 gives an REM picture of a pore-free full tone area. This full tone area was generated by a test printing device with the modified etch resist lacquer on e-copper substrate.

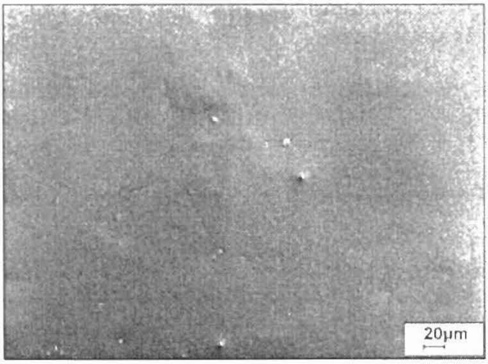

Fig. 9: Halftone electron microscope picture of a pore-free lacquer film

As expected, even at a thin lacquer film a pore-free full tone area is achieved when using a substrate with a smoother surface roughness. Table 1 compares the minimal thickness of the layer for e-copper and super-finished sheet copper substrate that in a series of tests was proven to be pore-free.

Substrate	R_z	Pore-free at film thickness
e-copper	2.5 μm	2.1 μm
super-finished c.	0.2 μm	0.7 μm

Tab. 1: Correlation between roughness of the surface of the substrates and minimal thickness of the pore-free lacquer film

The results show that the demanded thickness of the layer is in a range that is feasible by using offset printing ink and paper.
The problem now was to print the modified lacquer in waterless offset printing on copper substrate and to get a thickness of the layer that at least achieves the thickness according to table 1 – or it even succeeds. Of course in this case the printing plate must not tone.

The practician knows that in waterless offset printing toning can be removed by a reduced inking. With it in the present case, however, the achievable thickness of the ink layer is to thin.
Another way is to reduce the temperature of the plate. These tests did not fully lead to the demanded goal.

A third possibility is to change the consistency of the printing ink. In figure 11 is hypothetically shown the principal correlation between the viscosity of the ink and the thickness of the layer that can be printed below the tone limit. This figure is to make only clear the tendency in the correlation without being able to tell concrete measured values for the used lacquer.

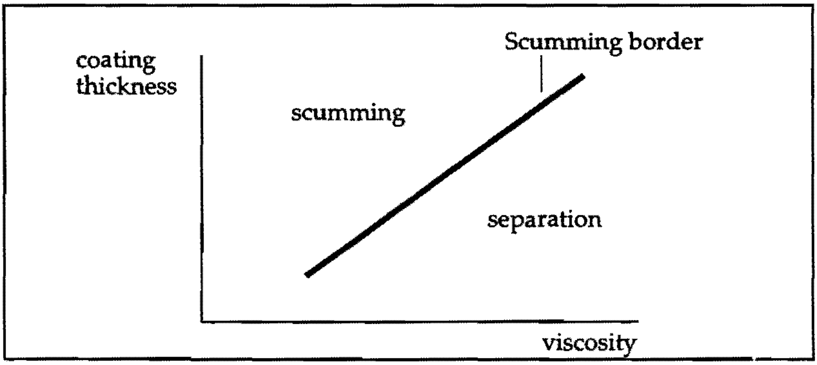

Fig. 10: Schematic representation of the tone limit in the thickness – viscosity diagram

In the present case the etch resist lacquer had room temperature and a viscosity of $\eta = 30$ Pa s without pre-shearing. The increase up to $\eta = 100$ Pa s resulted in a shift of the tone limit upwards so far that the lacquer films up to a thickness of several μm could be printed. This proof was furnished impressively while printing on art paper.

In printing on super-finished copper substrate the use of the highly-viscosity lacquer showed a printed image that was very pearly and often clearly diagonally streaky (fig. 11). The lacquer transfer from blanket onto substrate proved to be very instable.

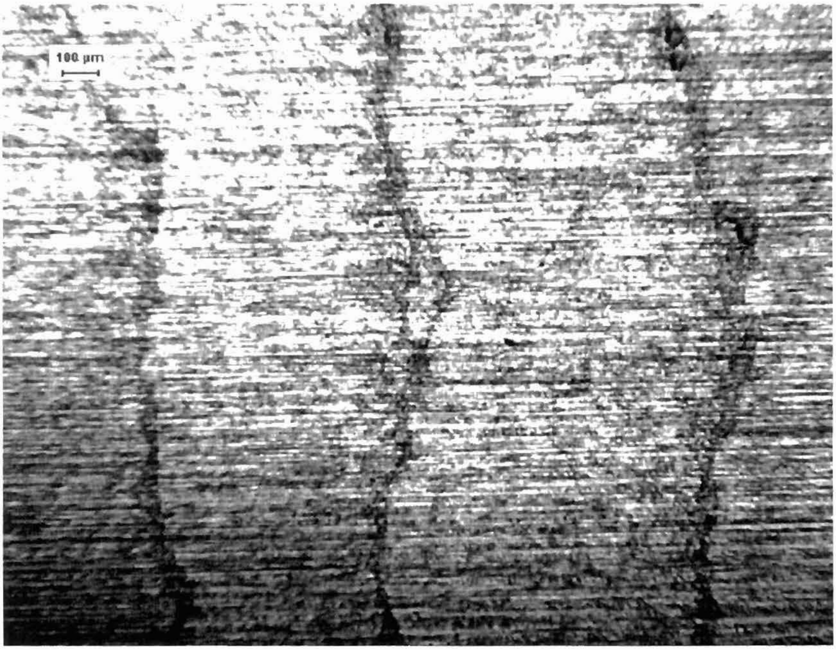

Fig. 11: Pearly, streaky print due to insufficient wetting

This effect indicates a poor wetting of the copper substrate by the lacquer – although the adhesion of the lacquer on the copper substrate was very good.

Surface Tension

The deciding improvement of the printing result was achieved by matching the surface tensions of lacquer and substrate with each other. Due to corrosion preventive reasons the manufacturer provided the copper surface with an organic passivation layer. This layer is very thin and does not produce an etch resistance. The surface tension of the passivated copper substrate σ_{total} = 31.8 mN m^{-1}, whereas the polar portion is σ_{polar} = 0.2 mN m^{-1}. Favorable wetting conditions are given if the substrate and the lacquer have comparable values in total of the surface tension as well as in the polar portion.

Figure 12 shows the micro picture of a detail of the printed image on the copper substrate.

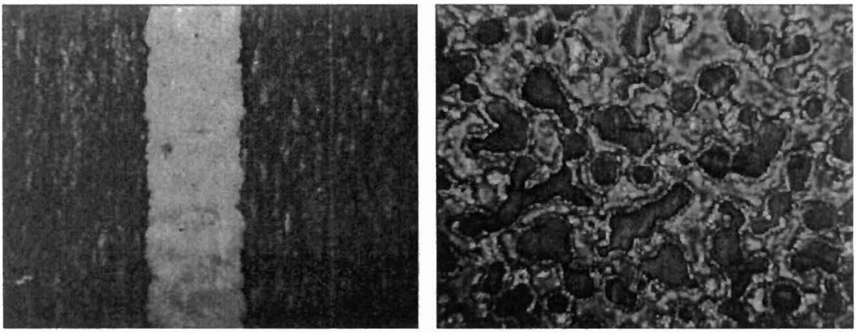

Fig. 12: Micro picture of a print with a pore-free lacquer film

The printed areas are completely coated and pore-free. Although the lacquer surface still shows a pearly structure all printed areas are coated. The etching of this pattern shows a faultless result on the surface (fig. 13).

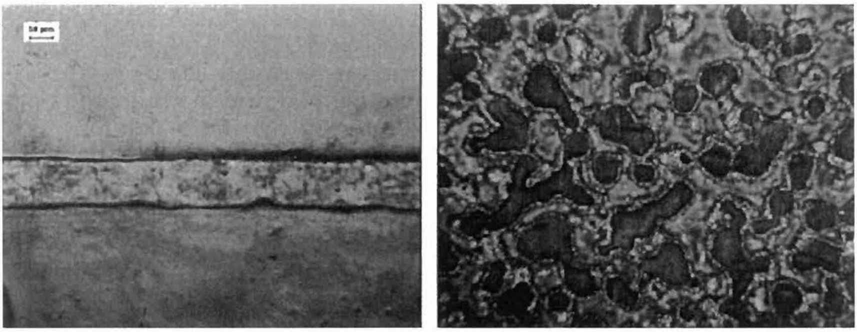

Fig. 13: Etch result of a print according to figure 12 (Etching:: ANDUS, Ch. Lehnberger)

With it the current state of the works is characterized.
The following necessary steps are:

- the formulation of standard printing conditions to control the widening of lines,
- the improvement of the edge quality with regard to outline sharpness and outline smoothness,
- the reliable control of fine structures, particularly also by including prepress processes and using a dust protected milieu for the printing process.

Knowing the current state of work the idea of being able to print and etch 50 μm structures in the near future seems to be real. The production of even finer structures is certainly no illusion.

We see the particular abilities of the presented procedure in the productivity which is several scales higher compared with the current photolithographical production process. Additionally, there are advantages due to being ecologically harmless compared to the photolithographic process. These result from the more economical use of etch resist lacquer and the reduction of wet-chemical process steps.

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Conclusion

It was proven that in waterless offset printing pore-free etch resist structures can be printed on copper substrate. Beyond printing brilliant visual information offset printing will in future enter the large field of producing technical structures, whereas the printing of etch resist masks for circuit boards will only be one area of a series of applications.

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