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Printing parameters and ink components affecting ultra-fine-line gravure-offset printing for electronics applications

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Abstract

The gravure offset printing method was examined for the manufacture of thick-film conductors on alumina, using Ag based inks. In this research, a roller type gravure offset manufacturing process was developed to give conductor lines and spaces down to 20 μm, together with a low square resistance. Novel hydrocarbon resin based inks have been used and compared to traditional ethyl cellulose based inks normally used in thick-film technology. The inks had a high viscosity compared to graphical inks due to their high solid content, which was necessary to enable a high printed mass. Different printing parameters were studied and printed sample properties were statistically compared. The results show that the cross sectional area of the lines is the best correlating measured property to describe the quality of the printing. 100% of the ink was transferred from the blanket to the substrate after 30 seconds. Prints from ink containing 85 wt.% of silver with optimised parameters resulted in a square resistance of 5 mΩ/sq. for 300 μm wide and 17 μm thick lines produced from a single print. These promising results are important requirements for high throughput electronics manufacture.

Keywords: Ag; Conductor inks; Gravure offset; Inks; Intaglio; Thick-films

1. Introduction

Electronics manufacture on ceramic hybrid substrates has been mostly realised previously using screen printing, but requirements are for an increased resolution and improved processes. Screen printing resolution (150–75 μm) is limited by the mesh number of the screen, properties of the paste, emulsion resolution and emulsion durability. Various thick-film manufacturing methods have been developed to offer a fine-line alternative. Thick films can be fine-patterned (~20 μm) with the use of Fodel inks, but this includes the slow steps associated with photo-chemistry.[1] Another alternative is ink-jet printing,[2] but this lacks in both speed and printed layer thickness. One promising method for cost effective printing of electronics is the use of gravure offset printing. Compared with emerging high-resolution (down to 0.1 μm) micro contact printing technology,[3] the gravure offset printing method has significant advantages of speed and pattern thickness in a less complicated manufacturing process.

In gravure-offset printing, the ink (or paste) is first doctored into the grooves of a gravures plate. An offset-pad or-roller, made of a rubber or silicone polymer, picks up the ink from the gravure grooves by pressing against it. Then the pad or roller transfers the ink to the substrate by pressing or rotating over it. After that, the conductor inks for ceramics are dried and fired at 600–900 °C.

In the previous papers the authors described the selection and optimisation process of the ink components for gravure offset printing.[4–6] Printing experiments have indicated that this printing method is highly dependent on the printing parameters. Two different types of inks were distinguished according to their printing properties: firstly, traditional ethylcellulose based inks and secondly novel hydrocarbon resin based inks. Previously, gravure offset inks for electronics applications have been diluted from ethyl cellulose binder based (mixed with terpineol) screen printing

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pastes. However, the resulting printed resolution and thickness have proved insufficient.[7] Novel hydrocarbon resin based inks are more pressure-withstanding during printing and have significantly better printing properties.[4,5]

Characterisation of the ink properties has been done using viscosity, elasticity and capillary number.[8–12] These methods give indirect results which cannot be directly compared in the case of different ink binder systems. Printing properties have been previewed based on the doctoring blade angle[10] and on the silicone oil content of the offset printing pad.[11] In this paper the references[10,11] have been used as a reference for observed effects of silicone filler oils and doctoring conditions.

In the literature, gravure offset printing results have been compared in terms of the line widening, line height, square resistance, printed mass and electrical performance of components.[10,13–19] However, there is no statistical comparison between these results to indicate which would the best one to adopt as a standard criterion to evaluate printing quality.

This paper presents the time and compression-thickness of the blanket parameters to be used in gravure-offset printing with the novel hydrocarbon resin based inks. The printing results were evaluated based on their printed mass, printed line width, printed line height, line cross section area and square resistance. The results have been compared in a correlation matrix. The goal is to print conductor inks on ceramic alumina and glass substrates with a high-resolution (down to 20 μm) and low square resistance (< 15 mΩ/sq.).

2. Experimental

Experiments have been done within various printing environments and with different inks. Prior to the printing, inks were measured in terms of the forces related to the surface energy and by rheological methods. The printing parameters were recorded during the printing process. After printing, the printed mass of the test pattern, the printed line height, printed line cross section area and square resistances of the conductor lines were recorded. Printed samples were weighed as 'wet' with an accuracy of 0.1 mg.

All printing experiments were done with a modified laboratory gravure-offset printer from Grauel GmbH. A pneumatic doctoring device was later installed, with fixed angles and a closed container.

The metal gravure was manufactured electrolytically by a novel method.[20] This enabled the creation of high-resolution (down to 9 μm) gravures with deep rectangular shaped grooves (~30 μm).

Silicone polymer offset printing blankets with a very smooth non-polar surface were used to permit narrow line printing. RT601 silicone polymer from Wacker-Chemie GmbH without filler oil was found to be the best material for the surfaces of the blankets. About 1 mm thick silicone polymer was moulded on top of the fabric to form the offset printing surface with a total hardness of ~60 Shore A. The blanket was on a roller with a radius of 3 cm.

The speed of the ink doctoring on the gravure was about 5–30 cm/s to allow all the ink to be doctored with sufficient doctoring pressure. The pickup speed of the ink from the gravure to the blanket was in the same range. Too slow a pickup speed (< 5 cm/s) of the ink causes low-viscosity inks to slip out of the grooves. Printing (laydown) speed over the substrate was adjusted to be in a same range. It did not have much effect on the printed results.

Conductor inks for ceramic alumina and glass substrates were made by Gwent Electronic Materials Ltd., using high (68–85 wt.%) concentrations of silver powder. The particle size of the silver was in the one to five micrometer range. The other component was 2.5 wt.% of glass-frit. The vehicle of the ink was composed of non-polar hydrocarbon binder and slowly evaporating solvent. The solvent evaporation rate was ~1% of all solvent from the printed sample in one minute. The inks had rheological elasticity, high shear thinning and some yield stress.

Rheological viscosity and yield stress measurements were made with a Bohlin CS Rheometer. The viscosity change was controlled by solvent concentration, solid percentage and binder type. Although yield stress measurement methods have received critique in the literature,[21] a textbook example of its definition was used:[22] Yield stress was estimated from two ranges of shear stress curves by drawing trend lines in a linear scale and determining the crossing point of the Y-axis.

Surface profiles and the maximum line heights were measured with a Veeco Dektak^{3}ST surface profiler. The maximum line height was defined as the highest point of the line cross section. The cross section area was calcu-

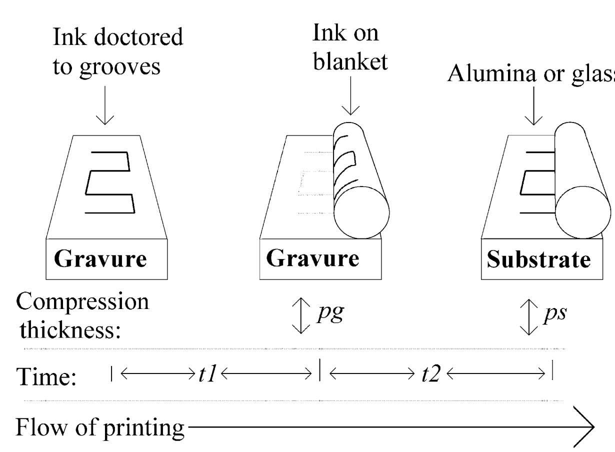


Fig. 1. Flow of roller type gravure offset printing.

lated with suitable base line correction by using a custom made program. Accuracy of the line cross section area measurement was 1–5% depending on the accuracy of measurement angle and the definition of the printed line bottom. The substrates used were glass and 96% alumina, which had about 1 μm Rz_{din} roughness. Glass was used when exact surface profiles of the printed lines were needed. To measure dried line height form and cross section, alumina samples were dried for 15–20 min at 180 °C.

The printing process is described in Fig. 1. Parameters recorded during printing were: the compression-thickness at the gravure when the ink is picked up (*pg*), the compression-thickness at the substrate at laydown (*ps*), the time from doctoring to pickup (*t1*), the time from pickup to laydown (*t2*) and the speeds of doctoring, pickup and printing (laydown). Compression-thickness to pressure correlation is shown in Eq. (1).[4]

$$\text{'Pressure in grams'} \ \alpha \ \text{'Pressure in millimeters'}^{3}; \quad (1)$$

After alumina samples had been fired for approximately 1 h in an 850 °C belt furnace, the square resistance was measured with a HP 3457A multimeter from the four-point measurements patterns shown in Fig. 2. The line length changed with different line widths. The acquired data were analysed with Microsoft Excel 97 and the Modde 4.0 factor-design software, which allows the use of MLR (multiple linear regression) and PLS (partial least squares) algorithms in finding the best-fit model for data.

3. Results and discussion

3.1. Ink content

A sufficiently high pressure and a low speed of the doctor blade are required for the doctoring of high viscosity inks. Hydrocarbon binder based inks had a maximum line widening of about 10%, but ethyl cellulose based inks could experience line widening in the worst case of about 100%. Line widening for both inks was dependent on the angle of the pickup direction (the same as the angle of doctoring): lines printed normal to the printing direction were wider. The mass of ink pickup from gravure grooves to blanket was up to three times higher with these inks than with ethyl cellulose based inks. One hundred per cent of hydrocarbon inks were transferred from the blanket to the substrate. For an industrially viable method, it is important that this transfer is complete because incomplete transfer means high variations in the printed results. In addition, cleaning the blanket after every incomplete print imparts increased stress and wearing of the silicone polymer due to the solvents or adhesive tape generally used in the offset material cleaning.

Fig. 2. Printed four-point measurement patterns of 300 μm and 150 μm wide lines, respectively.

Increasing the solid contents of the ink caused an increase in the printed mass (Fig. 3) and a decrease in the resulting square resistance (Fig. 4). Increase of solid content also increased viscosity and yield stress.

Increased printed mass has a high correlation to square resistance. Fig. 5 shows square resistance values vs. printed masses of different inks, for three line widths. The figure shows square resistance down to 5 mΩ/sq. for 300 μm wide lines with an ink containing 85 wt.% of silver. On the other hand, narrow (9 μm) lines were successfully printed only with the low viscosity inks (∼ < 10 Pas at 60 1/s).

3.2. Statistical analysis of the results

Ethyl cellulose binder based inks showed significant line widening that was affected by compression. Typical pad-printing inks belong to this group. Printing parameters *ps* and *t2* have only a minor effect on the printed

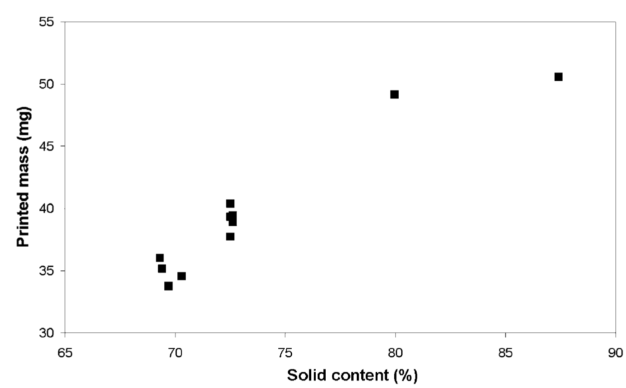


Fig. 3. Printed mass vs. solid content of inks.

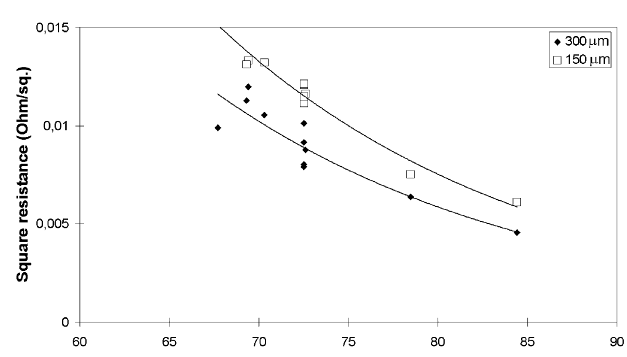


Fig. 4. Square resistance vs. solid content of inks for two line widths.

mass. Increasing the parameters *pg* and *t1* increased the printed mass in both cases. The minimum time for *t2* generally gives the best result. These inks do not transfer 100% from blanket to substrate.

The behaviour of the hydrocarbon resin based inks, as a function of the printing parameters, is shown based on a multivariable model in Fig. 6. The quality of the model is shown by R^2 and Q^2 values in the figure. Other inks based on similar type resin had slightly shifted optimum parameter values for maximum printed mass.

The multivariate model shows that the printed mass changes significantly with each variable parameter. Ink transfer of the hydrocarbon inks is described by an absorption transfer mechanism.[4] While ink is in the gravure grooves after ink doctoring, increasing *t1* causes the printed mass to increase. The effect is due to relaxation and cooling of the ink.[23] Increasing *pg* decreases the pickup mass. In order to achieve 100% ink transfer from a blanket to substrate, the ink has to remain for a minimum time ($t2 = 30$ s) on the blanket. This (*t2)* parameter interacts with the compression-thickness on the substrate at laydown (*ps*): significant increase of the one allows a decrease of the other, while still obtaining 100% ink transfer. *ps* has to have a minimum for 100% ink transfer.

A correlation matrix of the printed mass, the maximum line height, the cross section area and the square resistance is shown in Table 1. As expected, there is a strong correlation between the printed mass and the square resistance. The printed mass has higher correlations to cross section area and most importantly to the square resistance, than to line height. The printed mass could be used to compare printings if the same pattern is used with inks that have similar relationships between line height and line width.

Narrow lines of the test pattern are longer than wide lines (Fig. 2). It has been found that in gravure methods the error accumulating is affected by the line length, not by the printed area. Therefore narrow lines have more printing error accumulating in a test pattern. Also, roughness of the alumina substrates easily creates a non-uniform network-like structure of fired ink for thin layer thicknesses, as shown in the Fig. 7. This results in an increased accumulation of narrow conductor traces. The cross section area measurement method should be used when the square resistance cannot be measured sufficiently accurately.

The square resistance is a result of all the factors in the printing environment, ink settling, drying, and firing. It also shows up cumulatively non-uniform cross section areas of the printed line, over the long distances, unlike printed mass. Printed line cross section area can be used to study lines without random errors, independent of variations of line height.

3.3. Line shape and height

Printed and dried line shapes on glass are shown in Fig. 8. This figure shows that the maximum line height decreases when the printed line becomes narrower, as shown for different types of ink in Fig. 9. Cross section areas and the maximum line heights from Fig. 8 are shown in Table 2.

Ink A (in Fig. 9) is hydrocarbon ink, and inks from C to H are ethyl cellulose based inks. From the latter inks it can be seen that there is no dependence between line

Table 1
The correlation matrix of response values: printed mass (Mass), printed line height maximum (Height), printed line cross section area (C.s. area) and square resistance (Sq. resistance) for two line widths

	Mass	Height	C.s. area	Sq. resistance
300 µm wide lines				
Mass	1	0.80	0.90	−0.89
Height	0.80	1	0.94	−0.85
C.s.area	0.90	0.94	1	−0.88
Sq. resistance	−0.89	−0.85	−0.88	1
150 µm wide lines				
Mass	1	0.57	0.69	−0.96
Height	0.57	1	0.93	−0.68
C.s.area	0.69	0.93	1	−0.76
Sq. resistance	−0.96	−0.68	−0.76	1

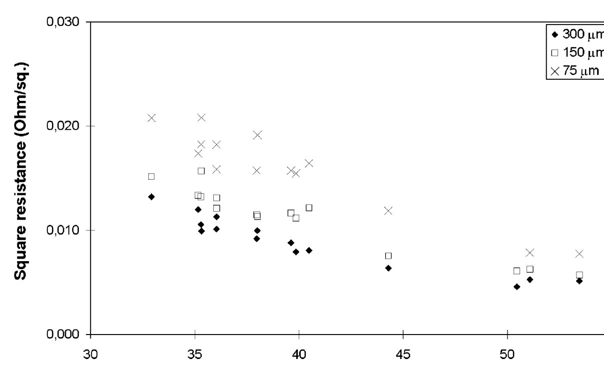


Fig. 5. Square resistances of inks with three printed line widths. 300 µm wide line was 34.7 mm, 150 µm was 64.9 mm and 75 µm was 129.4 mm long.

Table 2
Cross section areas and the maximum line heights of printed pattern in Fig. 8

Width/µm	280	200	140	100	70	50	35	25	18	13
C.s.area/µm^2	1700	1200	870	550	320	200	110	72	36	20
Height/µm	10.9	9.2	9.8	8.1	7.3	6.0	4.0	3.6	2.4	1.82

height and line width for lines wider than 100 μm. This points to the existence of a maximum ink thickness that can be picked up from the gravure.

The cross section area of the fired line divided by the line width gives the average line height, and that correlated best with square resistance. This comparison is shown in Fig. 10 for two inks containing the same hydrocarbon resin components. Ink B has a 15% higher silver content than ink A. The widest lines printed with ink B are also the highest, and have the lowest square resistances. However, ink A without solvent is able to print narrower lines, as shown by the trend line crossing

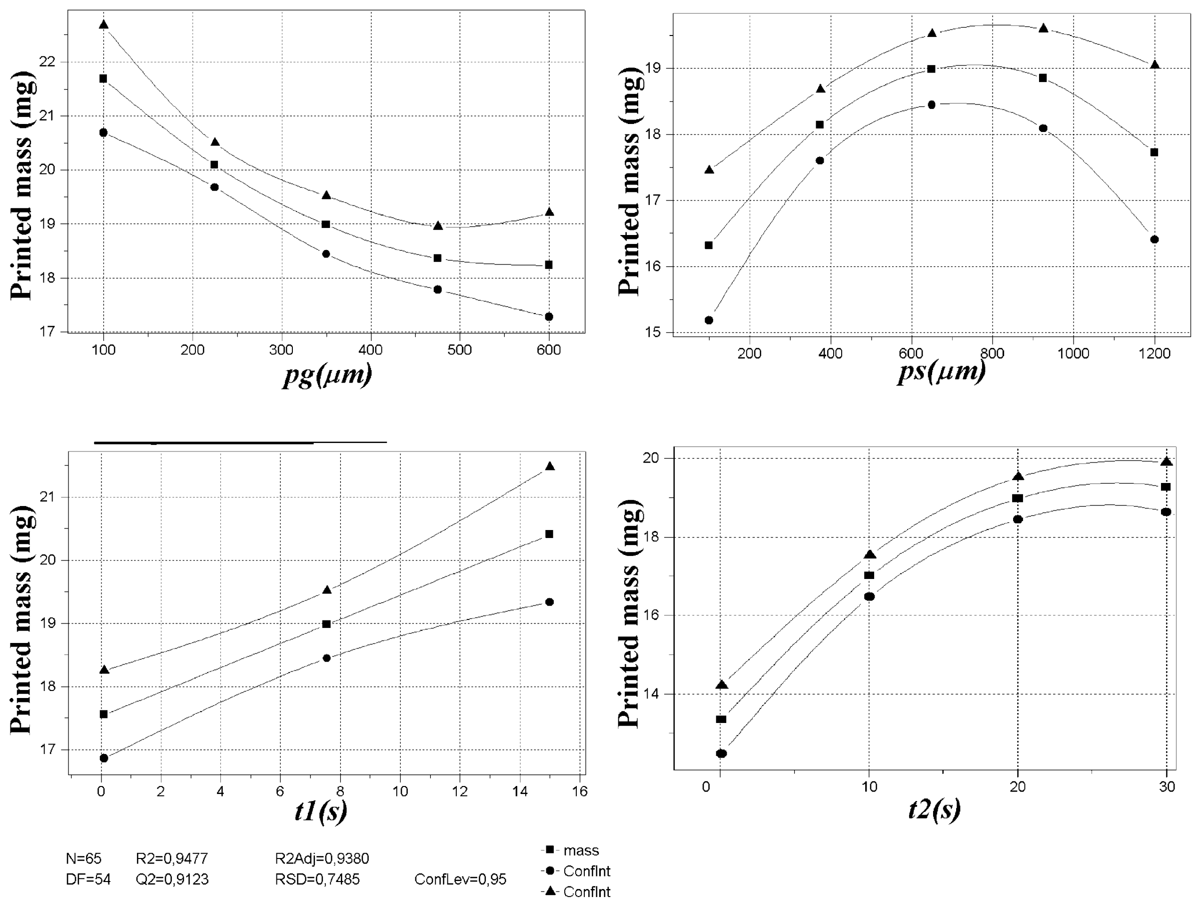


Fig. 6. Best-fit multivariate model made with Modde 4.0 from hydrocarbon inks. Printed mass on substrate with 95% confident limits as functions of compression-thickness [μm] of gravure (*pg*) and substrate (*ps*) and times [s] of doctoring to pickup (*t1*) and gravure to substrate (*t2*).

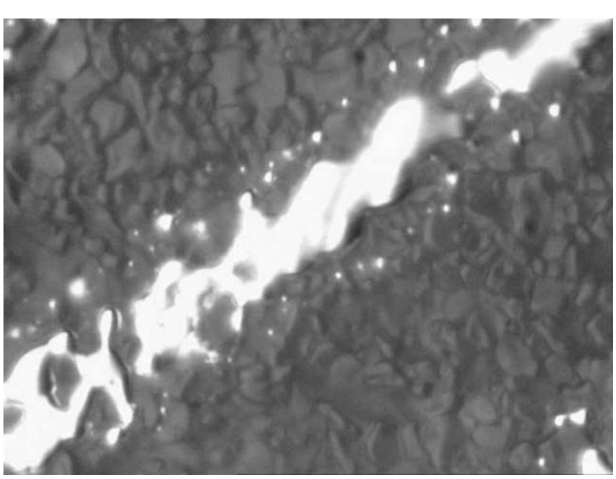


Fig. 7. A 20 μm wide printed and fired line on alumina. There is insufficient ink to form a conductive trace due to roughness of the substrate.

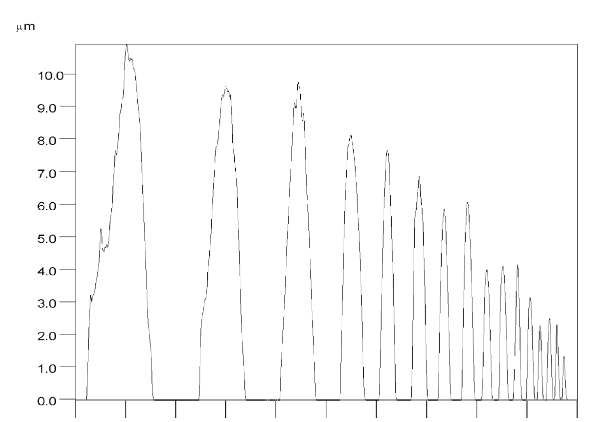


Fig. 8. Printed and dried ink 'A' line profiles printed on glass of 280, 200, 140, 100 μm wide lines and pairs of 70, 50, 35, 25, 18 and 13 μm wide lines.

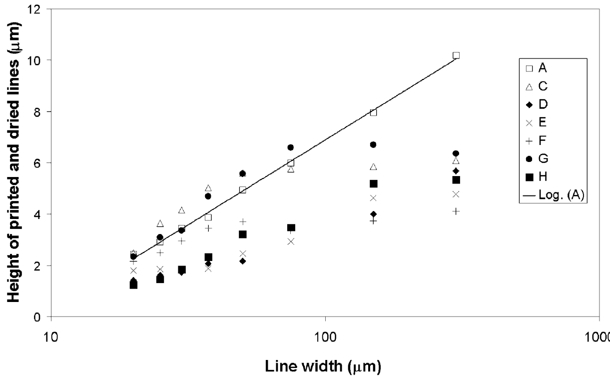


Fig. 9. Dried conductor line height vs. printed line width of different kinds of (hydrocarbon and ethyl cellulose based) of inks.

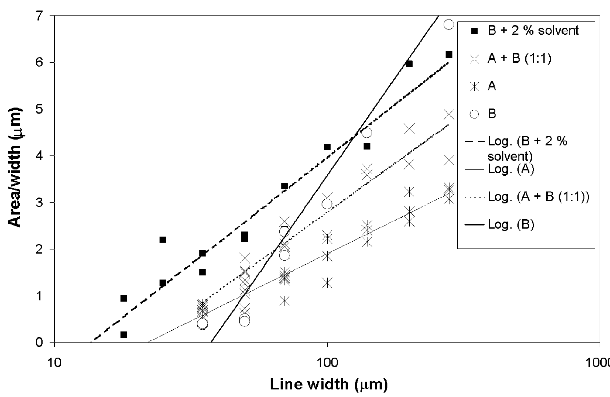


Fig. 10. Fired line cross section area/designed line width (normalized height) vs. designed line width.

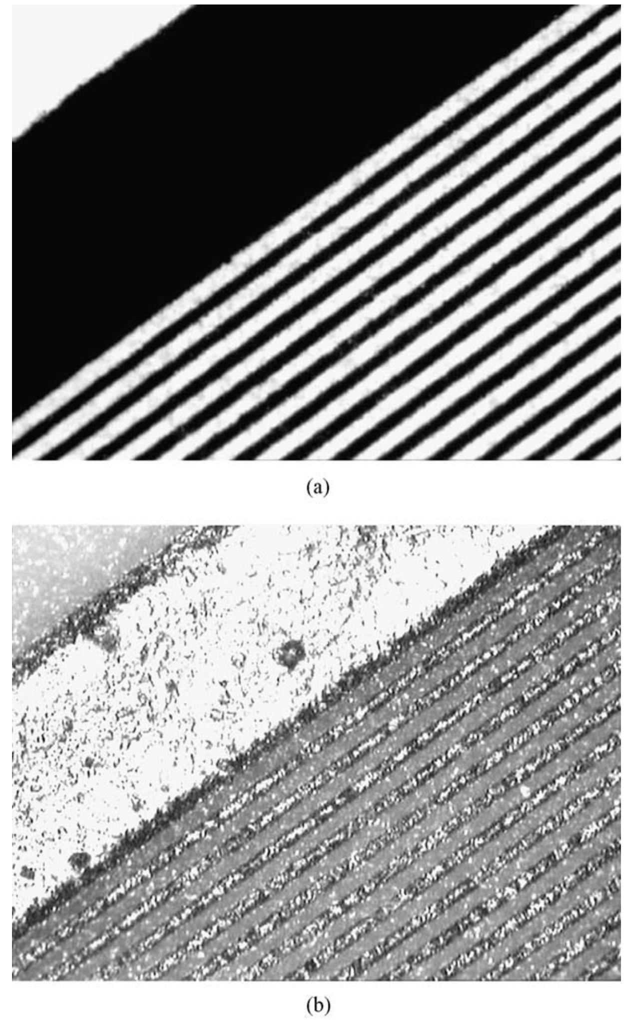


Fig. 11. Ink A, 300 and 20 μm wide dried lines, (A) light through and (B) light from top.

the x-axis. A mixture ratio 1:1 of inks A and B shows the expected behaviour between trend lines of these inks. With the addition of solvent (2 wt.% of hydrocarbon solvent, mixed on a 3-roll-mill), the semi-logarithmic angular coefficient of ink B decreased and the crossing of the x-axis moved towards smaller line widths. Therefore, the best results from the narrow line point of view, with a minimum effect on wide lines, are achieved by using ink B with added solvent. However, the practical limitation in the use of ink B is gravure groove blocking during long print runs.

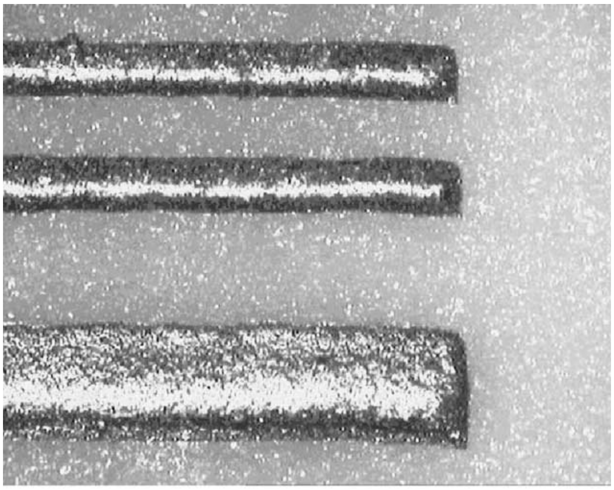
The printing results achieved with ink A, from a 30 μm deep gravure, are shown in Figs. 11 and 12. Light through the substrate enabled more accurate observation of printed area edges, whereas light from the top shows the surface forms on the printed ink.

4. Conclusion

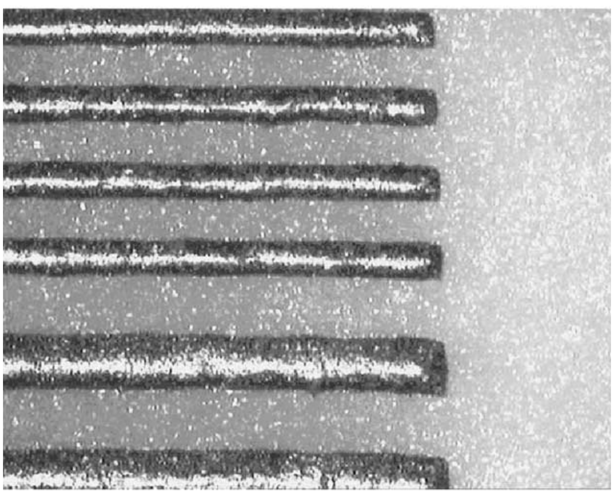
Hydrocarbon resin based inks have significantly better printing quality compared to the traditionally used ethyl cellulose binder based inks and are superior in all other printing result values tested. As long as gravure groove blocking is not a severe problem and sufficiently narrow lines and spaces can be printed, inks having high viscosity and high internal cohesion give the best printed results. Ink containing 85 wt.% of silver has resulted in resistance values down to 5 mΩ/sq. for 300 μm wide lines. This is a promising result for an electronics manufacturing product, because the printing was done while 100% of ink was transferred from the blanket to the substrate. The process is being developed further with respect to the printing delay parameter and its effect on resolution and resistance.

When thick lines must be printed, the associated issues of selecting the right ink content and required minimum line width must be addressed. A non-polar and smooth surface silicone blanket and effective doctoring were major requirements for good results. Better blankets and improved inks are still required.

Based on the results of the correlation matrix of printed sample measurements, it is found that the printed line cross section area is the best response for comparison. However, for uniform lines, the square



(a)



(b)

Fig. 12. (a) 75 and 150, (b) 37.5 and 50 μm wide dried lines printed with ink A. Because light is coming from the top, the surface shapes of printed lines are shown.

resistance can be used as a highly correlating response. If the same pattern, line width and ink are used, then the printed mass is a good response for the comparison of similar printings.

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