1. INTRODUCTION

Screen printing, sometimes referred to as silk screen printing or serigraphy, is a stencil printing technique used in many different industrial production processes, where thick film deposition is required. It is a low cost technology and is frequently used for printings in advertising, for printing decors on dishes or textiles, for the printing on glass in automotive industries, for decorative applications and for electronic devices.

The screen printing procedure, a stencil process, comprises the printing of a viscous paste through a patterned fabric screen and is usually followed by a drying process. The method can be applied to flat or cylindrical substrates. Depending on the substrate materials and the requirements for the printed structures, a high temperature densification can also be necessary.

Low temperature processes (T < 150°C or UV-curing) to cure prints on organic substrates are also well established for almost all kinds of materials.

Screen printing procedures in combination with high temperature processes (T > 500 °C) are most commonly used to obtain abrasion resistant and chemically durable decors e.g. in house ware industry or to obtain functional prints in electronic and automotive industry. The printed objects are glass, ceramic or metal substrates.

In electronic industries, the screen printing technology is used for the production of electronic devices with resolutions down to 100 µm line space width [1]. For this application, different pastes for the obtention of resistors, capacitors, conductors, isolators or solder glasses are processed in successive steps: printing, drying and firing procedures.

Additionally, pastes containing metal pigments are used for the printing of conductive electronic and sensor components, e.g. in solar cells, gas sensors and solid oxide fuel cells.

The densification temperature of the prints on glass substrates is usually lower than on metal or ceramic ones. Therefore, special glass frit binders with low melting points have been developed. Such pastes containing metal or color pigments are used e.g. for the printing of heating wires or decors for automotive windows and architectural glazings.
Recent developments utilized the screen printing technology for the production of glass based plasma discharge panels where fine structures of fluorescent pigments, conductors and spacers have to be printed with high structure heights and high resolution.

2. THE SCREEN PRINTING PROCESS

The screen printing process utilizes a screen as the carrier of the to-be-printed pattern.

The screen consists of the screen frame usually made of aluminum and the screen web covered with a photosensitive emulsion layer. The screen webs made of silk, nylon, polyesters or stainless steel, have usually mesh counts from 10 to 450 meshes per inch. Screens with high mesh counts and small thread diameter are suitable for the printing of fine structures. For example, a stainless steel web with 400 mesh per inch, a thread diameter of 18 µm and a mesh opening of 45 µm was successfully used to print sharp edged lines with 100 µm width or dots of 70 µm on glass substrates for electronic application [2].

To transfer a given setting copy to the screen, the photosensitive emulsion layer on the screen is exposed to UV light through a film containing the pattern. Unexposed areas of the emulsion layer are dissolved, leaving the pattern as free spaces in the screen.

The printing process is divided into two sections both shown in figures 1 and 2. In the flood stroke (figure 1), the paste is spread on the fixed screen so that the openings in the screen are filled with the paste. At this time, the screen does not get into contact with the substrate. During the print stroke (figure2), the screen contacts the substrate while the squeegee presses the paste through the screen openings and transfers it onto the substrate.

Squeegees are available in different shapes, such as U- or V-shapes, different hardnesses and materials. Squeegees of polyurethane and a hardness between 60 and 80 shore A are commonly used.

To obtain high quality printing results, parameters regarding the web material, the emulsion, the printing procedure and the printing paste have to be optimized [1]. This involves the web tension and thickness, the mesh count, the emulsion thickness, the squeegee hardness, shape and pressure, the printing velocity, the accuracy of the positioning and the paste parameters. The paste parameters are described in detail in the next section. A detailed mathematical treatment of the screen printing process is given in [3].
3. PASTE REQUIREMENTS, COMPOSITION AND CURING

Screen printing pastes mainly consist of four components: binders, screen printing oils, additives to adjust the rheological properties of the paste and functional pigments [3, 4].

Polymer binders like acrylates are used for low temperature applications. They are cured by thermal treatment or UV-irradiation to induce adhesion on the glass and cohesion with the pigments.

Usually, high temperature binders consist of glass frits (including crystallizing frits), which melt at temperatures of 550 – 850 °C. Depending on the substrate, the melting temperature has to be adjusted by incorporating high amounts of heavy metal ions (Pb, Zn, Bi, Cd) or, more recently, high amounts of Sn, alkaline, earth alkaline or rare earth metal ions. Adhesion to the substrate and cohesion of non-sintered particles is induced by melting of the binder.

For special applications, inorganic low temperature binders are required to reduce the burn out loss during firing of the dried pastes. For this purpose, aluminum phosphate [5] and sol gel materials were investigated [19].

In high temperature enamel pastes, polymer binders and high temperature binders are used together to achieve both a sufficient green hardness and a high mechanical and chemical durability after the firing process.
Screen printing oils as e.g. ethylene glycols, α-terpineole and ethylene glycol butyl ethers are used to dissolve and disperse the additives and pigments and to avoid the drying of the paste during the printing process.

The rheological properties of the paste are of great importance for the printing process, especially in high quality fine line printing [1, 3]. On one hand, after filling the screen openings, the printing paste has to remain in the screen. On the other hand, during squeegee crossing, the former high viscosity of the paste must decrease so that the paste can flow through the screen openings. Additionally, the low viscosity at this time leads to a smooth surface after the snap off of the screen. A small line broadening is only achieved if the viscosity increases shortly after the snap off. These properties are usually achieved by incorporating additives as cellulose derivatives to adjust a thixotropic rheology.

The pigments could be either organic or inorganic, metal or semiconductor particles are also possible.

The thermal treatment of high temperature enamel screen printing pastes includes a drying process at 120 to 180 °C and a successive sintering process at 550 to 850 °C in tunnel or muffle furnaces. The drying process should diminish the solvent content and should harden the green material for safe handling and successive prints. During the high temperature curing, solvent residues should first evaporate, then in a second step the complete burnout of organic additives is required and at last the pigment-glass frit composite should be densified.

4. SOL-GEL-MATERIALS IN SCREEN PRINTING PROCESSES

The sol-gel technique has been frequently applied for the production of nanoscaled powders (zirconia [6, 7], titania [8, 9], PZT [10], SnO₂ [11], etc.) which are later on incorporated into screen printing pastes for thick film applications. To achieve the required properties, a final thermal processing including the total burnout of organic additives is necessary.

Beyond this, the combination of the sol-gel technology and screen printing process has rarely been used. As an example for a low temperature application, alkoxides of titanium, zirconium and silicon were chosen as precursor materials for sol-gel/graphite [12, 13] or sol-gel/gold composite materials [14] including biological active components. They are used to fabricate electrochemical sensors, allow low curing temperatures (4°C) [13] and may replace cellulose binders and common screen printing oils [15].

Titanium alkoxide solutions as precursors for titania film for anti reflection coatings on solar cells have been incorporated into screen printing pastes without the addition of any particles. Required properties are achieved by the in situ sol-gel-process and by final thermal curing [16].

A new approach for high temperature binders in screen printing pastes is given by the application of liquid sol-gel materials which can replace conventional glass frits, screen printing oils or rheological additives [17]. These materials offer remarkable advantages as increased degree of pigment filling (e.g. for
conductive pastes), improved degree of homogenization compared to glass frits pastes and the (partial) replacement of organic additives which have to be burned out under oxygen containing atmospheres [19]. This approach is especially useful, if the printing is covered by a second glass during firing like side 2 or side 3 decorations in couple-bending of automotive windshields [18].

Mixing a water based sol of PbO-SiO$_2$-B$_2$O$_3$-ZnO and black enamel pigment without any organic binders and screen printing oils, a printable paste was produced for the decoration of glass. It had rheological properties similar to that of conventional pastes and could be densified between 560° and 640°C achieving good mechanical durability [19].

Sol-gel materials based on silicon alkoxides have been used as substitutes for glass frit binders in conductive pastes [17] and in heavy metal free ceramic pigment pastes [17], each for printing and firing on soda lime glass substrates. Conducting silver lines with improved line resistance (due to higher degree of filling) and improved acid resistance could be achieved after firing at 670°C for 5 minutes [17].

A second application of sol gel technology in screen printing technology is the micro encapsulation of pigment powders [20] with sol-gel derived xerogels utilizing spray drying of composites of sol-gel-materials and pigments. Benefits may be a lower annealing temperature, the replacement or at least the decrease of binder content and the incorporation of redox sensitive pigments [20].

The sol-gel technology has also been used for the preparation of a Cu- and Cr-free black pigment suitable for recyclable black decorations on automotive windows [21, 22]. The pigment is based on a SiO$_2$-SiC-C-composite system, which is obtained by the hydrolysis and condensation of methyl substituted silicon alkoxides. The sol is spray-dried and the obtained fine xerogel powder is heat treated at about 1400°C in a falling-tube-furnace. The pigment particles withstand the firing process in state-of-the-art glass frits at temperatures between 400 and 600 °C without bleaching. However, during the recycling process in a float glass melt at about 1500°C (50 % cullet), the carbon compounds are oxidized completely, and a clear glass with suitable optical properties is obtained [22].

5. REFERENCES

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