The Glass Surface and Ways of Its Modification

Ferdinand Trier, Munich University of Applied Science, Germany

Ulrich Ranke, Ormo Print GmbH, Germany

1. Introduction

The material glass is used in a variety of products. In many cases, the properties of a glass product shall be optimized. This can be done by changing the chemical composition of the glass. Some effects can also be achieved by changing the surface of a glass product.

2. What is a glass surface?

The glass surface seems to be an abrupt change between solid glass (which is defined by its chemical composition) and the surrounding air. A closer investigation of the glass surface gives a more detailed view, the abrupt border is vanishing and different zones of transition between glass and environment are appearing.

In the core of a soda-lime glass there is a network of silicon dioxide molecules. Between these, calcium and sodium ions are embedded (***fig. 1***).

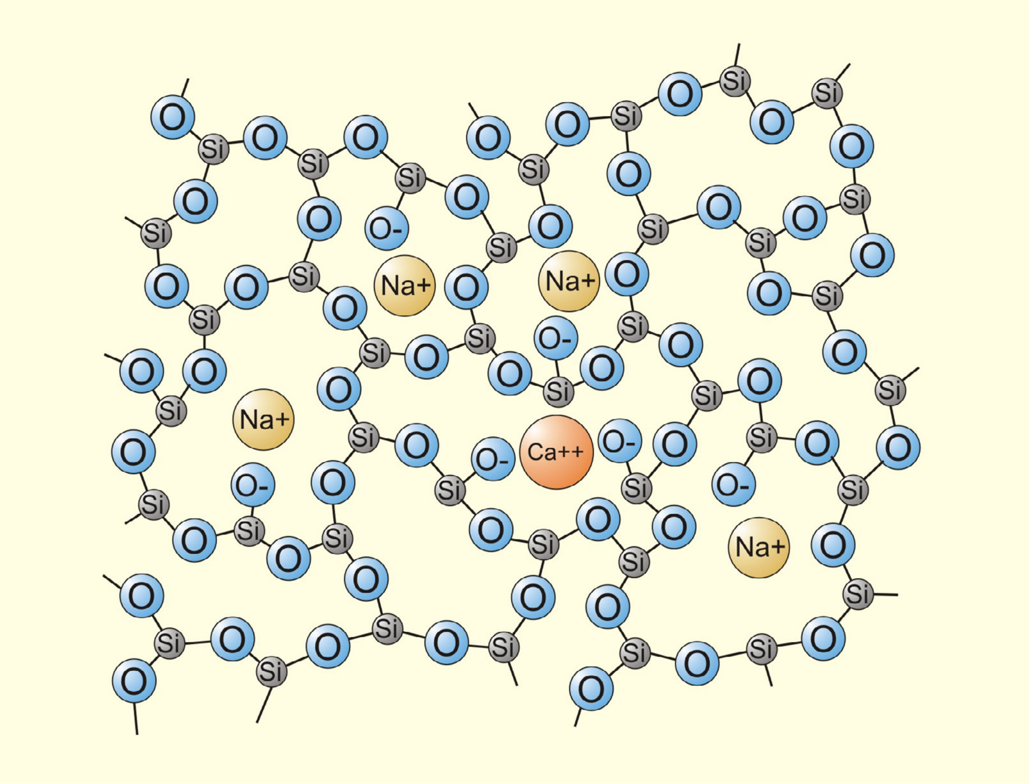

Fig 1: Scheme of a soda lime glass [1]

If we approach from bulk of a glass to the surface, the water content of the glass is rising, because glass is attracting water from the atmosphere. Water is able to break some of the connections in the silicon dioxide network and further diffuse from the surface and micro-cracks into the glass bulk (***fig. 2***).

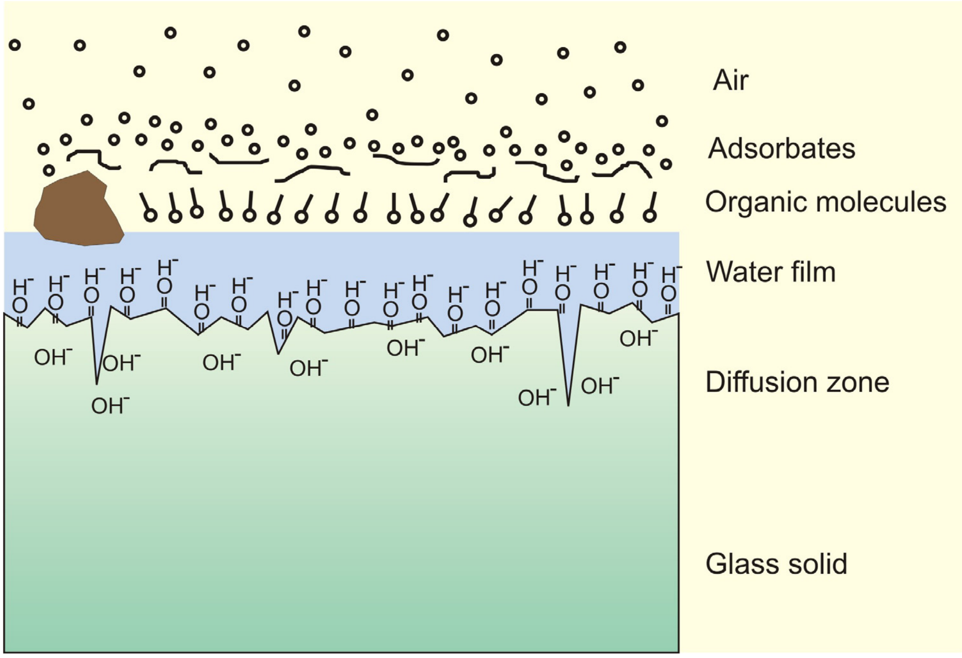

Fig. 2: Typical glass surface before coating

The sodium content near the surface may differ from the bulk material, because sodium is volatile under conditions of the heat treatment of the glass, so it may vaporize in some regions of the glass, but may also condense in other regions.

At the point, where the network of silicon dioxide ends, the network is continued with chemisorbed water molecules (***fig. 3***). This chemically absorbed water film goes over in a physically absorbed water film, which also collects various adsorbates from the atmosphere, like organic molecules and dirt particles.

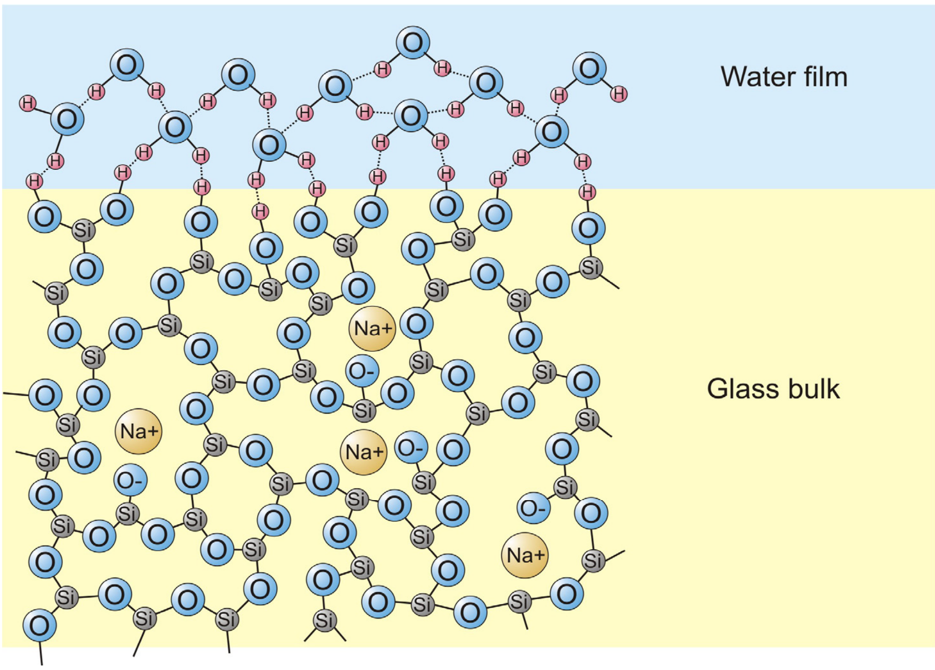

Fig. 3: Sodium-silicate glass with water film

The condition of the glass surface depends in a high degree from the history of the glass. It is already changed at the manufacturing, but also while the storage of the glass. Everybody who is concerned with glass should be aware of this fact.

3. Properties how to change the properties of a glass surface

Modifications at a glass surface can be classified as following:

- methods, which generate a new surface by removing material from the original surface
- methods, which do not form a new surface, although the original surface is modified by exchange of material
- methods, which generate a new surface by adding additional matter to the original surface

For these methods, there exists a variety of methods (***fig. 4***)

Different Ways for Surface Modifications

Removal of material from surface	**Modification by material exchange**	**Addition of material to surface**
Mechanical: • Grinding • Polishing **Chemical:** • Etching	**Diffusion:** • Glass staining • Chemical toughening	**From plasma:** • Ion plating • PECVD **From gas phase:** • Sputtering • PVD • CVD **From liquid/solid phase:** • Paint • Ceramic coatings • Au/Pt/Ag Coatings • Sol-gel • Hybrids

Fig. 4: Ways for surface modification - overview

4. Modification by removing matter from the original surface

4.1 Mechanically ablating methods

At a mechanically ablating process, little particles are broken out of the glass surface by the impact with a grinding matter. Usual techniques are grinding, polishing and blasting. Mechanically ablated surfaces always become rough, but the grade of roughness can be well controlled, so that even optically smooth surfaces are attainable. Grinding methods are necessary, in case the shape of the glass part must be defined very exactly, e.g. for optical parts.

Blasting is often used to get a surface with a certain roughness, without special attention to the mechanical precision (***fig. 5***). A probable disadvantage of a blasted surface is the high number of micro-cracks, which are generated at the process. Micro-cracks are suspected to weaken the mechanical strength of the part. On the other hand, surface frosting by blasting is typically cheaper than by etching.

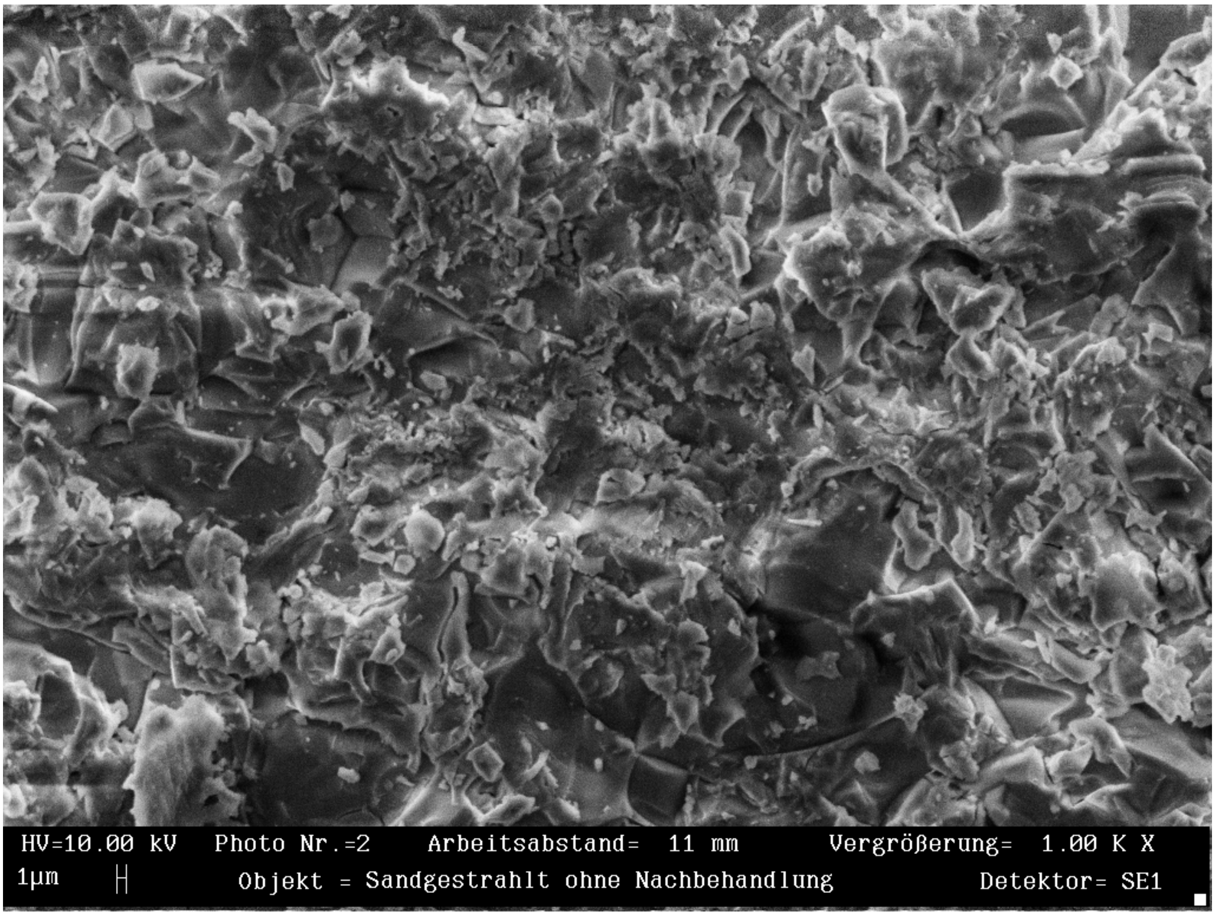

Fig 5: SEM picture of a blasted glass surface

4.2 Chemically ablating methods

Ablating by etching will typically have a smoothening effect to the surface. This polishing is often the motivation for the procedure. Another motivation is to replace the original surface, which is probably undefined, soiled or affected with micro-cracks with a newly created surface. The effect is a surface cleaning.

It is also possible to create a rough surface by etching. With acid frosting little crystals are settling at the glass surface and stop the acid attack at the covered areas, while the etching is between the crystals is not obstructed. The surface structure, which is generated by that, is an image of the crystals (***fig. 6***).

Compared to blasted surfaces, acid frosted surfaces have a very fine structure and a smooth touch.

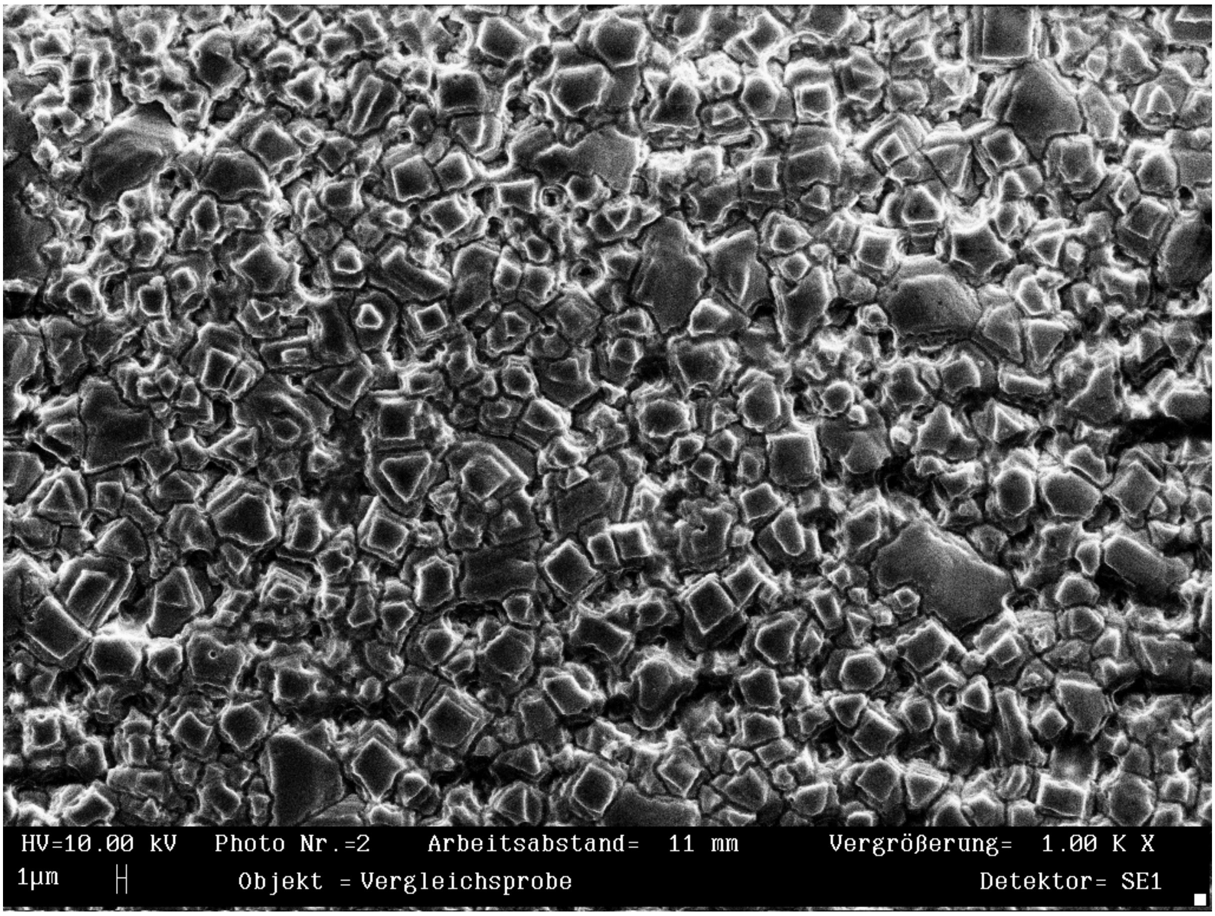

Fig. 6: SEM picture of an acid frosted surface

5. Modification of the existing glass surface

Behind this term hide two traditional techniques, the glass staining and chemical toughening. Also newer techniques, which influence the surface energy of glass, belong to this category.

5.1 Glass staining

For glass staining, silver is brought in the glass over a surface diffusion process. The yellow to orange-brown colour is generated by the formation of silver clusters. The diffusion process is conducted at high temperature for several hours from a silver containing paste, which was applied to the glass.

5.2 Chemical toughening of glass

Chemical toughening of glass is also a diffusion process. Sodium ions, which are present in the glass are partially replaced by potassium ions. Due to the higher diameter of the potassium ions, the volume of the potassium enriched volume is increased. Resulting mechanical stress leads to a higher mechanical strength of the part, like with thermal tempered glass. The process is conducted at high temperature by immersing the glass part into a molten potassium salt (***fig. 7***).

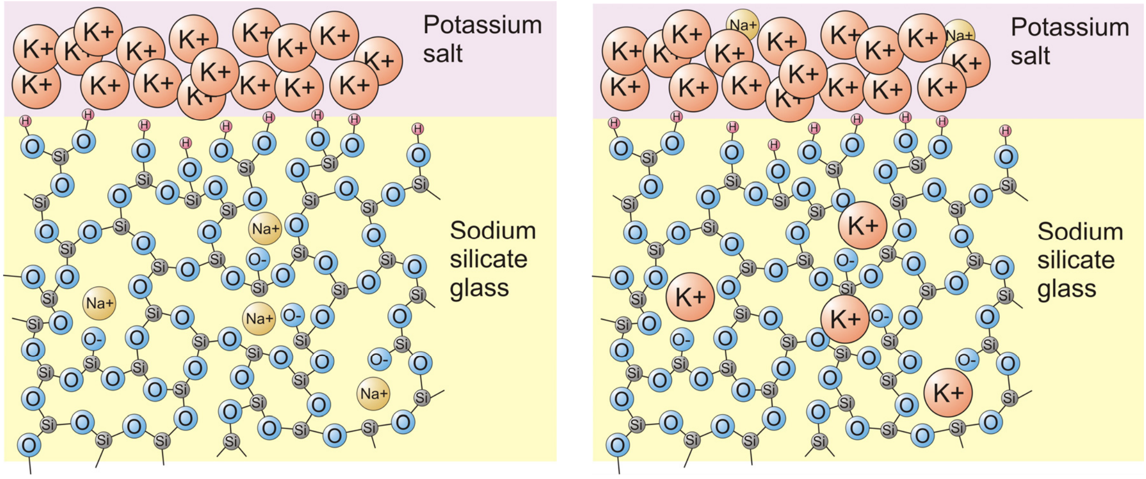

Fig. 7: Scheme of chemical strengthening:

7a: before ion exchange (left) **7b: after ion exchange (right)**

6. Modification by adding matter to the original surface (coating)

For the surface modification by coating, very different techniques are in use. The field can be roughly distinguished into 4 sections.

6.1 Physical vapour deposition (PVD)

For this process the coating material is evaporated in high vaccum by high temperature and condensated at the glass surface (***fig. 8***). The growing rate of the layer can be controlled by special measurement equipment. Often more than one coating are applied. So mirrors or antireflection coatings can be applied by a sequence of coatings with high and low refraction index. PVD coatings are used for antireflection coatings and metal oxide vaporized mirrors.

6.2 Sputtering

Sputtering is a high vacuum process as well, with a certain similarity to PVD. In opposite to PVD, the coating material is not thermally evaporated, but released by ion bombardment of a target. The matter, which is released from the target, is settling on the glass surface (***fig. 9***). Sputtering is more versatile compared to PVD, it is e.g. also possible to sputter materials with a very low vapour pressure.

Sputtering meanwhile became the standard procedure for low-E coatings for window glass.

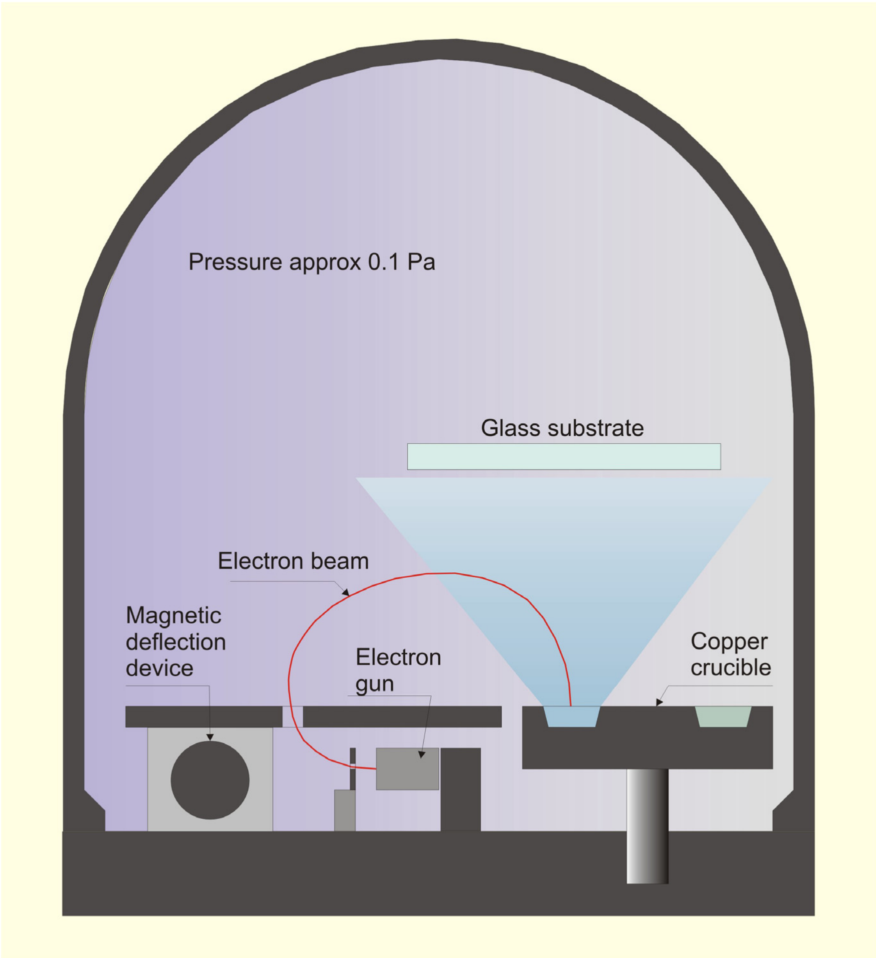

Fig. 8: Scheme of an Electron beam physical vapour deposition (EBPVD) plant

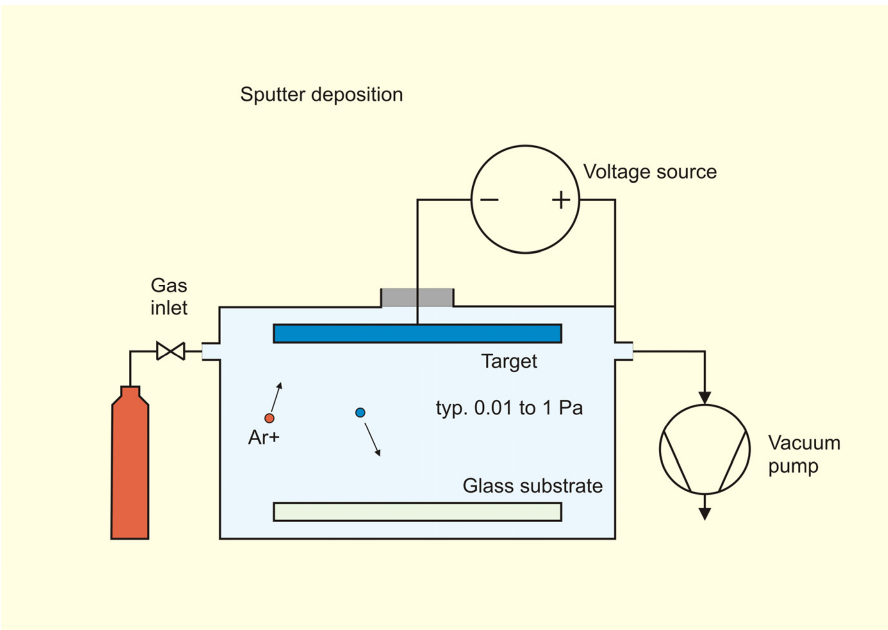

Fig. 9 Scheme of sputter deposition

6.3 Chemical Vapour deposition (CVD)

The CVD process is characterized by the fact, that a solid coating is formed from one or more vaporized chemical precursors (***fig. 10***). Depending on the nature of the chemical reaction, such a process may also be conducted at atmospheric pressure.

A typical PVD process a atmospheric pressure is the hot-end coating of container glass. Here a volatile, tin-organically substance is reduced at the hot glass surface to tin oxide.

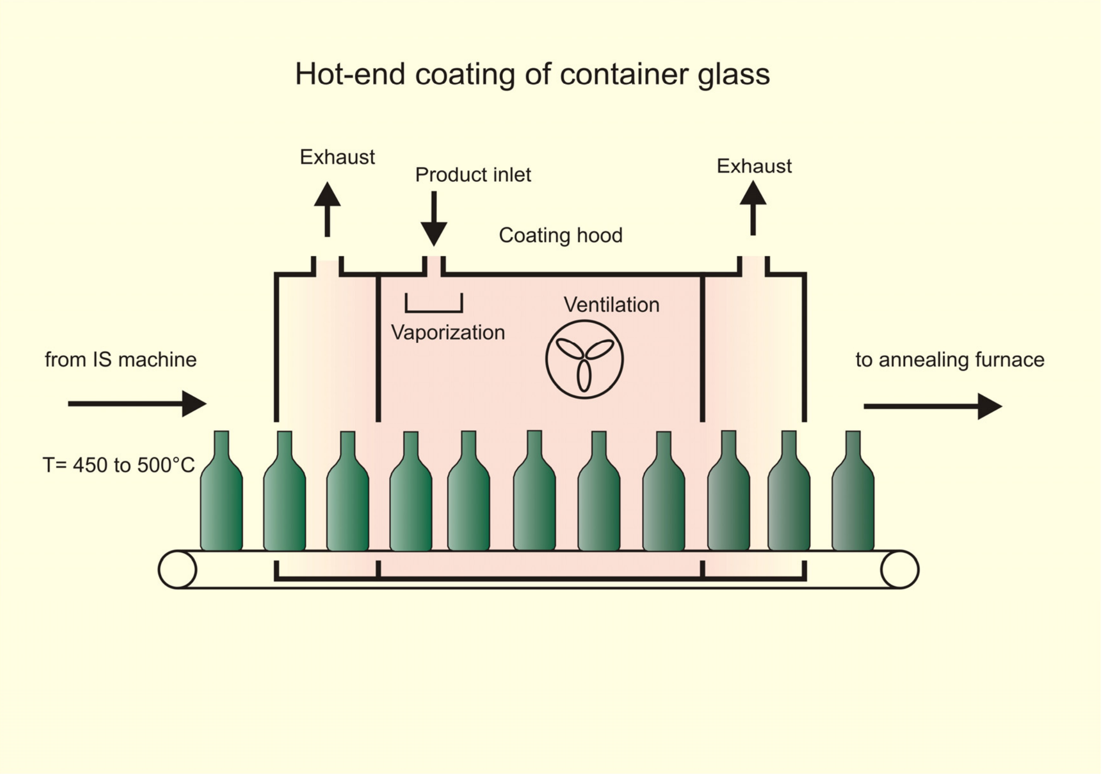

Fig. 10: Hot-end coating of container glass

6.4.1 Wet coatings.

For wet coatings, a paste or liquid is applied to the glass surface. By either a chemical and / or physical process the wet layer is hardened to a coating. Depending on the process, the coating needs an additional curing process to achieve the final durability.

6.4.1.1 Inorganic coatings

Inorganic coatings are known under the name „ceramic coatings” or „Sol-Gel“. Inorganic coatings are applied as fluid or paste. A first drying is typically conducted by solvent evaporation. To achieve full hardness, these coatings need to be fired at a high temperature, the upper temperature is typically limited by the properties of the basic glass.

6.4.1.1.1 Ceramic coatings

Ceramic coatings are mostly a dispersion of a glass powder, which is melting on the basic glass while curing. It is necessary that the transformation temperature of the coating is below the transformation temperature of the basic glass. Colour effects can be achieved with colouring metal salts. Ceramic paints give durable and robust coatings.

A special case is the precipitation of precious metals (gold, platinum) on glass. Such formulations are based on metal salts, which are reduced to the metal at firing.

Ceramic coatings have a wide field of application for flat glass as well as for hollow glass. A typical application is the black print around the rim of a car windshield. Here the gluing of the window shall be covered – not only for nice appearance – but also to protect the glue from the harmful influence of sunlight.

6.4.1.1.2 Sol-gel

The classical sol-gel method gives inorganic coatings as well. These are formed from a colloid by evaporation of the liquid phase. The solid phase of the colloid is synthesized from a solution of precursors (***fig. 11***).

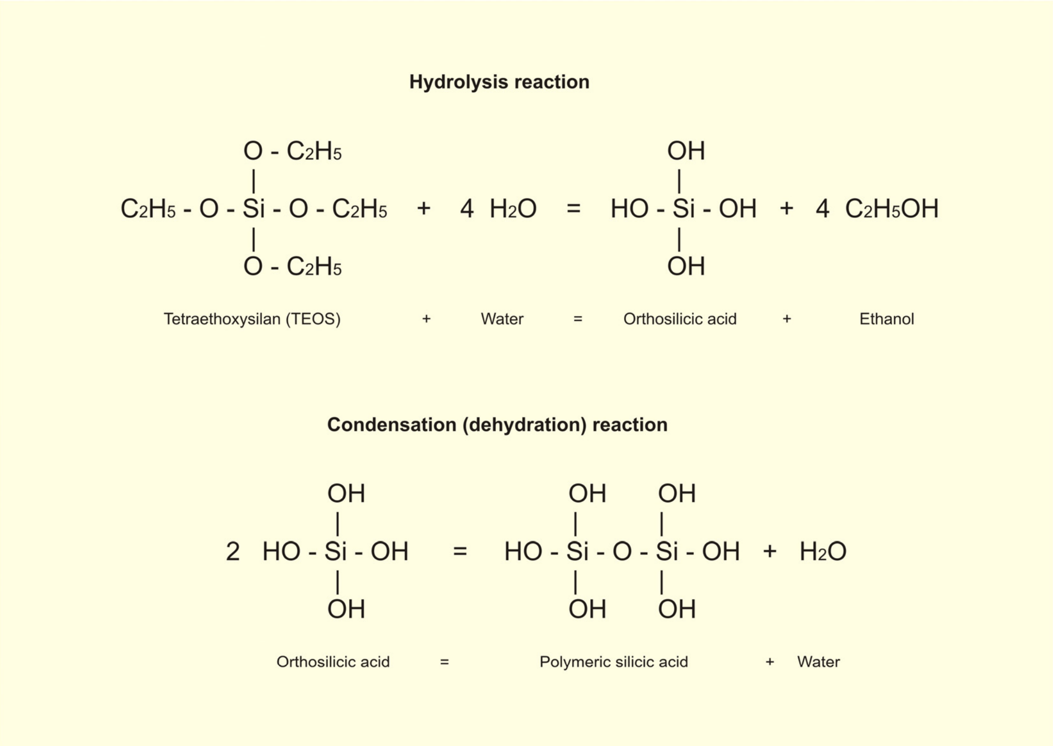

Fig. 11: Basic chemical reactions for Silica deposition by sol-gel

Usually oxide coatings can be generated with sol-gel, typical are coatings made of silicon oxide.

The coatings are massively shrinking while the curing process, which is a result of the loss of the liquid phase. This is why only thin layers are possible, thick layers are cracking.

Sol-gel is often used for interference coatings.

6.4.1.2 Organic coatings

Glass can be decorated with organic paints as well. Based on usual industrial coatings such coatings are modified for glass coating. One- ore two-component systems or powder coatings are usual. Some important quality criteria for an organic glass paint are:

- o good adhesion to glass (even under influence of water)
- o high gloss
- o high scratch resistance
- o good levelling
- o high transparency

Due to the easy application and curing, organic paints are often used for glass decorations. The durability of ceramic coatings is generally not obtained by organic coatings.

6.4.1.3 Hybrid coatings

Hybrid coatings were developed from sol-gels to overcome the limitations to layer thickness as well as to improve chemical resistance. Hybrids contain inorganic as well as organic matter. So the shrinking of the coating is reduced which makes thicker coatings possible, compared to sol-gels. Due to the thicker layers, colorants

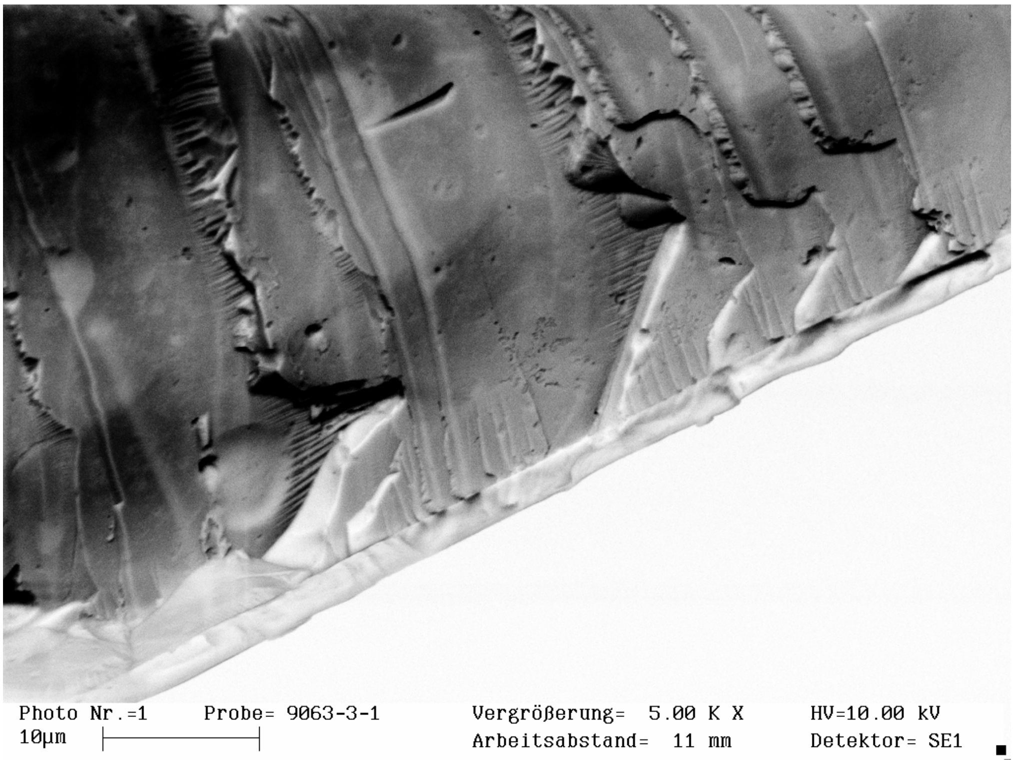

Fig. 12: SEM view on a broken glass, which has previously been coated with a sol-gel hybrid

can be introduced in the coating, so transparent or opaque decoration coatings are possible. Typical decoration coatings have a thickness between 1 and 10 micron. So hybrids are still thinner than organic coatings. That does not only result in economical advantages, also the appearance profits from the thin layers (***fig. 12***).

7. Examples for application techniques with wet coatings

For the surface removing techniques, as well as for the vacuum techniques, the process is rather defined by the technical procedure. For the wet coatings, everything is possible, which leads to a success. In the following section, some application techniques for wet coatings shall be introduced.

7.1 Standard techniques

Standard techniques for coating are dip coating (***fig. 13***), spray application (***fig. 14***) and brush painting (***fig. 15***). Dip coating and spray coating can be automated easily und are often used in mass production.

7.2 Felt pen

Application by felt pen has – compared to brush painting – the advantage, that the painting can be done continuously, because the paint flow works automatically. Lines, which fit to the width of the tip are easier to draw than with a brush

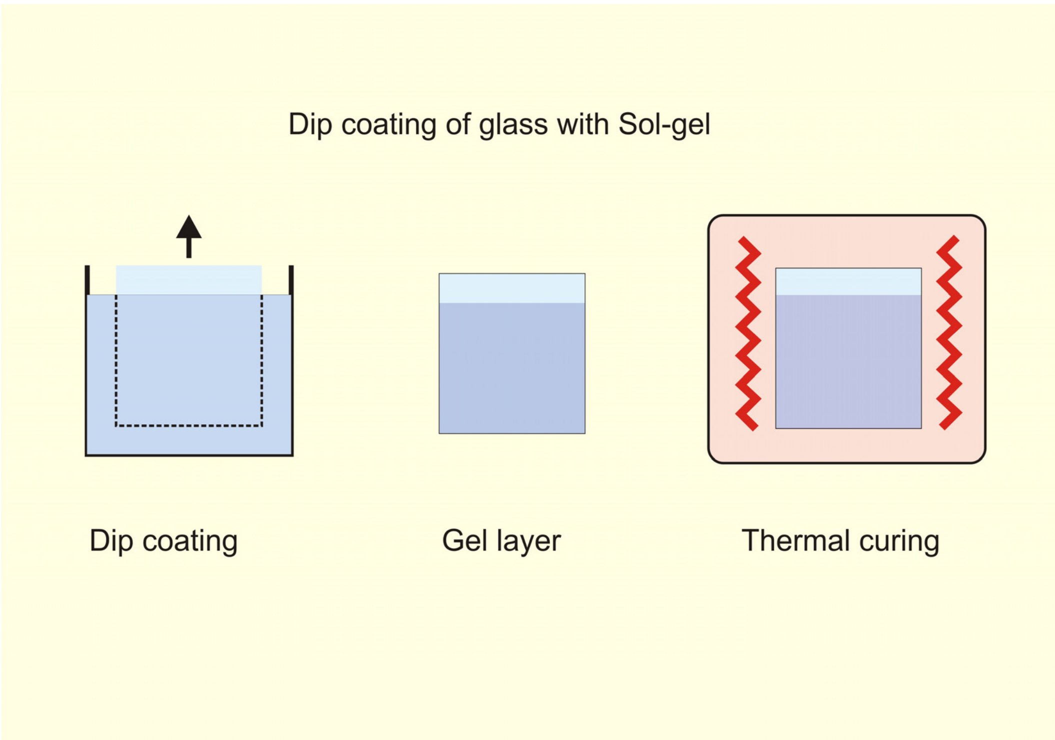

Fig 13: dip coating

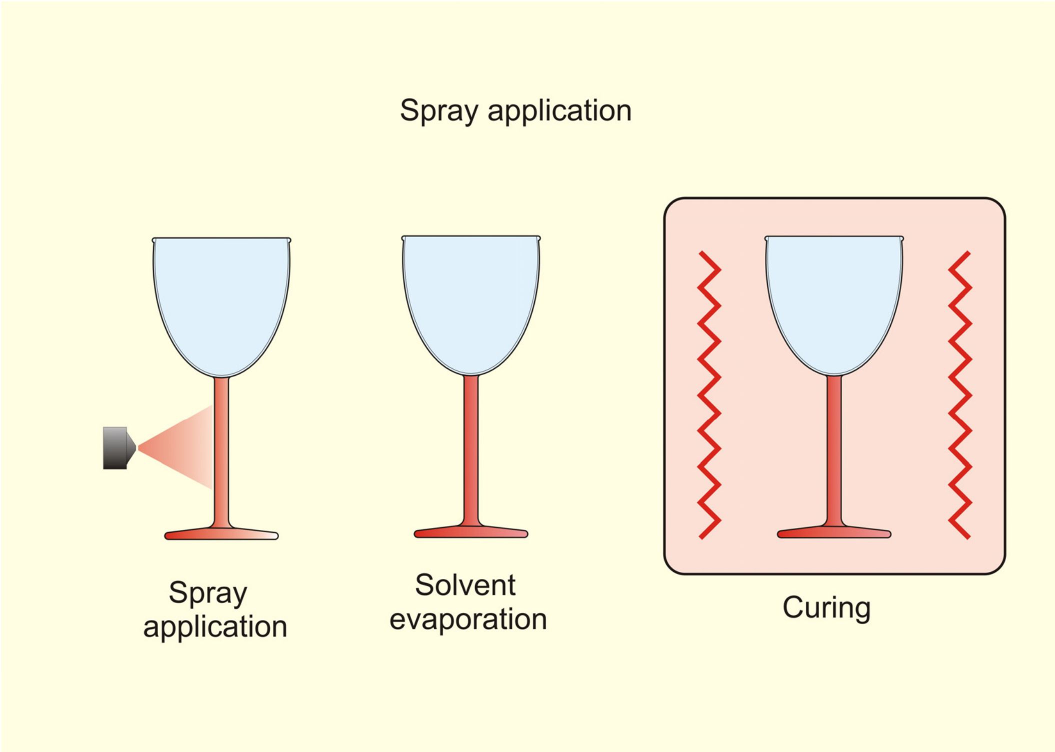

Fig 14: spray coating

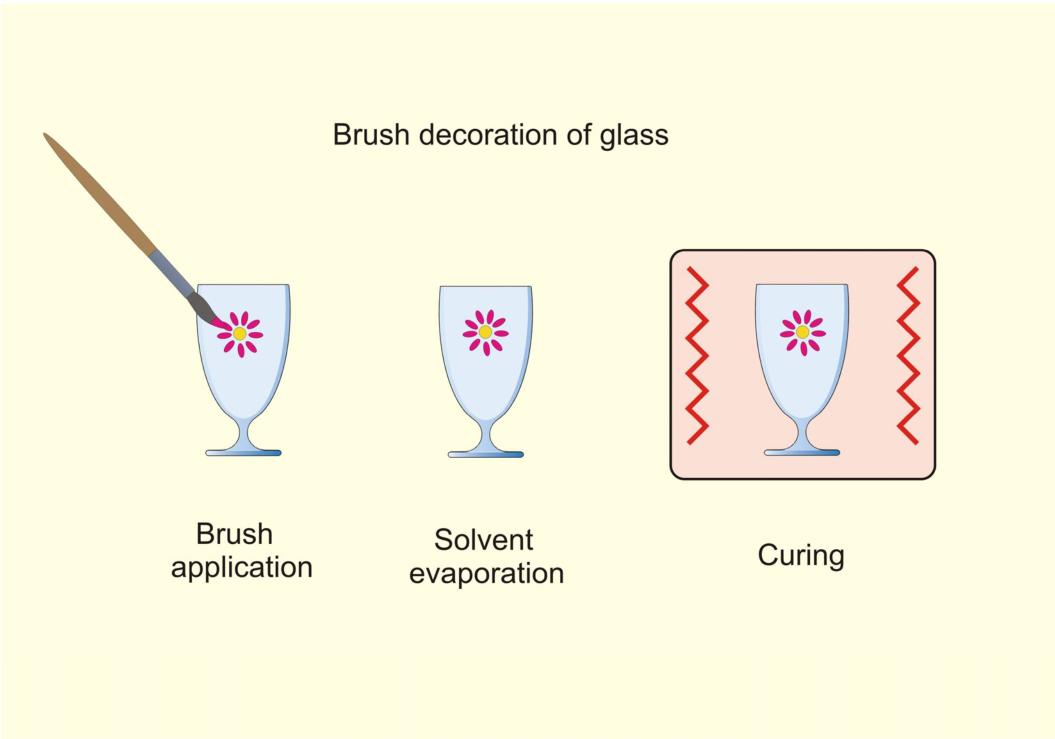

Fig 15: brush coating

7.3 Coating of bulk material

For bulk material a solvent based system can be applied. The bulk material (grains or beads) are intensively mixed with the paint, so that the paint spreads equally over the whole surface of the bulk material. After that, the solvent is blown out, so the paint is fixed and can be cured afterwards (***fig. 16***). It is important, that the paint spreads easily over the material and that the paint does not glue the material together.

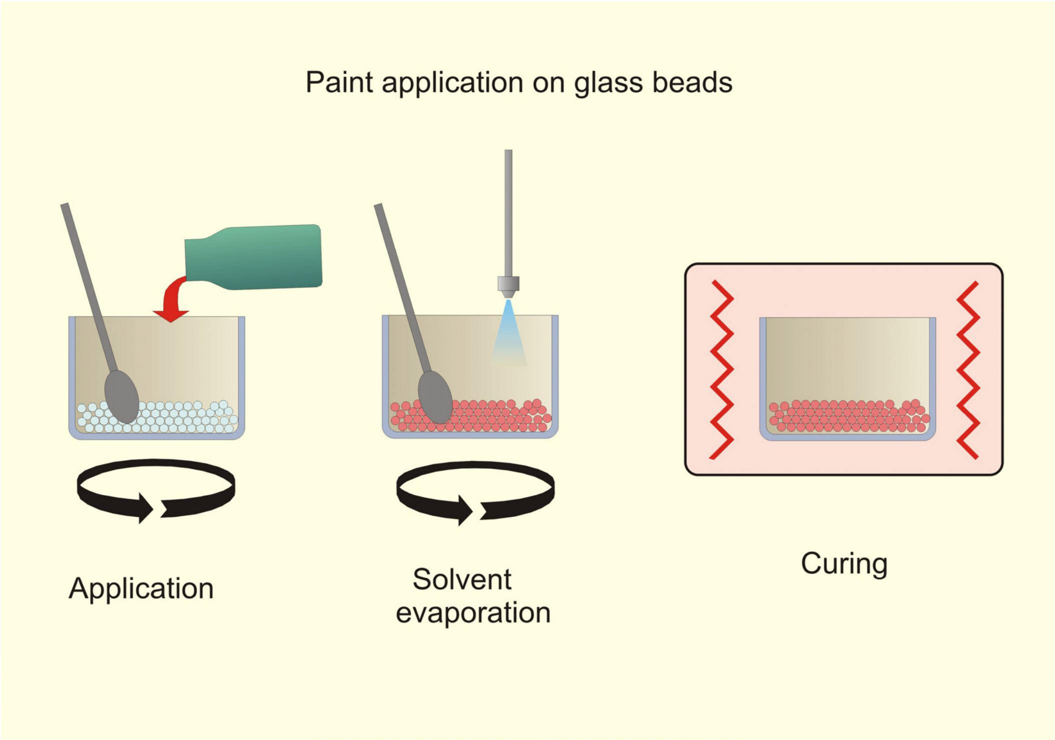

Fig. 16: Paint application on glass beads

7.4 Inside-coating of tubes Innenbeschichtung von Röhren

An interesting technique is the inside coating of tubes with a homogenous coating. This can be done in analogy to a dip coating process, by filling the tubes with paint and running it out after that. It is not trivial to get homogenous layers over the length of the tube. For solvent based paints, a defined ventilation of the tube is helpful to fix the coating (***fig. 17***).

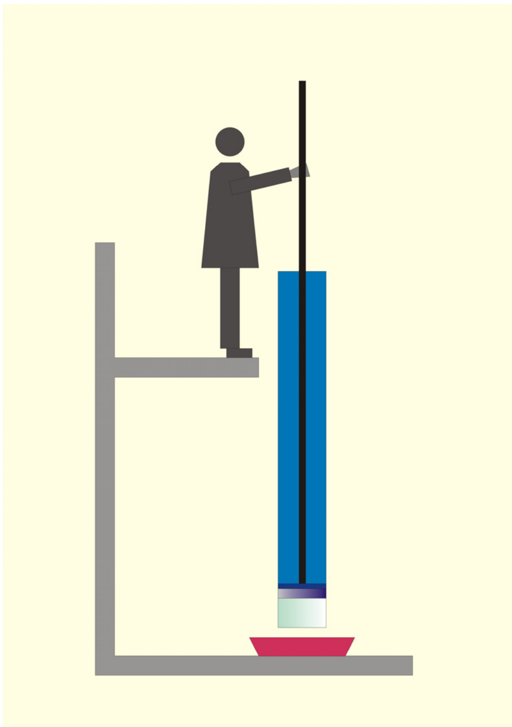

Fig. 17: inside coating of glass tubes

7.5 Digital printing

For hybrid paints, two interesting digital printing techniques have been developed.

7.5.1 Airbrush print

For airbrush printing, the paint is sprayed to the glass with digitally controlled nozzles. Colour generation works by sequential application of the basic colours cyan, magenta, yellow and black. The pictures are created pixel by pixel. The resolution is 42 dpi (dots per inch) (***fig 18***). The maximum size of the print is 3.5 x 6 metre.

Fig. 18: Print on glass with Ormojet Airbrush hybrid paint, printed on a TCG Michelangelo printer

7.5.2 Ink-jet Print

The viscosity of the hybrid ink can be made so low, that it can be printed even with an ink-jet printer (***fig. 19***). For ink-jet, a piezoelectric printing head can be used. Often Epson heads are used, which make a resolution of 1440 dpi possible. The size of a single ink droplet is 2 picolitre. With hybrid paints, prints with good resistance on glass are possible. The ink can be coloured either with dies or with pigments. A white ink is also available.

At the moment, different flat-bed plotters are offered, which allows prints on glass with a size up to 2.5 x 3.5 m. For cylindrical hollow glass, the first prototypes wave been successfully tested and we expect in future the development of printers for printing on irregular shapes.

Fig. 19: Inkjet print on a glass plate with Ormojet hybrid ink, printed with a Technoplot printer

8. Summary

Many properties of a glass object are determined by the properties of its surface. This is why many techniques have been developed to change the original glass surface to make the glass object either more decorative or to improve its functionality. This paper gives a short overview of the most important techniques of surface modification techniques on glass.

9. References

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Prof. Dr.-Ing. Ferdinand Trier, Munich University of Applied Sciences, Laboratory for Measurement Techniques Consultation for Glassing and Glasscoating, Lothstrasse 34, D-80335 München. e-mail: trier@fhm.edu

MEng. Dipl.-Ing. (FH) Ulrich Ranke, Ormo Print GmbH, Fuststrasse 8, D-80638 München. e-mail: ranke@lrz.fh-muenchen.de