Original Paper

Firing PbO-free glass enamels using the cw-CO_2 laser

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The firing of glass enamels, which are applied to decorate glass products, is usually done in a furnace. A new and suitable technique for firing glass enamels is to make use of the high-power cw-CO_2 laser. Its beam (wavelength 10.6 µm) induces a very fast heating of the enamelled glass within a small surface layer. This makes it possible to fire glass enamels at temperatures above 1000 °C, without any deformation of the substrate glass body. In this temperature range an amount of the harmful component PbO in the glass enamel is no longer necessary. The PbO-free glass flux of the enamel is made easily by milling the substrate glass (float glass). The gloss and smoothness of the laser-fired enamel are comparable to the conventionally fired enamel. The absence of PbO and the high firing temperatures are very advantageous to the chemical resistance of the enamels, meaning excellent dishwasher durability.

Einbrennen PbO-freier Glasemails mit dem cw-CO_2-Laser

Das Einbrennen von Glasemails, die zur Glasdekoration verwendet werden, wird üblicherweise in einem Ofen durchgeführt. Ein neues und geeignetes Einbrennverfahren für Glasemails stellt die Nutzung des cw-CO_2-Hochleistungslasers dar. Dessen Laserstrahl (Wellenlänge 10,6 µm) bewirkt eine sehr schnelle Erwärmung des emaillierten Glases innerhalb einer dünnen Oberflächenschicht. Dies ermöglicht eine Einbrenntemperatur für Glasemails über 1000 °C, ohne daß eine Verformung des Trägerglases stattfindet. Bei diesen Temperaturen ist es nicht mehr notwendig, daß das Glasemail schädliches PbO enthält. Der bleifreie Glasfluß des Emails wird einfach durch Aufmahlung des Trägerglases (Floatglas) hergestellt. Glanz und Rauhigkeit der mit Laser eingebrannten Emails sind mit den konventionell eingebrannten vergleichbar. Die Abwesenheit von PbO und die hohen Einbrenntemperaturen wirken sich vorteilhaft auf die chemische Resistenz der Emails aus, d.h. hervorragende Spülmaschinenbeständigkeit wird erreicht.

1. Introduction

In order to apply enamels to glasswares, a firing procedure is necessary. During heating in a furnace the individual enamel particles soften, melt and finally flow together, eliminating the voids between them. They must also bind to the glass substrate. This process has to take place at temperatures below the softening point (T_s) of the glass object, e.g. 630 °C for flat glass [1] in order to avoid deformation of the glass body. Only low-melting glass fluxes based on high amounts of harmful PbO are used today. They have low chemical resistance, and often show unfitness in the Coefficient of Thermal Expansion (CTE), meaning lower mechanical strength of the coated glass [2 and 3].

The cw-CO_2 laser (cw = continuous wave) is an attractive and suitable tool for firing glass enamels containing large quantities of lead oxide, as shown in preliminary experiments at this institute [4]. The laser technique makes it possible to treat glass surface layers without any influence on neighbouring regions of the glass [5]. Due to interaction with CO_2 laser radiation the temperature of the glass surface rises rapidly above T_s without any deformation of the glass body. Furthermore, heating enamels with CO_2 laser makes low-melting glass fluxes superfluous; completely new glass combinations are possible and the harmful lead oxide can be avoided.

2. Aim of this work

The aim of this work was to make use of the advantages and good features of high-power laser radiation for firing glass enamels. First of all a reduction of the PbO amount in the enamel should be achieved. An industrial, high lead-containing enamel (with a mass fraction of 57% PbO), PbO-reduced enamels (mass fraction 24% PbO) and completely PbO-free enamels were glazed, using the cw-CO_2 laser. These enamels, coloured with pigments or oxides, were examined in order to investigate the behaviour and influence of colour.

Another aim was the measurement of the surface temperature with a pyrometer during the firing process. This should lead to the optimum of the parameters feed rate and energy density which will promote small roughness and good lustre of the enamels.

Dishwashing durability tests of the different enamels were also performed in this work in order to test the chemical and erosive resistance.

Received November 11, 1995.

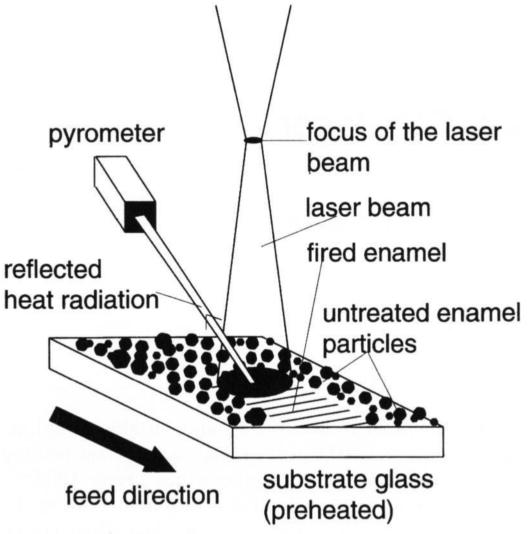


Figure 1. Firing process of glass enamel with CO_2 laser radiation.

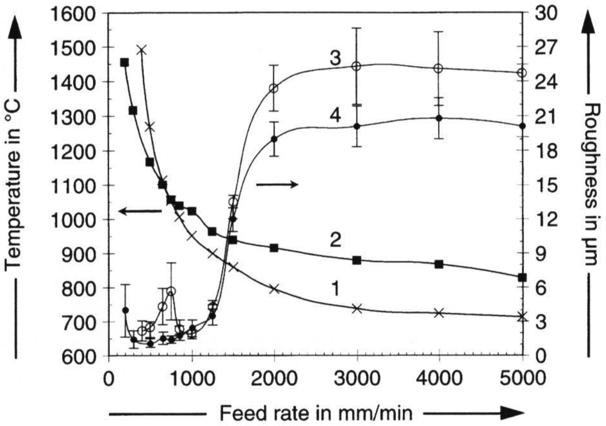


Figure 2. Temperature and roughness of laser-fired enamels; power density 180 W/cm^2, spot diameter 2 cm. Curve 1: colourless enamel, temperature; curve 2: black enamel, temperature; curve 3: colourless enamel, roughness; curve 4: black enamel, roughness.

3. Experimental

A 4 kW CO_2 laser was used, operating at a wavelength of 10.6 µm over a power range of 500 to 4000 kW. Plane metallic copper mirrors guided the laser beam to the sample and a convex mirror focussed the beam to a small point. The variation of the distance between this mirror and the sample surface made it possible to change the width of the laser beam. Thus, the experiments could be performed with spot radii up to 1.5 cm. Unfortunately, there was inhomogeneous power distribution across the beam resulting in heterogeneously melted enamel.

The CO_2 laser is one of the most important laser systems for material processing, especially for metals. There is a relatively high efficiency using the continuous wave radiation mode of this laser. Common glasses are nontransparent to infrared radiation above 4.5 µm. According to their compositions, glasses absorb 70 to 80 % of the laser radiation. The wavelength of the CO_2 laser light is located at a broad absorption band of silicate glasses between 10 and 11 µm [6]. For this reason, laser radiation leads to very fast heating of glass surfaces. The penetration depth is only a few micrometres, whilst deeper regions of the glass are only affected due to heat conduction [7 and 8].

This way of producing enamels differs from conventional methods. Because there was no low-melting glass flux required, it was simply made by milling commercial glass (soda–lime–silica glass (Flachglas AG, Weiherhammer (Germany)) or lead silica glass, containing a mass fraction of 24 % PbO) to the grain size of d_{50} = 20 µm. The enamels were coloured with a mass fraction of 20 % of a commercial black pigment (main ingredients CuO and Cr_2O_3; d_{50} = 1 µm), respectively, with 6.5 % CoO. The pigment was mixed with the glass flux, and CoO was embedded into the glass during an extra melting process. The colourless enamel without any PbO had the same CTE as the substrate glass.

Soda–lime–silica glass with dimensions of $(50 \times 50 \times 2)\,\mathrm{mm}^3$ was prepared for enamelling. The samples were coated via direct screen-printing or transfer. In a furnace the substrate glass samples, coated with enamel particles, were preheated at 500 °C. At this temperature soda–lime–silica glass endures highly inhomogeneous heat distributions without cracking. The organics of the screen-printing oil were eliminated during preheating, too. Figure 1 shows the formation of the enamelled surface during the "laser-enamelling" process. The sample is on a table, which can be moved with speeds from 0 to 5000 mm/min. The surface temperature during the laser treatment is measured by an infrared pyrometer, working in the spectral range of 4.8 to 5.2 µm. After firing the samples were cooled down in a furnace. The laser output power, the diameter of the laser spot and the feed speed determine the energy density to which the glass is exposed. Variation and examination of different laser parameters resulted in optimum experimental conditions for firing the different enamels.

4. Results

4.1. Melting behaviour

In figure 2 the measured temperatures of two enamels and the resulting roughness for different feed rates are presented. A colourless and a black lead-free enamel were fired with laser radiation. The power density was 180 W/cm^2 and the spot diameter 2 cm.

The dependence of temperature upon speed decreased with increasing feed rate. The roughness of the treated surface did not show any changes at high speeds. A significant modification took place around a feed rate of 1500 mm/min; here the temperature was high enough to allow the particles to flow together. In the area around speeds of 1000 mm/min the firing conditions for both, black and colourless enamels, were best, with yielded roughnesses of about 1.5 µm and low variation. Roughness and its standard deviation increased as bubbles disturbed the homogeneous enamel surface at slow speed and very high temperatures.

The temperature difference between black and colourless enamels at high feed rate was caused by their different absorption capability for laser radiation, whilst at slow speed chemical reactions of the black enamel dissipated energy (the enamel colour changed to green). The extremely fine black pigment particles decreased the roughness of black enamels at high feed speed.

There were four regions distinguishable at firing enamels using laser radiation:

region I:	incompletely melted enamel particles,
region II:	optimum melting behaviour of the particles,
region III:	overheated enamel, showing blisters and bubbles,
region IV:	deformation of the 2 mm thick glass substrate.

Figure 3 shows the four regions for a blue-coloured (mass fraction 6.5 % CoO) lead-free glass enamel transfer. The power density and the feed rate were varied.

The transitions from one region to another were not sharp. If working in region I, near region II, one could already find well melted areas in the enamelled surface. At the edge of region II to region III, local blisters dimmed the surface. The main reasons were the inhomogeneous power distribution of the laser beam and the fluctuation of laser output, which effected temperature differences of ± 20 K at the same laser power.

Higher power densities caused higher temperatures. If the power density is raised by 50 %, well melted enamels could be achieved by twice as high feed rates. Therefore, it is possible to accelerate the working velocity by raising the power density. The optimum melting of enamel particles with laser light was observed at temperatures between 900 and 1000 °C for all colours. A smooth and homogeneous enamel surface could be achieved without any cracks and peeling. The measured roughness in region II for blue, lead-free enamels and for different power densities is shown in table 1. It is seen that low power density produced the best results. The particles had more time to melt together as their interaction with the laser beam lasted longer at low power range. But one must be careful to avoid region IV, so the power should not be arbitrarily low.

Table 1 also shows that with transfers a lower roughness than with directly screen-printed enamels resulted. The transfers were printed in a more equal and compact way. Therefore, the distance between the particles was smaller and they could melt together more readily. The transfer led to 15 µm, the direct screen-printing technique to 30 µm thick coatings. Good melting of directly screen-printed enamels began at slightly lower feed rates than shown in figure 3, and region II became narrower. The PbO-containing enamels showed better lustre than lead-free enamels, as it had been expected by Berger [9].

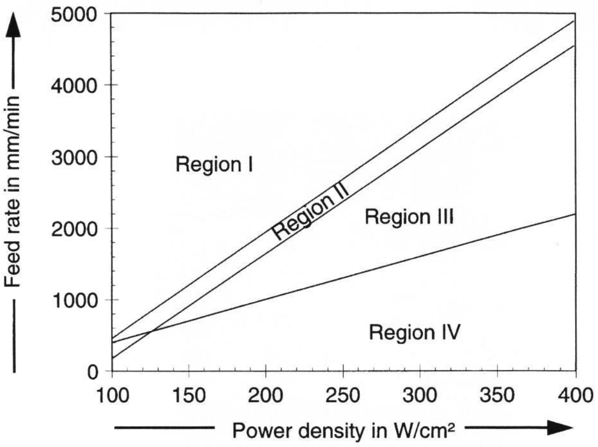


Figure 3. Classification of the melting behaviour of a blue-coloured lead-free glass enamel transfer; region I: incompletely melted enamel particles, region II: optimum melting behaviour of the particles, region III: overheated enamel; showing blisters and bubbles, region IV: deformation of the 2 mm thick glass substrate.

Table 1. Roughness of blue, lead-free enamels; best firing conditions

power density in W/cm^2	roughness in µm	
	screen-printing	transfer
130	1.5 ± 0.5	1.0 ± 0.2
180	2.0 ± 0.4	1.5 ± 0.8
265	2.5 ± 0.7	2.5 ± 0.6
350	3.0 ± 1.0	3.0 ± 1.0

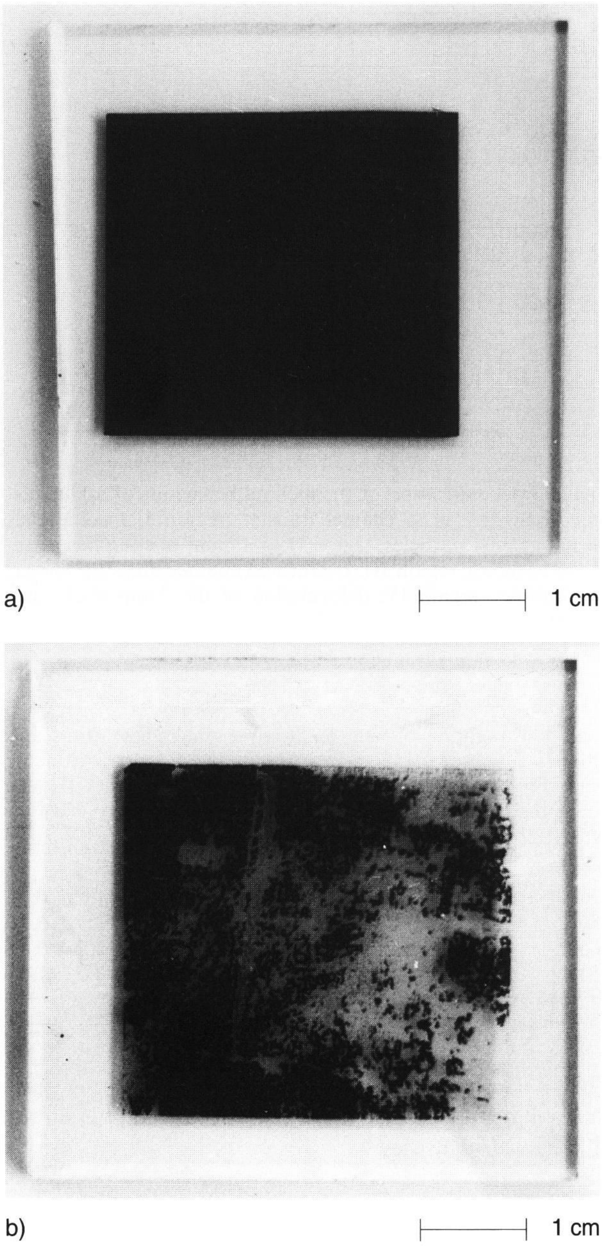
Their “region II” was broader than for lead-free glass fluxes, but was located at the same feed rate interval for given power densities.

4.2. Dishwasher durability

The corrosion tests of the glass enamels had been done in a household dishwasher according to DIN 50275 [10]; their stability was examined at every 100 cycles. Three different black-coloured enamels were tested: an industrial (mass fraction (in %): 57 PbO), a PbO-reduced (24 PbO) and a lead-free transfer, all coloured with 20 black pigment. To avoid effects induced by power fluctuation of the laser beam, the transfers were fired on one substrate at the same time. The power density was 180 W/cm^2, and the feed rate was 1000 mm/min. In order to make comparisons the industrial transfer had been fired conventionally in a furnace at 630 °C for 30 min [3].

Figures 4a and b show that the conventionally fired enamels did not resist more than 400 dishwashing cycles.

Even if these high lead-containing glass enamels were fired by laser radiation, the durability did not increase very much, as figures 5a to c show. The composition of this enamel, especially the low amount of SiO_2, caused poor chemical and erosive resistance.

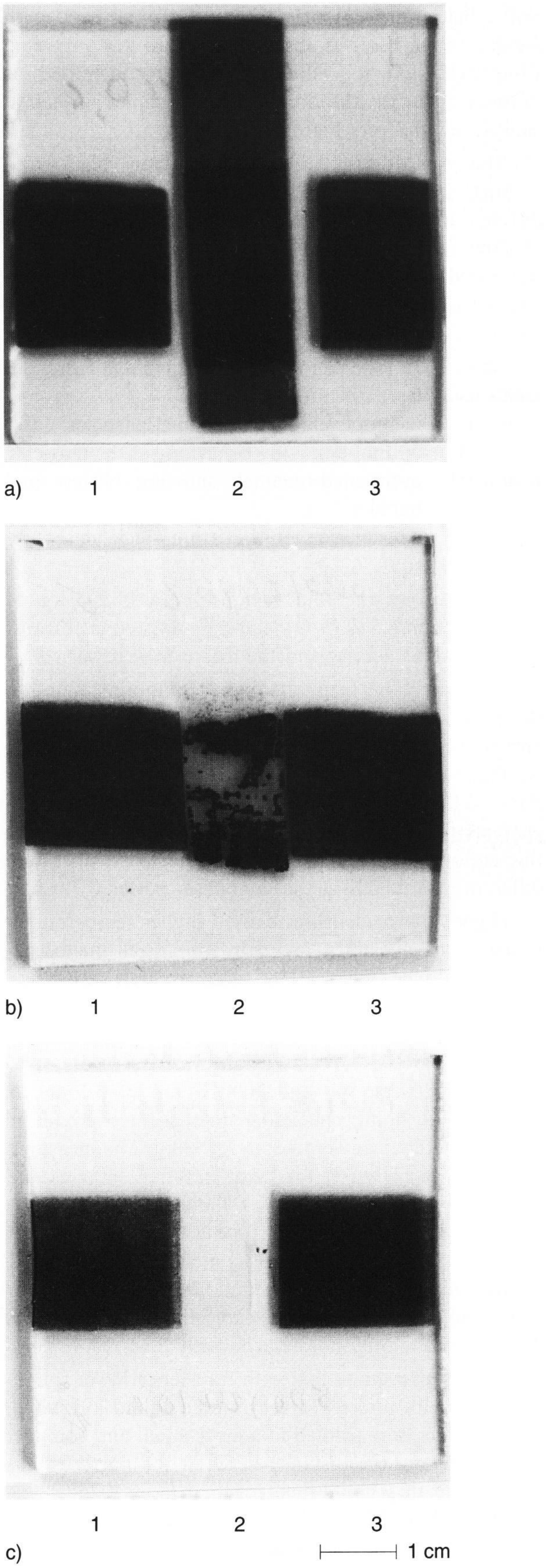


Figures 4a and b. Dishwasher durability of a conventionally fired black glass enamel after a) 0 dishwashing cycles, b) 430 dishwashing cycles.

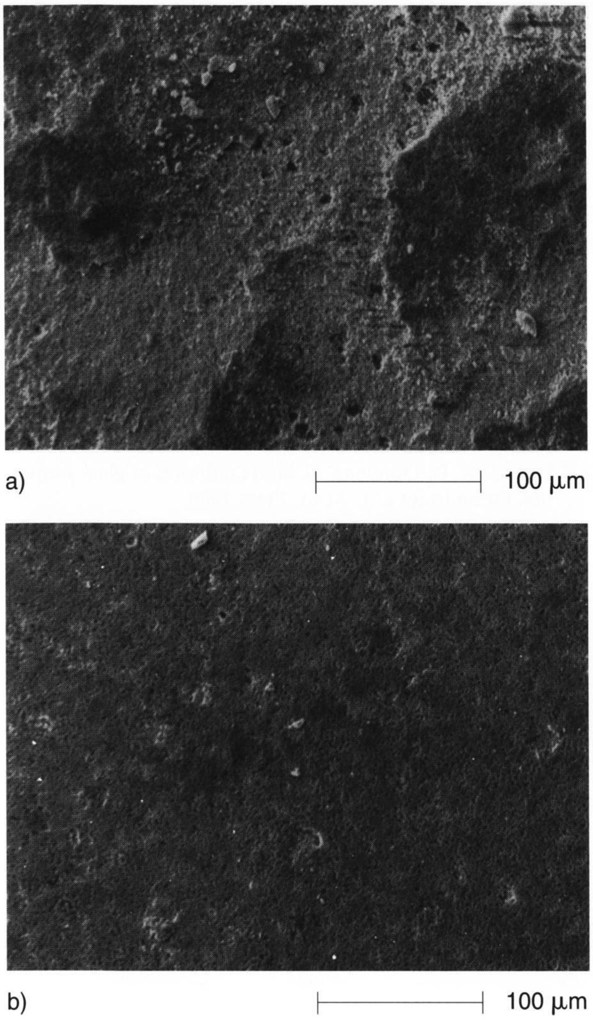
The preheating temperature of 500 °C made the whole high lead oxide-containing enamel soften; on the other hand, the preheating temperature was not high enough for the two other enamels to melt. They were fired only at the laser-irradiated area (figure 5a).

The lead-free and the lead oxide-reduced enamels showed no significant differences in their dishwashing durability as it is seen in figures 5a to c. Both enamels survived even 1000 dishwashing cycles, but with visible damages.

The Scanning Electron Microscope (SEM) photographs in figures 6a and b show the different appearances of the furnace-fired and the laser-fired enamel



Figures 5a to c. Dishwasher durability of three laser-fired black glass enamels (1: PbO-free, 2: with 57 % PbO, 3: with 24 % PbO) after a) 0 dishwashing cycles, b) 500 dishwashing cycles, c) 1000 dishwashing cycles.



Figures 6a and b. SEM micrographs of two black enamel samples, a) conventionally fired enamel after 300 dishwashing cycles, b) laser-fired enamel after 300 dishwashing cycles.

after 300 dishwashing cycles. The lead-free enamel (figure 6b) was much less corroded than the commercial one (figure 6a).

The blue-coloured enamels, on the other hand, possessed an additional improved chemical and erosive resistance, as CoO had been introduced into the glass matrix by an extra melting process. 1000 dishwashing cycles caused only low damages to this enamel.

4.3. Laser firing of different glass systems

Firing of glass enamels with the laser beam was not only examined for a float glass. Also lead silica glass and borosilicate glass (DURAN, Schott Glaswerke, Mainz (Germany)) were milled and used as a colourless enamel. Lead silica glass was covered with lead silica glass powder, borosilicate glass with borosilicate glass powder and float glass with float glass powder, via direct screen-printing.

For the different glass systems the optimum melting behaviour of their particles was located at different intervals of temperatures. These optimum regions are illustrated in figure 7. It is significant that the good melting was observed around the working point of the glasses at viscosities between 10^5 and 10^4 dPa s. So it will be possible to estimate the optimum firing temperature for another glass system. If the range of temperatures is wide where the change of viscosity from 10^4 to 10^5 dPa s takes place, these glasses are favoured for laser firing. This is the case for lead silica and borosilicate glass. Similar to industrial manufacturing "long" and "short" glasses are distinguishable. A "short" glass for laser firing, e. g. float glass, needs a homogeneous power distribution of the laser beam and the laser parameters must not be changed largely.

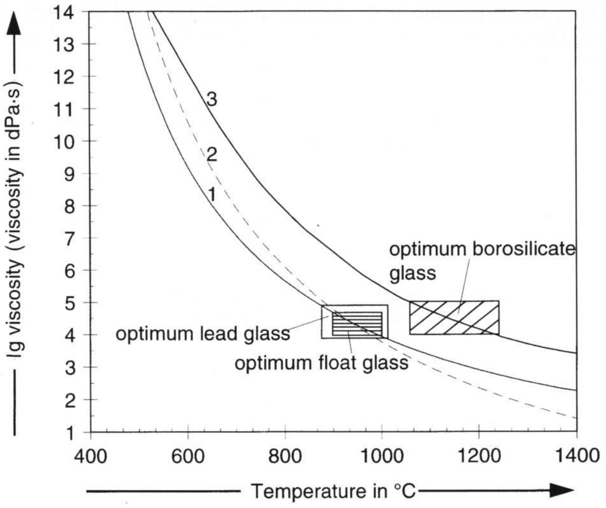


Figure 7. Viscosity curves [11] and ranges of optimum firing results with laser radiation for different glasses. Curve 1: lead glass, curve 2: float glass, curve 3: borosilicate glass.

5. Conclusion

The results of this work show that the cw-CO_2 laser is very suitable for firing glass enamels. The time of heating was long enough even for lead-free glass fluxes to soften and melt together. Other parts of the glass body were not influenced by the laser irradiation. Therefore, the enamelling procedure could be executed at temperatures of 900 to 1000 °C for lead silica and soda–lime–silica glass or 1100 to 1200 °C for borosilicate glass without any deformation of the substrate glass. In these temperature ranges the viscosities were low enough to make the enamels melt excellently into the substrate glass. The ingredients of enamels were changed arbitrarily and adapted to the glass body. Thus, lower corrosion and susceptibility to erosion are achieved, meaning a great improvement of the dishwashing durability. The roughness of enamels fired by laser irradiation did not differ much from conventional enamels fired in a furnace. If a small amount of PbO is tolerable, even the impression of colour and lustre fits the demands.

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These investigations were conducted with the kind support of the Arbeitsgemeinschaft industrieller Forschungsvereinigungen (AiF) Köln, (AiF no, 9295) under the auspices of the Hüttentechnische Vereinigung der Deutschen Glasindustrie (HVG), Frankfurt/M., utilizing resources provided by the Bundesminister für Wirtschaft, Bonn. Thanks are due to all these institutions.

6. References

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