Original Paper

The firing of enamels onto borosilicate glass through the selective absorption of infrared radiation[1]

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Gradations and other markings on laboratory glassware are made mainly with glass enamels. Firing temperatures of around 600 °C (i.e. 70 to 80 K above the transformation temperature of the glass) are needed in order to reach sufficient chemical and mechanical resistance. This can lead to alterations in the volume of the flasks. Due to the uneven temperature distribution in continuous or batch furnaces some flasks may undergo a volume change that is greater than the accepted margin of error of the calibration.

The aim of this study was to find a firing process for glass enamels that ensures the same chemical resistance as the furnace firing but without the risk of changing the volume. This was obtained by a combination of conventional heating by a hot-air blower and selective heating by absorption of infrared radiation. A halogen lamp and an Nd-YAG laser were used as infra-red sources. The use of the laser clearly showed better results. By firing-on blue lead-enamel with a laser a chemical and mechanical resistance comparable to that of furnace firing was achieved without altering the volume of the measuring container.

Einbrennen von Emails auf Borosilicatglas durch selektive Absorption von IR-Strahlung

Skalierungen und Beschriftungen auf Labor-Volumenmeßgefäßen werden überwiegend mit Glasemails aufgebracht. Um eine ausreichende chemische und mechanische Beständigkeit zu erreichen, sind Einbrenntemperaturen von ca. 600 °C, d.h. ca. 70 bis 80 K über der Transformationstemperatur des Glases, erforderlich. Dabei treten Volumenänderungen auf, die, bedingt durch die ungleichmäßige Temperaturverteilung in den üblicherweise verwendeten Kammer- oder Durchlauföfen, bei einem Teil der Meßgefäße bereits die zulässige Toleranz überschreiten.

Ziel dieser Untersuchungen war es, ein Einbrennverfahren für Glasemails zu finden, mit dem die chemische Beständigkeit des konventionellen Ofeneinbrandes erreicht wird, jedoch ohne daß beim Einbrand eine Volumenänderung auftritt. Dies wurde durch eine Kombination von konventioneller Erwärmung mit Heißluft und Erwärmung durch selektive Absorption von Infrarotstrahlung erreicht. Von den beiden dazu eingesetzten IR-Strahlungsquellen, Halogenlampe und Nd-YAG-Laser, lieferte der Laser eindeutig die besseren Ergebnisse. Bleihaltiges blaues Glasemail ließ sich damit mit einer dem Ofeneinbrand vergleichbaren chemischen und mechanischen Beständigkeit einbrennen, ohne daß dabei eine Volumenänderung an den Meßgefäßen auftrat.

1. Introduction

Gradations and other markings on laboratory glassware such as beakers, flasks and measuring containers (volumetric flasks and cylinders, pipettes and burettes) must, to a large extent, be resistant to acids and alkalis, as such glassware comes into contact with these aggressive chemicals in daily use and during cleaning. Glass enamels are often used for these markings.

Glass enamels are capable of producing markings in many colours and contrasts. Glass enamels are glasses with a low melting-point and consist of a glass flux (frit) and colour pigments (the actual colouring compounds) [1 to 6]. The glass enamel powder must be mixed to a paste with special oils. After the markings have been applied, by screen-printing, tampon-printing or knurling, or else in the form of transfers, the containers are first dried and then fired in a continuous furnace, or, in the

case of small runs, a batch furnace. In the process of heating the enamel paint, any organic residues disappear. The firing process starts at about 550 °C. The glass flux melts or sinters upon being heated, includes the colour compounds and at the same time bonds to the base glass [2].

Most enamels contain lead oxide or lead borate. These compounds cause a lowering both of the firing temperature and of the surface tension, thus enabling a thin layer of colour to flow on smoothly [1 and 5]. As lead is a poisonous heavy metal, its use in glass enamels should be avoided where possible and some manufacturers already offer pigments which are lead-free or contain only a small amount of lead. The avoidance of lead, however, entails a higher firing temperature.

Commercially available enamels containing lead achieve the degree of resistance to acids and alkalis, which is required of laboratory equipment, by being heated to a temperature of at least 580 °C for 15 min. The chemical resistance increases with the firing temperature and the length of time the process takes [7]. The heating of glass containers beyond their transformation

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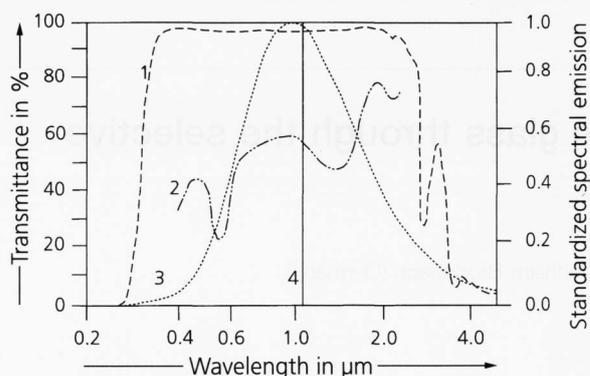Glastech. Ber. Glass Sci. Technol. 72 (1999) No. 7

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Figure 1. Transmittance of borosilicate glass 3.3 (curve 1), of blue lead-enamel (curve 2); and spectral emission of the halogen lamp with a filament temperature of 3000 K (curve 3), and of the Nd-YAG laser (line 4).

temperature can lead to alterations in the volume, caused by sagging of the glass. The longer and higher borosilicate glass is heated beyond T_g of 530 °C, the greater the deformation [8]. This can have serious consequences, given the very narrow margin of error allowed in volumetric containers. Morever, both the continuous and the batch furnaces normally used by the producers of laboratory glassware can have uneven temperature distribution, which adds to the problem. Containers in the cooler parts of the furnace end up with markings of insufficient chemical resistance, while containers in the hotter parts of the furnace can exceed the permitted margin of error through deformation. Therefore, allowance must always be made for rejects.

The aim of this investigation was to find a firing process for glass enamels by which the chemical durability of the conventional furnace firing could be attained without altering the volume of the container. This was to be achieved by warming with a hot-air blower and the simultaneous application of infra-red radiation. By this method it was hoped to avoid rejects through wrongly-calibrated containers or insufficiently durable markings such as occurs with furnace firing. Another aim of this investigation was to test whether, by this new firing process, volumetric containers could be marked with lead-free enamels without alterations to their volume and with a chemical durability comparable to that of the lead-enamels.

In order to heat the glass enamel with infra-red radiation without, at the same time, heating the base glass directly, the radiation should only be able to be absorbed by the enamel and not by the container. Radiation with a wavelength of about 2.5 to 4.5 µm is partly absorbed by borosilicate glass and, with a wavelength greater than 4.5 to 5 µm, fully absorbed by it. Between 0.35 to 2.5 µm, on the other hand, this glass is completely transparent, that is to say, the radiation should be at this wavelength. This requirement is fulfilled to a large degree by halogen lamps with a filament temperature of 3000 K (see figure 1). Nd-YAG lasers also radiate

in this area ($\lambda = 1.064$ µm) and have a high energy density. The degree of absorption required for the selective heating of the enamel at this wavelength is effected by the metal oxides of transition elements.

For the firing of a glass enamel, the base glass is heated, together with the enamel, to a temperature no higher than the transformation point of the base glass. The additional heating for the firing of the enamel is effected through the infra-red irradiation.

In order to effect a complete melting of the enamel and a proper fusion with the base glass, without overheating and forming bubbles, the beam of radiation must be moved over the surface of the glass more or less quickly, depending on its energy density. The high energy of a laser beam allows the fusion of a layer of enamel with a thickness of several µm to happen so quickly that very little heat energy flows into the base glass, the temperature of which is raised only minimally [9 and 10]. The absorption of the radiation from the halogen lamp or the Nd-YAG laser occurs in the coloured parts of the enamel, i.e. the oxides of the transition elements, through the transfer of electrons. As well as the Nd-YAG laser, the CO_2 laser, which emits a wavelength of 10.6 µm, is also suitable [11 to 14]. At this wavelength, the absorption of the radiation takes place through molecular vibrations. Irradiation by a CO_2 laser causes the oscillation of Si−O-bonds in silicate glass. With this radiation, in contrast to that of the Nd-YAG laser, not only the enamel frit, but also the base glass is heated. The strong absorption of the laser beam causes the heating of the surface layer of the base glass to a temperature of about 1000 °C [11 and 12]. In order that the enamel marking lies well within the area covered by the laser beam, the width of the beam must be greater than the width of the marking. In the case of the CO_2 laser, this leads to intense heating of the adjacent glass surface. The CO_2 laser is therefore not suitable for selective firing of glass enamels, i.e. firing without simultaneous direct heating of the base glass. With selective firing, the base glass adjacent to the enamel is heated only indirectly, by conduction from the enamel to the glass.

2. Experimental

2.1 The glass enamels tested

The experiments were carried out using blue enamels with and without lead content (H14116, royal blue, with lead and H52113, blue, lead-free, producer: Heraeus Hanau (Germany)) as blue is the most common colour for the markings on volumetric containers. This colour has the advantage that its high cobalt content allows infra-red radiation to be easily absorbed without the need for additional compounds. The high lead content normal for glass enamels (50 to 55 wt% PbO) is replaced in the lead-free enamel by Bi_2O_3. In order to arrive at a lower firing temperature, the lead-free enamel is more finely ground than that containing lead [15]. The

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producer recommends for both enamels a firing temperature, for furnace firing, of 580 to 630 °C with a firing time of 10 to 15 min.

2.2 Production of samples

The intention here was to investigate the firing of rings onto volumetric flasks, which are subject to a very narrow margin of error. By firing with infra-red radiation, only the neck of the flask needs to be heated, so borosilicate glass tubes were used instead, as these were sufficient for the investigation of the conditions necessary for the firing and also the chemical durability of the enamel. Flasks were only used to investigate the occurrence of alterations to the volume.

In order to mark the rings, the tubes were put in a jig and slowly turned by a motor. The coloured enamel paste was applied from a container onto the revolving tube by means of a knurling wheel, leaving a ring. Thick rings about 2 mm wide (average thickness ca. 15 μm, average mass ca. 7 to 8 mg) were used in order to have enough material for measuring mass loss in the chemical durability test. Thin rings about 0.3 mm wide as are common in commercial products were used in other experiments. After the colour had been dried, the organic matter (screen-printing oil) was removed by slowly heating to 450 °C for 1 h.

2.3 Firing by halogen lamp or laser

Figure 2 shows the experimental set-up for the firing of a ring marking onto borosilicate glass tubes or volumetric flasks. The marked tubes were placed in a chuck and revolved by a motor at a constant speed. Bearing in mind the possibility of a further production step, the firing process should not take longer than 0.5 to 1 min. This means that the tube must turn with a minimum frequency of 2 min^{-1}, at which speed most of the experiments were carried out. The marked borosilicate glass tubes or flasks were heated with a hot-air blower to a temperature no greater than that of the transformation point of the glass and were placed with the middle of the tube or neck of the flask positioned in the testing chamber, which had been pre-heated by the hot-air blower. When the required temperature had been reached, the glass enamel was selectively heated to a higher temperature than the base glass by irradiation with a halogen lamp (stated capacity 80 W, diameter of beam ca. 5 mm, energy density ca. 0.6 kW/cm^2) or an Nd-YAG laser (Spectron, Model 1302, capacity 120 W, continuous wave, multi-mode, $\lambda = 1064$ nm, diameter of beam 2 to 2.5 mm, energy density ca. 3 kW/cm^2) and by this means melted or fired on.

The temperature of the enamel layer was measured by a pyrometer (Kleiber Model 260, range 200 to 1200 °C) with a short response time (≤ 2 ms) and a particularly small measuring surface (radius ca. 1 mm). This was set at 90° to the spot at which the beam of the halogen lamp or laser was directed. This arrangement
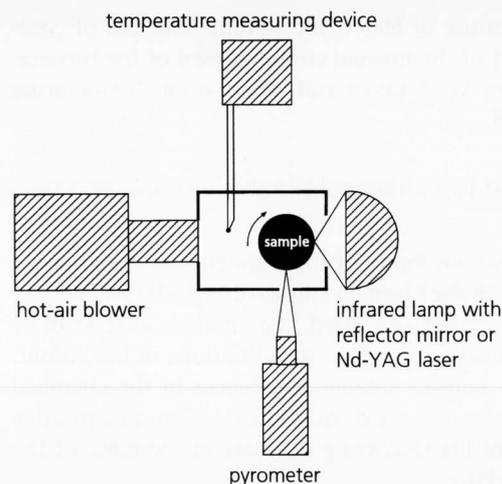

Figure 2. Schematic sketch of the experimental set-up for the firing-on of coloured enamels with a halogen lamp or with the Nd-YAG laser.
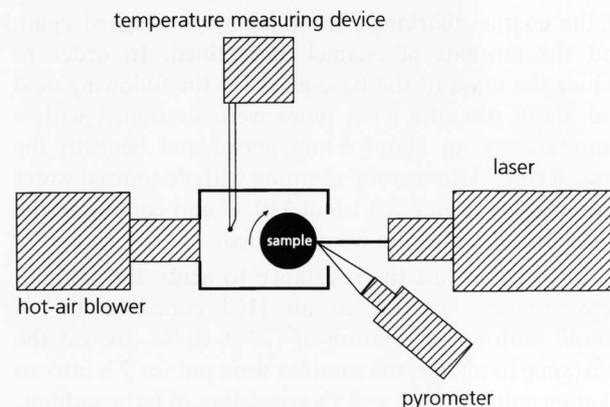

Figure 3. Experimental set-up for pyrometric measurement of the enamel temperature directly at the point of incidence of the laser beam.

was necessary (at least for the halogen lamp) for geometric reasons and because the pyrometer reacts to a part of the lamp's spectrum. Because the measurement is taken slightly later than the irradiation (being offset by 90°), the temperature measured is not the same as the temperature reached in the beam. This arrangement was used in most cases and allows the measurement of the pre-heat temperature and a comparison with the firing temperatures.

The temperature of the enamel layer can only be measured by the pyrometer directly at the point of irradiation if the firing is carried out by the laser (figure 3). This was only done in a few cases, as the adjustment is complicated.

2.4 Furnace firing

For comparison, the enamels were also conventionally fired in a forced-air furnace (Naber, Model N 120/A). The heating rate was 5 K/min and the firing took place

at a temperature of 600 °C for 15 min. The rate of cooling was that of the normal cooling-down of the furnace. The samples were taken out when room temperature was reached.

2.5 Testing the chemical durability of the enamel layer

The chemical durability of the enamels was tested in accordance with the German standard DIN-ISO 4794 [16]. After being rinsed and dried, the enamels were visually examined for loss of colour or alterations in the colour. In order to register smaller differences in the chemical durability the test was quantified. The quantitative measurement for this was a decrease in the mass of the enamel marking.

Tubes of borosilicate glass about 14 cm long were carefully cleaned with de-ionized water and acetone, dried in a drying chamber for 1 h at 110 °C and weighed after cooling in a desiccator. Ring markings 2 mm wide were then applied and dried at 450 °C. After the firing of the enamel markings, the tubes were weighed again and the amount of enamel ascertained. In order to reduce the mass of the base glass for the following acid and alkali test, the glass tubes were shortened with a diamond saw to about 5 mm above and beneath the enamel ring. After careful cleaning with de-ionized water and acetone, drying for 1 h at 110 °C and cooling in the desiccator, the samples were weighed.

In order to test the resistance to acids, the samples were exposed for 1 h to an HCl concentration of 2 mol/l with a temperature of (23 ± 5) °C. To test the resistance to alkalis, the samples were put for 2 h into an alkaline solution (pH = 9.7), consisting of tetra-sodium-diphosphate and dodecyl-benzene-sulphonate, which contained a wetting agent. Following that, the samples were again thoroughly cleaned and dried and the mass loss of the enamel was ascertained by weighing. Blank values for the acid- and alkali-resistance tests were determined with glass tubes of the same size, but without enamel rings.

2.6 Scratch test

In order to test the mechanical strength of the enamel layer, a scratch test was carried out, in which a metal gouge (after Clemen) moved across the enamel with a force of 5 N. At this force, the gouge left no trace on well-fired enamel layers but a distinct scratch on poorly-fired layers.

2.7 Exact determination of the volume of the flasks

In order to detect whether the volume of the volumetric flask had been altered by the firing process employed, the volume had to be very exactly determined, both before and after the firing. To this end, the weight of the flask was determined, both empty and after filling with de-ionized water to the point where the meniscus just touched the upper edge of the mark (inspection with a magnifying glass). The mass of the water was calculated from the difference between the two weights, after corrections for the buoyancy of the air. Division by the density of the water gave the volume of the vessel at the temperature at which the measurement was carried out. In order to ascertain the volume at the reference temperature of 20 °C, the expansion of the glass between reference and measuring temperature had to be taken into account [17].

3. Results and discussion

3.1 Temperature increase of the enamel layer during irradiation

The temperature of the enamel layer was measured by a pyrometer. The pyrometer employed records radiation between 4.8 and 5.2 µm. Radiation from the surface contributes most to the formation of the signal, as the intensity of the radiation from deeper layers declines exponentially through absorption. The law of absorption for radiation states that the depth at which 1 % of the radiation can still be registered, amounts to 0.5 to 0.6 mm in borosilicate glass [18 and 19]. With laser radiation, a temperature gradient between the surface and the inner portion of the glass has to be taken into account, as glass possesses minimal heat conductivity. Because of this the temperatures recorded by the pyrometer at the point of incidence of the laser beam are lower than the actual temperature of the surface of the enamel. In most of the tests, the temperature of the enamel layer was measured only after the sample had turned by 90°, equivalent to a delay of 7.5 s at a rate of rotation of 2 min^{-1}. During this time, the temperature gradient between surface and deeper layers had become so small, that the temperature measurement was no longer distorted. The surface temperature dropped so much, however, with the delay, that these measurements are only useful for comparisons.

Before irradiation with the halogen lamp or the laser, the sample was pre-heated with the hot-air blower. Because the infra-red radiation causes a boost in temperature, it was reasonable to make the pre-heating temperature as high as possible. The upper limit was the transformation temperature of the borosilicate glass, as above this point there was a danger of volume alterations. Low pre-heating temperatures entail correspondingly lower firing temperatures. A pre-heating temperature of less than 450 °C can lead to cracks in the borosilicate glass, through localized heating with the laser beam.

Figure 4 shows the increase in temperature through irradiation of the sample by the halogen lamp or the laser, measured after a 90° turn of the sample (equivalent to a 7.5 s delay). The sample was heated before irradiation to about 525 °C with the hot-air blower. After 1 min irradiation with the halogen lamp, an increase in temperature of ca. 60 K above the initial

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temperature was observed and after 1 min with the laser, an increase of about 120 K. The temperature, measured with the pyrometer directly at the point of incidence of the laser beam, amounted to 800 to 900 °C, corresponding to an increase in temperature of 275 to 375 K.

The temperature of the enamel increases through laser radiation, therefore, by an average of ca. 330 K more than the initial temperature and decreases in the 90° rotation by an average of 210 K. The cooling is caused by loss of heat to the surroundings (through radiation and convection) as well as through conduction of heat from the enamel to the glass underneath or to the side of it.

The temperature reached at the point of incidence of the beam from the halogen lamp is not directly measurable, as the pyrometer reacts to a part of its spectrum of emission. It is clearly lower than the temperature attained at the point of incidence of the laser beam, as the increase in temperature after a 90° turn was observed to be only half as great.

The difference in the increases in temperature between halogen lamp and laser can be explained by the difference in power density, beam diameter and wavelength of the two sources of radiation. The halogen lamp has a considerably lower power density than the Nd-YAG laser. This is partly compensated for by the fact that the duration of its effect on the enamel is twice as long (the diameter of the beam is about twice as great). The infra-red radiation of the halogen lamp is absorbed by a wide absorption band of cobalt oxide, of about 1.5 μm, while the absorption of the laser radiation takes place only in the short-wave part of this wave-band. In both cases, only a small part of the radiation is absorbed, as the layer is very thin (ca. 15 μm).

An unmarked glass tube was irradiated with the halogen lamp and the laser and, after 1 min, an increase in temperature of about 30 and 40 K, respectively, was observed.

Because glass absorbs practically no radiation from either the halogen lamp or the laser, this temperature increase is due mainly to the heating-up of the testing chamber through absorption of the radiation energy into its walls.

The glass surrounding the enamel ring is heated indirectly by the heat coming from the ring. As glass is a poor conductor of heat, the temperature drops quickly. Only 4 to 5 mm away from the enamel ring, which has been heated to a temperature of 800 to 900 °C by laser radiation, the temperature of the glass is approx. 600 °C.

3.2 Chemical and mechanical durability of the enamel

The quality of the firing of the glass enamel is ascertained above all by its chemical resistance to acids and alkalis. This is determined by the loss of mass as a per-
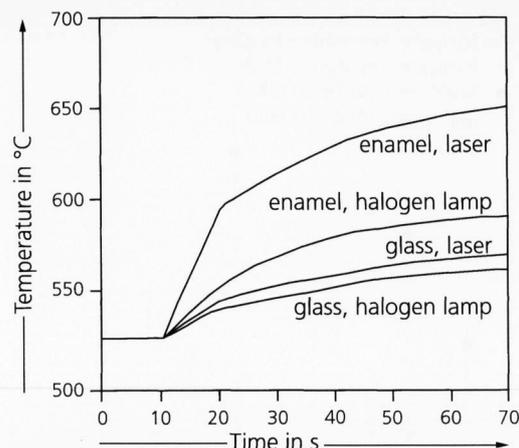

Figure 4. Pyrometrically measured temperature change of the sample during irradiation with the halogen lamp and with the Nd-YAG laser (120 W). The experimental set-up is the same as in figure 2.
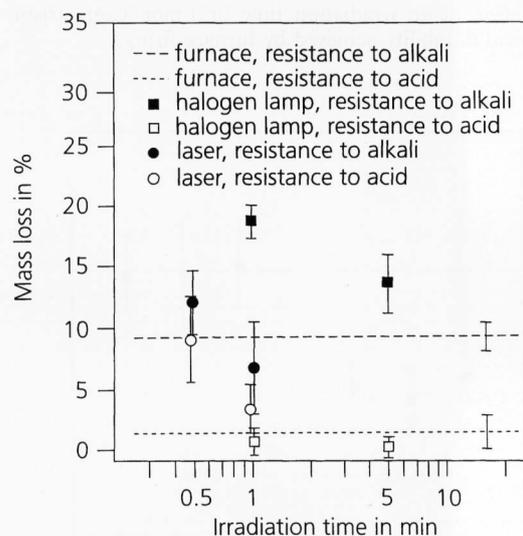

Figure 5. Relationship between the chemical durability of the blue lead-enamel and the type of radiation source and duration of the irradiation process (rotation rate 2 min⁻¹). Comparison with chemical durability achieved by furnace firing.

centage of the mass of the enamel. Figure 5 shows the relationship between the chemical durability of the blue enamel containing lead and the duration of the irradiation process. The durability increases with the increased duration of the irradiation. Irradiation by laser for 1 min affords a resistance to acids and alkalis which is comparable to conventional furnace firing. With the halogen lamp, one minute's irradiation suffices only for resistance to acids; a resistance to alkalis comparable to that achieved by furnace firing is reached only after irradiation for 5 min. Furnace firing and irradiation by laser afford a greater mechanical stability than with the halogen lamp. Therefore, with regard to achieving a high chemical and mechanical durability with as short a process time as possible, firing by laser radiation is to be preferred.
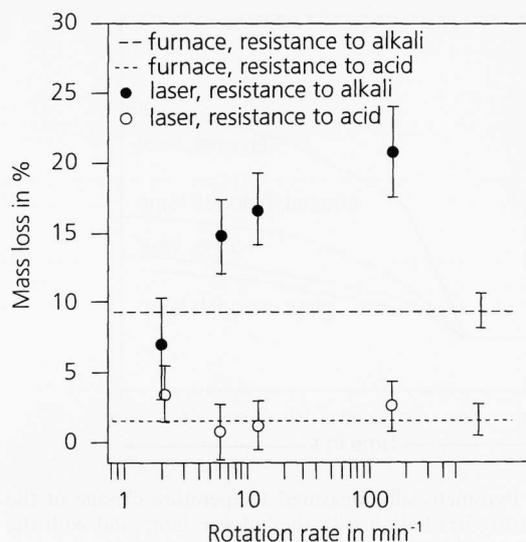
Figure 6. Relationship between the chemical durability of the blue lead-enamel and the rate of rotation during firing with the Nd-YAG laser, at an irradiation time of 1 min. Comparison with chemical durability achieved by furnace firing.
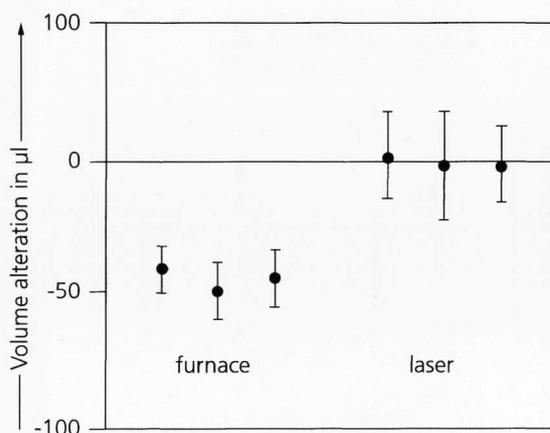

Figure 7. Comparison of the volume alteration of volumetric flasks (250 ml) after firing by forced-air furnace and the Nd-YAG laser, respectively.

At a rotation rate of $2\,min^{-1}$ and a firing time of 1 min, the enamel moves through the laser beam twice. The heating is very uneven, as in this way, the enamel becomes very hot within a second and then cools down for 29 s, when the process is repeated. Attempts were made to achieve a more even heating, through a faster rotation rate at a constant irradiation time of 1 min. The result of these, however, was that an increase in the rate of rotation led to a sharp reduction in the resistance to alkalis, while the resistance to acids remained unchanged (figure 6). A rotation rate slower than $2\,min^{-1}$ is useless, as, even at this rate, the middle part of the enamel ring, where it is thickest, exhibits a slight discoloration due to overheating. This, however, does not affect the chemical durability. Firing tests with the Nd-YAG laser at a capacity of 120 W, a firing time of 1 min and a rotation

rate of $2\,min^{-1}$ gave a result comparable in chemical durability to that of furnace firing. Firing tests under these conditions were carried out on volumetric flasks.

The chemical and mechanical durability of the lead-enamel was not achieved in the case of the lead-free enamel. This was not resistant to a hydrochloric acid concentration of 2 mol/l, regardless of firing conditions. The mass loss was between 65 and 100 %. In the scratch test, the enamel was completely removed by the gouge, regardless of which firing method was used (halogen lamp, laser or forced-air furnace).

The resistance to scratching was also considerably poorer than that of the lead-enamel, both after the alkali test and directly after the firing. The various firing methods seemed to have no significant effect on the resistance to scratching. The mass loss in the alkali test was between 16 and 33 %, depending on the firing conditions. The (qualitative) degree of resistance to alkalis according to DIN-ISO 4794 was fulfilled by the lead-free enamels. However, because of their insufficient resistance to acids, they are unsuitable for use on laboratory equipment.

3.3 Volume alterations to volumetric vessels during the firing process

Volumetric flasks (250 ml) were marked with thin (ca. 0.3 mm), blue rings of lead-enamel and the volumes at the mark were ascertained very exactly several times. After firing by laser at 120 W for 1 min, or in a forced-air furnace at 600 °C for 15 min, the volume of each flask was again ascertained several times. The results are shown in figure 7. Firing in a forced-air furnace showed a reduction in volume of about 50 µl (1/3 of the tolerable margin of error). Because in the calibrating of volumetric flasks the individual values do not lie in the middle of the margin of tolerance, but are spread over it, some of the vessels would be outside after firing. In addition, the temperature distribution in the normal industrial batch furnace is more uneven than in the forced-air furnace, so that in practice even greater volume alterations to individual flasks must be taken into account. In contrast to this, the laser firing showed no detectable volume alterations. The base glass was only indirectly and briefly heated at the mark, through heat conduction from the enamel and in this way an alteration to the volume could effectively be avoided. Consequently, laser firing of the lead-enamel markings affords a quality comparable to that of furnace firing, without the concomitant undesirable alterations in volume.

4. Summary

The firing of blue lead-enamels having a resistance to acids equivalent to that attained by furnace firing was achieved using a halogen lamp, with a firing time of 1 min. An equivalent resistance to alkalis was, however, not achieved, even with a firing time of 5 min. On the

other hand, both of these criteria were fulfilled by firing with the Nd-YAG laser with a capacity of 120 W a power density of about 3 kW/cm^2, a rotation rate of 2 min^{-1} and a firing time of 1 min. For this reason, firing with a laser is to be preferred, if a short process time is desirable.

Lead-free blue enamel can be fired-on with infra-red radiation, but regardless which form of firing it undergoes (halogen lamp, laser or forced-air furnace), it does not attain the degree of resistance to acids necessary to make it suitable for use in the chemical laboratory.

The firing of blue lead-enamel markings onto volumetric flasks (250 ml) in a forced-air furnace resulted in a volume reduction of about 50 µl. Laser firing, on the other hand, enabled alterations in volume to be effectively prevented.

Compared to conventional furnace firing, which, with heating-up and cooling takes several hours, the firing-on of enamel markings to a similar degree of chemical durability by means of the Nd-YAG laser takes only a few minutes, including the heating-up and cooling.

Laser firing is limited, at the moment, to those coloured enamels which absorb infra-red radiation, such as blue enamel containing cobalt compounds. This method can be extended to other colours through the addition to the enamel of infra-red absorbing materials, which are colourless.

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