SILICATE ENAMELS FOR STAINLESS STEEL

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Silicate Enamels for Stainless Steel

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Abstract For the development of enamels with different properties an experimental design was used in which the composition of different raw materials was varied. The enamels were applied on three stainless steel grades with a spray gun and fired at 820°C. Different pre-treatment methods (degreasing, pickling and blasting) for stainless steel sheets were used to find the method which leads to the best enamel adhesion on stainless steel. Blasting with corundum results in sufficient adhesion for all enamelled sheets. The analysis of statistical design shows the influence of the enamel raw materials on the different properties measured (e. g. chemical stability, coefficient of thermal expansion). The reasons for the limits of applicability of differently composed enamels on stainless steel substrates with defined coefficients of thermal expansion are discussed. Furthermore, colouring possibilities of direct-on enamels for stainless steel are mentioned.

Key words enamelling, stainless steel, corrosion protection, substrate pre-treatment, statistical design and analysis of experiments

Introduction

Enamelling of stainless steel seems to be an unnecessary rise in cost of an already expensive product. In many cases stainless steel is used because of its higher application temperature and its higher chemical stability. However, extreme conditions (e. g. contact with acid condensates or gases under oxidising conditions at high temperatures) can cause a measurable corrosion of the stainless steel.

Enamels provide an additional corrosion protection and increase the product lifetime of the equipment for the chemical industry. Another advantage is protection of the environment against toxic components released from the alloy (e. g. Ni or Cr). This is of special importance for pharmaceutical, food and housewares industries.

Furthermore, an enamelled stainless steel surface may avoid uncontrolled catalytic effects which can take place in chemical syntheses by contact of the alloying elements (Ni, Mo, W) with the reaction mixture. Other advantages are a better hygienic behaviour concerning the adhesion of spores and sufficient cleaning possibilities and the opportunity of design in terms of colour, e. g. for tubes.

However, chrome-nickel steel is difficultly to be enamelled because of its high coefficient of thermal expansion (CTE). This fact can cause high stress in the enamel coat so that the enamel can chip off. Microstructural changes during heating can cause poor adherence of the enamel on chrome steel.

The main research objective of this work was the systematic development of single-layer enamels for stainless steel substrates with CTEs of 122 … 193 · 10^{-7} K^{-1}, with chemical and optical properties comparable to standard quality enamels.

A secondary objective was to examine the colouring possibilities of such enamels, based on previous results [3].

To adapt enamels on stainless steel substrates, different ways of solution were possible. The following factors had to be varied:

- metal substrate
- metal pre-treatment
- enamel composition (chemical components and phases)
- baking conditions (temperature, time)
- coating (one-coat or two-coat enamel).

A variation of the metal substrate could only be realised by a selection of different commercial types of stainless steels, while a stepwise changing of composition of the stainless steels was not possible in this project. Different methods of pre-treatment have been tested. The sheets were pre-treated by degreasing, pickling or blasting. Baking conditions were at 820 °C for 4.5 min and an one-coat enamel was used. The chemical composition of the enamel was varied by a statistical design of experiments.

Statistical design of experiments

The method of statistical design of experiments is used to reduce the number of experiments and to still get more information per test series [6], [7].

Classical test series only change one parameter per experiment (One-factor-at-a-time). Thereby many individual tests are needed to cover all test alternatives and to interpret certain differences in the results. In contrast to this, by using the method of statistical design of experiments, several parameters can be changed at the same time. Therefore, less individual tests are needed and more data can be obtained for every test result (Fig. 1).

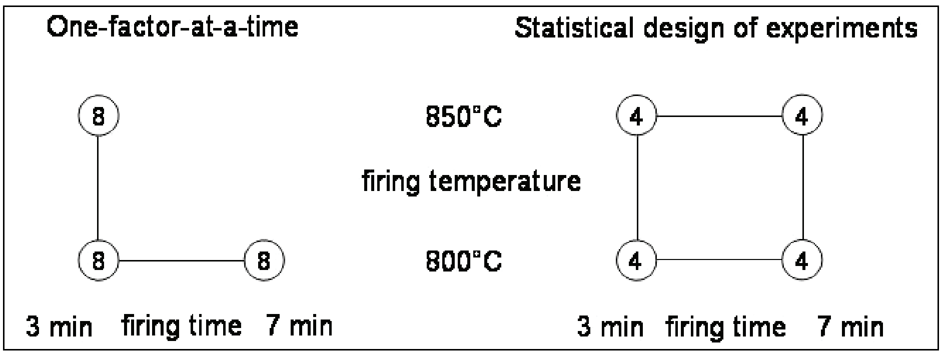

Fig. 1 Difference between classical and statistical design of experiments

With the aid of suitable software, a mathematical correlation can be established between parameters and target factors, thus objective statements about the influence of these parameters can be made. Furthermore, optimised enamel compositions can be calculated if the composition is within the area of investigation. Extrapolations beyond are not allowed.

Varied factors for experimental design were the raw materials quartz, soda, borax, barium carbonate and lithium carbonate. Constant factors were calcium carbonate, manganese oxide and cobalt oxide (Table 1). The target factors investigated were the coefficient of thermal expansion, softening point, glass transition temperature, chemical stability and visual appearance of the enamel surface and gloss.

Table 1 Fraction of the factors for experimental design

Raw materials	%
Quartz	45 to 60
Soda	10 to 35
Borax	10 to 25
Li_2CO_3	0 to 5
$BaCO_3$	0 to 2
$CaCO_3$, MnO_2, CoO	constant at 8

The composition of the frit, which represents the basis of the statistical design of experiments, is listed in Table 2.

Table 2 Composition of the basic frit according to HILLER [1]

Oxide	%
SiO_2	57
Na_2O	22
B_2O_3	14
CaO, MnO, CoO	7

Samples and sample preparation

Three different grades of stainless steels were used (Table 3).

Table 3 Coefficients of thermal expansion of the stainless steels used

Sample number	E1	E2	E3
Grades	Ferritic	Duplex	Austenitic
$CTE_{20\text{-}375°C}$ [$10^{-7}K^{-1}$]	122	151	193

The stainless steel E1 was ferritic steel with a low CTE, E2 was Duplex steel with a higher CTE, and E3 was austenitic steel with a very high CTE.

For sample preparation, different steps were necessary. First, the raw materials had to be weighed and mixed for producing enamel frits. This mixture had to be melted in a fireclay crucible at 1300°C and quenched then in cold water. The stainless steel plates for the experimental design were pre-treated by blasting them with corundum. The enamel slurry was made by grinding the frits with water and mill additions, and then it was applied with a spray gun on the stainless steel sheets. These enamelled sheets were dried and fired then at 820 °C for 4 min.

Results

Influence of pre-treatment of stainless steel

The following different pre-treatment possibilities were tested to elucidate their influence on the adhesion of enamels on stainless steel (q. v. [2]):

- degreasing
- pickling with hydrochloric acid
- blasting with corundum.

Fig. 2 shows the effect of the pre-treatment methods on the enamel adherence on stainless steel.

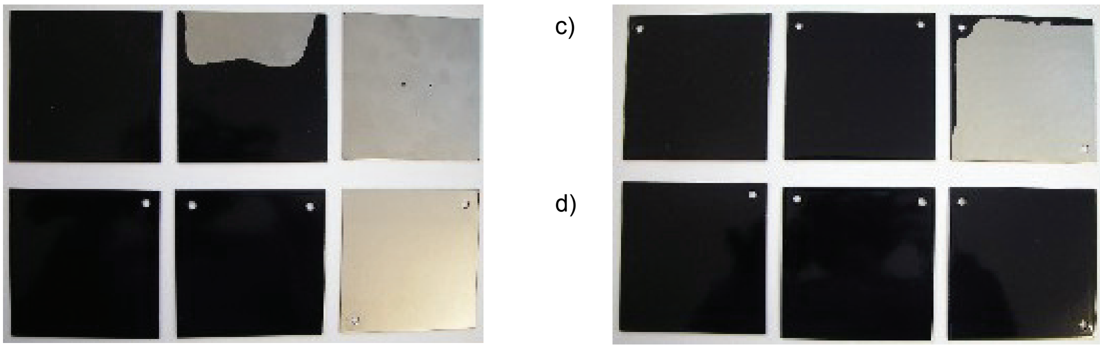

Fig. 2 Comparison of enamelled sheets after different pre-treatment methods
a) degreased; no adhesive oxide in the enamel; b) degreased; with 1 g CuO / 100 g frit
c) pickled in hydrochloric acid; with 1 g CuO / 100 g frit; d) blasted with corundum; with 1 g CuO / 100 g frit

The experiments of the different pre-treatment possibilities for stainless steel sheets show that corundum blasting of the sheets achieves the best adhesion of enamel on stainless steel. The enamel adheres well on all three types of stainless steel. After degreasing and no additional adhesive oxide in the frit, the enamel only adheres on chrome steel, which has a low coefficient of thermal expansion. The two other types (Duplex steel with middle CTE and chrome-nickel steel with high CTE) show no adhesion with the enamel; it chips off immediately after firing. The addition of 1 g CuO / 100 g frit leads to an enamel adhesion on the stainless steels E1 and E2. Pickling of stainless steel sheets does not improve the enamel adhesion.

Fig. 3 displays the differences in surface quality of stainless steel grades used after degreasing and after pickling. The influence of pickling is obvious only on stainless steel 1. The surfaces of stainless steels 2 and 3 show no differences between the two pre-treatment methods. This is due to a higher content of alloying additions of the chrome-nickel steel which leads to a higher corrosion resistance of this steel.

Fig. 3 Microscopic images of surfaces of the stainless steels, 100 x magnified
(a) degreased; (b) pickled

Influence of blasting process on the surface quality of the enamel

Problems with changing of the quality of the enamel surface led to new conclusions about the optimised blasting process. The enamel surface of some samples showed many pin holes. Other samples did not show these defects, although the stainless steel substrates, the enamel and the firing conditions were the same. The different appearances of the enamel surfaces could only be explained by the fact that the substrates were blasted on different days by different persons. It is supposed that the main cause for pin holes on the enamel surface is a too long blasting process and a too rough stainless steel surface. To corroborate this assumption, test series were performed with different times of blasting. The enamel surface of long blasted sheets showed pin holes, the surface of short blasted sheets did not. The different roughnesses of the sheets were verified by a measurement with a profilometer. The too long blasting time caused an inclusion of bubbles during the blasting process. These bubbles could leave the molten enamel layer too late and led to pin holes on the enamel surface.

Formation of a wavy enamel surface

A formation of a wavy enamel surface was observed during the heat-up phase only on chrome-nickel steel while firing the enamel. This effect was mainly noticed for enamels with more than 60 % SiO_2. Increasing SiO_2 content means lower CTE and higher viscosity [4], [5]. The formation of a wavy enamel surface is caused by a very high CTE of the chrome-nickel steel and by tearing open of the enamel biscuit layer during firing (see Fig. 4). Increasing the time of firing does not allow the molten enamel layer to be smoothened because of its high viscosity.

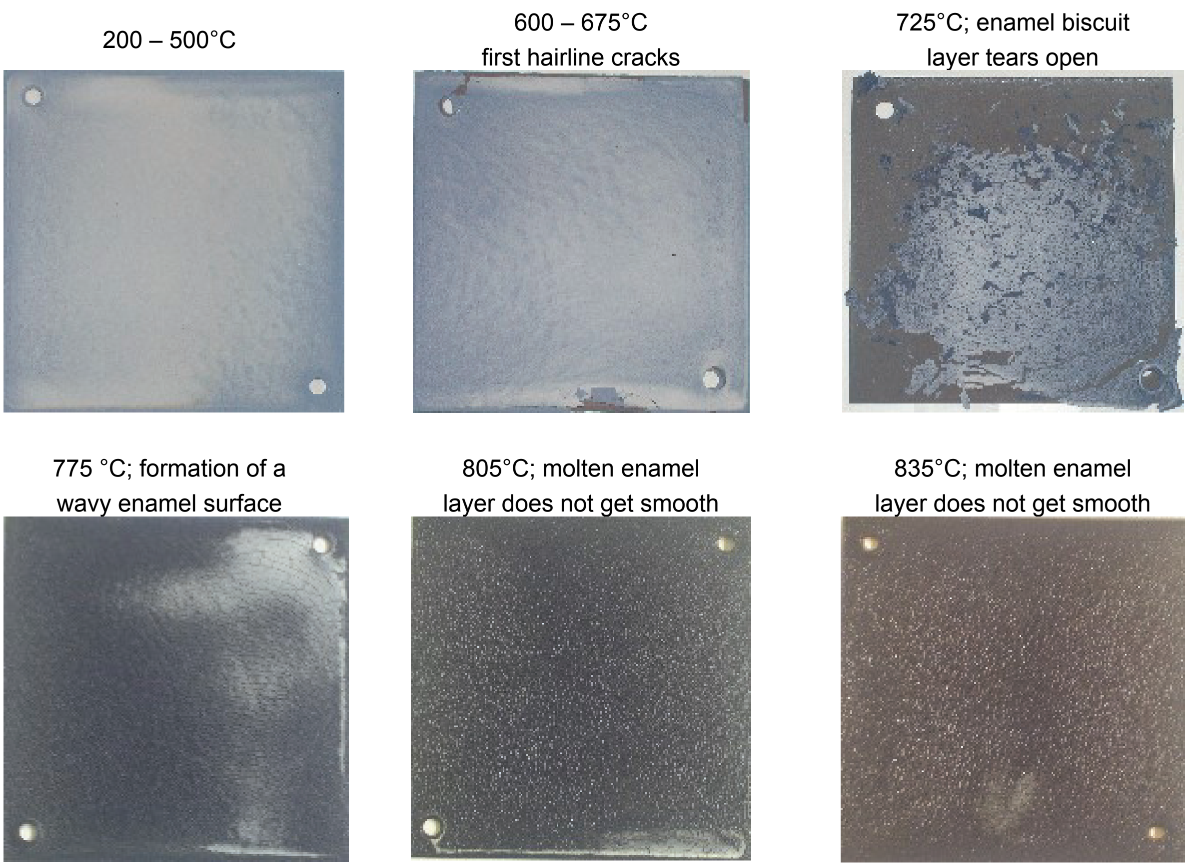

Fig. 4 Formation of a wavy enamel surface with increasing temperature

Computer-based evaluation of the influences of raw materials on desired properties

The enamels developed show very different property data (see Table 4). Thus the CTE, for example, varies from 99 to 146 · 10^{-7} K^{-1}, so that it is possible to find an appropriate enamel for any stainless steel grade.

Table 4 Summary of property data of the enamels developed

Property	Data
Chemical resistance	0.1 – 6.3 g/m²·d
Relative flow length	0.6 – 1.5
Coefficient of thermal expansion	$99 – 146 \cdot 10^{-7} K^{-1}$
Glass transition temperature T_g	431 – 498°C
Softening point T_{SP}	477 – 554°C

The analysis of statistical design shows the influence of the individual enamel raw materials on the different properties measured (e. g. chemical stability, CTE). Its impact may be seen from coefficient plots, as illustrated in Fig. 5. The bars specify direction and size of the effect and the 95 % probability confidence interval indicates the coefficient value being in this interval.

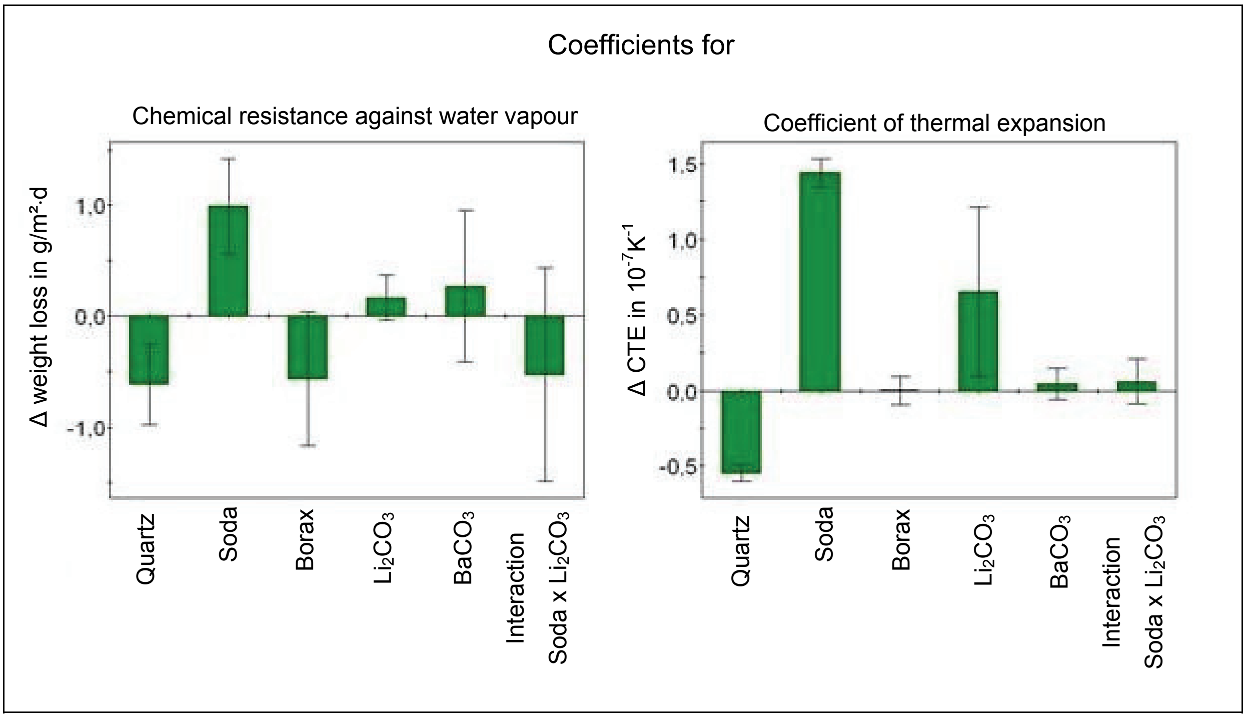

Fig. 5 Coefficient plot for enamel properties „Chemical resistance against water vapour" and „CTE"

The statistical analysis of the results displays the following influences when increasing the content of the raw materials:

- Quartz reduces the weight loss by chemical corrosion, relative flow length and CTE, and increases T_g and T_{SP}
- Soda increases the weight loss, relative flow length and CTE, and reduces T_g and T_{SP}
- Borax increases the relative flow length and CTE
- Li_2CO_3 increases the relative flow length and CTE, and reduces T_g.

Colouring possibilities

When developing coloured enamels for stainless steels, one first has to remove all colour oxides originally present in the mixture. Colour pigments were added then with two different contents (2 % and 5 %) to the mill batch. The colour pigments used are described in [3]. The colour intensities and shades obtained are illustrated in Fig. 6.

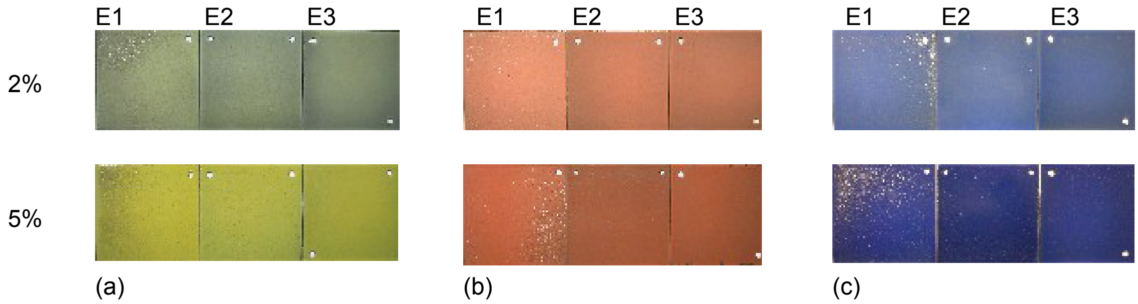

Fig. 6 Colour intensities and shades of enamels on different stainless steel substrates:
(a) with chromium-rutile-colour pigment; (b) with zircon-iron-pink-colour pigment; (c) with cobalt-spinel-colour pigment

As displayed in Fig. 6, different colour pigments developed a different covering power. Increasing the content of colour pigments intensified the colour and varied the shade. The surface quality of the enamels was dependent on the stainless steel grade used. Coloured enamels applied on stainless steel 1 always showed a much blistered surface. Most trials showed a more or less blistered enamel surface with pin holes. Because of a late degassing, bubbles could not leave soon enough the molten enamel layer.

Summary

The results of the investigation show that a corundum blasting of stainless steel sheets results in sufficient adherence against impact load for all enamelled sheets. A sufficient enamelling at the edges was found for most of the enamelled sheets. The best results were achieved with a raw material composition of ≈ 45 % quartz, 20 % soda and 25 % borax (for 820 °C as a firing temperature).

The three stainless steels used have different preconditions for a successful enamelling. For the chrome steel, the CTE of the enamel frit has to be $< 130 \cdot 10^{-7}\ K^{-1}$, otherwise tensile stresses develop. Chrome-nickel-molybdenum steel is easy to enamel, shows a smooth enamel surface in most experiments and there are no problems with an aligned CTE of the enamel frit. When using chrome-nickel steel as a substrate for enamelling, compressive stress can develop if the CTE of the enamel frit is too low.

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