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Vitreous Enamel Coating Surface Defects and Evaluation of the Causes

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Abstract: Enamel is composed of oxide forms, applied on a metal substrate with a firing temperature range of 800-870°C. Vitreous enamel coatings play a very important role in the coating production process of steel in accordance with the technical and aesthetic properties. Surface quality of the enamel coating can be affected by various defects. In this study, most common enamel surface defects obtained during laboratory trials have been investigated and elimination actions have been discussed.

Keywords: Vitreous enamel, Enamel surface defects, Fish scales, Impurities, Burn off, Poor adherence, Blisters.

I. INTRODUCTION

Vitreous enameling is only one of several surface protective processes, but one which holds a leading position from the aspect of quality. This derives not only from the excellent properties of vitreous enamel, but also from the fact that only finished enamel ware which meets the high quality requirements is allowed to leave the shops. The most important aim in quality assurance, therefore, is a good quality for the lowest costs and delivery within shortest time [1].

Defects that cause rejection regarding quality standards for production of enamel coated materials are termed as enamel defects [2]. It can be locally limited interruptions of the compactness or structure of the glass like coating [1]. When enamel coatings are discussed, repair or recycle processes are quite difficult to proceed for defected enamels. For this purpose, main point should be prevention of failure and achieve product liability [2].

Although the formation of defects can often be attributed to a combination of several unfavourable parameters, which leads to a practically infinite number of individual faults, quite often one factor dominates a typical defect type. Therefore, the defects are classified in groups according to the underlying base materials and application processes [1].

A. Fish Scales

Fish scales are steel-related defects which are half-moon shaped cracks in ground or cover coats, which occur immediately or even hours or days after the firing operation. They can occur individually with a typical size of 1-5 mm in diameters. They are the result of hydrogen diffusion through the steel and into the enamel layer; they only occur on pieces enamelled on both sides. The hydrogen formed at the steel surface during firing according to the reaction;

$$Fe + H_2O \rightarrow FeO + H_2$$

H_2 is dissolved in atomic form and after cooling remains in the steel as supersaturated solution. The separation of hydrogen from the steel takes place by recombination to molecules at the steel/enamel phase boundary, then building in pressures of up to 200 atmospheres, which causes scaling [1]. Surface with fish scales is shown in Fig.1.

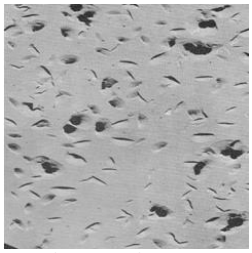

Fig. 1 A surface with fish scales defect [3]

B. Poor Adhesion

Adhesion of the enamel coating explained with two basic adhesion mechanism; chemical theory and mechanical theory. Chemical theory indicates that; a continuous shift of the type of bond must be achieved in the region of the phase boundary from the metallic bond of the base metal via an oxide adherence layer to the ionic bond of the enamel

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layer. Mechanical theory is defined by; the prerequisite for good adherence is roughening of the interface surface leading to a tight mechanical clinging of the enamel to the steel surface [4-8].

The adherence of the enamel coat can be ascertained by destroying it by means of mechanical deforming. The deformation can be achieved in a dynamic manner by impact caused by a falling weight. The remaining amount of enamel after the impact and determined by visual inspection, is a measure of the adherence between steel and enamel. Classification of adherence is standardised in EN 10209 as 1 equals to very good and 5 stands for poor adherence [1].

Poor adherence of the enamel is a very severe quality spoiling appearance which can lead to rapid destruction of the steel/enamel composite. Poor adherence can have very different origins, ranging from non-suited steel grades over poor pre-treatment, application of enamels with too low cobalt/nickel oxide content to under- or over-firing [1].

C. Blisters

Blisters are hollow holes through the fired enamel, having a diameter of up to 1 mm, which may remain intact in the enamel surface, but can also blow off leaving a funnel shaped recess. The common cause of this defect, also called re-boiling or carbon boil, is a local strong gas development during firing, with the gas containing hydrogen as well as carbon monoxide [1].

Pickling residues, through their (gaseous) decomposition products can bring up very heavy boiling-up with enamel and steel. Due to the diffusion of the hydrogen thus arising, impurities can also be observed on the opposite side of the sheet steel. Often, blisters are observed with hollow ware where in sealed rings or badly shaped handles obstinate residues of pickling acid accumulate [1].

D. Impurities

Impurities in base coat enamelling can range from sheet steel contamination to scale deposits. Often, it is very difficult and time consuming to find the origin because impurities can be introduced in all steps of the enamelling process. The most frequent ones are;

- Fine iron particles from cutting and welding
- Residues from pre-treatment agent
- Coarse particles from milling and balls (white spots)
- Coarse (ungrounded) mill additions
- Dust from cover coat enamel
- Scale deposit from firing tools [1].

E. Burn-Offs

Burn-offs are localised areas of iron oxide eruptions through the enamel coating. The main causes for these defects are a too thin enamel thickness or an insufficient amount of refractory mill additions. In the first case, the excess iron oxide which is not solubilised in the base enamel penetrates from the phase boundary to the surface [1].

II. EXPERIMENTAL MATERIALS

A. Steel Substrate

Due to their low carbon contents, two different steels have been utilized during experiments; DC 04 EK and DC 04 ED. Chemical compositions for these steels are shown in Table I.

TABLE I
CHEMICAL COMPOSITIONS OF STEEL SUBSTRATES (WT %)

Steel	C %	Mn %	P %	S %	Si %	Cr %
DC 04 EK	0,0384	0,168	0,0076	0,0183	0,0176	0,0283
DC 04 ED	0,0053	0,144	0,0101	0,0183	0,0106	0,0311

B. Enamel Frit

According to final product's area of usage, two different enamel powders have been applied on steel substrates. White is for white wares and black is for baking tray manufacturing. Chemical compositions for both enamel frits have been shown in Table II.

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TABLE II
CHEMICAL COMPOSITIONS OF STEEL SUBSTRATES (WT %)

Frit Composition	SiO_2 %	B_2O_3 %	TiO_2 %	Na_2O %	K_2O %	CoO %
White	43,30	17,20	19,37	13,00	7,10	0,03
Black	58,70	18,20	4,50	9,70	6,50	2,40

III. EXPERIMENTAL PROCEDURE

During laboratory studies, electrostatic powder coating method were used. Before enamel coating was applied, substrates have been prepared with cutting the steel sheets into 10 x 10 cm pieces. Surfaces were pre-treated via sand blasting for increasing roughness. Then, washing with degreasing agent at 65°C for 30 min in order to clean surfaces from rolling oil, rinsing in distilled water and drying in oven at 100°C for 10 minutes steps followed respectively.

After substrates were prepared, white and black enamel powders were applied for different applications in different thicknesses. Coated samples were fired in the oven at 840°C for 4-6 min. After firing, samples were visually inspected. In case of surface defect existence, SEM analysis was utilized for enamel coating-metal substrate interface and surface examination to evaluate the causes of the defects. Samples were placed in bakelite for cross-sectional examination and bakelites were subjected to abrasion and polishing before examination if necessary.

Defects encountered are discussed in detail in Results section.

IV. RESULTS

During experimental studies, fish scales, burn-offs, blisters, poor adhesion and impurities have been detected.

A. Fish Scales

Sample with fish scale (Fig. 2) has been examined via SEM analysis. Small piece was cut for cross-sectional examination. Chemical composition of the defect-free and defective areas were compared (Table III). SEM image for these areas is shown in Fig. 3.

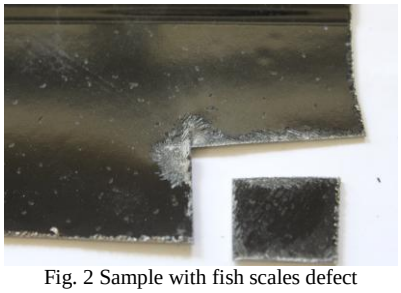

Fig. 2 Sample with fish scales defect

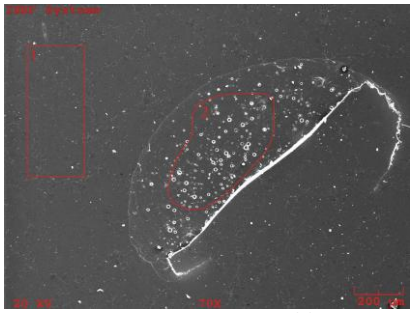

Fig. 3 Scanning electron micrograph of fish scales defect

TABLE III

EDS ANALYSIS OF DEFECT-FREE AND DEFECTIVE POINTS FOR FISH SCALE

Areas	O %	Na %	Al %	Si %	Cl %	K %	Ti %	Fe %	Zr %
Defect-free (1)	33,78	9,45	0,98	43,14	0,09	4,15	6,13	1,98	0,36
Defective (2)	35,72	8,18	0,78	41,99	0,06	5,23	4,46	3,21	0,20

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Main reason for fish scale is hydrogen diffusion through the steel and into the enamel layer. As seen from the EDS elemental analysis, defect-free and defective points almost have the same chemical content. That proves visual inspection comment was correct. Defect was not caused by an impurity but hydrogen presence due to insufficient drying. In the trials to come, as a preventive action, substrates were dried for 10 minutes after surface cleaning step, defect had been eliminated.

B. Poor Adhesion

In some cases, poor adhesion was observed after impact tests. Samples showing good adhesion (Fig.4a) and poor adhesion (Fig.4b) were compared via SEM cross sectional analysis (Fig. 5a and 5b) to understand the failure cause.

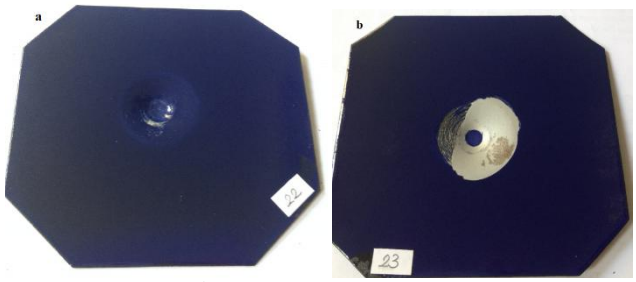

Fig. 4 Impact test results of samples showing a) good adhesion, b) poor adhesion

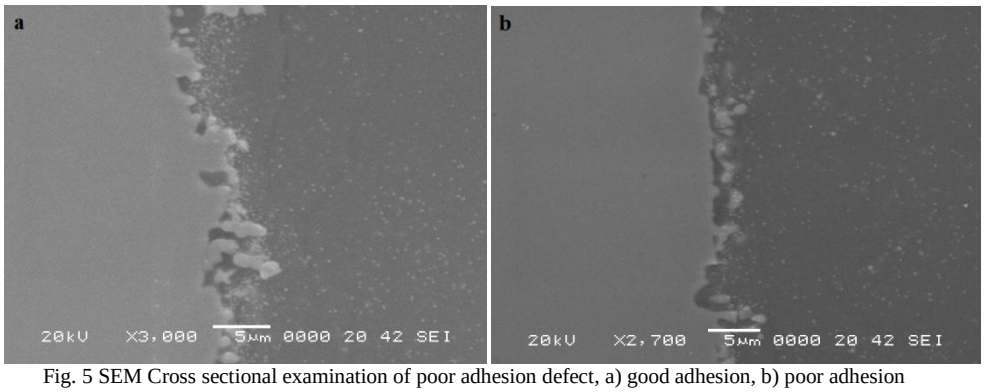

Fig. 5 SEM Cross sectional examination of poor adhesion defect, a) good adhesion, b) poor adhesion

Adhesion can be both mechanical and chemical. Mechanical side is achieved by dendrites along the enamel-steel interface. In Fig.5, two different interfaces from two different samples were shown. Both samples were prepared with the same enamel powder, in the same thickness and fired at 840°C. Firing duration was 6 minutes in Sample b where it was 4 minutes in Sample a. As seen from the micrograph, as duration increases, dendrite formation started to break away from interface. Due to loss of interlocking, after an optimum firing duration, adhesion gets worse. In the trials to come, as preventive actions, optimum firing parameters were set and substrate was changed to a different chemical composition with lower C content, from EK to ED. By using ED, outgassing during firing is reduced and surface quality of the final product was promoted.

C. Blisters

Especially in white enameled samples, blisters were visually detected at the surface (Fig.6). Sample was prepared for elemental analysis with EDS SEM to determine whether local gas development or impurities were the main reason for these formations.

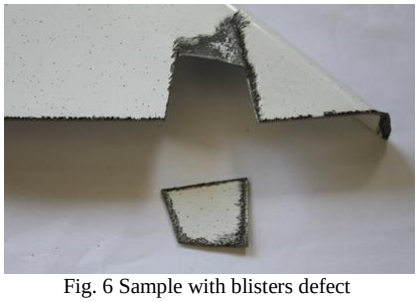

Fig. 6 Sample with blisters defect

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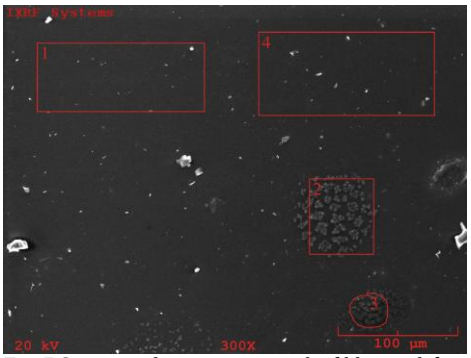

Fig. 7 Scanning electron micrograph of blisters defect

Both defect-free and defective areas were examined via EDS SEM analysis. Area 1 and 4 were defect-free areas. In Area 2 and 3 blisters were detected. Chemical analysis results were shown in Table IV.

TABLE IV
EDS ANALYSIS OF DEFECT-FREE AND DEFECTIVE POINTS FOR BLISTERS

Areas	O %	Na %	Al %	Si %	Cl %	K %	Ti %	Zr %
Defect-free (1)	36,27	7,42	1,24	29,64	0,13	7,81	14,85	2,64
Defect-free (4)	34,17	8,35	1,16	29,97	0,092	7,72	15,85	2,68
Defective (2)	33,83	10,25	1,57	17,59	15,16	5,62	13,24	2,74
Defective (3)	26,02	13,83	1,51	19,27	16,81	10,62	9,18	2,76

From EDS elemental analysis results, it was clearly stated from the increment in Cl content that, blisters were formed due to the residues of alkali surface cleaners which were utilized in substrate preparation stage to clean rolling oil. With addition of an extra rinsing step with distilled water to substrate preparation stage, blisters had eliminated in the trials to come.

D. Impurities

Sample with impurity defect (Fig.8) was examined via SEM analysis. Defect-free and defective areas, shown in Fig.9, were compared to understand the cause in Table V.

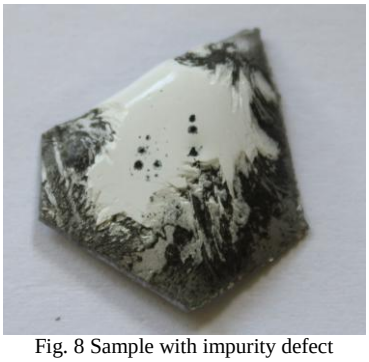
Fig. 8 Sample with impurity defect

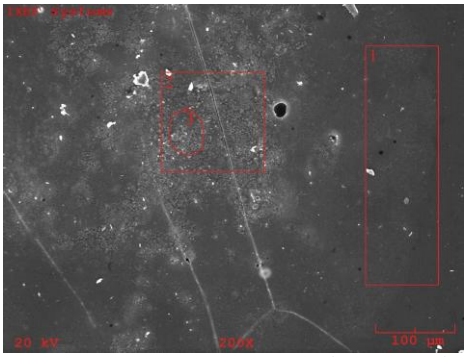

Fig. 9 Scanning Electron Micrograph of impurity defect

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TABLE V
EDS ANALYSIS OF DEFECT-FREE AND DEFECTIVE POINTS FOR IMPURITIES

Areas	O %	Na %	Al %	Si %	Cl %	K %	Ti %	Zr %	Fe %	Ca %	Cr %
Defect-free (1)	23,65	7,13	1,28	31,90	0,11	10,39	14,85	2,64	2,39	5,36	0,30
Defective (3)	9,73	10,85	0,72	12,07	0,41	2,34	3,70	2,79	42,31	14,92	0,16

EDS analysis showed that, an increment in Ca, Na and Fe contents was determined. Ca and Na increment was caused by alkali residues from substrate preparation stage. The change in Fe content was significantly noticeable. Due to surface discontinuities caused by alkali residues, enamel coating was not applied homogeneously. After firing, Fe content from steel substrate had come up beneath coating and caused this sudden increase. With utilization of a rinsing chemical in substrate preparation stage, defects caused by impurities had been eliminated.

E. Burn-Offs

Burn-offs were determined visually. Due to insufficient coating thickness caused burn-offs in some samples (Fig. 10). Via increment thickness with specific parameter optimization, defect had been eliminated. It was proven that thickness must be minimum 150 µm to receive a smooth surface at 840°C firing temperature for 4-6 minutes firing duration.

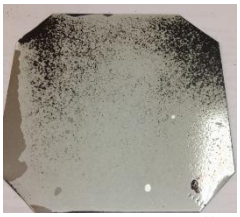

Fig. 10 Sample with burn-off defect

V. CONCLUSIONS

This experimental investigation reveals that enamel coating on a steel substrate is a highly delicate process. Not only raw materials and application stages but also production parameters are extremely effective on final product. Steel substrate composition, homogeneity of enamel powder, cleanliness of application equipment, preparation and firing parameters must be controlled regularly.

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