

# DESIGN AND APPLICATION OF TRANSPARENT AND TRANSLUCENT ENAMELS ON ALUMINUM

#H. AHMADI MOGHADDAM, M. SALEHI

*Department of Inorganic Pigments and Glazes, Institute for Colorants, Paints and Coatings,  
Ministry of Science, Research and Technology,  
No.55, Vafamanesh St., Tehran, Iran, 1668814811, P.O.Box: 16765-564*

#E-mail: ahmadi@icrc.ac.ir

Submitted November 14, 2011; accepted June 25, 2012

**Keywords:** Glass enamels, Opacity, Dipping, Sintering, Interfacial adhesion

*Transparent and opaque glass enamels for aluminum plates were designed with a minimum or with no heavy atom oxides such as lead and bismuth oxides. The thermal properties of the enamels were studied by DTA and their stability as measured by the difference of glass transition and crystallization onset temperatures was determined. Bending and rapid deformation (impact) tests indicated the interfacial adhesion. The enamel/aluminum interfacial qualities were viewed and examined by scanning electron microscopy (SEM). A large amount of NaF and P<sub>2</sub>O<sub>5</sub> in their formulation created opaque enamels. The three methods of melt dipping, pouring, and sintering were used to apply layers of enamels on aluminum plates. The novelty of the pouring and spreading method and its advantages over other methods, were in the use of lower stability and higher melting point enamels, without thermally/mechanically damaging the aluminum. Observations suggested that the interfacial contact and adhesion properties were good, particularly with the transparent or glassy state enamels.*

## INTRODUCTION

Aluminum is a distinctive metal for its low density, good conduction, and corrosion resistance properties. It may be coated with the aim of extending its service life against chemical attacks, in particular with acidic and erosive environments. Inorganic coating layers on aluminum, referred to as enamels, can act as barriers to heat transfer and electricity. Generally, enamels improve thermal and electrical resistance properties, and prevent deformation, especially at relatively high temperatures (500°C); In addition, they increase the surface scratch resistance. Enamels may improve the surface qualities of aluminum generating a smoother surface and a lower coefficient of friction. Aluminum products used in industries and in particular those utilized in aeronautical applications are favoured for their corrosion and erosion resistances. Aluminum may also be enamelled for decoration, and to give attractive tinted surfaces for aesthetic purposes. There are varieties of coated aluminum sheets and panels known as aluminum curtains, which are offered in a range of colours and artistic impressions. They are used occasionally for decorating the interior and exterior of buildings [1-2].

Thermal property matching and adhesion between the aluminum surface and the enamel are the preliminary requirements in tailoring suitable enamel compositions. The low temperature properties, i.e. relatively low melting temperatures, low viscosity-temperature depen-

dence, high thermal expansion coefficient, and low heat conduction besides low thermal shock resistance, are the main objectives and therefore, constrain the choice of appropriate ingredients in the enamel formulations. In glass-based enamels, the glass formers of low melting point such as B<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> might be included in the formulations to make relatively low temperature property enamels. However, the resulting enamels could have a reduced chemical resistance. On the other hand, alkali oxides, as modifiers, reduce the melting temperature, but weaken the acid resistance properties. Thus, in tailoring enamel formulations, proper counterbalances between glass formers: SiO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, and GeO<sub>2</sub>, intermediate glass formers: Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and modifiers: alkaline and alkaline earth oxide, heavy metal oxides, e.g., PbO and others, should exist. Other chemicals such as different metal fluorides or chlorides may be employed to introduce some physical or processing properties to enamels. Great efforts have been made to choose and to balance appropriate constituents in their relative amounts. They may have a counteracting effect on each other, but could contribute to the total desired overall enamel properties [3-5].

Addition of some transition element oxides, e.g. CoO, NiO, MnO<sub>2</sub>, etc, to enamels, is recommended for iron based substrates and is believed to be responsible for achieving the desired adhesion for which different theories have been suggested [6-9]. In practice, this has been found to be also applicable to aluminum substrates [10].

Adding oxides of large and asymmetric metal ions, e.g. PbO, promotes overall adhesion by lowering the surface tension of the molten enamel, so extending the area of surface which is wetted, whilst the decrease in viscosity, due to the presence of the mentioned heavy metal oxides, also promotes spreading of the enamel melt. Hence, the interfacial surface area increases [11].

Fluoride metal salts, particularly alkaline based, decrease melt viscosity, and facilitate enamel film formation. However, they may precipitate and/or induce devitrification during enamel solidification allowing opaque, translucent, semi-, or totally transparent enamels to be obtained [12].

Lastly, adding refractory oxides, such as, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, to the enamel formulations, enhances the body strength of enamels and lowers their expansion coefficients besides increasing the thermal properties [8].

In this investigation, the aim is to construct, test and assess suitable low melting enamels with good adherence to aluminum plates based on low content lead or lead free glasses using combinations of the additives listed above

Table 1a. Tailored formulations for aluminum enamels.

Batch materials	Chemical formulation (mol. %)					Base chemicals
	5S10	4S9	3S1	2S3	1S2	
SiO <sub>2</sub>	–	–	–	–	–	SiO <sub>2</sub>
H <sub>3</sub> BO <sub>3</sub>	37.9	32.0	21.4	18.1	11.4	B <sub>2</sub> O <sub>3</sub>
P <sub>2</sub> O <sub>5</sub>	–	5.1	23.7	19.1	32.4	P <sub>2</sub> O <sub>5</sub>
Li <sub>2</sub> CO <sub>3</sub>	22.0	18.5	12.5	–	–	Li <sub>2</sub> O
Na <sub>2</sub> CO <sub>3</sub>	26.6	22.4	14.4	32.5	12.8	Na <sub>2</sub> O
K <sub>2</sub> CO <sub>3</sub>	7.0	5.9	3.9	4.5	4.2	K <sub>2</sub> O
Al(OH) <sub>3</sub>	2.6	2.0	14.3	24.7	11.7	Al <sub>2</sub> O <sub>3</sub>
TiO <sub>2</sub>	–	–	–	–	–	TiO <sub>2</sub>
Pb <sub>3</sub> O <sub>4</sub>	3.0	–	–	–	–	PbO
Co <sub>3</sub> O <sub>4</sub>	0.9	0.7	1.0	1.1	1.1	CoO
NaF	–	13.2	8.9	–	26.4	NaF

Table 1b. Processing and test results of tailored aluminum enamels.

Samples		5S10	4S9	3S1	2S3	1S2
Batch melting temp. (T <sub>m</sub> ) °C		800	800	1100	1200	1200
Ramping time (hr)		1	1	1.5	1.5	1.5
Heating period at max. temp.(min)		30	30	30	30	30
Structure		Multi phase	Multi phase	Single glassy phase	Single glassy phase	Single glassy phase
Colour		Blue	Blue	Dark blue	Dark blue	Dark blue
Optical properties		Opaque	Opaque	Transparent	Transparent	Transparent
Adhesion quality grade		2	3	2	1	2
Thermal analysis (DTA) °C	T <sub>g</sub>	480	–	–	510	410
	T <sub>x</sub>	600	–	–	690	640
	T <sub>m</sub>	–	–	–	–	–

## EXPERIMENTAL

### Sample preparation

An aluminum sheet of Alloy 6000 Series with 2 mm thickness was cut into plates of 20×100 mm<sup>2</sup> [13]. In the surface treatment, we first cleaned and degreased the aluminum plates with a hard sponge soaked in standard dishwashing detergent. Then they were placed in 10 g per liter of 50:50 (by weight) Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> dissolved in distilled water, at 60-70°C for 5 minutes. After careful rinsing in hot and then in cold distilled water, plate surfaces were oxidized by immersion for 15-20 minutes in a 67.5 g per liter solution maintained at 85-95°C of 15:2.5:50 fractions by weight of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>:NaOH:Na<sub>2</sub>CO<sub>3</sub> salts dissolved in distilled water. The treated plates were annealed in a furnace at 550°C for 5 minutes [10, 14-16].

### Raw materials and compounding

Chemicals with 99-99.7 % purities were mostly obtained from Aldrich and Mercury companies. They were first ground to fine powders (<300 μm) in a jar mill, and then were weighed using a balance with two digits accuracy in accordance with the designed formulations, see Tables 1, 2, and 3 parts (a). 50 g batches were compounded by tumble mixing in a jar for about 2 minutes. Wet mixing, for preparing uniform 50 % slurries in different media, were performed in a Frisch Pulverisette 6 planetary mixer at 300 rpm for 15 minutes. The media were distilled water, aqueous sodium silicate, and some organic solvents (a mixture of ketones, alcohols, esters etc.) produced by the Helios Company.

### Melting

Batch melting was performed inside 50 and 100 ml alumina crucibles in a lifting furnace at different temperatures ranged from 800 to 1200°C, for a period of 1 hour. The aim was to use consistent melting procedures, since there were volatile chemical ingredients such as B<sub>2</sub>O<sub>3</sub> and PbO in the formulated batches. See Tables 1, 2, and 3 parts (b).

## Sample preparation

Three methods were used:

1. Dipping aluminum plates into enamel melts (dip coating),
2. Pouring molten enamels, at appropriate viscosities, carefully on to the surfaces of the plates to produce uniform films, and
3. from the original melts left from the preceding methods, frits were made, ground and sieved. Loose pastes (thickened slurries) using different liquid media were prepared. An applicator with a gauge less than 300  $\mu\text{m}$  was employed to apply it uniformly onto the aluminum plates.

In the second method, prior to pouring the molten enamels, aluminum plates were preheated to 500°C, intended to ease melt spreading at a lower viscosity. Subsequently, they were transferred back to the furnace at 500°C, and the furnace was set to cool down slowly to 50°C over 24 hours, in order to have a low cooling rate and to avoid possible interfacial failures or glass enamel shattering. See Figure 1 to view the prepared test

samples. Samples were coded according to the reference numbers in the Tables and their appearance order from left to right in Figure 1.

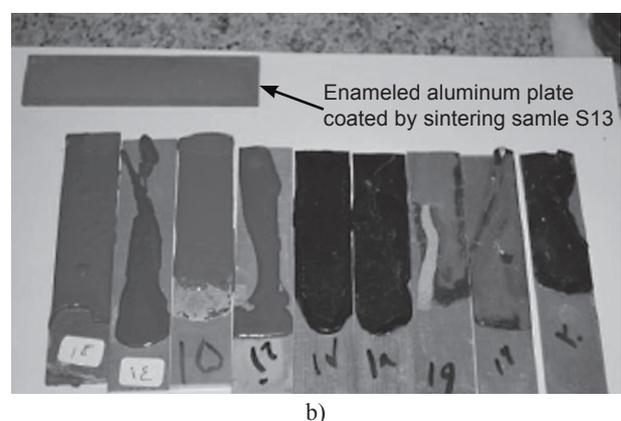
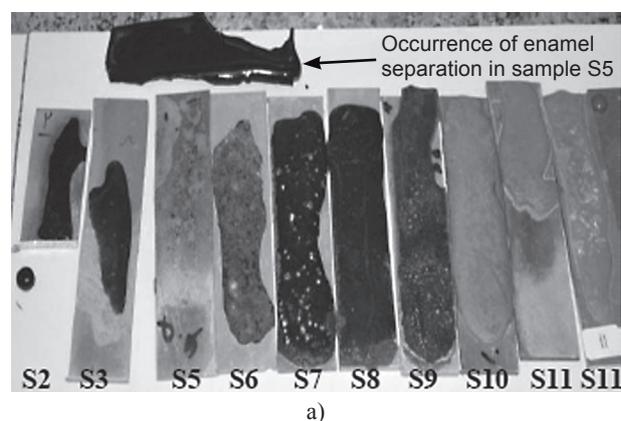


Table 2a. Tailored formulations for aluminum enamels.

Batch materials	Chemical formulation (mol. %)						Base chemicals
	11S16	10S15	9S14	8S13	7S12	6S6	
SiO <sub>2</sub>	20.1	17.2	11.5	11.7	11.2	29.2	SiO <sub>2</sub>
H <sub>3</sub> BO <sub>3</sub>	19.2	19.7	19.8	20.2	19.4	10.1	B <sub>2</sub> O <sub>3</sub>
P <sub>2</sub> O <sub>5</sub>	3.0	3.1	3.1	3.2	3.1	3.2	P <sub>2</sub> O <sub>5</sub>
Li <sub>2</sub> CO <sub>3</sub>	11.2	11.5	23.0	11.7	11.3		Li <sub>2</sub> O
Na <sub>2</sub> CO <sub>3</sub>	16.2	16.6	11.1	22.7	27.2	33.9	Na <sub>2</sub> O
K <sub>2</sub> CO <sub>3</sub>	7.1	7.3	3.7	3.7	3.6	11.2	K <sub>2</sub> O
Al(OH) <sub>3</sub>	2.7	2.7	2.7	2.8	2.7	2.8	Al <sub>2</sub> O <sub>3</sub>
TiO <sub>2</sub>	–	–	–	–	–	8.7	TiO <sub>2</sub>
Pb <sub>3</sub> O <sub>4</sub>	3.6	4.6	7.8	6.4	4.5	–	PbO
Co <sub>3</sub> O <sub>4</sub>	0.9	0.9	0.9	0.9	0.9	0.9	CoO
NaF	16.0	16.4	16.4	16.7	16.1	–	NaF

Table 2b. Processing and test results of tailored aluminum enamels.

Samples	11S16	10S15	9S14	8S13	7S12	6S6
Batch melting temp. (T <sub>m</sub> ) °C	800	800	800	800	800	1000
Ramping time (hr)	1	1	1	1	1	1
Heating period at max. temp.(min)	30	30	30	30	30	30
Structure	Glass-ceramic	Glass-ceramic	Glass-ceramic	Glass-ceramic	Glass-ceramic	Unstable
Colour	Blue	Blue	Blue	Blue	Blue	Dark blue
Optical properties	Glass-ceramic	Glossy-opaque	Glossy-opaque	Glossy-opaque	Glossy-opaque	Devitrified
Adhesion quality grade	3	3	2	3+	3-	3
Thermal analysis (DTA) °C	T <sub>g</sub>	350	350	360	375	356
	T <sub>x</sub>	435	435	450	440	435
	T <sub>m</sub>	–	–	–	–	–

Table 3a. Tailored formulations for aluminum enamels.

Batch materials	Chemical formulation (mol. %)									Base chemicals
	20S20 (S20m4)	19S19 (S19m3)	18S18 (S18m2)	17S8	16S11	15S17 (S17m1)	14S7	13S5	12S4	
SiO <sub>2</sub>	6.3	10.8	11.7	8.9	10.8	15.2	13.1	42.9	42.5	SiO <sub>2</sub>
H <sub>3</sub> BO <sub>3</sub>	53.9	42.0	45.6	30.6	28.0	34.2	26.3	13.9	9.2	B <sub>2</sub> O <sub>3</sub>
P <sub>2</sub> O <sub>5</sub>	–	–	–	–	–	–	–	–	–	P <sub>2</sub> O <sub>5</sub>
Li <sub>2</sub> CO <sub>3</sub>	–	–	11.8	17.8	21.7	20.3	17.3			Li <sub>2</sub> O
Na <sub>2</sub> CO <sub>3</sub>	18.2	15.7	17.1	21.5	26.2	14.8	25.3	36.4	36.0	Na <sub>2</sub> O
K <sub>2</sub> CO <sub>3</sub>	4.0	6.9	3.8	5.7	6.9	3.2	2.8	3.4	3.4	K <sub>2</sub> O
Al(OH) <sub>3</sub>	3.0	5.6	6.2	2.1	2.6	2.9	2.1	2.5	–	Al <sub>2</sub> O <sub>3</sub>
TiO <sub>2</sub>	–	–	–	–	–	–	–	–	8.0	TiO <sub>2</sub>
Pb <sub>3</sub> O <sub>4</sub>	5.2	3.0	3.3	–	2.9	1.4	–	–	–	PbO
Co <sub>3</sub> O <sub>4</sub> (MnO <sub>2</sub> )	0.5	0.5	0.5	0.7	0.9	0.8	0.7	0.9	0.9	CoO (MnO <sub>2</sub> )
NaF	9.0	15.5	–	12.7	–	7.2	12.4	–	–	NaF

Table 3b. Processing and test results of tailored aluminum enamels.

Samples	S20	19S19	18S18	17S8	16S11	15S17	14S7	13S5	12S4
Batch melting temp. (T <sub>m</sub> ) °C	800	800	800	800	800	800	800	1000	1000
Ramping time (hr)	1	1	1	1	1	1	1	1.5	1.5
Heating period at max. temp.(min)	30	30	30	30	30	30	30	30	30
Structure	Single glassy phase	Glassy +glass-ceram.	Single glassy phase	Unstable glass	Glass-ceramic	Single glassy phase	Unstable glass	Single glassy phase	Single glassy phase
Colour	Dark blue (brown)	Blue (bej)	Dark blue (brown)	Dark blue	Blue	Dark blue (brown)	Blue	Dark blue	Blue
Optical properties	Transparent	Translucent	Transparent	Opaque	Opaque	Transparent	Opaque	Transparent	Transparent
Adhesion quality grade	2	3	2	3	3	1	3	4	3
Thermal analysis (DTA) °C	T <sub>g</sub>	380	380	395		360	310		
	T <sub>x</sub>		550	540		510	475		
	T <sub>m</sub>	680	700	800		780	545		

Because of the presence of hygroscopic and volatile oxides such as B<sub>2</sub>O<sub>3</sub> and PbO in the formulae, which might affect the equipment, and reduce the accuracy of the tests, only small sample (<75 mg) were tested. The curves obtained were studied and compared for any discrepancies. The DTA curves for the translucent (devitrified enamel) samples did not display pronounced transition temperatures, T<sub>g</sub>s or crystallization temperatures, T<sub>x</sub>s, since the glass phase in them was minimal (see Figure 2). Since the TG curves of the tested samples were similar and did not exhibit significant differences, they have not been presented.

XRD and XRF tests were carried out to study the formation of any possible crystal phases in the transparent enamels and any effective changes in the enamel ingredients during melting respectively.

To evaluate enamel/substrate adhesion strength a bending experiment by a cylindrical mandrel in accordance with the standard test [17], was implemented. The best adhesion strength quality was rated as level '1', for which no or a minimum enamel separation was observed

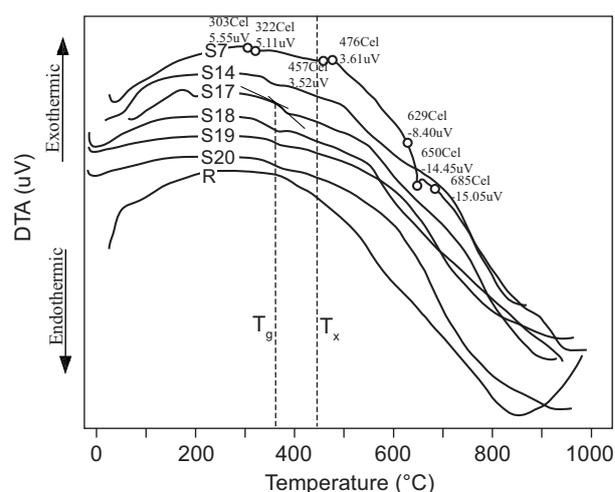


Figure 2. Depicting similarity in the DTA traces of samples (trace R indicates the result for DTA test without a sample). The first depressions on the curves close to the vertical line represent T<sub>g</sub> and the onsets of the subsequent low hills represent T<sub>x</sub>.

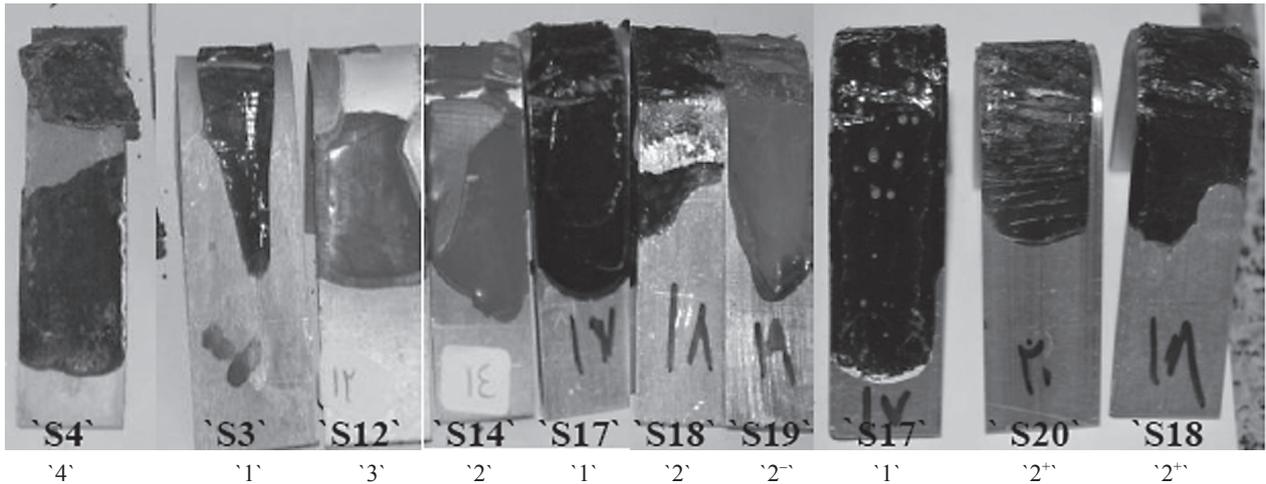


Figure 3. Different failure modes of enameled aluminum samples in the mandrel bending test suggesting adhesion quality level (adhesion quality grades: '1' - enamel cracks with no or very small interfacial separated pieces, '2' - enamel cracks with patchy interfacial separation, '3' - complete interfacial separation, '4' - interfacial separation before bending).

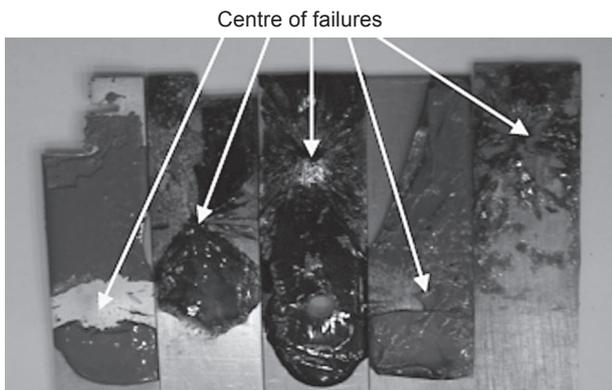


Figure 4. Results from the falling ball impact test. Enamel failure in the depressed regions, for S16 was a complete interfacial separation, for S18, S19 and S20 were combination of interfacial separation and cracks, and for S17 was only small radial cracks.

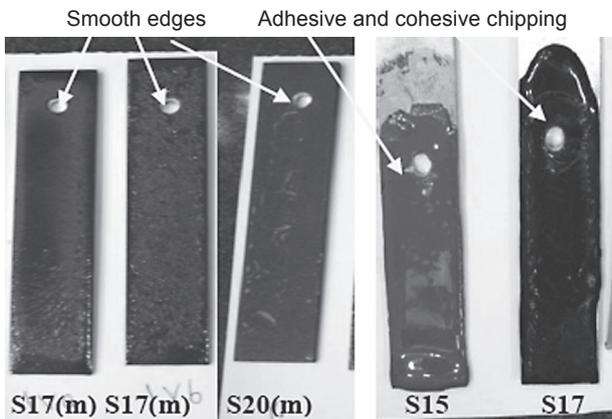


Figure 5. Effects of drilling on different samples: a) enamels sintered at 500°C (thickness 60 μm), b) melt poured (thickness 300 μm).

at the most curved or bent part of the aluminum plates (see Figure 3). Higher numbers indicated lower adhesion qualities; for example, '4' was the worst quality level or grade, for which separation occurred before bending was applied to the test sample (see Tables 1, 2, and 3 part b).

The falling ball impact test (rapid deformation) was executed on the samples according to standard [18]. The imposed energy was calculated as 0.12 Nm. The deformation created on the enamelled side of the plate was observed and examined after each test. For the best enamel adhesion, i.e., sample S17, no separation was witnessed. However, radial cracks were generated from the centre of the deformations (see Figure 4).

Other mechanical application tests, such as cutting and drilling, from both the enamelled and aluminum sides, were executed. No cracking or chipping of the enamels was observed for samples with thin enamel layers (see Figure 5).

## RESULTS AND DISCUSSIONS

### Materials and formulations

In enamels, mostly based on oxide glasses, challenges lie in the best choice and combinations of glass formers and modifiers. Results presented in Tables 1 (a) and (b) suggest that the addition of  $P_2O_5$  raises the melting point in comparison with  $B_2O_3$  in the glass, but it generally aids glass forming and stability [8]. In total, a combination of glass formers such as  $B_2O_3$  and  $P_2O_5$  lowers the fusing or melting characteristic of the glasses in the presence of  $SiO_2$ . This is most apparent when both  $B_2O_3$  and  $P_2O_5$  are present in equimolar proportions and can be regarded as  $BPO_4$  in the corresponding phase diagrams [19, 20] (see Tables 2). However, they impart poor chemical durability, when comparing with  $SiO_2$ .

Although, the  $\text{BPO}_4$  based enamels showed relatively high stability and transparency with satisfactory adhesion, they did reach a suitably low viscosity for pouring below  $1100^\circ\text{C}$ . In addition, their DTA results for  $T_g$  and  $T_x$  were high (see Table 1 part b). Samples 4S9 and 5S10 were melted at a lower temperature, but were not homogeneous and transparent. Therefore, these enamels may not be suitable for enameling by a sintering method. Results for 2S3 in comparison with others in the table may suggest that  $\text{P}_2\text{O}_5$  could replace  $\text{PbO}$  by an appropriate proportion in the formulae.

Samples in Tables 3 were tailored with a view to improve enamels; they adhered well to aluminum surfaces and resulted in transparent enamels. Relatively poor thermal properties and adequate adhesion strength were the prime challenges. Concerning the former, the transition temperatures,  $T_{gs}$ , of the enamels were required to be above the temperatures at which the aluminum would start deforming under the service tension. In this respect, the correlation between the enamel and aluminum regarding thermal expansion property, would depend on the enamel design parameters, such as thickness, shape, strength, and mechanical tolerances. In an overview of the samples in the Table 3, one may note that those with appreciable higher  $\text{SiO}_2$  contents, i.e. samples: 12S4 and 13S5 showed complete melting above  $1000^\circ\text{C}$ . Whereas, in comparison with others, samples 14S7, 16S11, and 17S8, with insufficient glass formers, and too high glass modifier concentrations, are unstable glasses, and exhibit lower melting points. The rest of the enamel samples, as indicated in Table 3, have formed stable glass layers on aluminum.

$\text{NaF}$  was added to impart a lower melting temperature and improve film formation. It can also act as an effective nucleating agent above a certain concentration [12]. In the sample 19S19 comprising more than 15 mol. %  $\text{NaF}$ , immiscible glass and crystalline regions appeared (see Figure 6). In this sample most of the glassy phase was located at the aluminum/enamel interface. The presence of crystallites in the enamel, may improve optical properties, especially from the diffuse reflection property point of view [21, 22].

Refractory oxides such as the  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  generally enhance chemical resistance properties, but also increase melting point. Thus, a proper balance of these intermediate glass formers in the presence of appropriate modifiers and the above strong glass formers in the enamel formula are necessary.

$\text{ZnO}$  and  $\text{CuO}$  can be included in formulations instead of refractory oxides, as an alternative way to improve chemical attack resistance while keeping the melting temperature low; however,  $\text{Al}_2\text{O}_3$  also promotes adhesion of the enamel to aluminum [10]. This may be ascribed to the presence of a layer of oxidized aluminum created on the substrate surface during the treatment [14-16].

The attainment of appropriate stable glassy states which possess the highest possible,  $T_g$ , and the lowest  $T_x$  requires a suitable combination of glass formers and

modifiers. While, in enameling aluminum by a sintering method, instead of  $T_x$ , the sintering temperature is rather to be considered, because the sintering must be done at a temperature below that which will spoil the mechanical properties of the annealed aluminum. The results in Table 3b introduce formulations for stable glassy enamels with low thermal properties, i.e. 15S17, 18S18, 19S19, and 20S20; satisfy the above requirements for both sintering and pouring enameling methods. Sintering in these enamels was done at  $500\text{-}550^\circ\text{C}$  (see Figure 5).

In some low stability glass based enamels, the tail of the characteristic crystal nucleation curve could extend to near or even below the ' $T_g$ ' value. If this were the case here, it would limit the enamel service temperature and their applications as a thermal barrier, because crystal nucleation might occur before the enamel reached its dilatometric softening point. Nucleation was not witnessed within the heat-treated sample 15S17, as shown by the Optical micrographs in Figure 7. In addition, the result obtained from XRD test suggests glassy phase for 15S17 (see Figure 8).

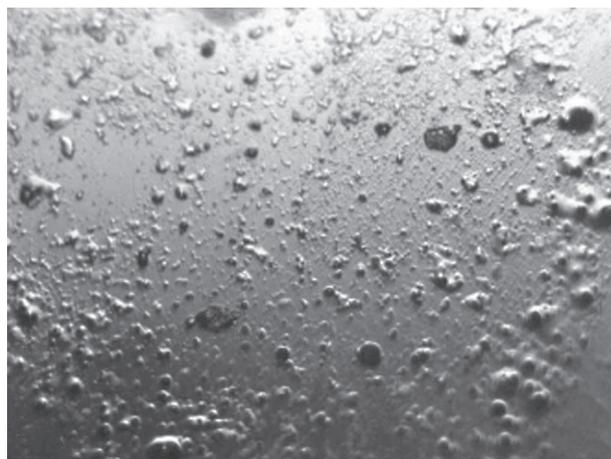


Figure 6. A reflectance microscope view of sample S19, showing immiscible phases of: the glass-ceramic (background) and glassy phase (enclosed).

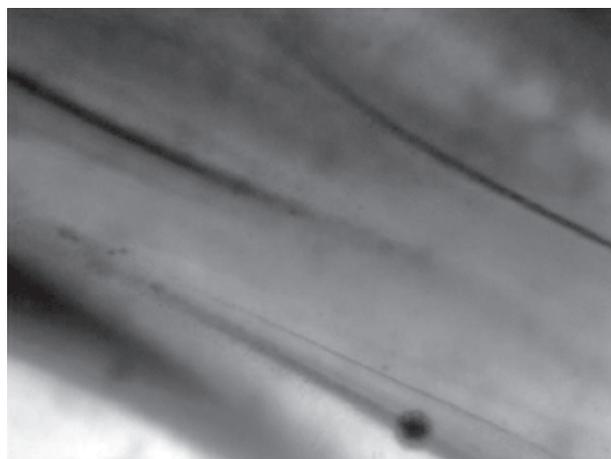


Figure 7. A reflectance microscope view of sample S17 (400 $\times$ ), showing single glassy phase with no inclusion.

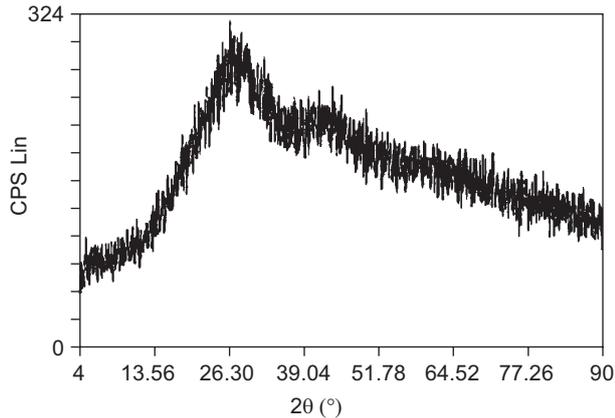


Figure 8. XRD trace of sample S17 indicating a glassy structure.

Generally, applications of enameled aluminum for thermal protection must avoid enamels with excessive firing or melting temperatures, particularly if using direct pouring or dipping techniques. On the other hand, enamels with too low a transition temperature, might not grant enough thermal protection to the aluminum. In this respect, lower values of the glass stability,  $\Delta T = T_x - T_g$ , may be desirable. For self-induced glass-ceramic based enamels,  $\Delta T$  would only matter, if the crystallization in enamels were not completed during initial deposition. Otherwise the enamels could experience some changes in their morphology and appearance, as a result of post crystallization and deformation in some service condition. Additionally, the interfacial adhesion may weaken, if the enamels have a lower surface energy, Surface contact separation may occur as a consequence of the enamel's contraction during treatment processes.

In the  $\text{SiO}_2\text{-B}_2\text{O}_3\text{-PbO}$  phase diagram [23], the melting point,  $T_m$ , rises to from 500 to 750°C as  $\text{B}_2\text{O}_3$  increases, since the corresponding compositions are moving away from the eutectic region. Similarly, addition of  $\text{B}_2\text{O}_3$  causes  $T_m$  to increase. Results in Figure 9 suggest little decreases in  $T_g$  as  $\text{SiO}_2$  increases for the glass forming system and as alkaline oxides in total decrease. This can be ascribed to the effect of the addition of  $\text{K}_2\text{O}$  to the formula. In Table 2 b, the almost constant  $T_x$ s suggest that the nature of the crystalline phase remains the same with increasing  $\text{SiO}_2$  content. Consequently, the glass stability,  $\Delta T$ , will increase (see Figure 10). The observed discrepancies in samples 8S13 and 9S14 compared with 7S12 are believed to be due to their higher PbO content. Besides, 9S14 contains a greater amount of  $\text{Li}_2\text{O}$ , which is replacing  $\text{Na}_2\text{O}$  in 7S12 and 8S13. This might raise the  $T_m$  of 9S14 comparatively. By keeping a proper balance in the constituents  $\text{B}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{PbO}$ , desirable values of the glass stability range i.e.,  $\Delta T$  may be achieved (see Table 3). If sample S10, in Table 1, is considered as the zero  $\text{SiO}_2$  content enamel member of Table 3, the considerable increase in stability with increasing  $\text{SiO}_2/(\text{SiO}_2+2\text{B}_2\text{O}_3)$  molar

ratio, indicates the versatility of these glass systems in design (see Figures 11 and 12), despite a general decrease in their thermal properties,  $T_g$ ,  $T_x$  and  $T_m$ , is observed. Enamels, with high amounts of  $\text{PbO}$  in their glassy structures, showed steep viscosity temperature dependent properties. In these cases, the temperature limit for the occurrence of devitrification is favoured to be narrow, and stable glasses are expected to form [11, 24].

Introduction of alkaline oxides, especially of low atomic weights, e.g.  $\text{Li}_2\text{O}$ , into enamel formulae, lowers the viscosity by weakening the network structure. Moreover, they can counterbalance the changes in thermal and chemical properties induced by refractory oxides such as  $\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2$  [3, 6]. Therefore, the corresponding coating temperature is expected to be lower. However, alkaline oxides reduce the chemical durability of the enamels. [12]. In the melt pouring

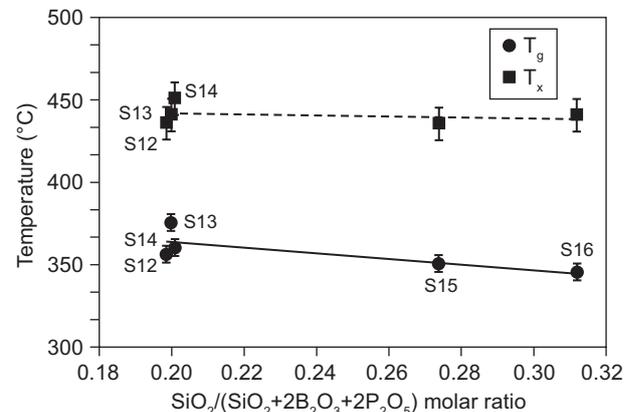


Figure 9. Indicating relatively small decreases in the glass transition ( $T_g$ ) and crystallization ( $T_x$ ) temperatures of translucence enamels by increasing  $\text{SiO}_2$  in the glass former system ( $\text{SiO}_2+2\text{B}_2\text{O}_3+2\text{P}_2\text{O}_5$ ) and decreasing total alkaline oxides ( $\text{R}_2\text{O}$ ) contents (Table 2a).

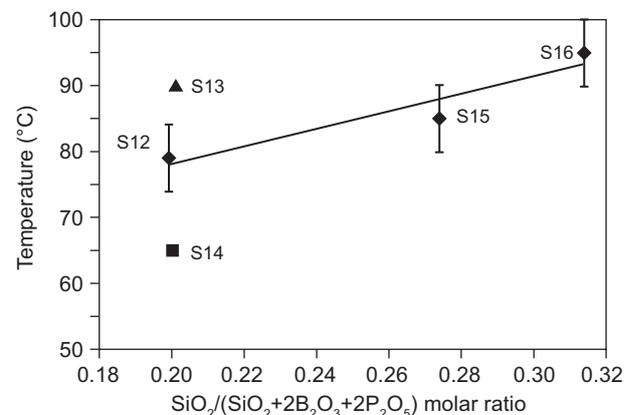


Figure 10. An almost linear increase of stability ( $\Delta T = T_x - T_g$ ), of translucence enamels by increasing  $\text{SiO}_2$  in the glass former system ( $\text{SiO}_2+2\text{B}_2\text{O}_3+2\text{P}_2\text{O}_5$ ) and decreasing total alkaline oxides ( $\text{R}_2\text{O}$ ) contents (Table 2a).

technique, the molten enamel can spread over the surface uniformly without needing high surface wetting effects, if the amount of molten enamel poured onto the aluminum surface, is sufficient to form a stable continuous film. Subsequently, the film thickness will depend on its viscosity, surface tension, and density values. The pouring temperature and the cooling rate as well as the substrate temperature also govern film spreading and uniformity. A relatively low surface tension value for an enamel melt plays an important role in wetting and spreading, and can be assisted by a high surface energy for the treated substrate [25-27]. Shartsis, et al. [28], measured and studied surface tension temperature dependence and its variation with PbO contents in binary systems PbO-B<sub>2</sub>O<sub>3</sub> and PbO-SiO<sub>2</sub>. Figure 13 displays the extent of film (no. 1) and droplet (no.'s. 2-5) formation with different contact angles, which were poured at different melt viscosities and temperatures, the melting crucible having been allowed to cool out of the furnace.

In samples with glassy structures, addition of K<sub>2</sub>O lowers melt surface tension and increases substrate wettability. In comparison with the smaller alkaline

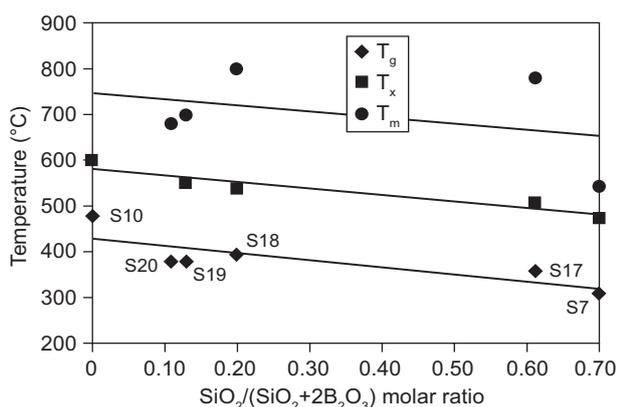


Figure 11. Linear increase of the glass transition ( $T_g$ ) and melting ( $T_m$ ) temperatures of stable transparent aluminum enamels by replacing B<sub>2</sub>O<sub>3</sub> with SiO<sub>2</sub> (Table 3a).

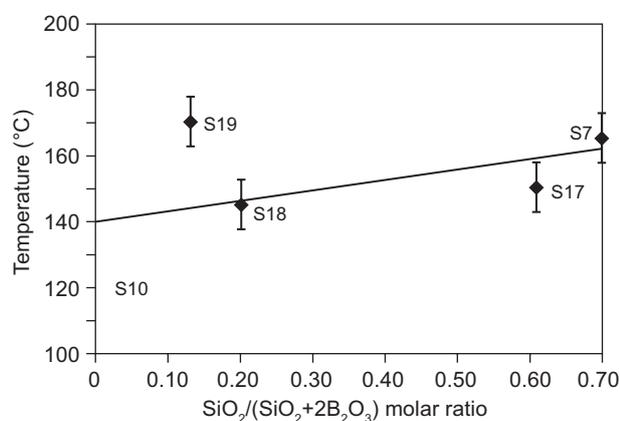


Figure 12. Decrease of stability ( $\Delta T = T_x - T_g$ ) with SiO<sub>2</sub> replacing B<sub>2</sub>O<sub>3</sub> in the transparent (glassy) enamels formula (Table 3a:  $T_m - T_g$  indicates the thermal processing limit).

atoms oxides, i.e. Na<sub>2</sub>O and Li<sub>2</sub>O, melt flowability or film formation may be decreased though [3, 6]. See Tables 1, 2 and 3. The role of PbO in the formulations, when comparing samples 7S12-9S14, in Table 2, is good film formation as a result of better surface wetting and adhesion [29]. These samples have a high gloss and smooth surfaces [21], particularly sample 7S14, which does not have an orange peel appearance. The lower  $T_g$  of sample S14 is believed to be attributed to the presence of heavy Pb atom in the network, which enhances disordering in the glassy structure of the enamel. Besides, PbO can decrease the enamel melt surface tension appreciably by which the interfacial contact area is extended, and so adhesion may improve [14, 30].

The strong opacification of uniformed glossy samples 7S12-11S16 and partly 19S19 and S19 m<sup>3</sup> can be due to the presence of 16 mol. % of NaF in their formulas, which can nucleate and crystallize (see Tables 2 and 3 and Figure 1). It can be observed that in the absence of NaF or at lower concentrations (<9 mol. %), the enamels vitrify and appear single phase. P<sub>2</sub>O<sub>5</sub> can also induce crystal nucleus formation and facilitate crystallization with smaller crystals in the glassy phase background, which could impart scattering [12]. Samples: 3S1-13S5, 15S17, 18S18, and 20S20 in Tables 1 and 3, in comparison with samples 14S7-11S16, look transparent with the characteristic deep blue colouration of CoO. Microscopic views of samples 1S2 and others in Figures 14 show the existence of some inhomogeneous transparent crystal phases, especially pronounced in thicker parts of the enamels, where slower cooling rates would exist. Thus, the corresponding light scattering might induce darker blue shades, if the included phases had higher light absorption. Three blue coloured Co and two brown coloured Mn containing samples are shown in Figure 1. The pale blue color in uniform opaque 11S16 enamel is ascribed to heterogeneous dendrite glass-ceramic crystals forming on the surface [12, 22] (see Figure 15).

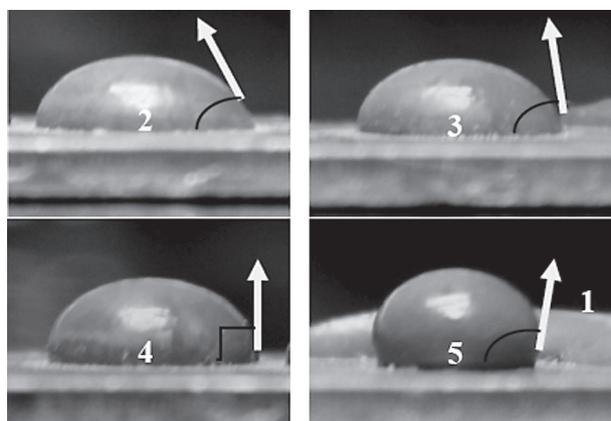


Figure 13. Wetting decreased as enamel poured on the hot aluminum substrate successively (1 to 5) as the melting crucible was allowed to cool.

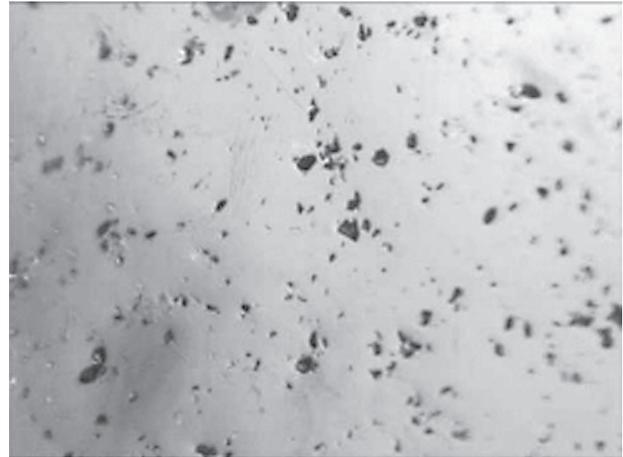
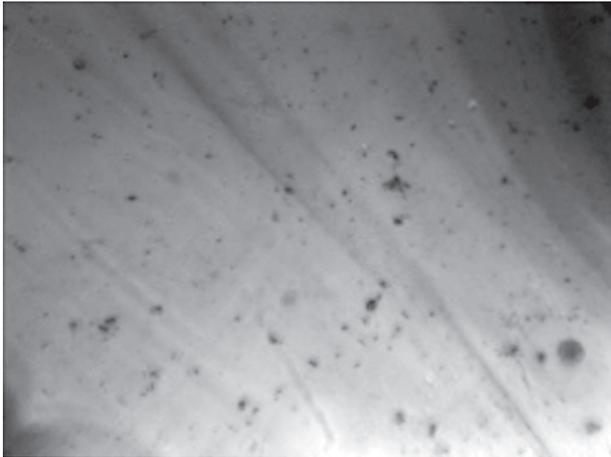


Figure 14. A reflectance microscope view of sample S2 (400 $\times$ ) showing transparent crystal phase inclusions).

Crystals of different morphology

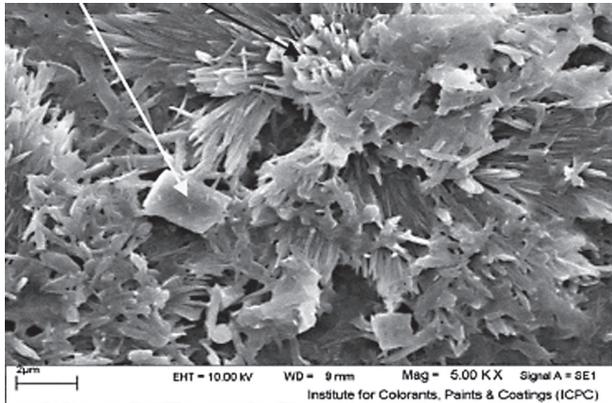


Figure 15. Exhibits dendrite crystals of S16 enamel on the aluminum (5KX).

### Adhesion

Regarding aluminum substrates, the presence of  $\text{Al}_2\text{O}_3$  assists diffusion at the enamel/substrate interfaces. Aluminum surfaces, for better adhesion, may be oxidized which deposits a strongly held, thin layer (0.012 $\mu\text{m}$ ) of  $\text{Al}_2\text{O}_3$  [13, 31]. Either different chemical agents applied before enameling or oxidizing molten enamels in the direct melt pouring method can oxidize the surface. In this respect introduction of  $\text{P}_2\text{O}_5$  as a glass former with high oxygen content could improve the glass adherence to the metals [10]. Figure 16 exhibits this oxidised layer caused by the enamel, which has been reduced at the interface.

Other phenomena, which are believed to have contributed to the general promotion of the interfacial adhesion, are the relatively high surface energy of the substrate created in the surface treatment, and the low surface tension of the enamels in the molten state, which allows the enamel to wet and spread on the surface more easily. Overall, a larger contact surface provides better adsorption, diffusion, or chemical surface reaction.

Stronger adherence will also be expected to exist at the enamel/substrate interface, if the differences in the enamels and substrates thermal expansion coefficients are not large enough to cause tension failure at the interface on cooling [32].

Diffusion was observed, because in poor enamel/substrate adhesion, fresh smooth interfaces were witnessed. Figure 16 depicts an SEM view of a surface, which had adhered strongly to the contact surface of the enamel layer to aluminum interface. In the more strongly adhering coatings, separation occurred at the interface between the enamel and its reduced part, when the samples were subjected to bending or impact. Some of the enamel fragments still remained firmly on the aluminum surface (see Figure 17). Shear cohesive failure was experienced in the thicker parts of the enamels of some samples, due to either the enamel weakness or improper annealing. Comparatively, adhesion properties observed in the opaque enamels were weaker than in the transparent ones (see Table 2). Figure 18 represents relatively a good interface contact in sample 15S17 and a poorer contact for sample 18S18. The higher adhesion in the clear glassy structure samples, 15S17, 18S18, and 20S20 than the translucent glass ceramic enamels,

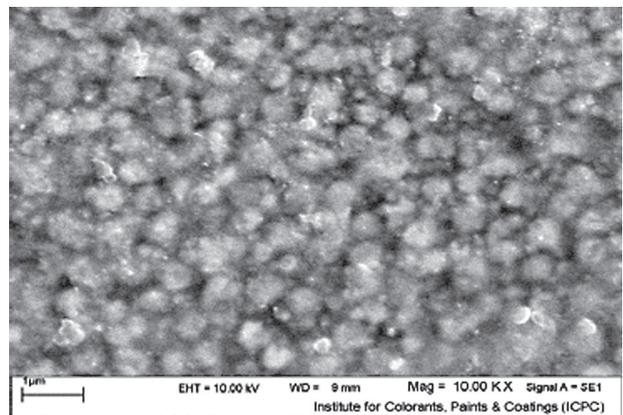


Figure 16. Surface of the smooth oxidized layer formed at the interface of sample S16 with aluminum (10KX).

8S13-11S16 could be explained by the absence of devitrified phases in them, because crystals in relation to amorphous phases possess lower surface energy [26-28]. A cohesive failure in the samples 8S13 was observed when subjected to shear impacted forces applied by sliding a slab of metal along the contact faces of the enamel droplets on the aluminum plate. (see Figure 19).

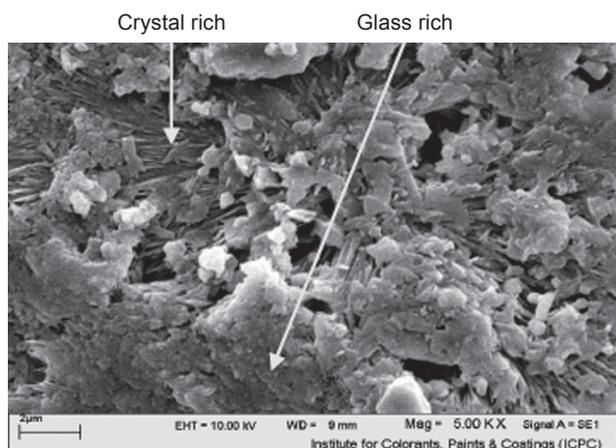
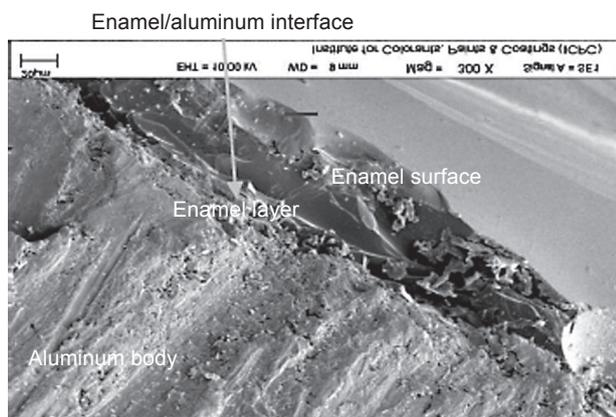
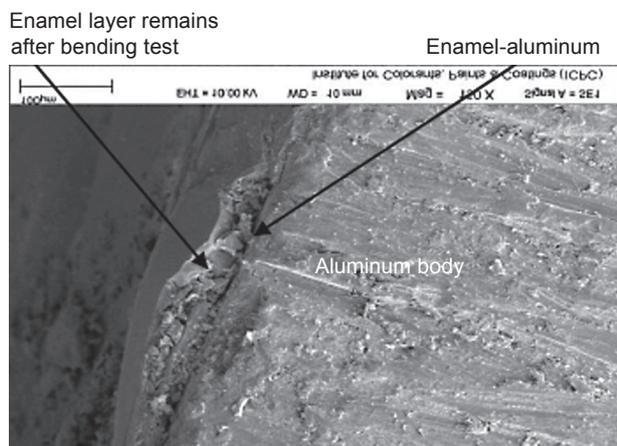


Figure 17. Exhibits remains of enamel on the aluminum surface after bending test and adhesive failure (5KX).



a) sample S17 depicting good interfacial contact (300×)



b) sample S18 depicting poor interfacial contact (150×)

Figure 18. SEM cross-sectional views of melt poured enamels.

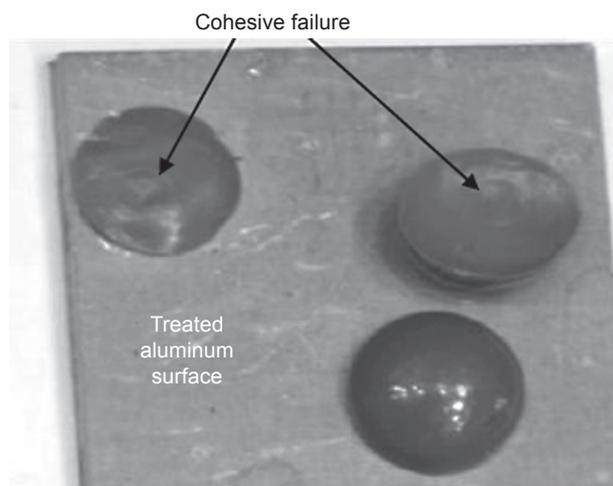


Figure 19. Exhibits a cohesive failure of a drop of sample S13 after exerting impact shear force.

Lastly, the XRF results for sample 20S20 were quoted in wt. % of constituted oxides and were almost in correlation with the tailored formulation, except for the heavy metal oxide PbO and the light glass former oxide B<sub>2</sub>O<sub>3</sub>.

## CONCLUSIONS

Transparent and opaque enamels on aluminum with a relatively high gloss have been obtained. The pouring and spreading enameling method allowed relatively higher thermal property enamels to be made on aluminum surface without affecting the aluminum properties. The presence of P<sub>2</sub>O<sub>5</sub> assisted self-induced glass ceramic enamels based on NaF system, which required a minimum amount in the formulations. Transparent enamels had better interfacial adhesion than opaque enamels but at the expense of the enamel strength. Low melting enamels possessing satisfactory adhesion but without or with a minimum amount of PbO in the formulations, were made.

## Acknowledgement

*I am sincerely grateful to Professor John M. Parker for his great helps and contributions concerning scientific issues and correcting English.*

## References:

1. *Global Update Report to the USW: Aluminum Industry Dynamics*, Potok & Co., Inc. New York 2005.
2. Andrews, A.L.: *Porcelain Enamels*, p.1-10, 133-135, 250-303, The Garrard Press, Publishers, 1961.
3. Eppler R., Eppler, D.R.: *Glazes and Glass Coatings*, p. 15-57, The Am.Ceram. Soc., 2000.

4. Masoudi Broujeni, F.: *Leab e Felez (Enamel)*, p. 201-205, Nasle Javan Pub., Tehran 1995. (in Persian)
5. Masoud E.: *Leab e Felez va karbord e an dar sanat (Enamel and its application in industry)*, p. 79-88, Navid Pub., Tehran 1996. (in Persian)
6. Norton F.H.: *Element of Ceramics*, p. 211-223, Addison-Wesley Pub. Co. Massachusetts, 1974.
7. Rawson H.: *Oxide Glasses*, J. Zarzycki, *Glasses and Amorphous Materials*, Ed. Cahn R.W., Haasen P., Kramer E.J., p. 279-330 Mats. Sci. & Tech., VCH Pub. Inc., NY 1991.
8. Babcock C.L.: *Silicate Glass Technology Methods*, p. 166-179, 254-263, Wiley & Sons Inc., New York 1977.
9. NACE Technical Practices Committee: *Glass Linings and Porcelain Enamel Coatings*, p. 137-146, 1986.
10. Yatsenko E.A., Zubekhin A.P., Shkurakova E.A.: *Glass and Ceramics, Coatings Enamels* 58, 27 (2001).
11. Rawson H.: *Properties and Applications of Glass*, p. 1-67, Elsevier, Amsterdam 1984.
12. Holland W., Beall G.: *Glass-Ceram. Tech.*, p. 75-191, The Am. Ceram. Soc., Westerville 2002.
13. Vargel C.: *Corrosion of Aluminum*, p. 9-19, 61-73, Elsevier, Amsterdam 2004.
14. Sheasby P.G., Pinner R.: *The Surface Treatment and Finishing of Aluminum and Its Alloys*, vol.1 p. 1-27, 155-229 and vol.2, p. 1267-1295, Finishing Pub. Ltd, Ohio, 2001.
15. Harrington, J.: *Industrial Cleaning Technology*, p. 270-285, Kluwer Academic Pub., Dordrecht 2001.
16. *Surface Preparation Specifications and Practices*, SSPC, the Society for Protective Coatings, p. 347-350, SSPC 05-03, 2005.
17. Institute of Standard and Industrial Research of Iran (ISIRI) 5908 The Iranian National Standard, 2001.
18. ASTM D 2794-93, 1999.
19. Horn W.F, Hummel F.A: *J. Soc. Glass Technol.* 39, 121 (1955).
20. Englert W.J., Hummel F.A: *J. Soc. Glass Technol.* 39, 128 (1955).
21. Fanderlik I.: *Optical properties of glass*, p. 50-225, Elsevier Science Pub. Co. Inc., New York 1983.
22. James P.F., Jones R.W.: *Glass ceramics*, p. 102-133, Blackie, Glasgow 1992.
23. Geller R.F., Bunting E. N.: *J. Research Natl. Bur. Standards*, (1939).
24. Marghoshian V.: *Glass (Structure, Properties and Applications)*, p. 216-238, University of Science and Industry Pub., Tehran 2003. (in Persian)
25. Satas D.: *Coating Technology Handbook 3*, p. 3-1 to 3-4, CRC Press, New Jersey 2007.
26. Bierwagen G.P.: *Surface Energetics*, p. 369-382, Koleske J.V., Gardner-Sward Handbook, ASTM Manual Series: MNL 17, 1995.
27. de Gennes, P.G.: *Rev. Mod. Phys.* 57, 827 (1985).
28. Shartsis, L., Spinner, S., Smock, A. W.: *J.Am.Ceram.Soc.* 31, 23 (1948).
29. Kumar G., Prabhu K.N.: *Advances in Colloid and Interface Science* 133, 69 (2007).
30. Xiaohong W., Wei Q., Bo C., Zhaohua J., Weiqiang L., Weidong H.: *J. materials processing technology* 200, 1 (2008).
31. Takabeya R.: *Corrosion Engineering* 36, 279 (1987).
32. Eppler R.A., Obstler, M.: *Understanding Glazes*, p. 214-231, The Am. Ceram. Soc. Ohio, 2005