**Effect of paint composition on the properties of black automotive glass enamel**

[***Selime ÖZTÜRK1,***](mailto:selimevarli@gmail.com)***[[1]](#footnote-1)\*[C:\Users\Abdullah\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ORCID-iD_icon-16x16.gif](https://orcid.org/0009-0005-5076-7722), İlknur KÜÇÜK2[C:\Users\Abdullah\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ORCID-iD_icon-16x16.gif](https://orcid.org/0000-0001-9203-0693), Buğra ÇİÇEK3[C:\Users\Abdullah\AppData\Local\Microsoft\Windows\INetCache\Content.Word\ORCID-iD_icon-16x16.gif](https://orcid.org/0000-0003-2477-4169)***

*1 Chemical Engineering Department, Yıldız Technical University, İstanbul, Turkey*

*2 Chemical Engineering Department, Yıldız Technical University, İstanbul, Turkey*

*3Metallurgical and Materials Engineering, Yıldız Technical University, İstanbul, Turkey*

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| **Abstract**  The main processes used in the production of automobile glasses are lamination, tempering, sag bending, and press bending. Laminated glasses can be produced by sag bending or press bending. Windshield glasses produced by sag bending process should ensure low tempering temperature, high chemical and physical properties and low UV transmittance means high optical density. Automotive glass enamels that ensure those specifications include 3 main components; high opacity low melting bismuth base frit, CuCr2O4 black spinel pigment, and an organic medium. The composition of the enamel as well as process factors such as frit production method, frit grinding types, frit particle size distribution, pigment particle size, media contents and final process steps also affect the final glass enamel paint properties. Present study, the effect of the composition of glass enamel paint on physical properties such as color, gloss, optical density, and chemical resistance was investigated. The structure, surface and physical properties of the automotive glass enamel applied on the substrate by silk screen printing method was characterized by using various techniques such as XRF, XRD, SEM, PSD, BET, color colorimetry |
| Keywords: Automotive, sag bending, lamination, black enamel, glass-ceramics |

1. **Introduction**

By increasing demand of automobiles during the years, windshield glasses and derivatives needs will increase. Windscreens are [laminated glass](https://www.sciencedirect.com/topics/engineering/laminated-glass) panes consisting of two individual panes and a polymer interlayer [1].

Automotive glasses utilize glass-ceramics, specifically glass-based paints, for various purposes. Glass enamels [2] consist of a high proportion of frit [3] which, in addition to bismuth oxides, includes silica (SiO2), boroxide (B2O3), sodium carbonate (Na2CO3), titanium dioxide (TiO2), and zirconium oxide (ZrO2). Total melting temperature, thermal expansion coefficient, chemical durability and stability depends on this composition.

Many studies on the production of windshield automotive glass paint can be found in the literature; nevertheless, research on how frit, pigment, medium, additive compositions affect the colour, gloss and opacity behaviour of glass enamel is limited.

In the present study, it was aimed to investigate effect of paint composition on the properties of black automotive windshield glass enamel which can be laminated PVB (polyvinyl butyral) and shaped with sag-bending process [4].

Glass enamel coatings ensure protection of glue from degradation of sunlight means high level of optical density [5], high chemical and mechanical strentgth, color stability depending on time under UV light, helps many design funcitons, environmentally friendly. For this purpose, glass paints having different complex inorganic colour pigments (CICP) , frit , organic medium [6] and additive contents were prepared and applied by silk screen printing [7] on a glass substrate that gives high color, gloss and opacity requirements of design function with high UV protection. They were characterized by using spectral and physicochemical characterization techniques such as XRF, XRD, SEM, PSD, viscosity measurement, color colorimetry, glossmeter and optical densometer.

1. **Materials and Methods**

Automotive Glass enamel paints contains 4 main contents; a bismuth base frit (Akcoat, Turkey), PBK-28 group CuCr2O4 inorganic black spinel pigment with 3 different brand (Shepherd, Belgium, solvent and water based organic mediums (Akcoat, Turkey) and additives surface modifiers (Evonik, Germany). Glass frits were produced in rotary kiln with 3 different bismuth oxide raw materials (Todini, Italy), (ZhuZhou Keneng, China), (Vital, Belgium). The standard procedure can be outlined as follows. Glass frit was melted to 1200 C◦ in rotary kiln as bismuth has high density and settle downs in continuous kiln and quenched in a cold water (25-35C◦) to ensure amorphous structure. Frit is dried and ball milled up to particle size D90 value 75 µm. Fine milling was done in bed type high air speed pressured pilot type jetmill. Final particle sizes were adjusted to D90 value 6-8 µm. Schematic presentation of bismuth glass frit powder production approach is shown in Figure 1.

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Figure 1. The framework of the bismuth glass frit powder production method

Frit glass powder should have a melting zone of 640-660 ◦C defined by hot stage measurement. Pigment is added on the medium in a high speed mixer and glass powder, additives were added at last stages of recipe process to make an efficient dispersion of all dense materials. All the samples were 3 roll-milled before silk screen printing (Figure 2)

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Figure 2. The framework of the glass enamel preparation and firing method

1. **Results and Discussion** 
   1. **Effect of bismuth oxide content, frit properties and pigment type on glass enamel**

XRF results and thermal expansion coefficient analysis of frits prepared by using different bismuth raw materials in the same ratio (60% bismuth oxide) are shown in Table 2. Hot stage microscopy provides insight into the melting behavior of the frit formulation. However, the analysis of the thermal expansion coefficient, as seen in Table 2, elucidates the mismatch between the glass substrate and glass enamel. The acceptance limits between 30-300°C are 74-80 x10-6, which is lower than that of sodium silicate glass itself, measuring at 83 x10-6.

**Table 2.** XRF results and thermal expansion coefficient of Frit A, Frit B and Frit C

|  |  |  |  |
| --- | --- | --- | --- |
| **Oxides** | **Frit A** | **Frit B** | **Frit C** |
| B2O3 | 42.8 | 38.5 | 46.4 |
| Bi2O3 | 36.52 | 38.95 | 33.19 |
| SiO2 | 16.53 | 17.88 | 16.29 |
| ZrO2 | 1.44 | 1.55 | 1.31 |
| Al2O3 | 1.36 | 1.58 | 1.64 |
| Cr2O3 | 0.49 | 0.53 | 0.459 |
| K2O | 0.399 | 0.427 | 0.358 |
| Na2O | 0.15 | 0.291 | 0.12 |
| CaO | 0.126 | 0.188 | 0.121 |
| TiO2 | 0.107 | 0.068 | 0.039 |
| MgO | 0.066 | 0.08 | 0.071 |
| Thermal Expansion Coeffienct(1/K)  (**30-300 C◦)** | 76x10-6 | 77x10-6 | 74x10-6 |

Following the jet mill processing of the frit, particle size distribution analysis was conducted using Mastersizer Malvern 3000 (Table 3). Also, after the jet mill process, scanning electron microscopy images were captured using Zeiss EVO® LS 10. SEM images showed that articles were detected like triangle crystals beside sphere and different size from 4-8 µm even it was cylonized and filtered during jetmill processing.

**Table 3.** Particle size distribution analysis results of Frit A, Frit B, Frit C

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **D (10) µm** | **D (50) µm** | **D (90) µm** |  |
| **Frit A (D13)** | 0.03 | 0.02 | 8.5 |  |
| **Frit B (D14)** | 0.73 | 3.16 | 6.35 |
| **Frit C (D15)** | 1.33 | 4.19 | 7.9 |
|  |  |  |  |

XRF, XRD (Figure 3) and BET analysis results (Table 4) clearly show that pigment types affect the colour, gloss, and optical properties of glass enamel when fired below 660 ◦C.

**Table 4.** XRF, PSD comparisons of Pigment A, Pigment B and Pigment C samples

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Oxides** | **Pigment A** | **Pigment B** | | **Pigment C** |
| Cr2O3 | 65 | | 69.3 | 70 |
| CuO | 35 | | 30.5 | 29.6 |
| Fe2O3 | 0.2 | | 0.05 | 0.12 |
| Al2O3 | 0.1 | | - | 0.08 |
| D (10) µm | 0.158 | | 0.053 | 0.02 |
| D (50) µm | 1.88 | | 1.57 | 0.06 |
| D (90) µm | 4.32 | | 4.46 | 0.29 |
| area(m2/g) | 2.13 | | 2.24 | 2.62 |

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Figure 3. XRD result comparison of pigment A, pigment B, pigment C

**3.2.Colour, opacity, and optical density results**

Colour L,a,b values were measured according to ASTM E-1164 standart with colour colorimetry instrument (Konica Minolta CM-700 D), gloss values were measured with glossmeter (TQC-Sheen GL0030-20◦/60◦/85◦) and 60◦ values were recorded, optical density results were obtained by optic densometer (X-rite 361 T) and ΔE values of test samples were calculated by an equation is given below.

Optical density is required deviation from standart D: ± 0.2D and gloss values G: ± 5 from the reference values are in the range of accaptance. Comparison of trial results can be seen in Table 5*.*

**Table 5.** Physical color, gloss and optical density measurements, ΔE comparisons

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Trial** | **Trial**  **Description** | **L** | **a** | **b** | **Gloss** | **Optical**  **density** | **ΔL** | **Δa** | **Δb** | **ΔE** |
| **STD** | Reference | 21.75 | -0.02 | -1.86 | 32 | 0.74 | ND | ND | ND | ND |
| **D1** | Pigment A | 21.50 | -0.12 | -1.86 | 37 | 0.73 | -0.25 | -0.10 | 0 | 0.27 |
| **D2** | Pigment B | 21.62 | -0.20 | -2.04 | 39 | 0.70 | -0.13 | -0.18 | -0.18 | 0.29 |
| **D3** | Pigment C | 23.81 | 0.01 | -1.58 | 31 | 0.66 | 2.06 | 0.03 | 0.28 | 2.08 |
| **D4** | Medium A | 19.42 | -0.17 | -1.78 | 44 | 0.71 | -2.33 | -0.15 | 0.08 | 2.34 |
| **D5** | Medium B | 21.23 | -0.10 | -1.79 | 33 | 0.71 | -0.52 | -0.08 | 0.07 | 0.53 |
| **D6** | Medium C | 21.13 | -0.20 | -1.92 | 38 | 0.65 | -0.62 | -0.18 | -0.06 | 0.65 |
| **D7** | Medium D | 16.88 | -0.13 | -1.99 | 50 | 0.71 | -4.87 | -0.11 | -0.13 | 4.87 |
| **D8** | Additive A | 22.76 | -0.09 | -1.89 | 30 | 0.58 | 1.01 | -0.07 | -0.03 | 1.01 |
| **D9** | Additive B | 22.31 | -0.09 | -1.71 | 26 | 0.60 | 0.56 | -0.07 | 0.15 | 0.58 |
| **D10** | Additive C | 21.43 | -0.10 | -1.83 | 35 | 0.56 | -0.32 | -0.08 | 0.03 | 0.33 |
| **D11** | Additive D | 22.72 | -0.07 | -1.88 | 32 | 0.63 | 0.97 | -0.05 | -0.02 | 0.97 |
| **D12** | Additive E | 21.25 | -0.13 | -1.86 | 32 | 0.64 | -0.50 | -0.11 | 0.00 | 0.51 |
| **D13** | Frit A | 21.40 | -0.06 | -1.66 | 49 | 0.60 | -0.35 | -0.04 | 0.2 | 0.41 |
| **D14** | Frit B | 19.15 | -0.05 | -1.58 | 53 | 0.56 | -2.60 | -0.03 | 0.28 | 2.62 |
| **D15** | Frit C | 19.77 | -0.01 | -1.61 | 48 | 0.58 | -1.98 | 0.01 | 0.25 | 2.00 |

When the bismuth rate increases from 36% to 38%, the brightness value increases from 32 to 53, indicating better melting. However, colour values with a ΔE value of 2.62 indicate over firing, which causes a greyish surface colour.

Chemical durability tests of samples were done according to ASTM C724-91. A drop of acid was applied to the enamel area of the fired glass and the stained area was covered with watch glass. The sample was washed with distilled water after 15 minutes and detection ranges were determined between 1-6. In this range, 1 indicates high acid resistance quality without leaving stains, while 6 indicates complete removal of glass enamel from the surface. Results can be seen in Table 6. Chemical stability test results show that the types of frit and pigments do not make a significant change on their chemical resistance.

**Table 6.** Chemical stability of samples

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| STD | 1 | D4 | 1 | D8 | 1 | D12 | 1 |
| D1 | 1 | D5 | 1 | D9 | 1 | D13 | 1 |
| D2 | 1 | D6 | 1 | D10 | 1 | D14 | 2 |
| D3 | 2 | D7 | 1 | D11 | 1 | D15 | 1 |

1. **Conclusion**

The glass ceramic coating composition consists of glass frit, a complex inorganic pigment and organic medium. The current study shows that the composition of glass enamel paint has an impact on physical properties such as color, gloss, optical density. While increasing the bismuth ratio improves melting and surface brightness, ΔE values show that it also cause undesirable greyish colour tones due to excessive firing. Pigment A and B can be chosen as an alternative depending on colour properties, BET and PSD analysis. Chemical durability can be affected by frit and pigment but medium and additives doesn’t affect. As a result, we believe that the suggested methods show a good result in the production of black automotive glass enamel process depending on the material choice upon recipe contents.

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1. \* Corresponding author. *e-mail address: selimevarli@gmail.com.* [↑](#footnote-ref-1)