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# The effect of pigment on the properties of black automotive enamel

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Lamination process of automotive glasses can be created through either sag bending or press bending. Especially front windshield glasses that are manufactured by sag bending process, must maintain low melting degrees, possess strong chemical and physical properties, and exhibit low UV transmittance, indicating high optical density. Automotive glass enamels meeting these criteria are composed of low-melting bismuth ingredient-based frit, $CuCr_2O_4$ black inorganic pigment, and an organic vehicle. All those components affect the final properties of cured glass paint characteristics. This study examines how different brands of black $CuCr_2O_4$ pigments, used in glass enamel paint, impact physical properties such as color, gloss, optical density and chemical properties.

**Keywords:** Laminated glass, enamel, paint glass-ceramics, pigment

## INTRODUCTION

Owing to increasing mobility and individual vehicle usage rates in recent years, vehicle sales have shown significant increases on both global and domestic markets. Consequently, there has been an acceleration in the demand for glass and processed glass used in vehicles. Especially in the automotive sector, laminated and tempered glasses are processed through sag bending or press bending processes and used on different surfaces of the vehicle [1, 2].

Front glasses, referred to as the 4th surface, use black enamel paints with high opacity, high chemical and mechanical resistance. The tempering temperatures, durations, and final customer test methods for these paints vary depending on the usage location and production processes. Black automotive glass paints consist of three main components [3-5]: a frit containing bismuth, $CuCr_2O_4$ black pigment, and an organic medium (vehicle) (Figure 1).

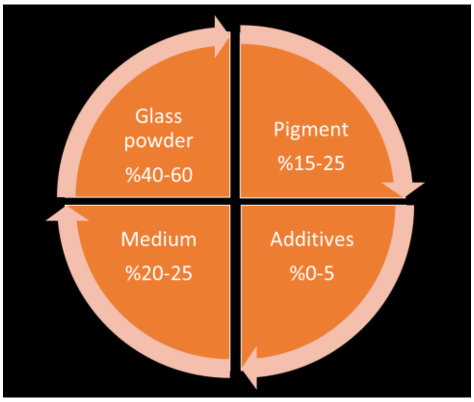


**Figure 1.** Automotive black glass enamel paint composition

The types of these components significantly affect the final paint properties. All these factors affect the color, gloss, optical density, chemical resistance, surface abrasion, and rheological properties that need to be controlled from both surfaces of the glass [6].

In this study, the effects of pigment on the paint properties of glass enamel applied on 10 cm×10 cm×4 mm glass substrate by using the screen-printing method were examined. The most suitable pigment option for the recipe and process were determined by characterizing it through XRF, XRD, PSD, BET, color measurement (L, a, b), gloss measurement, optical transmittance measurement, and chemical analysis tests. It was observed that when the pigment type, crystal structures in the pigment and particle size distribution changed, the color properties get greyish and acid resistance was negatively affected.

## EXPERIMENTAL AND MATERIALS

Automotive glass enamel paints contain 4 main constituents: a bismuth-based frit (Akcoat, Turkey), PBK-28 group $CuCr_2O_4$ inorganic black spinel pigment of 3 different brands (Shepherd, Belgium, solvent- and water-based organic media (Akcoat, Turkey), additives and surface modifiers (Evonik, Germany).

Glass frit was produced in a rotary kiln. The standard procedure can be outlined as follows. Glass frit was melted to 1200 ◦C in a rotary kiln as bismuth has high density and settles downs in a continuous kiln. It is quenched in cold water (25-35 ◦C) to ensure amorphous structure. The frit is dried and ball-milled up to particle size of D90 value 75 µm. Fine milling was done in bed type high air speed

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pressured pilot type jet mill. Final particle sizes were adjusted to a D90 value of 6-8 µm. Schematic presentation of bismuth glass frit powder production approach is seen in Figure 2. Frit glass powder should have a melting zone of 640-660 ◦C defined by hot-stage measurement. Pigment was added to the medium in a high-speed mixer; glass powder, additives were added in the last stages of the recipe process to make an efficient dispersion of all dense materials. All samples were roll-milled three times before silk screen printing (Figure 3).

## RESULTS AND DISCUSSION

XRF, PSD (Malvern Mastersizer 3000) and BET surface area (Quantachrome TouchWin) results of three different brand pigments are shown in Table 1. XRF provides insight into the chemical components of pigment recipe. The analysis by PSD and BET, as seen in Table 1, reveals differences in particle size distribution and surface total area. The acceptance limits of $Cr_2O_3$ should be as high as possible for less contamination. The higher the D90, the bigger are the pigment particles. BET analysis confirms that the particles are smaller, with larger surface which can easily and effectively be covered and coated by the medium.

XRD (Bruker D8 Advance Eco) tests were made to characterize the crystal phases of similar pigments.

**Table 1.** XRF, PSD comparisons of pigment samples

| Oxides | Pigment A | Pigment B | Pigment C |
|---|---|---|---|
| $Cr_2O_3$ | 65 | 69.3 | 70 |
| CuO | 35 | 30.5 | 29.6 |
| $Fe_2O_3$ | 0.2 | 0.05 | 0.12 |
| $Al_2O_3$ | 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 |
| Surface area ($m^2$/g) | 2.13 | 2.24 | 2.62 |

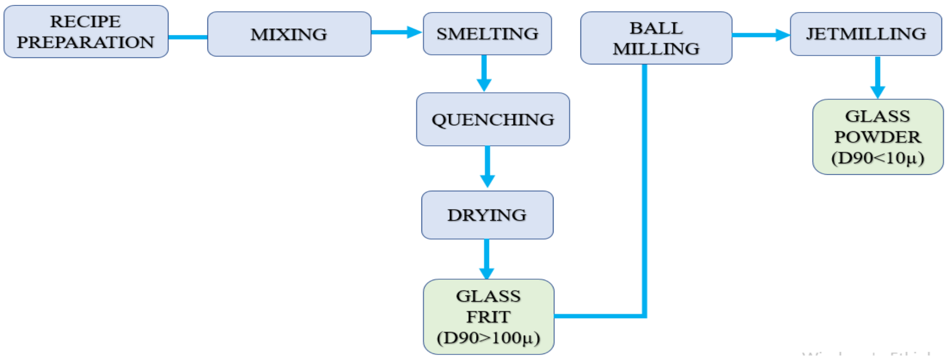


**Figure 2.** Flow diagram of the bismuth glass frit powder production

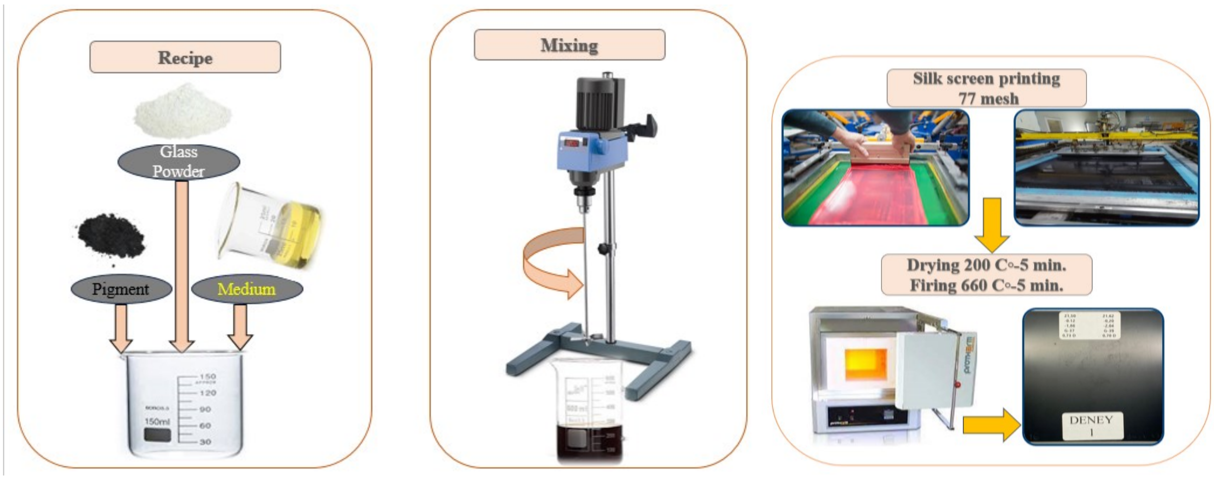


**Figure 3.** Schematic presentation of the glass enamel preparation and firing method

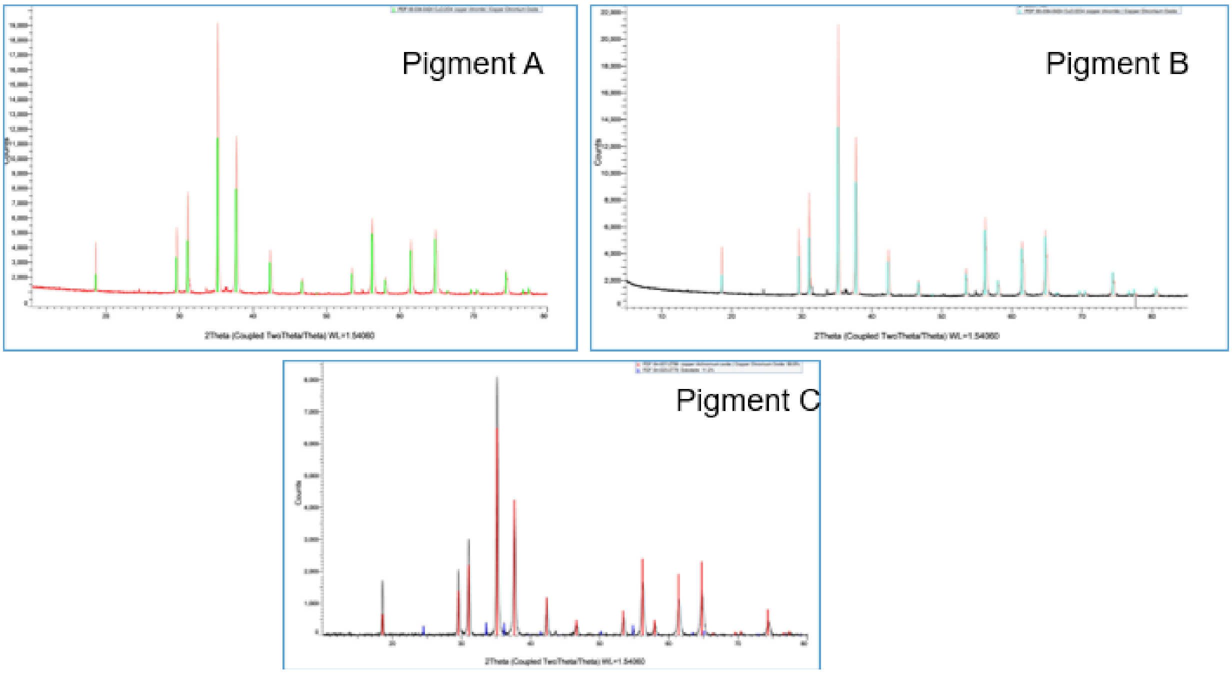


**Figure 4.** XRD analysis of pigments A, B, C

**Table 2.** Physical color, gloss and optical density measurements, ΔE values

| Experiment | L | a | b | Gloss | O.D | ΔL | Δa | Δb | ΔE |
|---|---|---|---|---|---|---|---|---|---|
| Reference | 21.75 | -0.02 | -1.86 | 32 | 0.74 | * | * | * | * |
| Pigment A | 21.50 | -0.12 | -1.86 | 37 | 0.73 | -0.25 | -0.10 | 0 | 0.27 |
| Pigment B | 21.62 | -0.20 | -2.04 | 39 | 0.70 | -0.13 | -0.18 | -0.18 | 0.29 |
| Pigment C | 23.81 | 0.01 | -1.58 | 31 | 0.66 | 2.06 | 0.03 | 0.28 | 2.08 |

As seen in Fig. 4, pigments A and B consist of 100% $Cu_2CrO_4$ while pigment C also contains 11.2 % eskolaite phase.

Color L, a , b values were measured according to ASTM E-1164 standard with colorimetric 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 densitometer (X-rite 361 T) and ΔE values of the test samples were calculated by the equation given below.

$$\Delta E *= \sqrt{(L2 - L *)2} + \sqrt{(a2 - a *)2} + \sqrt{(b2 - b *)2} \qquad (1)$$

Optical density deviation from standard D: ± 0.2D and gloss values G: ± 5 from the reference values are in the range of acceptance. Experimental results can be seen in Table 2.

When the pigment ratio is constant depending on the pigment XRF results itself, the brightness value increases from 21.5 to 23.81, indicating higher L values. However, color with a ΔE value of 2.08 indicates less firing, which causes a greyish surface color. Also pigment C causes lower gloss which means higher matness of the surface and supports that there is less firing on the glass enamel paint. Pigment B gives a higher gloss value of 39 compared to the reference glass paint. ΔE lower than 0.5 can be acceptable. Pigment C lowers the optical density the most which is unwanted condition for the UV protective automotive front glass enamels.

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 min and detection range was 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. Chemical stability of samples is given in Table 3.

**Table 3.** Chemical stability of samples

| | STD | D1 | D2 | D3 |
|---|---|---|---|---|
| Chemical stability | 1 | 1 | 1 | 2 |

Chemical stability results show that the different types of pigments display different chemical resistance. Pigment C has the lowest result with 2. When melting level is lower, chemicals attack the open pores on the glass enamel and react with pigment particles causing them to deform and change the color to the greyish side.

## CONCLUSION

The glass ceramic coating composition consists of glass frit, a complex inorganic pigment and organic medium. The current study was designed by keeping frit type, medium and additive type and % ratio, pigment % ratio as constants and changing only the pigment type.

The study shows that the composition, particle size distribution and crystal structure of the pigment and its derivatives have an impact on the physical properties such as color, gloss, and optical density.

Pigments A and B can be chosen as an alternative depending on color properties, gloss and optical density with the help of BET and PSD analysis. Chemical durability can be affected by pigment type. As a result, we believe that the suggested methods show a good result in the production of black automotive glass enamel depending on the material choice upon recipe contents. All components' ratios and types should be studied thoroughly by controlling all critical methods and factors.

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