

T.R.
GEBZE TECHNICAL UNIVERSITY
GRADUATE SCHOOL OF NANOTECHNOLOGY

**STUDYING THE EFFECT OF GRAPHENE ON THE
MECHANICAL PROPERTIES OF AUTOMOTIVE GLASS
ENAMEL**

SEÇİL AYDIN ASLAN
**A THESIS SUBMITTED FOR THE DEGREE OF MASTER OF
SCIENCE DEPARTMENT OF NANOSCIENCE AND
NANOENGINEERING**

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GEBZE

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T.C.
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NANOTEKNOLOJİ ENSTİTÜSÜ

GRAFENİN OTOMOTİV CAM
EMAYELERİNİN MEKANİK
ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİNİN
İNCELENMESİ

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SUMMARY

The sales revenue of the car industry reached a peak level of about 3 trillion US\$ in 2019 with almost 75 million cars produced worldwide. Even though a decline was observed as the result of the Covid-19 epidemic it still reached a turnover of 2.95 trillion US\$ with about 66 million cars produced in 2022. It still remained one of the most important industrial branches with a huge impact on other industrial branches like steel and glass industry and their suppliers. The global demand for glass enamels for the automotive glass industry is about 1500 to 2000 Mt/a which does not even consider the need of the replacement market.

Continuous effort is put into the improvement of safety and the technical performance of all parts of a car. Recently, carbon-based nanomaterials like nanotubes and graphene have found widespread applications in electronics and coating industry.

In the present study it was investigated how graphene, graphite and other carbon-based materials interact with the bismuth-based glass frit used in a glass enamel for automotive windshields at various stages of the production process. Modified glass enamels were prepared and tested under conditions typical for automotive applications.

Key Words: glasss enamel, windshield, automotive glass, silver hiding, nanotechnology, graphene.

ÖZET

Otomobil endüstrisinin satış geliri, dünya çapında üretilen yaklaşık 75 milyon otomobil ile 2019 yılında yaklaşık 3 trilyon ABD doları ile zirve seviyesine ulaşmıştır. Covid-19 salgını nedeniyle bir düşüş gözlemlense de en önemli sanayi kollarından biri olmaya devam etmektedir. Sektör, çelik ve cam sanayi gibi diğer sanayi kollarında ve tüm tedarik zincirini de tetikleyerek 2022'de üretilen yaklaşık 66 milyon otomobille 2,95 trilyon ABD doları ciroya ulaşmıştır. Otomotiv camı endüstrisi için küresel cam emaye talebi yaklaşık yenileme camları pazar payı hariç 1500-2000 Mt/yıl olmaktadır. Bir otomobilin tüm parçalarının güvenliğinin ve teknik performansının iyileştirilmesi için sürekli iyileştirme çalışmaları yürütülmektedir. Son zamanlarda, nanotüpler ve grafen gibi karbon bazlı nanomalzemeler, elektronik ve kaplama endüstrisinde yaygın uygulamalarda yer almaktadır. Bu çalışmada grafen, grafit ve diğer karbon bazlı malzemelerin, üretim sürecinin çeşitli aşamalarında otomotiv ön camları için cam emayede kullanılan bizmut esaslı cam frit ile nasıl etkileşime girdiği araştırılmıştır. Geliştirilen cam emayeleri, otomotiv uygulamaları için simüle edilmiş koşullar altında hazırlanmış ve test edilmiştir.

Anahtar Kelimeler: cam emayesi, ön cam, otomotiv ön camı, gümüş saklama, nanoteknoloji, grafen.

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LIST OF ABBREVIATIONS AND ACRONYMS

<u>Abbreviations and Acronyms</u>	<u>Explanations</u>
±	: Plus – Minus
°C	: Celsius Degree
a	: Redness – Greenness in Color Values
atm	: Atmospheric Pressure
b	: Yellowness – Blueness in Color Values
Cm	: Centimeter
g	: Gram
h	: Hour
K	: Kelvin
kg	: Kilogram
L	: Lightness – Darkness in Color Values
N	: Newton
wt.	: % Weight Percent
A	: Linear Thermal Expansion Coefficient
μm	: Micrometer
ACEA	: European Automobile Manufacturers' Association
ASTM	: American Society for Testing and Materials
CIE	: Commission Internationale d'Eclairage
CTE	: Coefficient of Thermal Expansion
DIN	: Deutsches Institut für Normung
DTA	: Differential Thermal Analysis
DSC	: Differential Scanning Calorimetry
FT-IR	: Fourier transform infrared spectroscopy
ICP-OES	: Inductively Coupled Plasma Optical Emission Spectroscopy
ISO	: International Organization for Standardization
SEM	: Scanning Electron Microscope
SLS	: Soda Lime Silicate glass
XRD	: X-Ray Diffraction
XRF	: X-Ray Fluorescence

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1. INTRODUCTION

1.1. Structure and Properties of Graphene

The name “graphene” was coined by Boehm et al. in a paper published in 1986 [1]. It is a combination of a word derived from “graphite” and the suffix “ene” indicating the polycyclic aromatic electronic structure. Graphene can be regarded as a mono-layered graphite, the structures of which are shown in Figure 1.

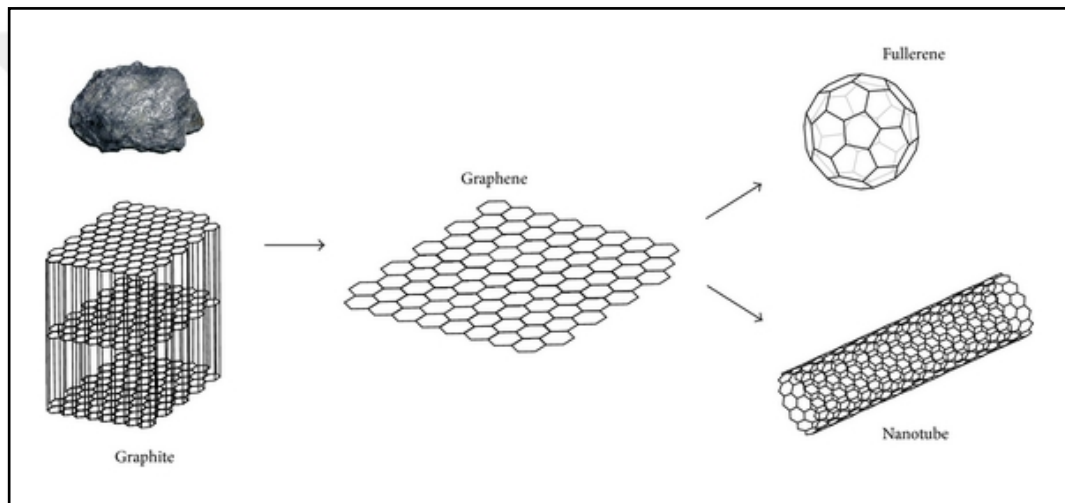


Figure 1.1: Structures of graphene and graphite[2].

Although there have been speculations over the existence of graphene for several decades it was isolated only in 2004 by Novoselov and Geim [3] by a technique that is called mechanical exfoliation. Both scientists were awarded with the Nobel Prize in 2010. Thanks to its unique properties graphene has found widespread application, mainly in electronics [4, 5]. With increasing number of applications there was an increasing demand for graphene syntheses in larger scales. An overview on synthetic routes is provided in several recent review articles [5-8]. For synthesis in large scale graphite can be used as starting material that is transformed to graphene oxide from which graphene is obtained by chemical reduction [9-12]. Interestingly, the formation of graphene by ball-milling of graphite is claimed in a patent [13]. While graphene is

stable at temperatures above 800°C in an inert atmosphere [42-44] it starts to decompose in air already around 500°C [45].

1.2. Automotive Glass Enamels

1.2.1. Glass Enamels and Glass Types Used in Passenger Cars

In a passenger car there 2 types of glass windows in use: laminated glass for the front windshields and tempered glass for the side windows and rear window, which is also called backlight. In some cases, there are also glass windows on the roof that are called sunroofs. Like backlights and side windows sunroofs are usually also made with tempered glass.

Tempered glass is produced by heating the glass to temperatures above the softening point and subsequent fast cooling of both surfaces by compressed air. By this process compressive stress is created on the glass surface, and the glass becomes mechanically stronger. However, if there is a strong impact, e.g., hitting the glass by a stone, the window may be shattered into many small pieces. For obvious reason this is rarely the case for backlights. For front windshields the situation is different. The chance that the windshield is hit by a stone is much higher. In the past, front windshields were also made with tempered glass. If it is hit by a stone, it broke into many small pieces by which a dangerous situation was created for the driver. For safety reasons this was changed later, and nowadays only laminated glass is used for front windshields.

In an automotive laminated windshield 2 glass panes of about 1.4 to 2 mm thickness and a foil of polyvinyl butyrate (PVB) in between form the laminate. The glass panes are shaped pairwise by heating to about 600°C. After slow cooling to ambient temperature a PVB foil is put in between the glass panes and the glass panes with the PVB foil in between is heated to about 130°C in an autoclave to form the laminate.

If an automotive windshield is hit by a stone the outer glass may break but the entire construction will still remain intact, which is much safer for the driver. Until the mid of the 1980's car windows were mounted to the car body by using a sort of plastic encapsulation around the edges of the glass panes. Because this was a time-consuming and labor-intensive process one started to glue the front windshields and the rear

backlight directly to the car body. In order to protect the polyurethane glue from degradation by sunlight it was necessary to apply a protective light-absorbing layer onto the glass edges that is stable to sunlight. Glass enamels based on low-melting glass frits and inorganic light absorbing components were found to be the best solution. In the beginning mixtures of inorganic transition metal oxides like chromium oxide, cobalt oxide, nickel oxide etc. were used in order to provide sufficient light absorption [14]. Later, however, the mixtures of inorganic oxides were replaced by lightfast inorganic pigments. The spinel-type black pigment CuCr_2O_4 has become one of the most commonly used black pigments for automotive glass enamels.

Black enamels are not only used in order to protect the glue from sunlight degradation, but they also have an aesthetic function as they hide the glue from being seen from outside the car. Very soon the black enamel has also become an essential design element, especially for the backlights.

1.2.2. Anti-Stick Enamels

Starting in the 1990's, the car design required strongly bent glasses for the backlights. More and more often bending in 3 dimensions took place. For the black enamel, which is screen-printed onto the glass prior to bending, this meant that traditional glass enamels that are also used for the decoration of architecture could not be used for strongly bent automotive glass anymore because the enamel would stick to the forming head by which the glass is shaped. By adding all kind of materials, it was tried to avoid sticking. For instance, the addition of metallic zinc powder was very popular in the early 1990's [15-17]. Addition of zinc powder did indeed improve the anti-stick properties. However, the color of the fired enamel was quite grey and the resistance of the enamel towards attack by acids was very poor. Addition of other metal in powder, e.g., tin, cadmium, manganese, iron, was also proposed [17, 18].

When working with zinc powder it was noticed that some glass frits underwent partial crystallization. It was found that zinc silicate, Zn_2SiO_4 , is formed. By adding finely milled Zn_2SiO_4 the anti-stick properties of glass enamels with zinc-containing frits could be improved [19]. If a mixture of Zn_2SiO_4 and Bi_2O_3 is added the anti-stick properties are claimed to be even better [20].

Although the anti-stick properties of glass enamels made from zinc-containing crystallizing frits could be improved by adding zinc silicate seed, there remained still

the problem of insufficient acid resistance for many applications. It was well known that low melting zinc frits are usually less resistant than lead-based frits. However, there was an increasing concern about the toxicity of lead. Nevertheless, glass enamels based on lead-containing frits were used for automotive laminated windshield glasses in Europe until the year 2003, mainly because there were no lead-free alternatives. For automotive backlights the situation was different. The reason for this is the different technologies used for making automotive windshields and backlights.

The firing temperature for bending windshield glasses is much lower than for backlight glasses. Therefore, in order to get a good fusion of the glass enamel the frit in the black enamel has to be quite low melting.

Unlike the windshield glasses the backlight glass is shaped in a relatively short firing process at a much higher temperature. After bending the glass in a press bender, the hot glass is quickly cooled by compressed air. This process, which is also called tempering process, leads to improved mechanical strength of the backlight glass. The glass frits used for backlight enamels are higher melting than frits in laminated windshield glasses. Acid resistant frits for use in backlight enamels were available already in the early 1990's in form of crystallizing bismuth-containing frits [21]. By adding seed powder in form of bismuth silicate, e.g., Eulytite ($\text{Bi}_4(\text{SiO}_4)_3$), partial crystallization and, hence, anti-stick properties could be enhanced [22].

Black enamels based on bismuth-containing frits have been used for more than two decades for the decoration of automotive backlights and after the ban of lead-containing glass enamels in 2003 also for the decoration of automotive windshields.

1.2.3. Silver Hiding Enamels for Automotive Backlights

Most of the black backlight enamels are overprinted with silver paste in order to provide heating tracks together with busbars bearing the connectors for the power supply. When a silver paste is printed onto a dried black enamel and then fired in the glass bending process the silver overprint becomes visible from the glass side as a yellow to brown colored shadow. The actual color of the silver tracks and the busbar depends on the side – air side or tin side – of the float glass that is carrying the print. When printed onto the tin side of the float glass the color of the silver track is darker than when it is printed onto the air side. It is generally accepted that the brown color is due to the formation of silver colloids in the float glass. The presence of Sn (II) on

the tin side of float glass is causing a softening of the soda lime float glass at the surface. Silver ions may therefore diffuse easier into the glass, where the brown silver colloids are formed.

If the silver paste is printed onto the air side of the float glass the color of the silver tracks is light yellow. For aesthetic reasons the darker reverse color of the silver tracks is more desirable. Therefore, for automotive application the silver paste and, hence, the black enamel, are always printed onto the tin side.

Soon after the technology of using screen-printable silver paste to provide conducting tracks for heating windshields has been introduced [23] the silver paste was also used in order to print aerals and information about the production process of the backlight onto the black enamel. Fig. 2 shows an example of a backlight provided with a series of silver overprints.

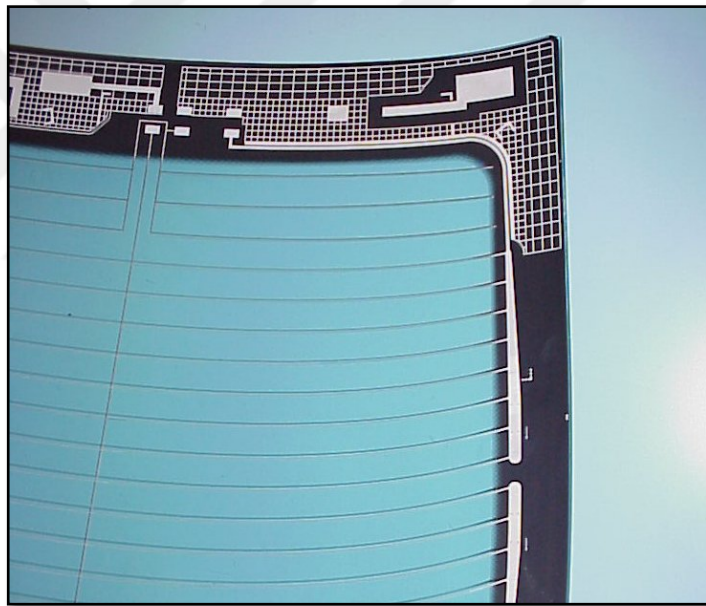


Figure 1.2: Part of a backlight with silver overprint.

It was understandable that the silver overprint should not be visible from outside the car in the form of brown shadows.

There have been several approaches to improve the appearance of backlights with silver overprint. In the beginning it was believed that the visibility of the silver overprint was related to the optical density of the black enamel [23] or the diffusion of the silver paste through the unfired black enamel. However, very soon it was

recognized that diffusion of silver ions through the frit part of the enamel is responsible for the visibility of the silver overprint. Since silver ions Ag^+ and sodium ions Na^+ have similar ionic radii of 116 and 129 pm [24], respectively, it is assumed that Na/Ag ion exchange at the silver/enamel and enamel/glass interfaces plays an important role. By using sodium-free glass frits Andrews and Kridler [17] could reduce the silver migration. Adding lithium oxide to the glass enamel had a similar effect [25]. In this case, the smaller Li^+ was successfully competing with Ag^+ in the ion exchange reaction at the enamel/glass interface. However, the Li/Na ion exchange may lead to high tensile stress near the surface of the glass that may reduce the mechanical strength significantly. In another patent application Sato et al. [26] proposed to put a layer of a higher melting, more viscous glass frit between the black enamel and the silver overprint. Of course, this required an additional print and was therefore economically not feasible. However, with the achievements made with digital printing by using ceramic inks for ink-jet printing [27-29, 35] this idea is worth to be reconsidered.

By adding powders of boron, carbon, lead, and silver [24] it was observed that not only anti-stick properties could be improved but also silver ion migration was reduced. A combination of boron and silver powder seemed to give the best results. Even with the addition of small amounts of silver powder (<1%) alone enamels could be produced that gave a very dark color without visibility of the silver busbar overprint, at least when viewed at diffuse daylight. Under the light of an intense lamp or in the light of intense sunlight the busbar became clearly visible. Due to the presence of the silver in the enamel the black enamel got a brownish color tone, and the color difference between the area that was overprinted with silver and the non-overprinted became smaller. Therefore, the silver overprint became visible only under intense light. Enamels like that were used until the end of the 1990's and marketed by both Johnson Matthey (now Fenzi) and Cerdec (later Ferro and now Vibrantz Technologies). Adding silver to the enamel, even in small quantities, was not only a cost factor but was also not desirable for aesthetic reasons. A "neutral" black was required by the car companies.

The addition of silicon powder [18] or alloys of silicon [30] helped to inhibit or, at least, to slow down silver ion migration in black enamels. Although the actual mechanism of silver migration was never elucidated in detail it is assumed that redox processes between the reducing additive and the frit surface during the firing process plays an important role in the retardation of the silver ion migration into the glass

surface. For bismuth-containing frits it is possible to carry out the redox process of the frit separately prior to making the enamel paste and to use the reduced frit in the black enamel [31]. Glass enamels made with frits produced by this process have a dark color and are very opaque, even without adding pigments. A similar effect was observed when sulphides or polysulphides were added to glass frit compositions during the melting process [32].

Interestingly, the addition of sulphides or polysulphides to the melting process of zinc borosilicate glass frits also lead to a significant suppression of silver ion migration [34]. Silver ions migrating into the enamel are either trapped as relatively temperature-stable silver sulphides or are reduced to elemental silver.

Unfortunately, this method cannot be used for bismuth frits. Attempts to add sulphides like zinc sulphides to the melting process of a bismuth frit led to uncontrolled reduction of Bi_2O_3 to elemental bismuth that was collected at the bottom of the smelter and led to a violent reaction when the melt was quenched into flowing water.

1.2.4. Silver Hiding Enamels for Automotive Windshields

In the past, conductive tracks were usually only printed onto backlights. However, there is a growing interest in having conductive tracks also on front windshields. This is because more and more devices like busbars for heatable windshields, heating grids for the wipers, rain sensors, antennae etc. are being placed on the windshield. In order to hide them from being visible from outside the car silver hiding black enamels is required. Solutions developed for backlights do not work on windshields since the glass enamels used on backlights are too high melting for use on windshields.

From the patent application [31] it is known that bismuth frits can be converted into silver hiding frits by calcination under reducing condition. However, this method requires an additional process step, and in view of the increased energy cost it becomes economically less feasible. Therefore, solutions that do not require additional energy intensive process steps would be most desirable. It would be most advantageous if the standard production process could be used in order to modify the product which is developed for windshields.

The individual steps of this process are shown below (see flow chart below).

- Weighing raw material

- Mixing raw material
- Smelting raw material in gas-fired smelter at 1200°C for about 1 hour
- Discharging the smelter and fast cooling/quenching of molten frit
- Milling of quenched frit by either (a) wet ball-milling and subsequent drying or (b) jet-milling
- Weighing components of enamel
- Mixing components of enamel
- Preparation of enamel paste



Figure 1.3: Flow chart of production process for glass enamel pastes (blue) and possible addition of carbon reductants (red).

If the silver hiding ability of the glass frit has to be increased without major modification of the entire production process addition of the reductant (carbon black, graphite, graphene or ethyl cellulose) to one the following process steps appears to be most suitable (see red arrows in the flow chart):

- Addition of the reductant prior to the smelting process,
- addition of the reductant to the ball-milling process or
- addition to the paste composition prior to the pasting process.

Frit smelting takes place at about 1200°C during a period of about 40 to 90 minutes. Both rotary kilns and continuous smelters are used for frit smelting. However, for smaller quantities (up to about 500 Mt/a) rotary kilns with a capacity of 300 to 500 kg are preferred. Moreover, smelting of bismuth-containing frits in continuous smelters may lead to uncontrolled reduction of bismuth oxide to elemental bismuth that is accumulated at the bottom of the smelting tank where it may drill holes into the refractory bricks. For lab trials alumina, cordierite or mullite crucibles with a capacity of about 0.5 to 1.5 kg frit are used.

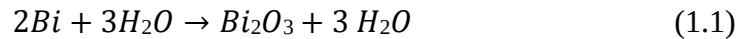
Prior to the melting process the raw materials are weighed off and then homogenized by intense mixing. Homogenization of the raw materials was found to give a more homogeneous glass melt, especially if stirring during the melting process, e.g., in a continuous smelter or in a crucible in the lab is difficult. The raw materials are usually used in form of oxides, carbonates, and borates. During the melting process the raw materials are converted into oxides, and a molten glass is formed. After the conversion of the raw materials into a molten glass the melt is rapidly cooled, either by pouring the melt into cold water or by pouring it onto water-cooled rotating steel cylinders. The latter method is usually applied in a continuous process whereas in a batch process cooling by water is preferred. The rapid cooling of the melt is called “quenching”. A quenched glass is called “glass frit”. Quenching is necessary in order to stabilize the glassy state of the frit that would otherwise undergo devitrification by forming phases with crystalline materials. Although partial crystallization of frits is desirable, e.g., in order to design anti-stick enamels that do not stick to the press head during the shaping process of automotive glass, devitrification by crystal formation during the discharge of frits at the end of the melting process should not take place. The minimum firing temperature of the enamel would increase and a number of properties of the fired enamel, e.g., the fusion, the color and the surface gloss, would be affected in an uncontrolled manner. In addition, spontaneous crystallization may often lead to crystals that have undesirable properties, e.g., too high a coefficient of thermal expansion or insufficient acid resistance. Therefore, it is preferred to start from crystal-free glass frits and to force crystallization during the press bending process by adding seed material to the enamel composition.

By heat treatment of bismuth frits in the presence of reducing compounds it was shown that silver-hiding properties of the frits could be generated [31]. However, an additional process step, namely calcination of the milled frit at about 500 °C, was required, which increased the production cost. Adding the reductant already to the melting process would therefore be an advantage. Since the melting process is carried out at temperatures of about 1200°C one should not expect different results for carbon black, graphite or graphene. None of these compounds would survive this high temperature for a long time. Therefore, we restricted our experiments in large scale (batch size of 500 kg) only to the addition of carbon black. In small lab scale (ca. 1 kg) we tried both carbon black and graphite (see Table 1.1). However, since the results were very similar it was decided to dispense experiments using expensive graphene.

Table 1.1: Overview on experiments using reducing additives.

#	Process step	Additive	Amount
1a	Melting raw material large scale (300 kg)	Carbon black	0.5%
1b	Melting raw material in lab scale	Carbon black	0.5%
1c		Graphite powder	0.5%
1d	Re-melting frit F1 in lab scale	Carbon black	0.5%
1e		Ethyl cellulose	0.5%
1f		MoS ₂	0.5%
2a	Dry ball-milling unground frit F1	Carbon black	0.5%
2b		Graphite powder	0.5%
2c		Graphene	0.5%
2d		MoS ₂	0.5%
2e	Dry ball-milling pre-milled frit F1	Carbon black	0.5%
2f		Graphite powder	0.5%
2g		Graphene	0.5%
2h		MoS ₂	0.5%
2i		Ethyl cellulose	0.5%
2j		Sugar	0.5%

Addition of carbon black to the melting process led to the formation of elemental bismuth. Since bismuth metal has a low-melting point of 271.2°C, a relatively high boiling point of 1564°C and a high density of 9.28 g/cm³ [34] it accumulates at the bottom of the smelter. In a continuous smelter this would lead to the destruction of the refractory material. When the melting process is carried out in a rotary kiln the bismuth metal would leave the kiln towards the end of the discharging process. When hot bismuth metal melt comes into contact with the water that is used for quenching it is causing a violent reaction in which hydrogen is liberated [46]:



Depending on the amount of bismuth reacting with water this may lead to an explosion and, hence, is considered to be too hazardous to be carried out in a production environment.

When the reaction was carried out in smaller laboratory scale the formation of bismuth metal was also observed. However, due to the smaller amount of material involved the reaction during the quenching process was less violent.

Apparently, the reaction of the reductant and the raw materials of the frit are difficult to control during the melting process. Some of the reductant might already been burnt off before the raw material has formed the glass composition. Therefore, it was tried to reduce the frit by re-melting the frit in the presence of reductant. This process resembles the reduction of the frit by heat treatment in the presence of reductants [31]. However, compared to the process described in this patent application, handling could be easier.

In principle, it should also be possible to modify the production process by adding the reductant to the frit after completing the melting process. The burners could be turned off, and after adding the reductant the molten frit could be stirred for some time before quenching.

In lab trials (1d, 1e and 1f, Table 1.1), the milled frit F1 was mixed with 0.5% (w/w) reductant and the heated to about 800 – 900°C for 15 to 20 minutes and then quenched into cold water.

Since pure carbon seems to be a very strong reductant for the bismuth frit F1 a somewhat milder reductant like ethyl cellulose was also tried (experiment 1 e).

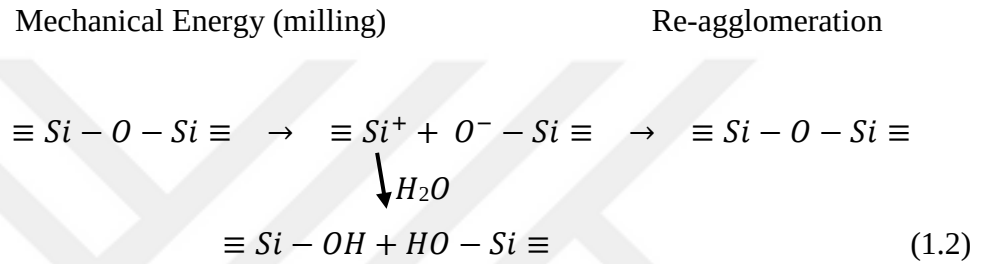
Addition of molybdenum disulphide (experiment 1 f) was also tried. Molybdenum disulphide was chosen because it has a similar layered structure like graphite [53].

Addition of the reductant during the milling process appeared to be the best method in order to control the reaction. Normally, glass frits for glass enamels are either milled by jet-milling or by ball-milling.

In a jet-mill the frit particles are colliding against each other under the influence of three high pressure (ca. 8 bar) air jets in an angle of 120°. At the exit of the jet-mill chamber there is classifier. By the rotation speed of the classifier one can control the particle size of the frit particles that leave the jet-mill: the higher the classifier speed, the smaller the particles but also the smaller the throughput. It is possible to reduce the particle size of frit particle to about $d_{90} = 6 \mu\text{m}$. The throughput can be increased by using a lower classifier speed. A particle size of $d_{90}=20 \mu\text{m}$ is sufficient for frits that are used for making screen-printable pastes. Due to the relatively low throughput and the high energy required to run the compressor, milling glass frits with a jet-mill is quite expensive. On the other hand, no drying is required.

Ball-milling in large ball mills with corundum milling balls and a capacity of about 2 Mt is probably the cheapest way to mill glass frits for glass enamel

applications. The particle size distribution of frits milled in conventional ball mills is much broader than for jet-milled frits. In order to obtain a powder that is suitable for screen-printable automotive glass enamels the frit has to be milled to a particle size of $d_{90} = 10\text{-}12\text{ }\mu\text{m}$. In this case, the maximum particle size is still in the order of $60\text{ }\mu\text{m}$, which is slightly smaller than the mesh size of printing screens used in the automotive industry. A particle size of $d_{90} = 12\text{ }\mu\text{m}$ is difficult to achieve by dry ball-milling. Extremely long milling time would be required that would lead to abrasion of the milling balls and, hence, to significant contamination of the frit. Therefore, water is added to the mill. Water prevents the re-agglomeration of small frit particles by reacting with the surface of the silicate-based frit according to the following scheme:



Under the influence of the mechanical energy provided by the ball mill the siloxane (Si-O-Si) is split. The resulting positively and negatively charged silicon species react with water to form silanol groups and prevent thus the re-agglomeration of the siloxane.

It is known that graphene has excellent properties as a lubricant [36]. However, addition of graphene to the wet-milling process is unlikely to have any effect as the frit surface has a high affinity towards water. On the other hand, it is known that glass frits can easily be coated with organic compounds in a dry ball-milling process [37, 38]. Moreover, addition of organic compounds to the dry ball-milling process could also accelerate the milling process. Frit powder that can be used for electrostatic spraying were produced in this way [38].

In order to bring graphene and also carbon black, graphite and molybdenum disulphide (MoS_2) into close contact with frit particles the milling process shown in the flow chart was modified. Instead of wet ball-milling a dry ball milling process is used. In this case the drying step that would normally follow the wet milling process would become obsolete. Dry milling usually takes a relatively long time to reach the desired particle size of about $d_{90}=10\pm2\text{ }\mu\text{m}$ with a maximum particle size of $<50\text{ }\mu\text{m}$. In addition, significant contamination of the frit by alumina formed by abrasion from

the Corundum milling balls may occur after extended milling times. Therefore, another modification of the process is taken into consideration: instead of using an unground frit a coarse pre-milled frit produced on the jet-mill at low classifier speed. The throughput of the jet-mill would be much higher in this case, which would reduce the cost significantly. In the subsequent ball-milling step the desired particle size could be achieved easily. It is expected that the added reductants (graphene, carbon black, graphite and molybdenum disulphide) will form a coating on the frit particles that both facilitates the milling process and provides a reactive reducing layer that forms an effective barrier for the silver ion migration.

By combining the high throughput jet-milling process to give a relatively coarse frit powder with the subsequent dry ball-milling the production cost can be kept low. No drying is required in this case, and the high energy consumption of the jet-mill in case of milling to small particle size could be avoided. This modified milling process should therefore be economically viable.

The process that would hardly lead to any cost increase, however, would include the use of standard frit powder and addition of the reductant during the final pasting step. In case of addition of boron, silicon, and silicon alloy powder this approach was shown to be successful [18, 23, 30, 39].

2. ANALYTICAL METHODS

2.1. Chemical Analysis

The chemical composition of the frit was determined using the Bruker S8 Tiger X-ray fluorescence (XRF) equipment and Agilent 5110 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis. Elemental compositions were measured to determine if the demanded composition was reached and to provide a more precise interpretation of the research.

2.2. Phase Analysis

X-ray diffraction (XRD) was used for the identification of crystalline phases in the glass enamels. Measurements were carried out with a Rigaku Miniflex 600 operating with CuK α radiation and a 2θ scanning range of 15°-70°.

2.3. Morphology Analysis

A scanning electron microscope (SEM) PHILIPS XL 30 SFEG was used to examine the microstructure of frit and additive after milling. Sputtering with gold was used to avoid charging of the samples.

2.4. Thermal Analysis

The optical dilatometer (Misura 3.32) was used to examine the sintering behavior of the produced frit. The melting temperatures of frit were found by heating the frit sample at a rate of 10 °C/min to the sintering, softening, sphere, halfsphere, and melting temperatures. The linear thermal expansion coefficient of the frit composition evaluated in this study was measured using a Netzsch thermal dilatometer Netzsch / DIL 402PC at 10°C/min to 300°C.

2.5. Particle Size Distribution Analysis

Particle size distribution of the frit powder was determined using Malvern Mastersizer 3000 with Hydro EV laser diffraction method. The parameters D10, D50 and D90 defining the highest particle diameter below 10, 50 and 90% of total volume, respectively, were determined.

2.6. Wet Film Thickness

The film thickness after screen-printing was controlled with an Erichsen wet film thickness gauge.

2.7. Acid Resistance

The acid resistance is assessed based on ASTM C724-91. Fired glass enamels are subjected to a 10% citric acid solution for 15 minutes and a 3.7% hydrochloric acid solution for 10 minutes at room temperature.

2.8. Color Measurement

The color values were measured using a Konica Minolta CM-700d spectrophotometer. The “specular reflection excluded” mode is used for the measurement of CIE Lab color parameters L^* , a^* and b^* .

2.9. Gloss Measurement

The gloss of fired enamels is measured at five different positions in 60° angle mode using a TQC Sheen Polygloss glossmeter.

2.10. Check for Microporosity

The presence of micropores in glass enamels is carried out by drawing a line over the fired glass enamel by using a felt-tip pen. In case of the presence of micropores

the ink of the pen penetrates into the pores, and the line drawn by the pen is visible from the reverse side, i.e., the non-decorated side of the glass. If the enamel is well fused, the ink will not penetrate the enamel. It is important that this test is carried out after the decorated glass is cooled to room temperature.

2.11. FT-IR Spectrum

The FT-IR spectra were recorded on an Universal Attenuated Total Reflectance FT-IR (UATR-FT-IR) Two-Spectrum PerkinElmer. FT-IR measurements were carried out for transmittance percentages at various wavenumbers.



3. EXPERIMENTS WITH GLASS FRITS

An overview of the experiments is shown in Table 1.1.

3.1. Frit Melting Experiments

Raw materials, the quality of which is controlled and approved by both chemical and physical methods, are weighed off according to the frit recipe. Raw materials are then homogeneously mixed with vertical type mixers suitable for dry powders. In the melting process, the homogenous raw material mixture is heated to a temperature high enough to convert them into oxides. The extra energy makes the molecules vibrate until they break the bonds holding them together and become a flowing liquid. This melt is directly poured into cold water. As the molecules lose energy by cooling to lower temperature, they are less and less able to move into an ordered position, and the result is what is called an amorphous solid or glass frit.

- Experiment 1a – Melting frit F1 without additives

298.5 kg of the raw materials used for making frit F1 in industrial scale are thoroughly mixed with 1.5 kg carbon black powder. This material is then filled into a gas-fired rotary kiln at ambient temperature. After charging the kiln the kiln is then heated with a natural gas/air mixture to a final temperature of 1200°C. This temperature is kept for 70 minutes. During the melting process the kiln is rotating back and forth in an angle of about 270°. After completion of the reaction the kiln is then discharged by pouring the molten glass slowly in a narrow stream into a container filled with water. For most of the time this quenching process went off as usual. However, towards the end of the discharging process a very violent reaction similar to an explosion took place. For health and safety reasons it was decided to stop experiments in large scale.

- Experiment 1b – Melting frit F1 in the presence of 0.5% carbon black starting from raw materials

995 g raw materials used for making frit F1 in industrial scale are thoroughly mixed with 5 g carbon black powder and then filled into a crucible. The crucible was heated in a gas-fired kiln until a homogeneous melt was received. It was then kept in the kiln for another 30 minutes. The melt was then stirred with a steel rod and kept for

another 10 minutes in the kiln before the melt was poured into a steel bucket filled with tap water.

- Experiment 1c – Melting frit F1 in the presence of 0.5% graphite starting from raw materials

995 g raw materials used for making frit F1 in industrial scale are thoroughly mixed with 5 g graphite powder and then filled into a crucible. The crucible was heated in a gas-fired kiln until a homogeneous melt was received. It was then kept in the kiln for another 30 minutes. The melt was then stirred with a steel rod and kept for another 10 minutes in the kiln before the melt was poured into a steel bucket filled with tap water.

Both in experiment 1b and 1c small metallic spheres were detected in the quenched frit granules.

- Experiment 1d – Re-melting frit F1 in the presence of 0.5% carbon black

995 g of industrially produced jet-milled powder of frit F1 was thoroughly mixed with 5 g carbon black powder and then filled into a crucible. The crucible was heated in a gas-fired kiln until a homogeneous melt was received. It was then kept in the kiln for another 10 minutes and then poured into a steel bucket filled with tap water.

Some small metallic spheres were detected in the quenched frit granules. There have been clearly less metallic particles than in experiments 1b and 1c.

- Experiment 1e – Re-melting frit F1 in the presence of 0.5% ethyl cellulose

995 g of industrially produced jet-milled powder of frit F1 was thoroughly mixed with 5 g ethyl cellulose and then filled into a crucible. The crucible was heated in a gas-fired kiln until a homogeneous melt was received. It was then kept in the kiln for another 10 minutes and then poured into a steel bucket filled with tap water.

Hardly any metallic particles were detected in experiment 1e.

- Experiment 1f – Re-melting frit F1 in the presence of 0.5% molybdenum disulphide (MoS_2)

995 g of industrially produced jet-milled powder of frit F1 was thoroughly mixed with 5 g molybdenum disulphide and then filled into a crucible. The crucible was heated in a gas-fired kiln until a homogeneous melt was received. It was then kept in the kiln for another 10 minutes and then poured into a steel bucket filled with tap water.

Numerous small metallic spheres were detected in the quenched frit granules.

The metallic particles detected in the quenched frit produced in experiments 1a – 1f were collected and thermal analysis was carried out.

3.2. Milling Experiments

100 g of unground frit F1 and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 6 hours the particle size was measured with a Malvern Mastersizer. The maximum particle size was still found to be $>100\text{ }\mu\text{m}$.



Figure 3.1: Malvern Mastersizer 3000.

In a second experiment, 99.5 g of unground frit F1, 0.5 g of graphite and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 6 hours the particle size was measured with a Malvern Mastersizer. The maximum particle size was still found to be $>100\text{ }\mu\text{m}$.



Figure 3.2: Rosetti Mill.

Hardly any effect was noticeable by adding graphite powder. Since frits with a maximum particle size of $>100\text{ }\mu\text{m}$ cannot be used for screen printing in the automotive glass industry it was decided to run all further trials with jet-milled frits as starting material.

Jet-milled frit F1 was used for all further ball-milling trials. After milling samples were taken for the measurement of the particle size and for the characterization of the morphology by SEM.

The particle size d90 values of the frit after 1 hour milling in the presence of 0.5 % additive are compiled in Table 2.1. Jet-milled frit F1 with a particle size d90 = $6.58\text{ }\mu\text{m}$ was used as starting material.

SEM images taken from jet-milled frit F1 and powders after co-milling with 0.5% additive are shown below (Fig. 3 and Fig. 3a-3e).

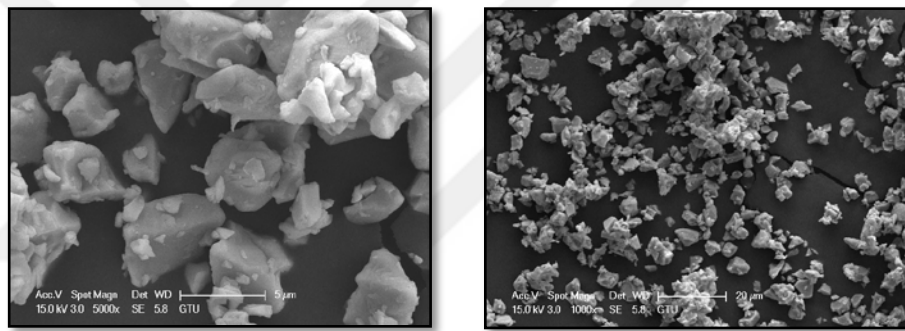


Figure 3.3: SEM images taken from jet-milled frit F1 that has been used as starting material for milling experiments.

- Experiment 2a – Milling in the presence of carbon black

99.5 g of jet-milled frit F1 with 0.5 g carbon black and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 1 hour milling time a sample was taken, and the particle size was determined with a Malvern Mastersizer. The results are shown in Table 2.1.

SEM images taken from the milled sample are shown below.

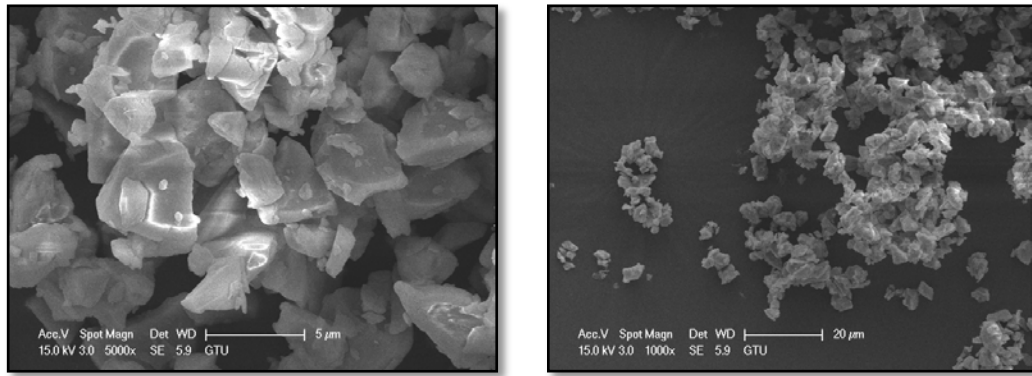


Figure 3.4: SEM image of the frit sample ball-milled with 0.5% carbon black for 1 hour (F1a).

- Experiment 2b – Milling in the presence of graphite

99.5 g of jet-milled frit F1, 0.5 g graphite powder and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 1 hour milling time a sample was taken and the particle size was determined with a Malvern Mastersizer. The results are shown in Table 2.1.

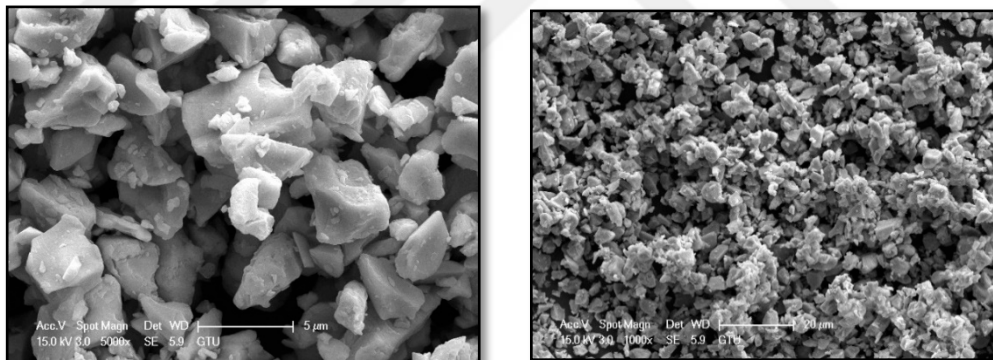


Figure 3.5: SEM image of the frit sample ball-milled with 0.5% graphite for 1 hour (F1b).

- Experiment 2c – Milling in the presence of graphene

99.5 g of jet-milled frit F1, 0.5 g graphene and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 1 hour milling time, a sample was taken, and the particle size was determined with a Malvern Mastersizer. The results are shown in Table 2.1.

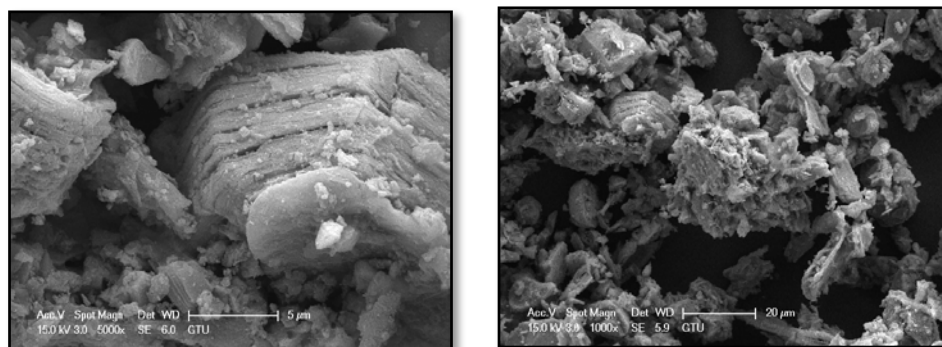


Figure 3.6: SEM image of the frit sample ball-milled with 0.5% graphene for 1 hour (F1c).

- Experiment 2d – Milling in the presence of molybdenum disulphide

99.5 g of jet-milled frit F1, 0.5 g molybdenum disulphide and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 1 hour milling a sample was taken and the particle size was determined with a Malvern Mastersizer. The results are shown in Table 2.1.

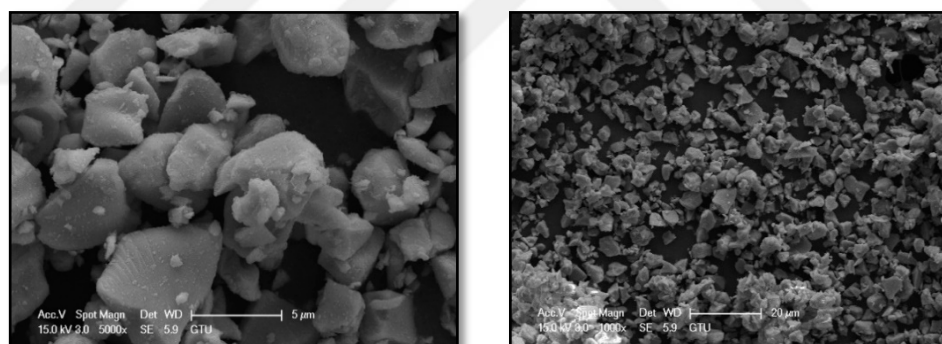


Figure 3.7: SEM image of the frit sample ball-milled with 0.5% MoS₂ for 1 hour (F1d).

- Experiment 2e – Milling in the presence of ethyl cellulose

99.5 g of jet-milled frit F1, 0.5 g ethyl cellulose and 4 corundum milling balls with a diameter of 10 mm were placed into a Rosetti mill. After 1 hour milling time, a sample was taken, and the particle size was determined with a Malvern Mastersizer. The results are shown in Table 3.1.

Table 3.1: Overview on frits used for making screen-printable pastes.

Frit	Experiment for producing frit	Type of milling	Particle size of frit (d90 in μm)	Remarks
F1	Standard frit made in large scale	Jet-milling	6.58	No milling additive
F1a	2e	Dry ball-milling	11.5 ¹⁾	Jet-milled frit with Carbon black as additive
F1b	2f	Dry ball-milling	8.39 ¹⁾	Jet-milled frit with Graphite as additive
F1c	2g	Dry ball-milling	9.28 ¹⁾	Jet-milled frit with Graphene as additive
F1d	2h	Dry ball-milling	8.71 ¹⁾	Jet-milled frit with MoS_2 as additive
F1e	2i	Dry ball-milling	7.47 ¹⁾	Jet-milled frit with ethyl cellulose as additive
F1f	2j	Dry ball-milling	5.64 ¹⁾	Jet-milled frit with sugar as additive

1) after ball milling for one hour

An overview on frits used for making pastes is given in Table 3.1.

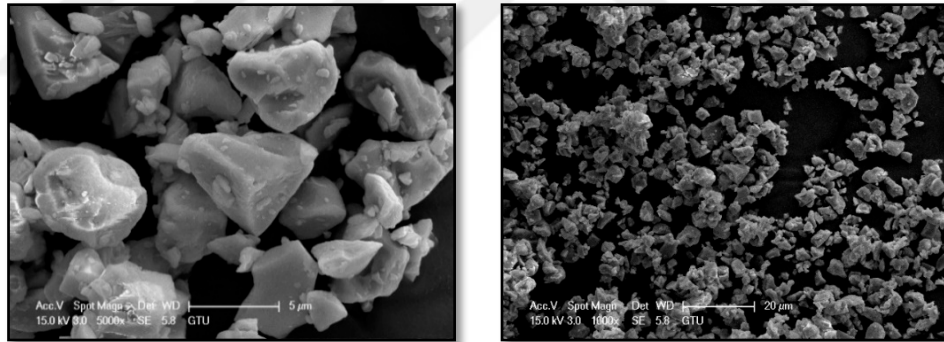


Figure 3.8: SEM image of the frit sample ball-milled with 0.5% ethyl cellulose for 1 hour (F1e).

Figure 3.3e: SEM image of the frit sample ball-milled with 0.5% ethyl cellulose for 1 hour (F1e)

3.3. Preparation of Pastes

All pastes were prepared by mixing 77 parts by weight of milled frit with 23 parts by weight copper chromite (III) black pigment.

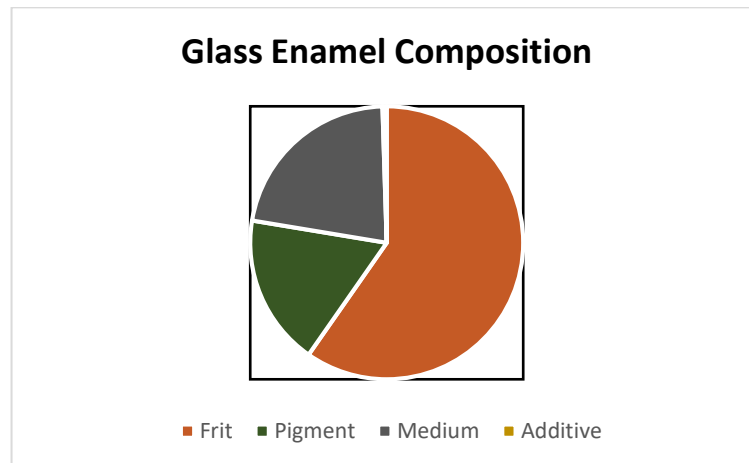


Figure 3.9: Glass enamel composition.

This powder was then dispersed in the screen-printing water-friendly medium produced by Zschimmer & Schwarz by adding the total amount of 20 parts by weight of medium in small portions and intense mixing with a stirrer.



Figure 3.10: Laboratory stirrer.

After the addition of medium was completed the highly viscous paste was further dispersed by passing it twice over a lab triple-roll mill (120S-450 supplied by Exakt).

After the addition of medium was completed the highly viscous paste was further dispersed by passing it twice over a lab triple-roll mill (120S-450 supplied by Exakt).

To produce homogeneous dispersion, graphene dispersion using ultrasonication (tip or bath sonicator) is commonly utilized in nanocomposites manufacturing [54]. Tip sonication is used for better dispersion of additives after preparation of glass enamel paste with additives.



Figure 3.11: Tip sonicator.

3.4. Assessment of Black Enamels

All black enamel pastes were made by pasting the frits (see Table 2.1.) and spinel type copper chromite black pigment in the water-friendly screen-printing medium. They were tested under the same condition.

Float glass plates of 100x100x4 mm³ soda-lime-silicate glasses were used in all trials. All pastes were printed onto the tin-side of the glass. Tin side of the float glass is determined by Advanced Optics Tin Side Detector/TS580 device. The design shown in Figure 4 was used to prepare the test specimens by hand screen-printing. A 77T screen and freshly prepared pastes were used for printing.

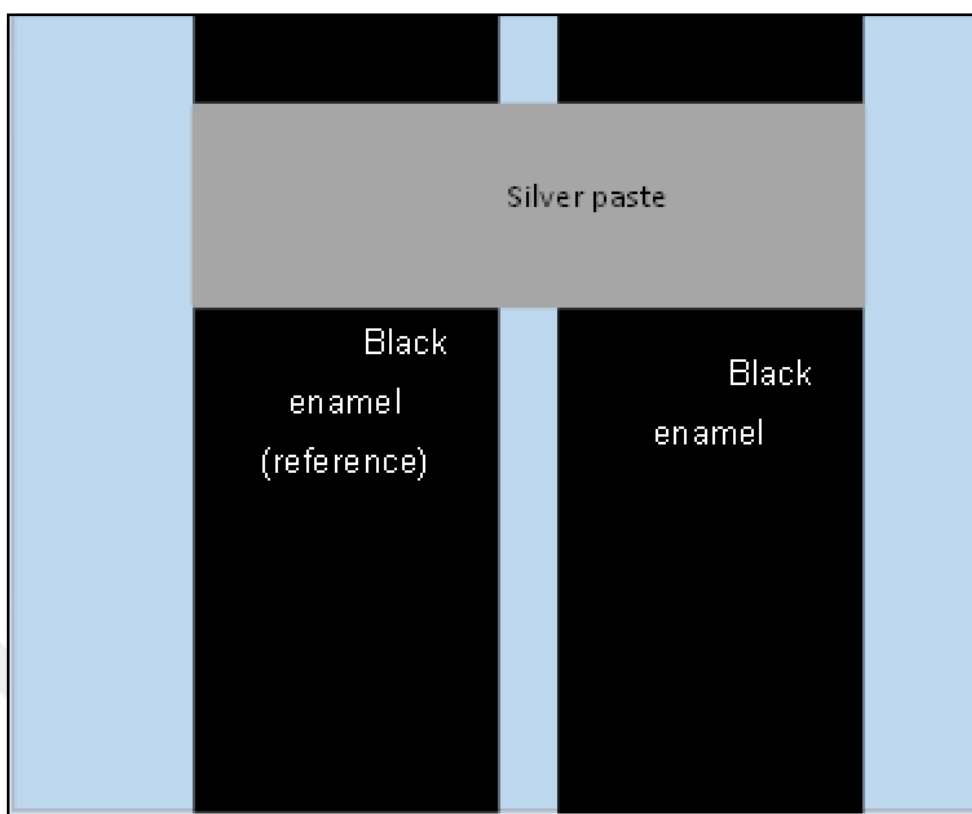


Figure 3.12:Design for testing black enamels.

Since a number of characteristics of the enamel depend on the layer thickness, e.g., the diffusion of silver ions, the optical density and the resistance against attack by chemicals, it was important to control the layer thickness. All pastes were prepared with the same powder-to-medium ratio. Therefore, it was sufficient to measure the wet layer thickness directly after printing. A film thickness of $25 \pm 2 \mu\text{m}$ for the black enamel and the silver paste was applied in all cases.



Figure 3.13:Screen printing setup.

The reference and the test sample were printed onto the same glass plate. After drying at 180°C in a drying oven for 5 minutes and cooling to ambient temperature both enamels were overprinted with silver paste as shown in Figure 2. Silver paste AG 2303-80 with a silver concentration of 80% supplied by Johnson Matthey was used to provide the silver overprint.



Figure 3.14:Bench type drying oven.

The dried glass plates are placed in box kiln that was set at 600°C and heated for 300 seconds. The glass plate was then taken out of the kiln and was allowed to cool down to room temperature.



Figure 3.15:High temperature furnace.

After cooling the glass plates to room temperature, the following tests were carried out:

- Check for microporosity,
- Measurement of the gloss of the black enamel,
- Measurement of the reverse color of the black enamel (without silver overprint),
- Measurement of the reverse color of the black enamel (with silver overprint).

A well fused automotive glass enamel must not show any microporosity. Otherwise, water may penetrate into the enamel causing a chemical reaction or enhanced mechanical stress that eventually will lead to the deterioration of the black enamel. A simple check on whether or not the enamel is well fused and does not show any microporosity can be carried out with a felt-tip pen. A line is drawn on the surface of the enamel. If there is still microporosity the ink of the felt-tip pen penetrates into the enamel and becomes visible on the reverse side.

The gloss of the black enamel correlates with the anti-stick properties of the enamel, i.e., the behavior of the enamel in the press bending process. Low gloss is desired for enamels that are used for press bending. In the patent [40] it is claimed that addition of graphite powder to the enamel will not only improve the mechanical properties like resistance against impact (ball-drop resistance) but also the anti-stick properties. Therefore, it was interesting to know if the additives used in combination with frit F1 also have an effect on the gloss.

The surface roughness is an important characteristic that affects the production process in the car industry. Since windshields are glued to the car body with the help of glue robots that apply the adhesive by moving the glue gun closely over the enamel surface high surface roughness may shorten the lifetime of the glue gun. An arithmetical mean of surface roughness $R_a < 1 \mu\text{m}$ is required for glass enamels used on automotive parts. If the enamel contains components that burn out late craters may be formed on the enamel surface that affect the surface roughness. The surface roughness is measured with an Erichsen surface roughness tester.

The reverse color is the color one can see on the reverse side of the glass plate, i.e., the undecorated side. This is also the color that is seen from outside the car. The color does not affect the technical performance of the enamel. However, it is of aesthetic importance. There are no strict guidelines for the color of automotive glass enamels. The actual requirements depend on the car model. There is a general trend towards darker neutral black color. The color can be expressed by the parameters L, a and b in the CIE lab system (see Figure 3.16).

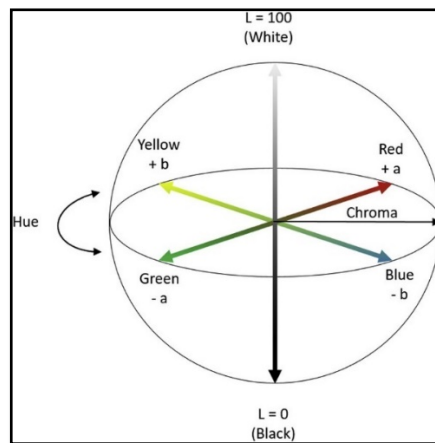


Figure 3.16: Color space according to CIE lab.

Neutral black means that the CIE lab parameters a and b are close to zero. A perfect black color would have the color values $L = 0$, $a = 0$ and $b = 0$. In practice, however, color values a and b for automotive glass enamels are in the range of 0 ± 1 . L values are usually < 8 , although for some car models $L < 5$ or even $L < 3$ are required. Specular reflection from the glass surface has to be excluded in this case. If the specular reflection is included the color L value is much higher (around $L = 25$). Commercially available colorimeters allow the measurement in both “specular reflection excluded” and “specular reflection included” mode.

A silver overprint reflects some heat. Therefore, the enamel under the silver overprint gets less heat than the parts of enamel that are not overprinted with silver. This means that the frit in the enamel under the silver overprint is less fused than in the non-overprinted areas. Due to light scattering at the glass-enamel interface caused by the frit particles the color appears greyer. If the firing temperature is increased the frit under the silver overprint will also fuse. The viscosity inside the frit particle will decrease, and diffusion of silver ions from the silver paste through the frit will take place. Eventually, the silver ions diffuse into the glass substrate, where they form silver colloids. Since the silver colloids absorb visible light in the range of 410 nm the color of the black enamel under the silver overprint appears brown. The silver overprint thus becomes indirectly visible as a grey shadow at low firing temperature and in form of the brown silver colloids at high temperature. A color difference – here between the area that is overprinted and the area that is not overprinted with silver – can be detected by a human eye if the difference of the color value ΔE is < 1 . Here ΔE is defined as

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2} \quad (3.1)$$

Δa , Δb , and ΔL are the differences of the color values a, b and L for the overprinted and non-overprinted areas of the black enamel.

For black enamels it is also possible to use the ΔL value instead of ΔE for the judgement of silver hiding, assuming that the color shade does not change.



4. MATERIALS

Carbon black powder was purchased from Cabot.

Graphite powder (99.9% purity with a particle size between 5 and 10 μm) was purchased from Nanografi Nanotechnology/Ankara.

Ethyl cellulose was purchased from Ashland as Aqualon ethyl cellulose.

Molybdenum disulphide was purchased from Nanografi Nanotechnology/Ankara.

Samples of graphene were kindly provided by Nanografi Nanotechnology/Ankara.

Copper chromite (III) black pigment 1G produced by Shepherd.

Water-friendly organic medium was provided from Zschimmer & Schwarz.

Silver paste AG2303-80 produced by AGT-Fenzi and kindly provided by Şişecam was used in all experiments without further dilution.

Sugar (saccharose), available in food stores, was used for a milling experiment.

5. RESULTS AND DISCUSSION

5.1. Characterization of the Frit

If a glass enamel is printed onto a glass, then heated to high temperature in order to fuse the glass enamel and finally cooled to room temperature it is important that the thermal expansion of the enamel is lower than glass substrate. Otherwise, tensile stress would occur on the enamelled surface, which would render the decorated glass very sensitive against scratches and would also lead to substantial weakening of the glass. Since soda-lime float glass has a linear coefficient of thermal expansion (CTE) of $90 \times 10^{-7}/K$ in the temperature range between $30^{\circ}C$ and $300^{\circ}C$ the glass enamel should have a coefficient of thermal expansion that is $<90 \times 10^{-7}/K$. Since the glass enamel comprises both a glass frit and a pigment, of which the CTE very often is not known, the frit should preferably have a CTE that is much lower than $90 \times 10^{-7}/K$. The coefficient of thermal expansion (CTE) of a specimen was calculated using experimental data for difference in length $30^{\circ}C$ and $300^{\circ}C$.

The material expands when heated, and it contracts when cooled. The linear coefficient of thermal expansion indicates the length change caused by temperature changes. The linear coefficient of thermal expansion of the frit is critical in order to avoid defects on the final product. Crack-free coatings are available for glass enamels with a linear coefficient of thermal expansion less than the glass substrate. The different materials of different atomic bonding used as layers like black glass enamel, silver paste and soldering increase the complexity of the coating system and generates thermal stress on the glass. The difference in the linear coefficient of thermal expansion on glass frit is one of the factors causing interlayer mechanical stress. Thermal expansion properties change over time and affect the performance and reliability of windshield. Coefficient of thermal expansion (CTE) of the frit was measured by dilatometry using a Netzsch DIL 402PC horizontal dilatometer operated at $10^{\circ}C/min$ on 5mm long glass specimen that was prepared by melting the frit and pouring it into a mold made of metal.



Figure 5.1: Preparation of F1 specimen for CTE measurement.

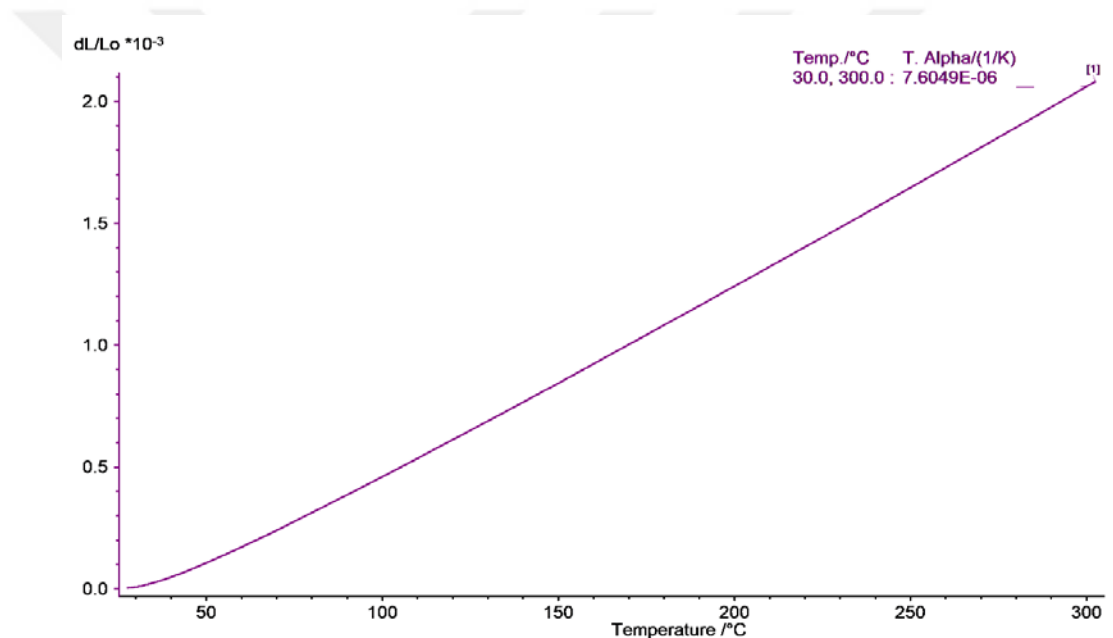


Figure 5.2: CTE of F1.

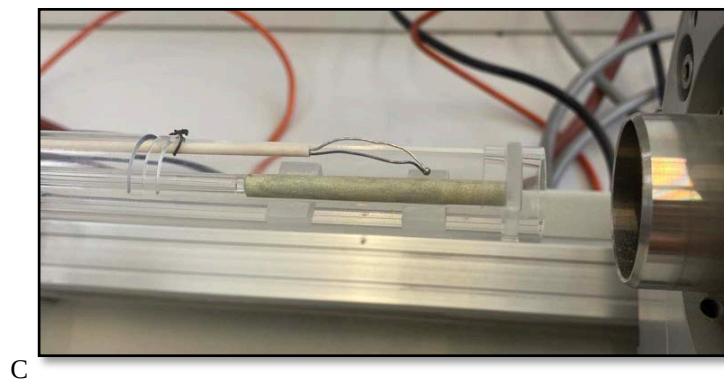


Figure 5.3: Dilatometry measurement setup.

By using a heating microscope, the change of frits during the heating process can be monitored. A small cube of jet-milled frit is shaped and then heated to a temperature above the melting point with a heating rate of 10°C/min. Throughout the experiment, one camera on the microscope bench frames captures each stage of the distinctive dimensional shape changes regarding with temperature change in air atmosphere. This is important to recognize material change procedure such as sintering, softening, sphere, half-sphere, and melting. The Optical Dilatometry Platform, ODP 868 by TA Instruments were used to determine the sintering, softening, sphere and melting points of produced frit.

Table 5.1: Stages observed in the heating microscope.

Point	Temperature, [°C]
Sintering	524
Softening	604
Sphere	642
Half Sphere	695
Melting	710

Taking into consideration the firing temperature of windshield enamels, the created frit should have a low melting point. The melting temperature 710°C proves that the frit is suitable for windshield glass production.

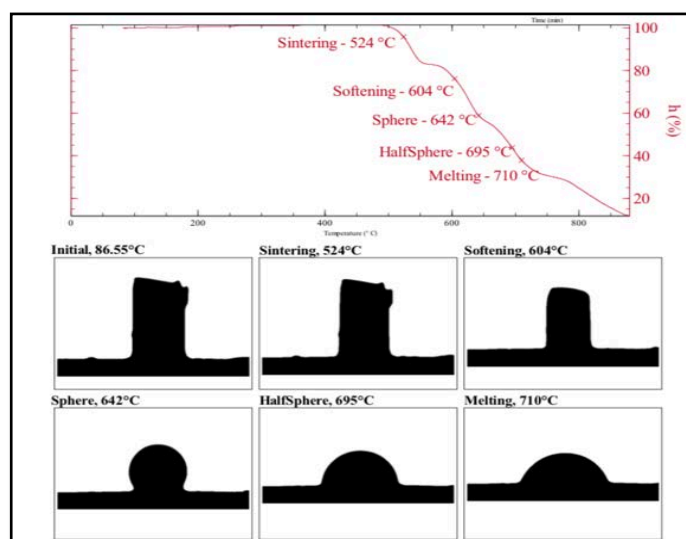


Figure 5.4: Heating microscopy result of F1.

Apart from the wide peak caused by the glassy structure, no special peaks were observed in XRD measurement which proves that the frit has an amorphous structure that has no crystal phase.

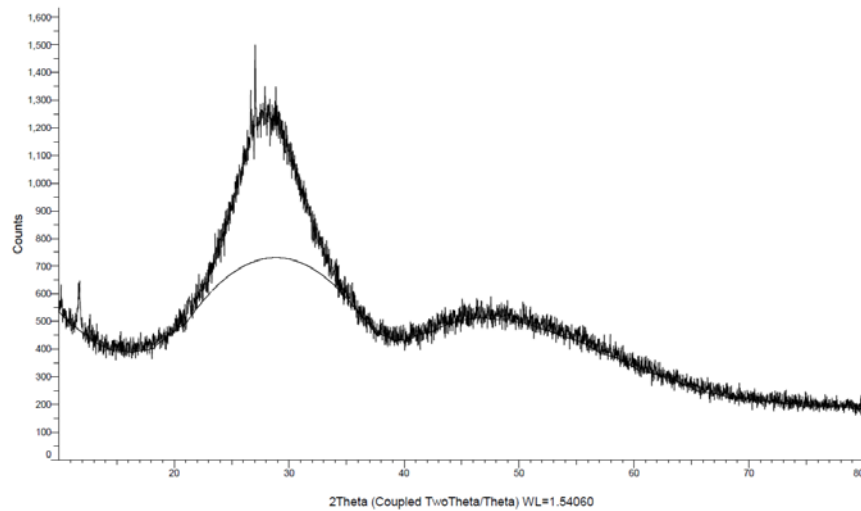


Figure 5.5: XRD pattern of F1.

By adding a number of potential reductants like carbon black, graphene, graphite, and ethyl cellulose to the frit smelting process in the lab it was intended to form small amounts of reduced bismuth species that may act as scavengers for silver ions and thus prevent silver ion migration into the glass. By intercepting silver ions on their way to the float glass surface hiding of a silver overprint on the final black enamel was hoped to be achieved.

However, when carbon black, graphene, graphite, or molybdenum disulphide were added in the melting process small pieces of metal were detected in the quenched frit. DTA measurements revealed that the melting point of the metallic particles isolated from the quenched frit was about 271°C suggesting that the metallic particles are metallic bismuth for which a melting point 271.3 °C is reported in the literature [47].

Bismuth metal is accumulated at the bottom of the smelter or crucible. When the kiln or the crucible is discharged the molten metallic bismuth undergoes a violent reaction with the quench water at the end of the discharging operation. A hazardous

situation is thus created for the operators. For health and safety reasons it was decided not to proceed this route in production scale.

Formation of elemental bismuth was also observed when MoS₂ was added to the molten bismuth frit. Since molybdenum oxide is a commonly known frit additive the reduction process must be due to the presence of sulphide. This is insofar interesting as compositions of frits comprising both bismuth and sulphur are claimed in a number of patents [48-50].

Addition of ethyl cellulose also leads to small amounts of metallic bismuth although far less reduction took place. The most likely reason is that a substantial part of ethyl cellulose, which is also a component of many organic screen-printing mediums, is evaporating before a glass melt is formed from the frit.

Obviously, it is difficult or impossible to avoid the formation of reduced metallic bismuth by adding reductant to the melting process. The presence of metallic bismuth in the frit will cause problems for quality assurance since the bismuth is not homogeneously distributed in the quenched frit. More importantly, however, bismuth metal is one of the few elements that expand during the liquid-solid phase transition. This characteristic may lead to tensile stress in the glass enamel and, hence, to weakening of the decorated glass. Therefore, frits containing metallic bismuth should not be used for automotive glass enamels.

5.2. Particle Size Distribution Analysis of Ball Milling

Adding a reductant to the milling process appeared as a better approach for the generation of a reducing environment. It was expected that the reductant will form a coating on the frit surface. When the glass enamel eventually is heated it is expected that the reductive coating will react with bismuth (III) species on the frit surface to form colloidal bismuth that will act as scavengers for migrating silver ions. This mechanism has been assumed for the silver-hiding effect of bismuth frits that have been reduced by cane sugar at elevated temperatures [31].

Ideally, the reductant would also accelerate the milling effect so that unground frits can be used as starting material.

Jet-milled frit F1 was used for all milling trials. The particle size distribution of this frit as well as the particle size distribution of this frit after ball milling for one hour in the presence of additives is shown in Table 5.2.

Table 5.2: Particle size distribution after ball milling in the presence of additives (milling time: 1 hour).

Frit	Additive	Particle size in μm			
		D10	D50	D90	Dmax
F1	No additive¹⁾	2.53	4.24	6.58	8.68
F1a	0.5% Carbon black	3.09	5.74	11.5	24.1
F1b	0.5% Graphite	3.67	4.94	8.39	12.7
F1c	0.5% Graphene	1.96	4.12	6.29	8.17
F1d	0.5% MoS₂	1.98	4.14	6.51	8.24
F1e	0.5% Ethyl cellulose	2.74	4.59	7.47	9.86
F1f	0.5% Sugar	0.03	0.14	5.64	7.65

¹⁾Jet-milled frit used as starting material

Apparently, none of these additives – except sugar - had a significant effect on further particle size reduction. Besides, both graphene and MoS₂ has an effect of accelerating milling the frit in ball milling process. In fact, a slight increase of both the maximum particle size and the d10, d50 and d90 values, respectively, was observed in carbon black and graphite especially. It is assumed that formation of agglomerates is the reason for the observed slight increase of the particle size. Agglomerated particles can be seen in some SEM images while hardly any differences in the primary particle size can be seen in the SEM of the jet-milled frit (Fig. 3.3) and the frit ball-milled in the presence of an additive (Fig. 3.3a – 3.3e). The SEM images of frit particles prepared by milling in the presence of additives look very similar for most additives (see Fig. 3a, 3b, 3d, 3e) whereas milling the frit in the presence of graphene gave a different morphology of the particles (see Fig. 3 and 6). For comparison, the SEM images recorded with the same magnification of the standard jet-milled frit F1 and this frit ball-milled in the presence of carbon black are shown in Fig. 5.7 and 5.8.

It is interesting that sugar had an entirely different effect on the dry milling process. A significant decrease of the maximum particles size and an increase of the number of fine particles was observed when the standard jet-milled frit was milled in the presence of 0.5% sugar. It is assumed that both the structure of the sugar and the fact that it melts at the relatively low temperature of 160°C, a temperature that is easily achieved during the ball-milling process. This is why sugar is more effective in particle size reduction than, e.g., ethyl cellulose, which has some structural resemblance but does not melt during the ball milling process.

5.3. Morphological Analysis of Ball Milled Samples

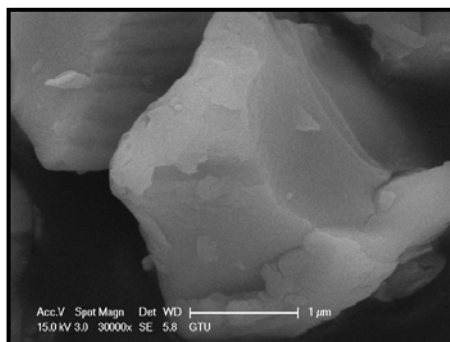


Figure 5.6: High-magnification SEM image of standard jet-milled frit F1.

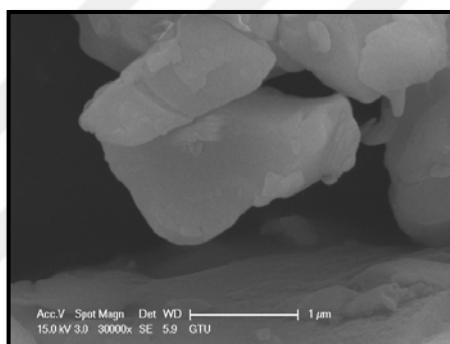


Figure 5.7: High-magnification SEM image of particles milled in the presence of 0.5 % carbon black (F1a).

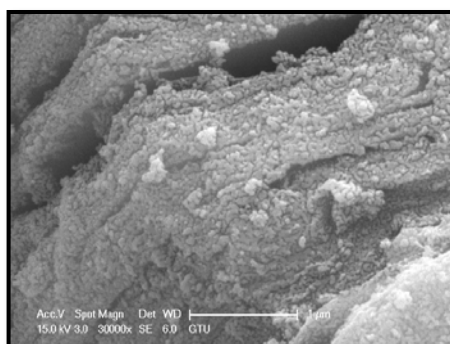


Figure 5.8: High-magnification SEM image of particles milled in the presence of 0.5 % graphene (F1c).

The jet-milled standard frit F1 and frit particles obtained by ball-milling frit F1 in the presence of carbon black have a very similar morphology. The frit particles

obtained by milling in the presence of graphene show a number of cracks across the frit particle and a large number of smaller particles on the surface. It is assumed that that this is either the result of local thermal shock the frit is facing during the milling process or due to the different coefficient of thermal expansion of the graphene coating and the frit. The high kinetic energy of the milling ball is causing scission of bonds within the frit particles when the milling ball hits a frit particle. At the same time some energy is converted into thermal energy. Due to the high thermal conductivity of graphene residing on the surface of the frit part of this thermal energy that is conducted to more remote regions where it may cause cracks.

Cracks can also be produced if the frit particle has a coating with a thermal expansion coefficient that is different from the frit. Frit F1 has a linear coefficient of thermal expansion of $76 \times 10^{-7}/K$ in the temperature range 30-300°C. For graphene a negative expansion coefficient is reported [51]. High tensile stress is thus created inside the frit if graphene-coated frits are heated, as this is the case during ball-milling. The tensile stress in the frit at the frit-graphene interface may lead to cracks in the frit particle.

A strong bond between the graphene coating and the frit must be formed in order to cause severe stress as the result of the thermal expansion mismatch. It is assumed that oxygen groups on the frit surface are involved in this bond. Attempts to find evidence for the bond between graphene and the glass frit by using Fourier Transform Infrared (FT-IR) spectroscopy failed. The C-O stretch vibration of graphene oxide was reported to occur at 1091.47 cm^{-1} [53]. Unfortunately, the FT-IR spectrum of the glass frit shows a very strong absorption in this region by which the much weaker signals of graphene [42] for the C-O stretch of graphene oxide is hidden (see Fig. 5.9).

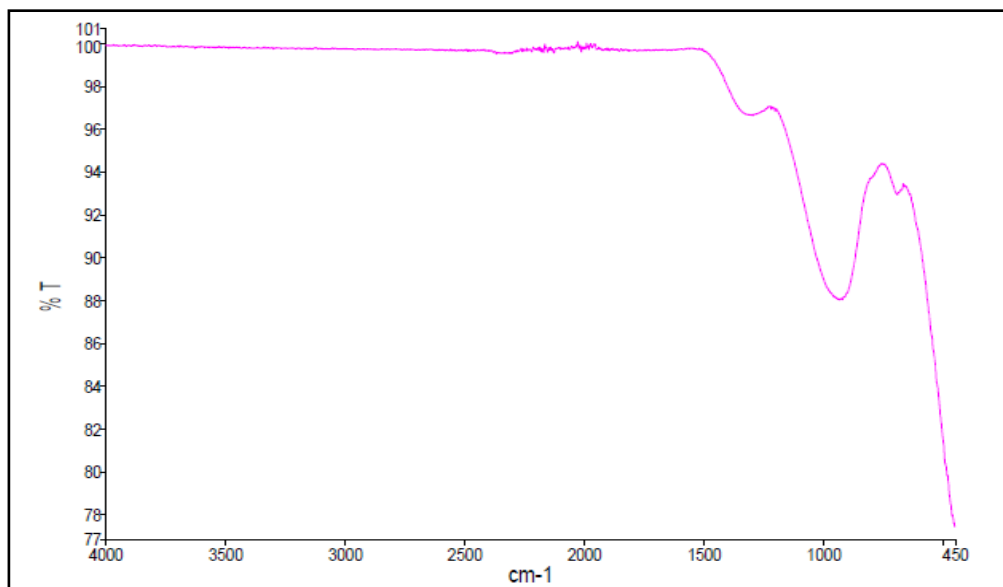


Figure 5.9: FT-IR spectrum of jet-milled frit F1.

Although the presence of reducing additives, except sugar, had no significant effect on the particle size distribution in the milling process they affect the performance of the enamels that have been prepared from these co-milled frits.

5.4. Differential Thermal Analysis of Ball Milled Samples

In order to get a better insight into the thermal processes that take place during the firing of the enamel DTA measurements with a heating rate of 10°C/min were carried out with the frit after milling in the presence of an additive. Although the DTA measurements were carried out in a temperature range up to 1000°C, only the part at temperatures below 700°C is relevant for glass enamels. The DTA trace of the untreated jet-milled frit F1 is shown in Figure 5.10.

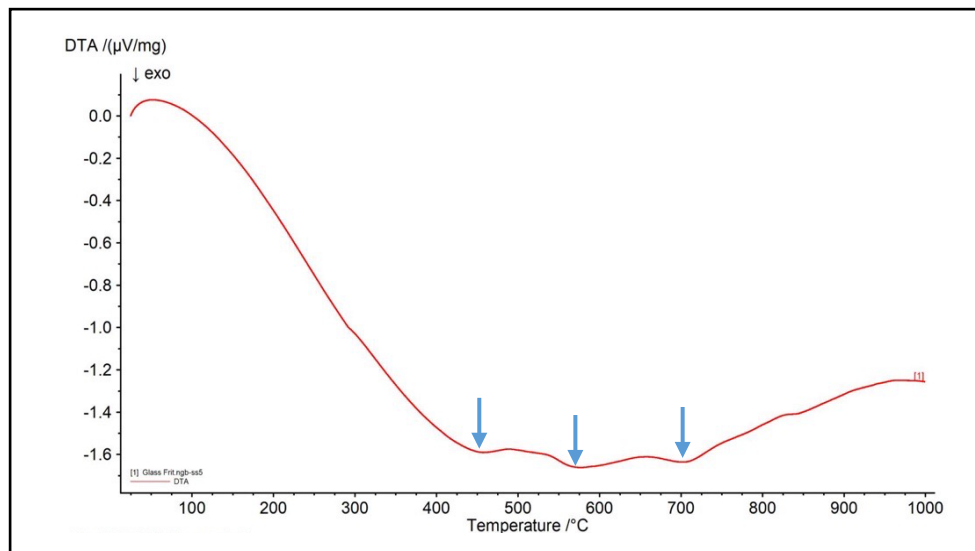


Figure 5.10: DTA curve of jet-milled frit F1.

A slight endothermic reaction until about 100°C was observed. This was observed also in all cases (see Fig. 5.11-16). Most likely this is related to the evaporation of moisture from the frit surface. The glass transition temperature of 458°C and the softening temperature of 520°C are indicated by the first 2 arrows (Fig. 10). Crystallization, which is an exothermic process, occurs at about 700°C. This is well below the maximum temperature reached in a normal firing range of automotive windshields, which is about 580°C to 640°C. This means that spontaneous crystallization is unlikely to appear during the normal firing process of windshields. Possible issues due to the spontaneous formation of crystalline phases with a high CTE, e.g. $(\text{BiO})_2\text{SiO}_3$, are not to be expected. However, if the firing temperature is increased, e.g., if the windshield should get a strongly bent shape, issues cannot be ruled out. More in-depth investigations are required in this case.

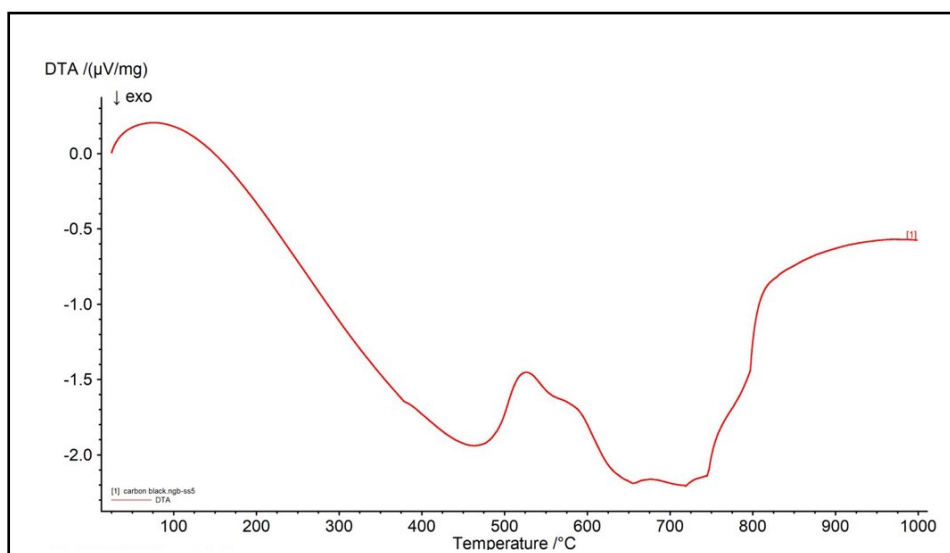


Figure 5.11: DTA curve of frit milled in the presence of carbon black (F1a).

The use of graphite as a milling additive lead to a much weaker reaction with the frit (Fig. 5.12). This is insofar surprising as there is a patent [13] that claims the transformation of graphite into graphene by ball milling.

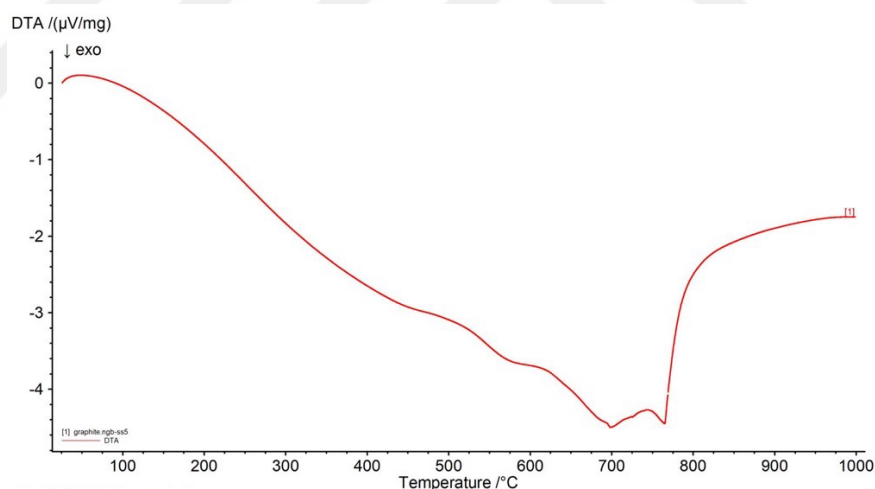


Figure 5.12: DTA curve of the frit milled in the presence of graphite (F1b).

However, the frit milled in the presence of graphene shows a different behavior compared to the aforementioned examples (Fig. 24c). Both endothermic and exothermic processes take place in the temperature region below 700°C. Which is in agreement with the previously reported thermal instability of graphene when heated to temperatures higher than 500°C [45]. A similar behavior was observed in case carbon black was used as milling additive (Fig. 5.11).

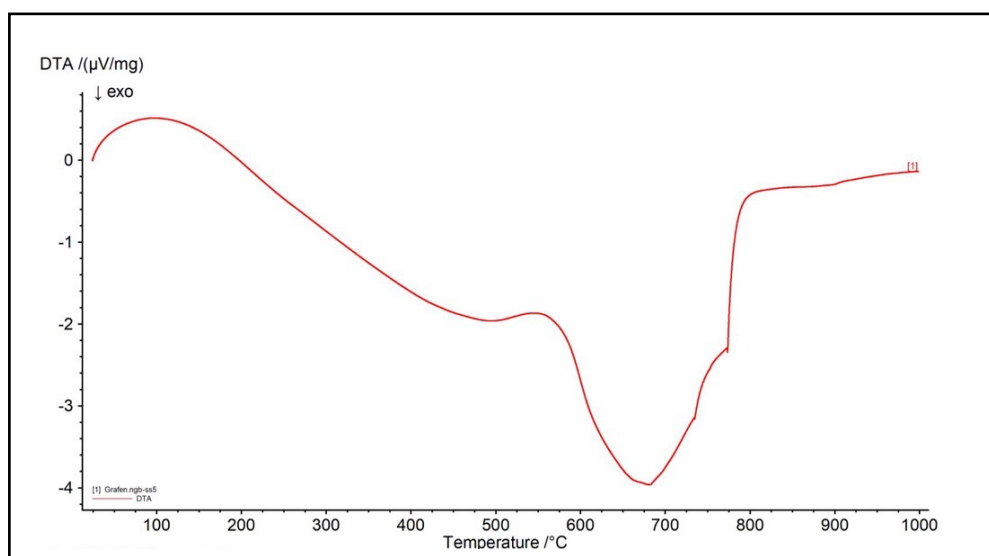


Figure 5.13:DTA curve of the frit milled in the presence of graphene (F1c).

The DTA chart of the frit milled in the presence of molybdenum disulphide also provides evidence for several exothermic and endothermic reaction in the for windshield enamels important temperature range below 700°C, though less pronounced than in case of graphene or carbon black. Overlapping steps in the DTA curve did not allow us to assign the exact temperatures for these events.

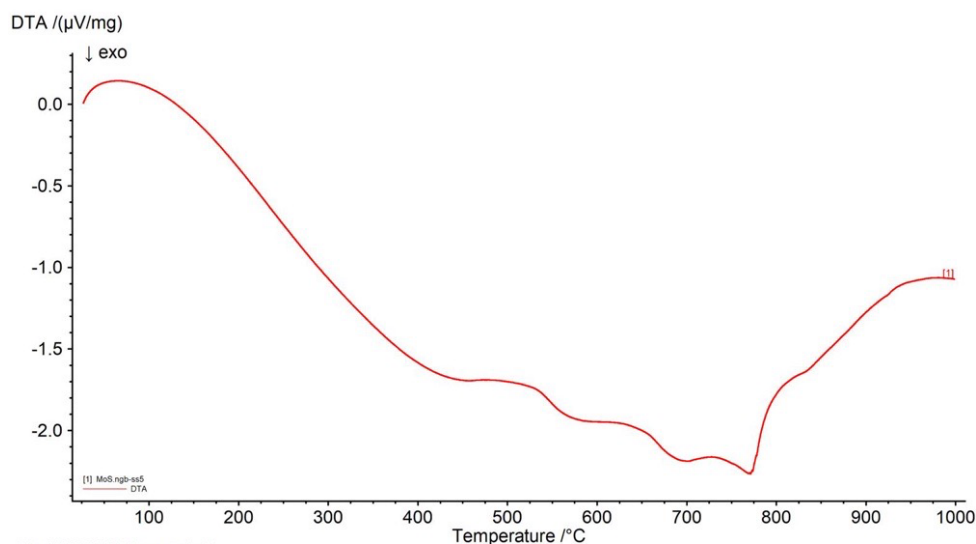


Figure 5.14:DTA curve of the frit milled in the presence of MoS₂ (F1d).

The frit milled in the presence of sugar or ethyl cellulose shows more or less the same behavior in the DTA measurement (see Fig. 5.15 and 5.16). There is no sign for crystallization at a temperature below 700°C.

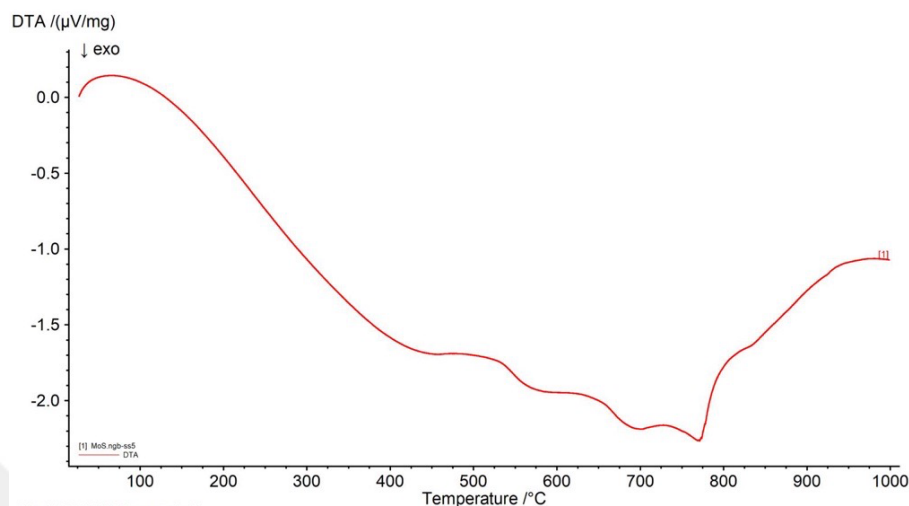


Figure 5.15:DTA curve of the frit milled in the presence of ethyl cellulose (F1e).

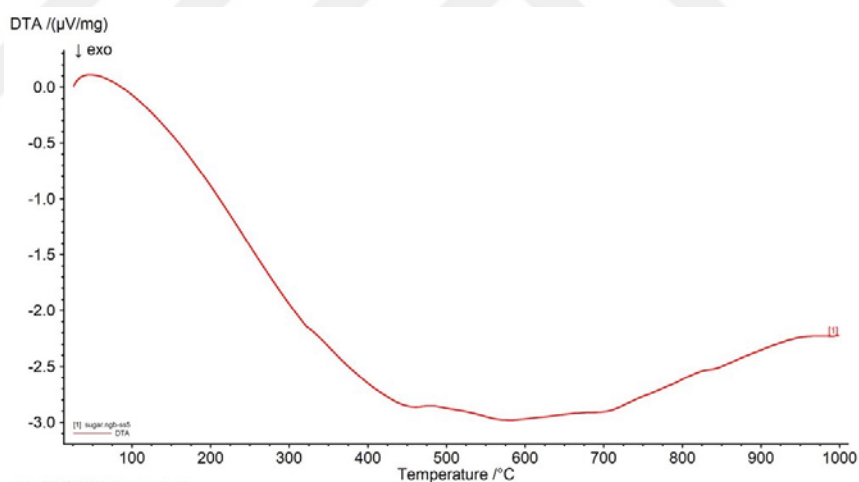


Figure 5.16:DTA curve of the frit milled in the presence of sugar (F1f).

5.5. Color Measurement of Prepared Glass Enamels

The results of the measurements of the reverse color, i.e., the color one can see through the glass, for the pastes with and without silver overprint fired at a temperature of 600°C for 5 minutes and the gloss measured on the surface of the fired enamel are summarized in Tables 5.3-5.9. The data for the standard enamel based on the jet-milled frit F1 are shown in Table 5.9 for comparison.

Table 5.3: Color values and gloss for the enamel based on the frit milled in the presence of carbon black (GE1).

	F1 + Carbon black (no Ag overprint)	F1 + Carbon black (with Ag overprint)	ΔL
L	11	13.07	2.07
a	-0.65	-0.58	
b	-1.61	-1.06	
Gloss	2.5		

Table 5.4: Color values and gloss for the enamel based on the frit milled in the presence of graphite (GE2).

	F1 + Graphite (no Ag overprint)	F1 + Graphite (with Ag overprint)	ΔL
L	5.96	9.46	3.50
a	-0.2	-0.3	
b	-1.54	-1.89	
Gloss	3.1		

Table 5.5: Color values and gloss for the enamel based on the frit milled in the presence of graphene (GE3).

	F1 + Graphene (no Ag overprint)	F1 + Graphene (with Ag overprint)	ΔL
L	11.96	13.74	1.78
a	-0.88	-0.72	
b	-1.81	-1.69	
Gloss	2.4		

Table 5.6: Color values and gloss for the enamel based on the frit milled in the presence of MoS₂ (GE4).

	F1 + MoS₂ (no Ag overprint)	F1 + MoS₂ (with Ag overprint)	ΔL
L	6.07	5.77	-0.3
a	-0.24	-0.06	
b	-0.17	-0.92	
Gloss	78.7		

Table 5.7: Color values and gloss for the enamel based on the frit milled in the presence of ethyl cellulose (GE5).

	F1 + Ethyl cellulose (no Ag overprint)	F1 + Ethyl cellulose (with Ag overprint)	ΔL
L	4.13	5.79	-1.66
a	0	-0.07	
b	-0.7	-1.54	
Gloss	54.3		

Table 5.8: Color values and gloss for the enamel based on the frit milled in the presence of sugar (GE6).

	F1 + sugar (no Ag overprint)	F1 + sugar (with Ag overprint)	ΔL
L	3.96	2.85	-1.11
a	-0.13	-0.07	
b	-0.86	-1.04	
Gloss	67.6		

Table 5.9: Color values and gloss for the enamel based on the standard jet-milled frit (GE0).

	F1 std (no Ag overprint)	F1 std (with Ag overprint)	ΔL
L	3.53	5.37	1.84
a	0.16	0.02	
b	-0.25	-0.3	
Gloss	90		

When black glass enamels are printed onto glass and then dried in order to evaporate the solvents of the medium the reverse color is grey. Upon heating to about 500 to 550°C the resins and polymers are burnt off and the frit starts to soften. The reverse color is still grey since the frit particles at the glass-enamel interface scatter the incident light. If the temperature is further increased the frit starts to flow and forms a tight bond with the glass surface. The light scattering is strongly reduced, and the reverse color is becoming darker. Depending on the type of glass frit and the amount and type of black pigment the color L value may either asymptotically reach its minimum value or starts to increase again. The latter is the case if the enamel is either crystallizing or the pigments are destroyed, which happens e.g., in case of copper (II) chromite pigments in a reducing environment. Crystals formed near the glass-enamel interface may also scatter the light, and the enamel thus appears grey again.

In case of an enamel based on the standard frit F1 and CuCr_2O_4 black pigment in the ratio 75:25 the minimum color L value is reached in the temperature range from about 590°C to 620°C. The exact temperature where the color reaches its minimum depends on a number of factors, in particular on the particle size and the type of medium. If the firing temperature is further increased the reverse color of the enamel becomes grey again. Although the DTA showed that the pure jet-milled frit does not crystallize in the temperature range below 700°C (see Fig. 24), the presence of a pigment with a high heat absorption may lead to different results.

The change of the color L value for the standard enamel comprising 75 parts by weight frit F1 and 25 parts CuCr_2O_4 as a function of the firing temperature is shown in Fig. 5.10.

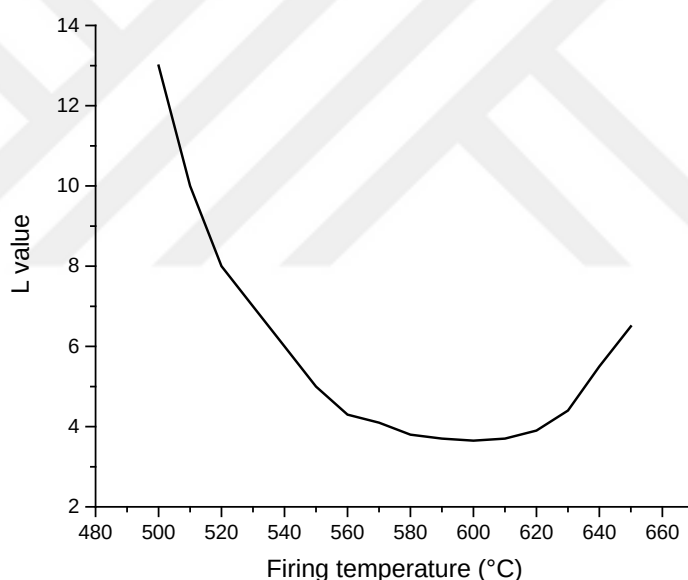


Figure 5.17: Color L value of enamel made from standard frit F1 measured at different firing temperatures.

The gloss is measured on the surface of the enamel. Like the color, it is also dependent on the firing temperature. For non-crystallizing enamels the gloss usually increases with increasing firing temperature. In case of crystallizing enamels, the gloss remains constant or is even reduced with increasing firing temperature. However, the gloss is not only determined by the fusibility of the frit and its ability to crystallize. The surface roughness also has an effect on the gloss measurement. If the enamel paste

contains organic components that burn out late craters on the enamel surface may be formed, and the gloss values are low. Therefore, a matt surface, even at high firing temperatures, is not necessarily linked to surface crystallization. The gloss on its own has no importance for automotive enamel. However, since the gloss, if it is linked to crystallization, shows a correlation with the anti-stick properties, gloss measurements are a helpful tool for the assessment of anti-stick properties. Enamels with high gloss usually stick in the press bending process whereas enamels with low gloss show good anti-stick properties, provided the low gloss is really the result of crystallization and not due to high surface roughness.

The highest gloss was measured for the enamel that has been made from amorphous structure, jet-milled frit. This is an indication that no or only little crystallization takes place when this enamel is heated. The color under the silver overprint is less dark than the non-overprinted parts. The color difference ΔL of 1.84 is quite high. The silver overprint is thus visible with the naked eye. In other words, the enamel does not hide the silver overprint. Since the silver layer reflects more heat than the uncoated black enamel the enamel under the silver overprint gets less heat than the non-overprinted enamel, and the black color is not yet fully developed, i.e., it is still more grey.

More or less the same behavior for the color L value is found for enamels based on the frit milled in the presence of ethyl cellulose. This is not too surprising bearing in mind that ethyl cellulose is a component used in many automotive screen-printing mediums. The color L value for both the silver-overprinted and the non-overprinted part are a bit higher than for the standard enamel. Apparently, the presence of ethyl cellulose leads to a slight delay of the temperature in the enamel. This is also in line with the lower gloss of the enamel, which is lower than for the standard enamel. The ΔL value is similar to the standard enamel and indicates the lack of silver hiding.

A different behavior was observed for the enamels containing carbon black, graphite and graphene on the one hand and molybdenum disulphide on the other hand.

The color L value of the enamel based on a frit ball-milled together with molybdenum disulphide is very similar for the area with and without silver overprint. The ΔL value is only -0.3. The silver overprint is hidden since the human eye cannot distinguish between this low a color difference. It is interesting that the L value for the area without silver overprint is slightly higher than for the overprinted area. This could be due to either some crystallization or to partial reduction of the black pigment.

5.6. Crystal Structure Characterization of Ball Milled Frits

The gloss value is significantly lower than for the standard enamel but still relatively high, especially when compared to enamels that are based on frits milled in the presence of carbon black, graphite and graphene, respectively.

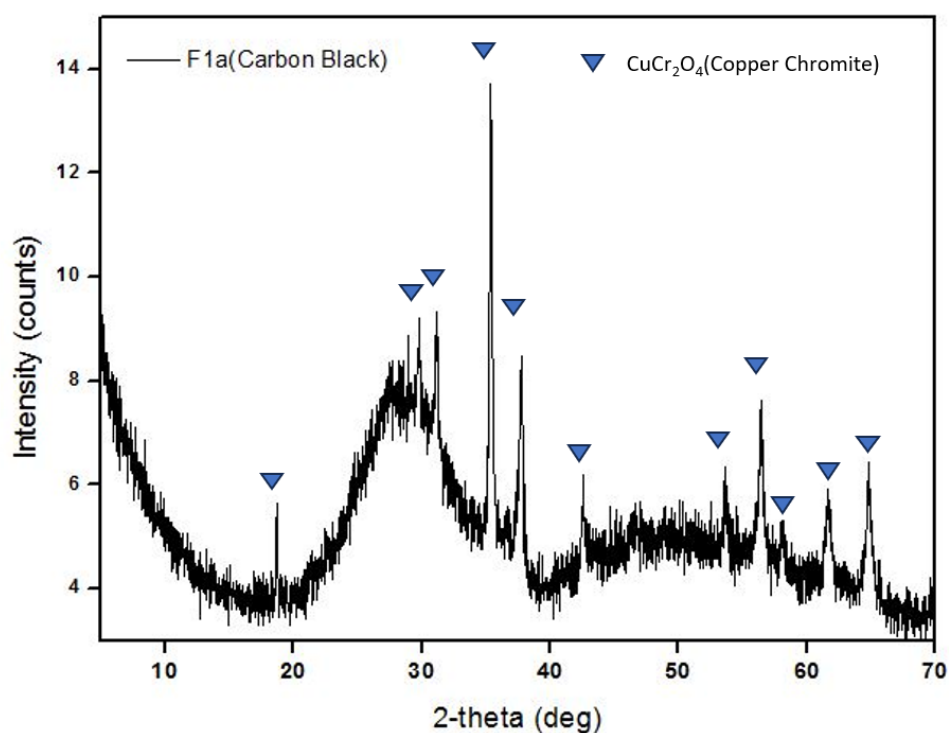


Figure 5.18: XRD of fired enamel based on frit F1 co-milled with carbon black (F1a).

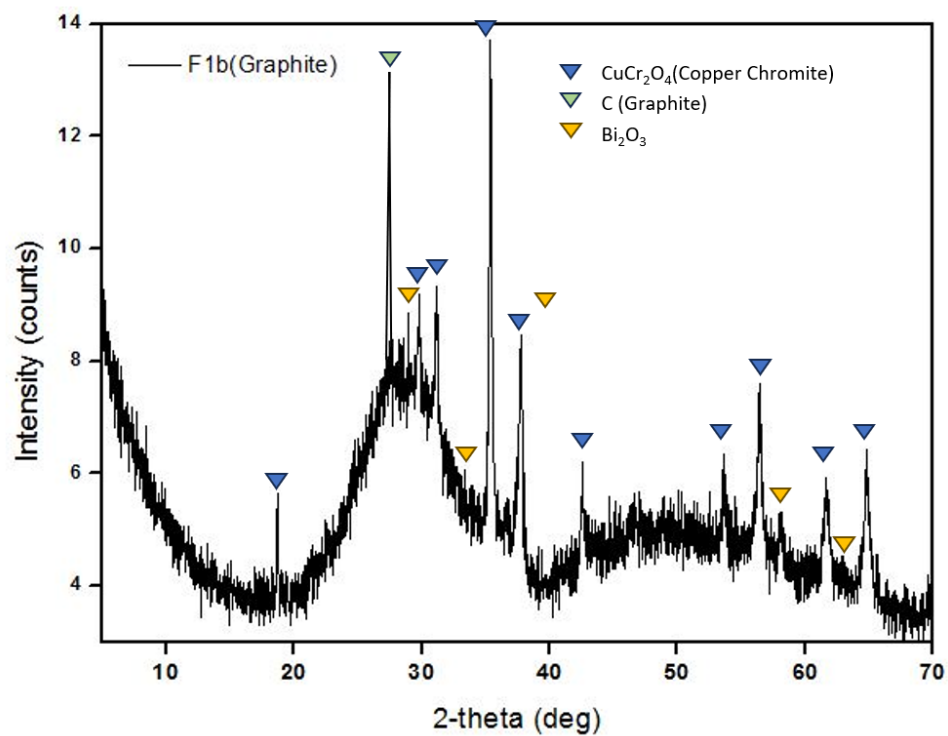


Figure 5.19: XRD of fired enamel based on frit F1 co-milled with graphite (F1b).

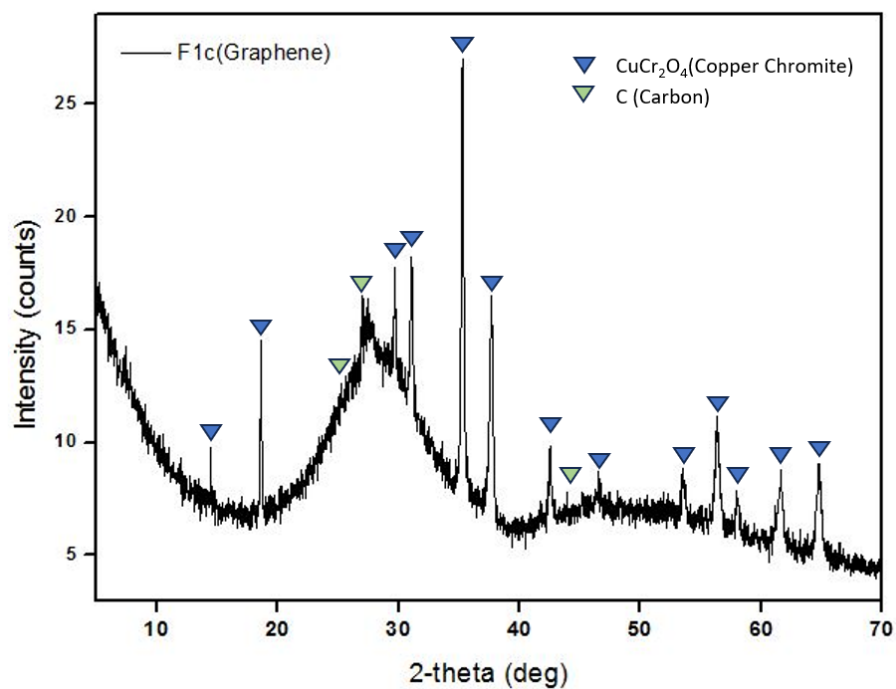


Figure 5.20: XRD of fired enamel based on frit F1 co-milled with graphene (F1c).

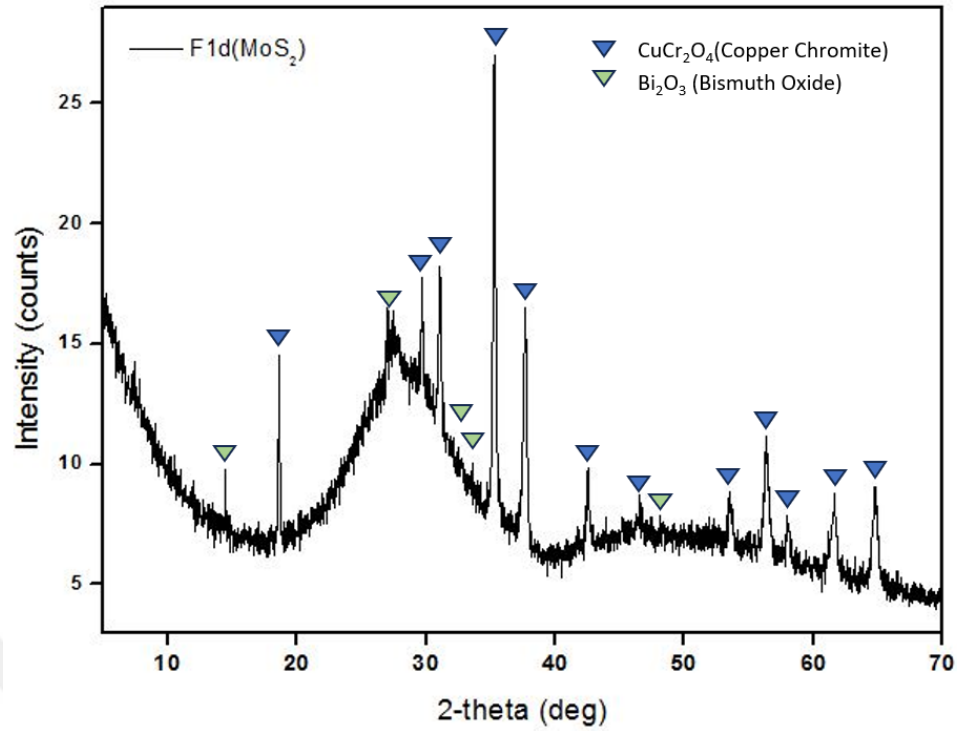
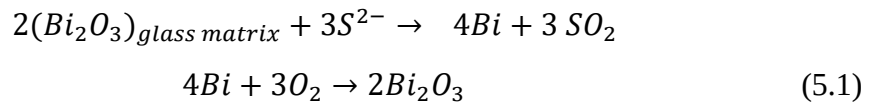


Figure 5.21: XRD of fired enamel based of frit F1 ball-milled in the presence of MoS₂ (F1d).

The X-ray powder diffraction chart (XRD) of the enamel recorded after firing at 600°C is shown in Fig. 5.11. As expected, the most intensive signals can be assigned to the pigment (CuCr₂O₄). In addition, there are also signals of low intensity that can be assigned to crystalline Bi₂O₃ and to partly reduced bismuth oxide. The most likely explanation for the occurrence of these signals is that Bismuth on the surface of the glass frit is reduced by sulphide ions during the firing process, which is then re-oxidized by air to give Bi₂O₃:



The reduction of bismuth oxide on the glass surface to colloidal bismuth retards the flow of the glass frit. The gloss after firing will thus be lower than in case of the standard frit.

The lowest gloss values were measured for enamel that are made from frits co-milled with carbon black, graphite, and graphene, respectively.

Enamels made from the frit co-milled with carbon black, graphite and graphene respectively give the lowest gloss upon firing at 600°C. If this was due to crystallization XRD should indicate the formation of new crystalline phases. However, the only signals with significant intensities can be assigned to the CuCr_2O_4 pigment (see Fig. 5.12-14).

Obviously, the low gloss is not the result of enhanced crystallization. It is assumed, that the low gloss is related to the formation of craters on the surface of the enamel. Craters can be formed if gases escape from the enamel after the frit in the enamel has begun to flow. Closer inspection of the enamel surface under an optical microscope has indeed confirmed that craters are formed. Due to the craters the surface roughness is higher and, consequently, the gloss is lower. This is in line with the high color L values that have been measured in these cases. Most likely, the carbon-based additives react with the pigment at higher temperatures as shown in the following equation:

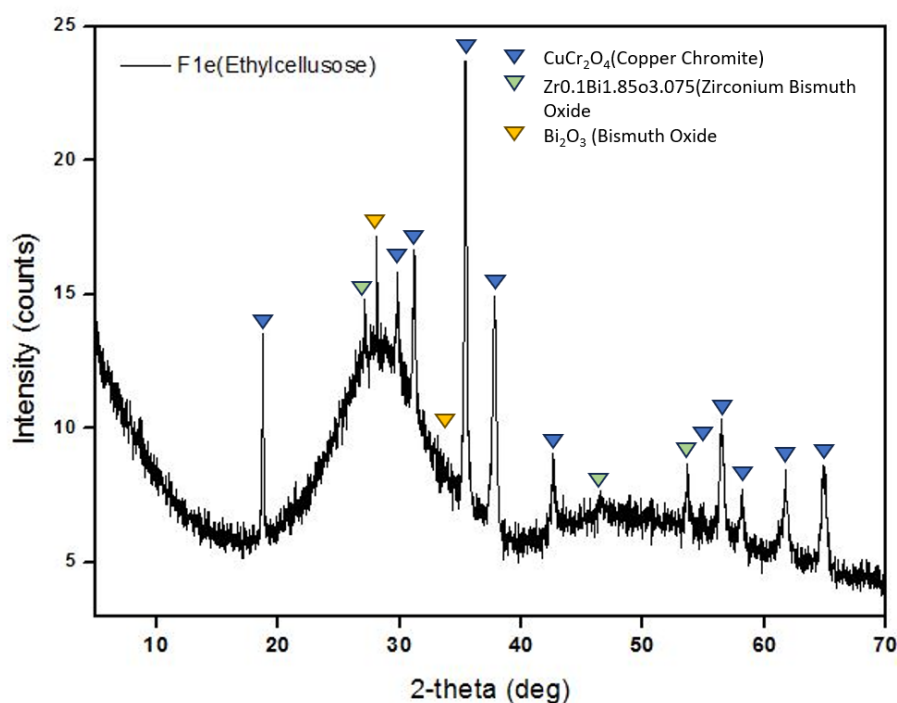


Figure 5.22: XRD of fired enamel based on frit F1 co-milled with ethyl cellulose (F1e) (with possible assignments).

The XRD of the fired enamel made from frit F1 co-milled with ethyl cellulose exhibits strong signals that can be assigned to the pigment. In addition, intense signals were found for $2\theta = 28.139^\circ$ and $2\theta = 27.135^\circ$ (Fig.15). Most likely, the signal at $2\theta = 28.139^\circ$ can be assigned to bismuth borate. No unambiguous assignment is possible for the signal at $2\theta = 27.135^\circ$. Both bismuth oxide and zirconium bismuth oxide show signals in this region. Considering the low concentration of zirconium oxide and the high concentration of bismuth oxide in the frit the signal is tentatively assigned to bismuth oxide, which may be formed by a similar mechanism as discussed for MoS_2 (see above).



6. CONCLUSIONS

In summary, it was found that graphene and MoS₂ have an accelerating effect on the milling process. Furthermore, the sugar (saccharose) that has a beneficial effect on the dry milling process. Due to the presence of hydroxyl groups and relatively low melting point of 160°C it can interact with the surface of the frit and, thus, prevent re-agglomeration during the milling process. These findings are worth to be explored further in another context. As the result of the large difference of thermal expansion of the frit and graphene cracks in the frit have been observed. XRD has provided some evidence for the redox process between the frit and the additives. However, except for molybdenum disulphide reduction of the bismuth frit was not sufficient to create a reducing environment in the frit that was able to stop silver migration. At a level of 0.5% graphene has a very similar behavior like other carbon-based additives except accelerating milling. Addition of sugar to the dry ball-milling effect had a surprising effect of increasing the milling efficiency although this is assumed to be due to the specific structure of having hydroxy groups that may interact with the frit surface rather than being a carbon-based molecule. Further exploration of this effect, which is outside the scope of this thesis, would certainly be worthwhile. In conclusion, nano sized MoS₂ can be studied both accelerating milling and hiding silver paste property in further studies.

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