

Introduction

Ferro GmbH, Glass Systems, can draw on decades of experience in the production and application of ceramic colours, media and silver pastes.

To secure our high share of the market in the future, our research and development in recent years has focussed on extending our range of high performance products.

Our objective is not only to satisfy current customer needs but to market products that already meet future standards for environmental compatibility and technological challenges. An excellent example was the introduction of the New Generation Antistick System in early 2006. This system passes the high chemical durability requirements which became standard in 2008.

With this brochure, we want to give an overview of our wide range of automotive glass enamels for the coating of tempered and laminated safety glass.

The different products are grouped by application:

- Automotive glass enamels for:
- **laminated safety glass**
sag bending and press bending
surface No. 2 printings

 - **tempered safety glass**
side and rear windows
sunroofs

This brochure also includes a selection of screen printing media for use with automotive glass. In the last few years, we have successfully introduced innovative and environmentally compatible products from this area, too.

Edition 09/2010

This brochure presents a representative selection of products for specific applications. For optimum selection of paste systems for your individual requirements, our customer service team will be pleased to advise.

Contact us at: Ferro GmbH
 Glass Systems
 Gutleutstrasse 215
 D-60327 Frankfurt am Main
 Telephone +49 (0) 69 271 16 - 0
 Telefax +49 (0) 69 271 16 - 379

We can offer package solutions tailored to your specific needs. Benefit from our experience and our global presence. We are your partner – WORLDWIDE.

The information and statements contained herein are provided free of charge. They are believed to be accurate at the time of publication, but Ferro GmbH makes no warranty with respect thereto, including but not limited to any results to be obtained or the infringement of any proprietary rights. Use or application of such information or statements is at user's sole discretion, without any liability on the part of Ferro GmbH. Nothing herein shall be construed as a licence of our recommendation for use which infringes upon any proprietary rights. All sales are subject to Ferro GmbH General Conditions of Sale and Delivery.

General Information

Composition of Ceramic Automotive Glass Enamels

Ceramic automotive glass colours are glass enamels that fire on to the glass during the bending process above 560 °C, forming a glassy inorganic layer. For screen printing, these consist of an inorganic component, the colour powder and an organic component, the medium.

The content of the colour powder in a screen printing paste varies between 75 and 86 wt. percent. The colour powder is a ground ceramic vitrifiable colour composed of glass frits, stain and any additives required.

As shown in the table below, the components of the colour powder largely determine the properties of the fired colour.

Component	Chemical composition	Function
glass frit 60 – 85 %	glass flux with Bi, B, Zn, Si oxides as the main components	forms the matrix of the enamel, strength, chem. resistance, melt-on behaviour; firing range
stain 15 – 40 %	oxides with Cu, Co, Fe, Ni, Mn, Cr	colour shade and light transmission
additives 0 – 15 %	oxides, sulphides, metal compounds	antistick effect, silver-non-bleed-through

The medium used determines the drying mechanism after screen printing. A differentiation is made between infrared drying (IR) and ultraviolet curing (UV) systems. The following table shows the differences between the chemical compositions and the drying / curing mechanism of the two systems.

Type	Chemical composition	Drying / Curing
IR	oils and organic resins in combination with solvents	physical drying by evaporation of the solvents, recommended glass temp. 80 – 150 °C
UV	monomers and acrylate compounds	photoinduced cross-linking by UV radiation; no evaporation of solvents, no heat required

The medium has a crucial influence on the screen printing properties of the paste and the adhesion of the dried enamels after they have been printed on the glass. The medium is also partly responsible for the storage stability of the paste.

Selected Requirements for Modern Automotive Glass Enamels

Associated with the development of automotive glass from simple protection of driver and passengers against wind and rain to multifunctional glass used as a stability component in the body of the vehicle, the requirements of the glass and car manufacturers for ceramic screen printing have steadily increased. While around 30 years ago, it was sufficient for the glass enamel to be “simply black”, today there is a growing demand for multifunctional automotive glass enamels. In the following, the higher requirements for ceramic screen printing are briefly explained:

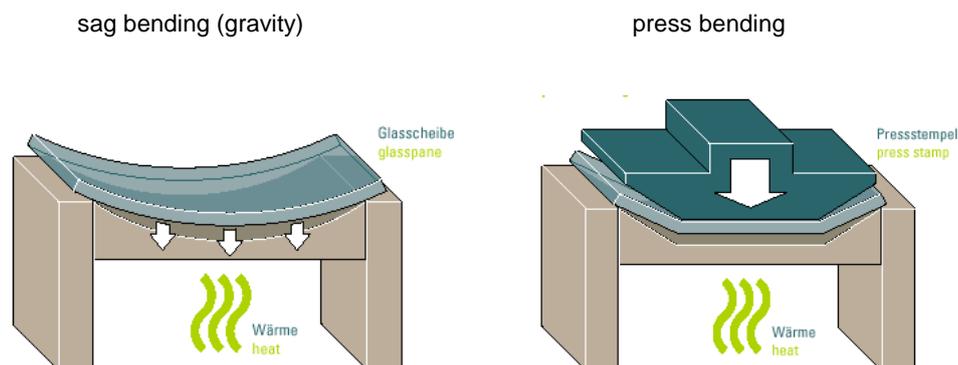
a) Heavy metal free composition

New legislation on environment protection, safety at work and the labelling of packaging for transport and handling in Europe were leading to complete prohibition on the use of lead, cadmium, hexavalent chromium etc.

Today, nearly all of our customers expect enamels to be free of toxic heavy metals. New types of glass panels are decorated almost exclusively with heavy metal free automotive glass enamels. Zn, Bi or Zn/Bi systems are used.

b) Antistick properties

The further development of glass bending technology from sag to press bending has enabled the production of glass panels with increasingly complex curvature and faster firing cycles (see schematic).



In press bending processes, the ceramic automotive glass enamel printed on the top surface of the glass comes into contact with the press ram during the forming process.

In this process, the melted enamel must withstand the pressure applied. The enamel coating should not be damaged and no traces of enamel should be left on the press cloth. The enamel should not stick to the press ram, as otherwise the softened glass deforms when the press ram is lifted away. The resulting deviations in shape are not tolerable. These antistick properties can be achieved by varying the product composition accordingly:

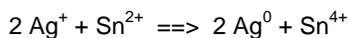
Either highly viscous systems with high surface tension, additive systems or reactive and crystallising systems are used. The antistick effects differ depending on the system. Ferro supplies automotive glass enamels from all three systems.

c) Silver-non-bleed-through

Car rear windows are generally printed with heat conductors from conductive silver pastes, which are fired together with the ceramic colour.

During firing, the silver ions (Ag^+) migrate from the overprinted silver layer through the not completely molten ceramic colour to the surface of the float glass. This migration is the result of ionic exchange processes, promoted by the capillary forces of the porous automotive glass enamel.

The reduction of the silver ions by the polyvalent tin in the surface of the float glass leads to the formation of colloidal silver complexes, which tint the glass a yellowish brown colour:



The bleed through of the silver busbars can be avoided by preventing diffusion of the silver ions and reducing them again within the enamel layer. Ferro supplies automotive glass enamels based on a patented process to achieve exactly this effect.

d) High opacity

There is a tendency that automotive and glass manufacturers more and more specify visible light transmission values of below 0.1 % for the printed glass. The optical density of the enamel depends primarily on the thickness and density of the fired layer.

Ensuring reproducible values is not just down to the colour paste supplier (e.g. with an appropriate pasting ratio, rheology, special high loading media), but is also partly the responsibility of the glass manufacturer as the printed layer thickness (wet film thickness) – and ultimately the thickness of the fired layer – is largely influenced by the printing viscosity, screen mesh, screen coating and the machine settings.

e) Chemical resistance / hydrolytic resistance

The standards for chemical resistance vary very widely around the world. The approval tests range from three minute exposure to hydrochloric acid (3 % HCl) at room temperature to a 140 hour sulphuric acid attack at 80°C. Depending on the region and nature of application, very different specifications are issued. In the last two years requirement on chemical resistance grew enormously. In 2008 the sulphuric acid test at 80 °C became standard for tempered glasses. Ferro can supply enamels to meet those specific requirements.

In the following section of the product information, the chemical resistance of the enamels is evaluated based on the following nomenclature:

Test method:	The sample is exposed during 5 min at room temperature with 3 % hydrochloric acid	
Classification:	Grade 1 -	no attack
	Grade 2 -	iridescent surface or just noticeable loss of gloss
	Grade 3 -	obvious matting without strong effect on colour respective surface changes
	Grade 4 -	strongly affected colour respective surface changes, not scratch resistant
	Grade 5 -	glass enamel disappeared, the glass substrate is free or partly free

On request, we can provide you with details on the performance of our various enamels in other test conditions, e.g. the sulphuric acid test at 80 °C.

Prospects

The requirements for the automotive glass enamels will continue to increase in future. Bending of the automotive glass panels will become increasingly complex, such that higher press forces during shaping can be expected. Additionally the firing cycles become faster, combined with lower temperatures to further increase the optical quality of the bended glass.

The standard for the opacity of the screen printed enamel will rise further, to improve the long-term UV protection of the adhesive - especially for primerless glueing application.

Finally we expect that the chemical resistance will remain as one of the key requirement around the world. As a manufacturer of ceramic colours, Ferro GmbH, Glass Systems Division, will in future be confronted by greater challenges requiring the elaboration of new solutions. We will face these challenges. As your partner – WORLDWIDE.

Automotive Glass Enamels for Laminated Glass

Heavy metal free enamels for Sag Bending

The main requirements are a wide firing range, gloss, good opacity and maximum blackness of the colour shade. The firing range is generally between 570 °C and 650 °C (laboratory values). The requirements for chemical resistance vary from low to very high.

We offer three product families for the standard application of sag bending process (surface No. 4).

Product No.	Frit system	Colour	Firing range (laboratory values)	Remarks
14 303	Bi-Si-B-Alkali	black, glossy	565 – 640 °C 4 – 8 min	excellent chem. resistance – passes 72 hrs Toyota test; good opacity, wide firing range; wet fire possible
14 300	Bi-Si-B-Alkali	black, glossy	560 – 630 °C 4 – 8 min	very good chemical resistance very good opacity wet fire possible lower melting
14 279	Bi-Si-B-Alkali	black, glossy	570 – 640 °C 4 – 8 min	very good chemical resistance very good opacity wet fire possible higher melting
14 301	Zn-based Bi-System	black, semi-matt	570 – 640 °C 4 – 8 min	good chemical resistance good opacity wide firing range wet fire possible

The new enamel 14 303 provides an excellent chemical durability and passes 72 hrs Toyota test (lab conditions).

The high bismuth containing enamels 14 300 and 14 279 fulfil highest requirements with regard to chemical resistance, colour shade, opacity and firing range.

14 301 is reduced in bismuth content and offer best value for all standard applications.

Heavy Metal Free Enamels for Press Bending

Press bending is not very common in the production of LSG in Europe. Particularly important requirements are very good breaking strength, fast maturing and good antistick properties. The firing range is between 580 °C and 620 °C (laboratory values).

Variations to adjust the firing range are available.

Product No.	Frit system	Colour	Firing range (laboratory values)	Remarks
14 259	Bi-Si-B-Zn-Alkali	black, matt	590 – 630 °C 3,5 min	chem. resistance 2

Surface No. 2 Enamels for Direct-Firing and Pre-Firing

These enamels are applied to surface 2 (sometimes surface 3) of the laminate to optically hide antenna, heat conducting and sensor connections in the increasingly complex composition of laminated glasses. They require a carefully co-ordinated colour powder-organic-system, special drying conditions after printing and special adaptation to the specific bending process.

Product No.	Frit system	Colour	Remarks
based on TDF 9185	Bi-Zn-B	black, matt	Direct-Firing drying > 130 °C necessary, no silver-hiding possible
14 330	Bi-Zn-System	black, matt	Pre-Firing wide firing range 570 – 620 °C silver-hiding possible higher melting
14 331	Bi-Zn-System	black, matt	Pre-Firing wide firing range 560 – 610 °C silver-hiding possible lower melting

Please contact our technical service to select the best product for your process. We can offer tailor-made products to existing product lines.

Automotive Glass Enamels for Tempered Glass

Heavy Metal Free Enamels for Side Windows

The requirements for these enamels include good opacity, maximum blackness of the colour shade and a wide firing range as well as good silver-hiding properties for specific applications (e.g. antennas and alarm circuits).

Product No.	Frit system	Colour	Firing range (laboratory value)	Remarks
14 622	No Bi Si-Zn-B- Alkali	black, semi-matt	660 °C 3,5 – 4,5 min	Non-Bismuth System chem. resistance 3
14 242	Si-Bi-Zn-B- Alkali	high blackness semi-matt	660 °C 3,5 – 4 min	chem. resistance 3 intermixable with 14 233
14 233	Si-Bi-Zn-B- Alkali	high blackness semi-matt	660 °C 4 – 4,5 min	chem. resistance 3 intermixable with 14 242
14 251	Si-Bi-Ti-B- Zn-Alkali	black, semi-matt	660 °C 3,5 – 4,5 min	chem. resistance 1 - 2 intermixable with 14 252
14 252	Si-Bi-Ti-B- Zn-Alkali	black, semi-matt	660 °C 4 – 5 min	chem. resistance 1 - 2 intermixable with 14 251

Heavy Metal Free Enamels for Rear Windows

The requirements for automotive glass enamels used on rear windows increased constantly over the last few years – especially with regard to antistick, busbar hiding, chemical durability and opacity.

The Ferro “New Generation” Antistick System fulfils and even surpasses the current specifications of the automakers and glass producers. In automotive glass fabrication processes, the new enamel series provides performance at faster cycle times and lower firing temperatures.

The Ferro “New Generation” Antistick System:

Product No.	Temperature range for application	Firing range (laboratory values)	Remarks
14 500	very low – low	650 °C / 3,0 - 4,0 min	<p>The “New Generation 14 500 family”</p> <p>Frit system: Si-Bi-Ti-B-Zn-Alkali</p> <p>excellent antistick and busbar hiding, excellent chemical durability, very good colour shade, very good opacity, very wide firing range</p> <p>intermixable system</p>
14 501	very low – medium	660 °C / 3,0 - 4,0 min	
14 502	low – high	660 °C / 3,5 - 4,5 min	
14 503	medium – high	660 °C / 4,0 - 5,0 min	
14 509	very low – medium	660 °C / 3,0 - 4,0 min	<p>The “New Generation 14 510 family” designed for Outside Pressbend Furnaces</p> <p>Frit system: Si-Bi-Ti-B-Zn-Alkali</p> <p>less crystallizing, deep black colour shade, excellent chemical durability, excellent busbar hiding, very good opacity, very wide firing range</p> <p>intermixable system</p>
14 510	low – high	660 °C / 3,5 - 4,5 min	
14 511	medium – high	660 °C / 4,0 - 5,0 min	

The Ferro Standard Antistick System:

Product No.	Temperature range for application	Firing range (laboratory values)	Remarks
14 260	low	660 °C / 3,0 - 3,5 min	The "14 25x family"
14 251	low – medium	660 °C / 3,5 - 4,0 min	Frit system: Si-Bi-Ti-B-Zn-Alkali good antistick, very good busbar hiding, very good chemical durability, very good colour shade, good opacity; intermixable system
14 252	medium – high	660 °C / 4,0 - 4,5 min	
14 253	high	660 °C / 4,5 - 5,0 min	

Automotive Glass Enamels for Sunroofs

For sunroof enamels it is particularly important to pass the ball drop test in accordance with the German industrial standard DIN 52306 (height of fall 3 m). This means that the enamels must not weaken the breaking strength of the glass. Ferro offers different lead containing and heavy metal free enamels for this specific application.

Please contact our customer service team who will recommend the best products for your requirements.

Media

The automotive glass enamels described can be supplied as infrared drying or ultraviolet curing pastes (except for the special enamels for surface No. 2 printing).

The solid concentrations specified for the ready-to-print pastes (=SC, specified in wt-percent) are empirical values and depend to a large extent on the properties of the colour powder used.

We specially recommend the use of the following media for screen printing:

Screen Printing Media IR-Oil Based

Data/Media	80 1018	80 007F	C80-1623
Flash point / °C	75	95	77
Density / 23 °C	0,93	0,94	0,88
Viscosity / mPa*s at 23 °C and D = 200 1/s	270	100	120
Solid content of lead free pastes	78 – 81	80 – 85	81 – 86
Thinner	80 063	80 007F	C80-1623
Cleaner	80 452	80 452	80 452

Due to optimum selection of solvents with slow evaporation rates, medium 80 007F guarantees long lasting on the screen.

With medium 80 007F and C80 - 1623, particularly high loading of the enamel pastes are possible. This allows extremely good opacity and improved busbar hiding by keeping very good printing properties. Both media are highly compatible with Ferro conductive silver pastes.

The universal screen printing medium 80 1018 features a medium drying rate and favourable firing behaviour. It allows high loading of the enamel paste (good opacity) and is highly compatible with Ferro conductive silver pastes. Multilayer printing is possible.

Screen Printing Media IR – Water-Soluble

Data/Media	80 1026	80 8003	C80-1565
Flash point / °C	> 100	> 100	> 100
Density / 23 °C	0,97	1,01	1,01
Viscosity / mPa*s at 23 °C and D = 200 1/s	340	210	220
Solid content of lead free pastes	77 – 80	77 – 80	77 – 80
Thinner	80 868 80 890	80 868	80 868
Cleaner	Water	Water	Water

These media feature water soluble solvents which facilitate both the use of the products and cleaning of the application tools.

They are intermixable without any problem.

The slow drying medium C80-1565 and the faster drying 80 8003 are also compatible with Ferro conductive silver pastes (oil and water based) and therefore especially suitable for side and rear windows.

Screen Printing Media UV

Data/Media	80 8004	80 8015	80 887/80 1708
Flash point / °C	> 100	> 100	> 100
Density / 23 °C	1,06	1,06	1,08
Viscosity / mPa*s at 23 °C and D = 200 1/s	220	235	150
Solid content lead free pastes	77 – 80	77 – 81	77 – 80
Reactivity	High	medium	medium
Thinner	C80-1709	80 8016	C80-1709
Cleaner	80 452	80 452	80 452

UV enamels cure after printing as the result of a photo-initiated cross linking reaction. No solvents are released in this process. Costly heating and cooling of the glass are not necessary.

80 8004, the new 80 8015 as well as the frequently applied blend of media 80 1708 and 80 887 are highly suitable for overprinting with Ferro conductive silver pastes.

In addition medium 80 8004 shows low sensitivity to humidity while 80 8015 shows excellent burn-out.

If you have any questions or require advice regarding the use of our products, please consult our customer service team.