



VIBRANTZ
TECHNOLOGIES™

Automotive Glass

High Chemical Durability
Excellent Non-stick Performance
Innovative Solutions for Windshield Application
Fine Line Silver Paste Systems



Vibrantz: enhancing life through superior materials performance

Headquartered in Houston, Texas, USA, Vibrantz is a world leading producer of Performance Materials, with operations in 20 countries across Europe, Asia and the Americas.

We apply core technologies in organic and inorganic chemistry to develop leading market positions in a diverse range of industries.

Our mission is "to achieve market leadership through a customer-focused and highly creative organisation committed to delivering top quality products and outstanding services to customers worldwide".

Our materials are used to add value to, and to improve the performance of products in a variety of end markets including building and renovation, home appliances, cookware, giftware and tableware, transportation, household furnishings, leisure, electronics and industrial products.

We are among the world's leading suppliers of ceramic glazes and colors, glass decoration, speciality glasses and porcelain enamel coatings. We pioneered the development of forehearth color technology for coloring of glass.

Our global commitment to quality, reliability, innovation and personal customer care is founded on over 80 years of experience in serving the changing needs of industry, from our international network of manufacturing plants and service centres. Our commitment to quality management has been recognised with the award of ISO9001 accreditation to all of our global manufacturing and research facilities.

Meeting the needs of the Color World calls for great foresight, flexibility and innovation ...

- Our global presence is a strong competitive advantage. Technical, marketing and management personnel are in continuous contact with customers in every major region. Multinational customers can be assured of standard products and consistent quality wherever they have operations.
- We co-ordinate our R&D activities globally and use our international talent to ensure that product specifications and performance are designed to satisfy the specific requirements demanded by regional markets.
- Vibrantz views the world-wide concern for the environment as an opportunity to develop improved products and also to participate in chemical industry efforts to address public concern. Environmental concerns are a major driving force behind the evolution of our lead- and cadmium-free technology and our low VOC decoration systems.
- The markets we cover are extremely service intensive. Vibrantz has established regional color matching, blending/pasting and technical support facilities, to provide the level of service demanded by our customers in all time zones. Think of us as High Performance Partners to manufacturers around the world ... Helping to create and enhance many of the products you use and enjoy every day of your life.

Technical Information

AUT04

Performance Coatings

Automotive Glass Enamels

Introduction

Vibrantz can draw on decades of experience in the production and application of ceramic colors, media and silver pastes.

To secure our high share of the market into the future, our research and development in recent years have focused 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 Windshield enamels 2012. These enamels pass the high chemical durability requirements which are actually requested by more and more carmakers.

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

In the last few years, we have successfully introduced innovative and environmentally compatible screen-printing media for use with automotive glass, and this brochure features a selection of these products.

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

General Information

Composition of Ceramic Automotive Glass Enamels

Ceramic automotive glass colors 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 color powder, and an organic component, the medium.

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

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

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	color shade and light transmission
additives 0 – 15 %	oxides, sulphides, metal compounds, silicates	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

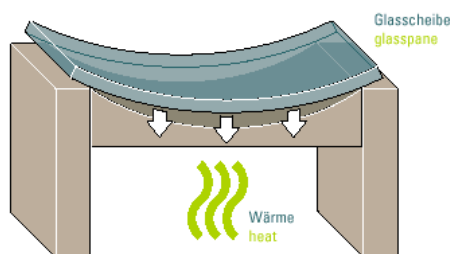
New legislation on environment protection, safety at work and the labelling of packaging for transport and handling in Europe were leading to complete prohibition on the use of lead, cadmium, hexavalent chromium etc.

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.

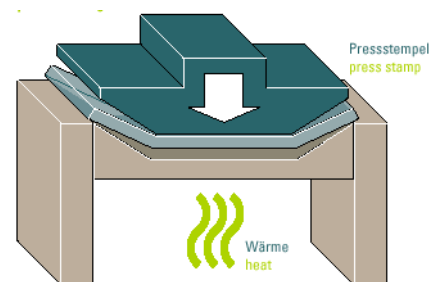
b) Antistick properties

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.



sag bending (gravity)



press bending

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:

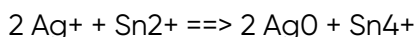
Either highly viscous systems with high surface tension, additive systems or reactive and crystalizing systems are used. The antistick effects differ depending on the system. Vibrantz supplies automotive glass enamels from all three systems.

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 color.

During firing, the silver ions (Ag⁺) migrate from the overprinted silver layer through the not completely molten ceramic color 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 color:



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. Vibrantz 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 color 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 and recently also for laminated glasses.

Vibrantz 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 color respective surface changes
	Grade 4 -	strongly affected color 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.

The Future

The requirements for 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 bent 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 primer-less gluing application.

Finally we expect that the chemical resistance will remain as one of the key requirement around the world. As a manufacturer of ceramic colors, Vibrantz 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 color 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	Color	Firing range (laboratory values)	Remarks
14 305	Bi-Si-B- Alkali	black semi-matt	560 – 640 °C 4 – 8 min	excellent chemical resistance – passes 72 hrs Toyota test, very good opacity, uniform gloss in the whole firing range, wet fire possible, low melting.
14 304	Bi-Si-B- Alkali	black, glossy	555 – 630°C 4 – 8 min	excellent chemical resistance – passes 72 hrs Toyota test; very good opacity wide firing range, wet fire possible lower melting.
14 303	Bi-Si-B- Alkali	black, glossy	565 – 640°C 4 – 8 min	excellent chemical resistance – passes 72 hrs Toyota test; very good opacity, wide firing range, wet fire possible higher melting.
14 300	Bi-Si-B- Alkali	black, glossy	560 – 630°C 4 – 8 min	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	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 enamels 14 303 and 14 304 provide an excellent chemical durability and pass 72 hrs Toyota test (lab conditions). In addition, the 14 305 provides a uniform gloss in the whole firing range. This allows a very uniform appearance of the fired enamel on the windshields even when larger temperature gradients occur.

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

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

Heavy Metal Free Enamels for Press Bending

Press bending became more and more common in the production of LSG in Europe in the past two years. Particularly important requirements are very good breaking strength, fast maturing and good antistick properties.

For some applications the enamels have to pass up to 72 hrs in the sulphuric acid test at 80°C. The firing range is usually between 580°C and 620°C (laboratory values).

Product No.	Frit system	Color	Firing range (laboratory values)	Remarks
14 310	Bi-Zn-System	black, matt	580 – 620 °C 6 min	passes > 8 hrs Toyota test wet fire possible
14 316	Bi-System	black, matt	570 – 640 °C 6 min	passes > 72 hrs Toyota test wide firing range, wet fire possible lower melting
14 315	Bi-System	black, matt	580 – 640 °C 6 min	passes > 72 hrs Toyota test wide firing range, wet fire possible higher melting

Surface No. 2 Enamels for 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 coordinated color powder-organic system and special adaptation to the specific pre-firing and bending processes.

Product No.	Frit system	Color	Remarks
14 331	Bi-Zn-System	black, matt	wide firing range 560 – 610°C silver-hiding possible lower melting
14 330	Bi-Zn-System	Black, matt	wide firing range 570 – 620°C silver-hiding possible higher melting
14 316	Bi-System	black, matt	570-640°C passes > 72 hrs Toyota test wide firing range, wet fire possible higher 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 color 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	Color	Firing range (laboratory values)	Remarks
14 624	No Bi Si-Zn-B-Ti	black, matt	660°C 3,5 – 4,5 min	Non-Bismuth System passes > 72 hrs Toyota test intermixable with 14 633
14 633	Low Bi Si-Zn-B-Ti (Bi)	black, matt	660°C 4 – 5 min	Low-Bismuth System passes > 72 hrs Toyota test intermixable with 14 624
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

Automotive Glass Enamels for Sunroofs

Vibrantz offers different heavy metal free enamels for this specific application. Please contact our customer service team who will recommend the best products for your requirements.

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 Vibrantz “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 Vibrantz “New Generation” Antistick Systems:

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

Vibrantz always works to improve and optimize existing product lines, even when they reach benchmark status. The latest development for application on deep bend tempered glasses provides a larger working range than the 14 500 family and passes up to 144 hours Toyota test.

The Vibrantz "New Generation" Antistick System:

Product No.	Temperature range for application	Firing range (laboratory values)	Remarks
14 530	very low – medium	650 – 710 °C 3 min	The "14 530 family" Frit system: Si-Bi-Ti-B-Zn-Alkali
14 531	low – medium high	660 – 720 °C 3 min	excellent antistick, deep black color shade, excellent busbar hiding range, very good opacity, very wide firing range, excellent chemical durability (passes up to 144 hrs Toyota test)
14 532	medium – high	675 – 730 °C 3 min	intermixable system

Automotive Glass Enamels with less than 5 % of Bismuth

Vibrantz has developed enamels for tempered glasses which contain maximum up to 5 wt% of Bismuth in the paste and still fulfils highest requirements to chemical durability, firing and busbar hiding range.

Product No.	Frit system	Color	Firing range (laboratory values)	Remarks
14 624	Zn-B-Ti-Si	black, matt	670 – 710 °C 3 min	passes > 72 hrs Toyota test intermixable with 14 633
14 633	Zn-B-Ti-Si (Bi)	black, matt	680 – 720 °C 3 min	passes > 72 hrs Toyota test intermixable with 14 624

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 color powder used.

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

Screen Printing Media IR - Oil Based

Data/Media	80 1018	80 007F	C80-1631	C80-1623
Flash point / °C	75	95	75	77
Density / 23 °C	0,93	0,94	0,99	0,88
Viscosity / mPa*s at 23 °C and D = 200 1/s	270	100	230	120
Solid content of lead free pastes	78 – 81	80 – 85	80 – 85	81 – 86
Thinner	80 063	80 007F	C80 1631	C80-1623
Cleaner	80 452	80 452	80 452	80 452

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

With medium 80 007F and C80-1623, and C80-1631 particularly high loading of the enamel pastes are possible. This allows extremely good opacity and improved busbar hiding by keeping very good printing properties. All three media are highly compatible with Vibrantz conductive silver pastes.

The universal screen printing medium 80 1018 features a medium drying rate and favorable firing behavior. It allows high loading of the enamel paste (good opacity) and is highly compatible with Vibrantz 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 Vibrantz 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 of lead free pastes	77 – 80	77 – 81	77 – 80
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 Vibrantz 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.

The information and recommendations contained herein are based on data we believe to be reliable and does not imply any warranty or performance guarantee, as conditions and methods of use of our products are beyond our control. The data herein is determined using Vibrantz's standard test methods. Hazard and safety information with respect to this product is available in the applicable SDS. Vibrantz will not be liable under any circumstance for consequential or incidental damages, including but not limited to, lost profits resulting from the use of our products.



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