

# Technical Information

HGS02

Performance Coatings

## Container Glass Enamel Decoration System – leaded

### Vibrantz System

Vibrantz’s container glass products are formulated to meet the needs of our customers from all market segments.



### Vibrantz Lead-containing systems

Market Segment	Vibrantz System	Firing Temp. (°C)
Page 10 Multi-trip bottles	VR	600-630
Page 12 Semi-resistant cosmetic bottles	VS	580-600
Page 14 Low firing cosmetic bottles	30	540-580
Page 15 Borosilicate glass	PR	620-640

Chrome VI and Mercury are not used in the manufacture of our heavy metal-free glass enamels.

## REACH update

Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is a European Union regulation which entered into force in June 2007. The scope of the REACH regulation is to address the production and use of chemical substances and their potential impacts on both human health and the environment. The registration process is an important part of the REACH regulation which requires each legal entity to file a dossier for chemical substances produced in Europe or imported into Europe. In 2010 the registration started with substances of annual volumes above 1000 tons, substances above annual volumes of 1 ton had been due by May 31, 2018. Depending on the volume the regulation of substances has different data requirements for registration. Companies planning to register a substance are members of consortia with the objective to organize data exchange and manage page 3/16 necessary toxicological and eco-toxicological studies. Data and cost-sharing is another fundamental aspect of the REACH regulation. Substances listed in Annex V of the REACH regulation like substances which occur in nature or non-hazardous[1] frits are exempted irrespective of the tonnage. The manufacture and importation of substances below 1 ton are also exempted from registration. Compliance with the REACH regulation is of the highest priority for Vibrantz. Vibrantz's REACH managers have checked the volumes of production and importation to decide which registrations are necessary. More than 200 substances have been registered by Vibrantz's legal entities since 2010. Additional registrations will be required also in the future if new raw materials are imported into Europe or new substances are produced. The REACH regulation sets up a system under which a hazardous substance may be subject to authorization. Substances which may be authorized in the future are listed on the candidate list or list of Substances of Very High Concern (SVHC). The presence of an SVHC substance is communicated to our customer in compliance with the REACH regulation. Vibrantz's policy is to manage any risks, so our research and development departments are continuously looking to replace these substances whenever possible.

## System test specification

### 1. Thermal expansion coefficient

Values quoted are measured between 25 – 300 °C (with 5 K/min), on the basic fluxes used in the systems concerned and they are indicative values.

### 2. Firing temperature

The optimal range shown is based on laboratory control tests, established during conception of each system.

Under industrial conditions, the actual firing cycle can be influenced by factors such as the type of kiln, the ware loading, the thickness and weight of the decorated articles.

We recommend setting the fire cycle with our systems on site, and our technicians will provide a full support to help achieve the optimal conditions.

### 3. Chemical durability

There are many tests available to judge the chemical resistance of glass enamels. The test results will depend, not only on the chemical formulation of the enamel, but also on the nature of the article, the layer thickness of the enamel and the firing cycle used.

Also for dishwasher resistance testing, the final results are influenced by the article, machine set-up, and the detergent type.

To try to overcome these testing variations, Vibrantz has created its own control tests to evaluate chemical resistance, with a visual testing scale to compare one system with another.

- Acid resistance test method – 10 % citric acid, 15 min at room temperature.
- Alkali resistance test method – 10 % NaOH, 4 h at 88° C.

The visual testing scale is as follows:

- (1) No attack
- (2) Iridescence or visible stain on the exposed surface when viewed at a 45° angle but not apparent at angles < 30°.
- (3) Definite staining which does not blur reflected images and is visible at angles < 30°.
- (4) Definite stain with gross color change or strongly iridescent surface visible at angles < 30° and which may blur reflected images
- (5) Surface dull or matt with chalking possible
- (6) Significant removal of enamel with pin holing evident
- (7) Complete removal of enamel in the exposed area

Additionally, we control upon demand our products according to the following market-specific International test methods:

- EN 1388-2 – designed specifically for the glass tableware market measurement of Cd & Pb released by exposure to 4 % acetic acid at 22°C for 24 h, to simulate the effect of exposure to food contact.

## Methods of use and recommendations

Glass enamels are ground mixtures of fluxes - formulated according to the fusibility and expansion of the glass substrate to be decorated - and inorganic pigments, which produce a wide range of shades after firing.

They can be blended with several types of medium system, depending on the final method of application (direct screening, decal, spraying).

Our colors from all systems are usually provided in the following forms:

- Powder form
- Water-friendly pastes for conventional and electrostatic spraying
- Oil-based liquid pastes for cold screen-printing
- Thermoplastic pastes for multi-color hot screen-printing
- Mediums suitable for all applications can also be provided separately (see separate medium section).

### 1. Storage and shelf life

Powders, medium and color paste systems should be stored in dry conditions and at room temperature (24°C).

Partly used tins must be tightly sealed after use. Pastes must be stirred thoroughly before printing.

If stored as recommended, the products are guaranteed with a minimum shelf life from production date:

- 6 months for the liquid paste.
- 2 years for the thermoplastic pastes
- Unlimited for the powders.

### 2. Recommendations for converting powders to pastes

#### 2.1. Cold Screen printing

The ratio powder/medium can be provided from our technical support technicians. The mixing should be performed using a mixer, followed by processing the paste through a triple-roll mill.

## 2.2. Spraying

Use the same process as in 2.1., then add 40 to 60 parts water to adjust the viscosity for final application. We recommend a spray viscosity of 25-30 s at 23°C, as measured with a No.4 (4mm) Ford flow Cup.

Typically, spray guns with a 1mm nozzle are used, with spray pressures set at 2.5 to 5 bars (35 - 75 psi).

We recommend stirring the spray paste in the tank to avoid sedimentation or settling.

## 2.3. Banding/Lining

Use the same process as in 2.1., except that the final viscosity should be adjusted with 25-30 % of our recommended medium, after roll milling. Test with a 6 mm flow cup to reach a viscosity of 25-30 s at 23°C.

## 2.4. Brushing

Typically, the powder is mixed with an oil-based medium and thinned with turpentine, following the usual safety precautions.

# 3. Recommendations for screen printing

## 3.1. Cold screen-printing

Our pastes can be supplied ready-to-use, although more typically our customers prefer to thin to a suitable printing viscosity on site. Printing viscosities in the range 18-23 Pas at 23°C are recommended.

Nylon or polyester screens – 120 to 300 meshes per inch (opening of 48-120 µm), may be used.

Squeegees should be made of hard rubber and sanded enough to avoid printing streaks.

Screens can be cleaned with a suitable solvent, generally ethanol, following the usual safety precautions.

## 3.2. Hot screen-printing (TP)

Thermoplastic glass enamels, which are solid at room temperature, need heat applied to become printable. The molten enamel is screen-printed through a heated metal screen, which can be heated either electrically or with IR-lamps.

Their main advantage is that each print-layer 'freezes' as it hits the colder glass, and therefore no drying is required between each successive print. This makes thermoplastics ideal for automatic multi-color printing machines.

## Pre-melting

TP inks perform best when pre-melted in temperature-controlled melting pots. We recommend melting at 65°–75°C. Avoid overheating, signified by smoke emission, as this may change the properties and printing behavior of the ink.

## Screens

We recommend stainless steel screens, with mesh size 150–300 meshes per inch (screen opening of 60–120 µm), dependent on the type of print.

For lead-free thermoplastic glass enamels, coarser mesh sizes are recommended, compared to those typically used with lead-containing enamels. This ensures good deposit weight and optimum brightness of the fired glasses.

Heated screens should be maintained at 70 – 90 °C and overheating (emission of smoke) should be avoided.

## Coverage

Around 1g of thermoplastic glass enamel will print a surface area of 100 cm<sup>2</sup>.

## 4. Drying recommendations

For oil-based pastes or wet spraying applications, the decoration must be dried prior to firing, if the ware is to be handled or is to be over-printed, or if the temperature at the kiln entrance exceeds 100°C. Decorated ware can be dried either at room temperature or in a drier. Alternatively, a hot-air draft over the decorated ware will speed up the drying process.

Tunnel-type driers can be used and are usually powered by gas or electricity. An adequate flow of air in the tunnel must be maintained to assist evacuation of the fumes via the chimney.

The heat input and drier length should be designed such that the decorated ware is at approx.40°C at the exit.

## 5. Thermal decomposition of the medium

During the firing of our glass colors:

- at around 70°C, there is an endothermic reaction, signifying the melting of the medium
- at 180–320°C, we observe an exothermic reaction, which signals the combustion of the major components of the medium, mainly waxes and fatty alcohols.
- at 320–520°C, a small exothermic reaction takes place, corresponding to the burnout of resins.

It is absolutely necessary that all medium components are burned off before the vitrification of the glass enamel powder components. If not, there is a potential to create defects, such as craters, bubbles and pinholes.

Whilst our systems are formulated to minimise such defects, we always recommend to adjust the firing cycle up-to 500°C, but especially between 250–320°C, so that the medium has sufficient time to burn out completely.

## 6. Firing recommendations

During the firing cycle, the organic components of the medium are burnt off and the enamel fuses to the glass surface to become a vitrified coating. Because of the presence of hydro-carbon organics in the kiln atmosphere, good ventilation must be maintained to minimise the possibilities of decoration defects.

Typical firing cycle profile:

- room temperature to peak temperature: 20–40 min.
- soak time at peak: 10–20 min.
- cooling zone cycle will be adapted to the type of decorated glass.

This typical cycle can be modified dependent on the glass thickness, to achieve optimal results.

With tempering glass cycles, the duration of the firing is reduced to a few minutes, dependent on the thickness of the glass.

## 7. Trouble-shooting guide

The most commonly noticed defects are:

- **bad aspect of Cd-containing reds and yellows**

Cadmium pigments are very sensitive to kiln atmosphere. Oxidising atmospheres are necessary for the good color development of cadmium-containing reds and yellows.

In addition, we recommend to manage a good extraction of the combustion gases from the kiln and to leave enough space between the decorated items in the kiln, for an improved air circulation.

- **« back-lapping »**

This is an irregular deposit on one of the sides of the ACL label, which can occur if the glass enamel is too fluid during printing.

Solution is to decrease the temperature of the heated screen.

- **blistering**

This is created by the formation of bubbles in the body of, or craters at the surface of the glass enamel. The defect is caused by a bad evacuation of the gases formed from the combustion of the medium (see 5).

There are several solutions:

- improve the extraction in the kiln
- decrease the speed of the kiln belt i.e. throughput
- increase temperature and/or speed of the pre-heat phase of the firing cycle

- **crawl**

This is where the glass enamel recedes from the glass surface, and is generally caused by oily deposits on the glass before decoration. Solution is to clean the glass before decoration.

- **drip-through**

In this defect, the glass enamel drips through the screen. Solution is to decrease the screen temperature, in order to increase slightly the TP ink viscosity.

- **tears**

This is where the glass enamel runs down the glass to form tears, and is often due to condensation of some of the waxes, onto cold items in the first zones of the kiln. Solutions are:

- improve the kiln extraction, especially in the first zones of the lehr
- increase the temperature in the pre-heat zone more rapidly
- increase the space between the decorated articles to improve the air circulation

## Medium system

### We offer 4 types of medium:

- Water-friendly mediums – these systems can be diluted with water; equipment can also be cleaned with water
- Oil-based mediums – these products must be let-down with solvent, not water
- Thermoplastic mediums – used for hot screen printing
- Pad printing Medium – used for pad printing process

## Recommended Vibrantz medium systems

Application Method	Product Reference	Medium Type	Properties
Direct screening	MX 54	Oil-based	Medium drying rate
	MX 44.62	Thermoplastic	
Spraying	80 1022	Water-friendly	Medium drying rate
Pad-printing	80 4084	Thermoplastic	Solid @RT
	80 4085	Thinner	Thinner for 80 4084

Generally the medium used is also used as the thinner.

## Indirect printing process

### Pad printing process:

The advantage of the Pad Printing process in comparison to the total transfer process is the higher resolution of the print. Sharper images can be achieved.

The film thickness of is lower than with the Total Transfer Process.

Our specially developed medium 80 4084 gives best properties that allow a very good transfer using the Pad Printing technique.

In order to achieve a good print result we recommend the following parameters (changes may be necessary depending on the machine and the setting of the machine, such as speed, etc.)

Pasting ratio: 10:5 – 10:7

Cliché temperature: app. 80° C

Pad/ Pulp temperature: 35° – 40° C

Glass temperature: 20° – 25° C

The temperature should decrease with each application step.

## Lead-containing system technical data

### VR System

#### Main market use

These enamels are recommended for decoration of soda-lime glass packaging, more particularly single-trip and multi-trip bottles.

This System can also be used for special applications, such as color-break enamels for pharmaceutical borosilicate glass ampoules.

#### Chemical composition

Colors in this System contain lead and cadmium. We guarantee a lithium content of maximum 30 ppm.

Color	Reference	Pantone	
Dark Green	VR 99.59	342 C	
Green	VR 231	370 C	
Blue	VR 209	2935 C	
Cobalt Blue	VR 208	2735 C	
Yellow	VR 241	109 C	
Yellow	VR 242	116 C	
Red	VR 270	1795 C	
Dark Red	VR 272	186 C	
Orange	VR 261	1505 C	
Brown	VR 280	175 C	
White	VR 290		
Flux	VR 725		
Black	VR 285		
Etch	VR 296		

*The Pantone references and color prints are provided as an indication of the shade only.*

*The above mentioned references are randomly selected color shades, please contact your respective Vibrantz Technical Service to get more information on further available colors.*

*The above mentioned references refer to the powder form only. If you want the thermoplastic paste, liquid paste or spraying form, make sure to add the suitable name of the medium – mentioned on page 5 – at the end of the reference.*

These colors are intermixable. We recommend performing preliminary tests before launching production with color mixtures from this System.

### **Expansion coefficient (c.o.e.)**

This system is suitable for most chemical compositions used in the production of soda-lime glass bottles.

### **Recommended firing conditions**

600°C to 630°C in a cycle of 1 h-1.5 h, with a soaking period of approx. 10 min, dependent on both the type of furnace and the volume of ware fired.

It is also possible to fire the VR System at a temperature of 600°C-700°C in short cycles, such as used for pharmaceutical glass bottles. Tests are recommended.

### **Chemical resistance**

Norm EN 1388-2 (tests on the basic flux system in laboratory conditions)

- Lead release is < 10 mg/dm<sup>2</sup> of the decorated surface.
- Cadmium release is < 1.5 mg/dm<sup>2</sup> of the decorated surface.

Acid resistance : 4

Alkali resistance : 4

See page 2 for details.

## VS System

### Main market use

These enamels are intended mainly for the decoration of tumblers, but are also used for cosmetic and perfume bottles.

### Chemical composition

Colors in this System contain lead and cadmium.

Color	Reference	Pantone	
Dark Green	VS 327	349	
Green	VS 321	362 C	
Royal Blue	VS 300	2727 C	
Cobalt Blue	VS 302	2747 C	
Blue	VS 3318	299 C	
Yellow	VS 68.59	109 C	
Light Red	VS 370	1795 C	
Dark Red	VS 372	187 C	
Orange	VS 361	151 C	
Brown	VS 73.59	483 C	
Black	VS 384		
White	VS 390		
Flux	VS 730		
Etch	VS 392		

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*The above mentioned references refer to the powder form only. If you want the thermoplastic paste, liquid paste or spraying form, make sure to add the suitable name of the medium – mentioned on page 5 – at the end of the reference.*

These colors are intermixable. We recommend performing preliminary tests before launching production with color mixtures from this System.

### **Expansion coefficient (c.o.e.)**

This system is suitable for most chemical compositions used in the production of soda-lime glass bottles.

### **Recommended firing conditions**

From 580°C to 600°C in a cycle of 1 h-1.5 h with a soaking period of approx.10 min, dependent on both the type of furnace and the volume of ware fired.

### **Chemical resistance**

Norm EN 1388-2 (tests on the basic flux system in laboratory conditions)

- lead release is < 25mg/ dm<sup>2</sup> of the decorated surface. Exception is VS 302 cobalt blue, with a lead release of c. 60 mg/dm<sup>2</sup> of the decorated surface.
- Cadmium release is < 3 mg/dm<sup>2</sup> of the decorated surface.

Acid resistance : 4

Alkali resistance : 5

See page 2 for details.

## System 30

### Main market use

These low-melting enamels are mainly used for the decoration of thin glassware which would deform at higher temperatures - such as lamps, fancy and small hollow glassware.

### Chemical composition

Colors in this System contain lead and Cadmium.

Color	Reference	Pantone	
Green	11 641	349 C	
Dark Green	11 667	3435 C	
Light Blue	12 530	293 C	
Dark Blue	12 602	Reflex Blue C	
Yellow	13 440	116 C	
Orange	13 464	166 C	
Red	17 395	186 C	
Black	14 171		
White	19 130		
Flux	10 042		
Etch	19 961		

*The Pantone references and color prints are provided as an indication of the shade only.*

*The above mentioned references are randomly selected color shades, please contact your respective Vibrantz Technical Service to get more information on further available colors.*

*The above mentioned references refer to the powder form only. If you want the thermoplastic paste, liquid paste or spraying form, make sure to add the suitable name of the medium - mentioned on page 5 - at the end of the reference.*

These colors are intermixable. We recommend performing preliminary tests before launching production with color mixtures from this System.

### Expansion coefficient (c.o.e.)

These enamels have a high C.o.E., and therefore it is advisable to take special care when applying these colors. Enamels with a higher C.o.E. than the glass substrate to be decorated, can weaken the glass. We recommend decorators make preliminary trials to check that the end results are in accordance with their requirements.

### Recommended firing conditions

From 540°C to 580°C with the higher temperature recommended for optimal transparency.

### Chemical resistance

Acid resistance : 7

Alkali resistance : 7

See page 2 for details.

## PR System

### Main market use

These enamels are specially designed for the decoration of borosilicate glasses.

### Chemical composition

Colors in this System contain lead, cadmium and lithium.

Color	Reference	Pantone	
Green	PR 106	349 C	
Blue Green	PR 109	323 C	
Ultramarine Blue	PR 113	2945 C	
Royal Blue	PR 108	Reflex Blue C	
Blue	PR 102	2727 C	
Yellow	PR 107	012 C	
Orange	PR 101	021 C	
Medium Red	PR 100	186 C	
Dark Red	PR 118	200 C	
Brown	PR 105	470 C	
Black	PR 112		
White	PR 104		

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*The above mentioned references refer to the powder form only. If you want the thermoplastic paste, liquid paste or spraying form, make sure to add the suitable name of the medium – mentioned on page 5 – at the end of the reference.*

These colors are intermixable. We recommend performing preliminary tests before launching production with color mixtures from this System.

### **Expansion coefficient (c.o.e.)**

Average C.o.E. measured on the basic frit System is  $57 (+/- 4) \cdot 10^{-7} K^{-1}$ .

The enamels are specially formulated for application onto borosilicate glass and they should be tested for suitability to the expansion of the glass to be decorated. The 'fit' of these enamels is also dependent on application weight and to avoid microcracking or fracture problems, they should not be applied too thickly.

### **Recommended firing conditions**

From 620°C to 640°C in a long cycle; from 630°C to 700°C in a short cycle. Tests are recommended.

### **Chemical resistance**

Norm EN 1388-2 (tests on the basic flux system in laboratory conditions)

- lead release is  $< 10 \text{ mg/dm}^2$  of the decorated surface.
- Cadmium release is  $< 1 \text{ mg/dm}^2$  of the decorated surface.

Acid resistance: 4

Alkali resistance: 4

See page 2 for details.

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.