
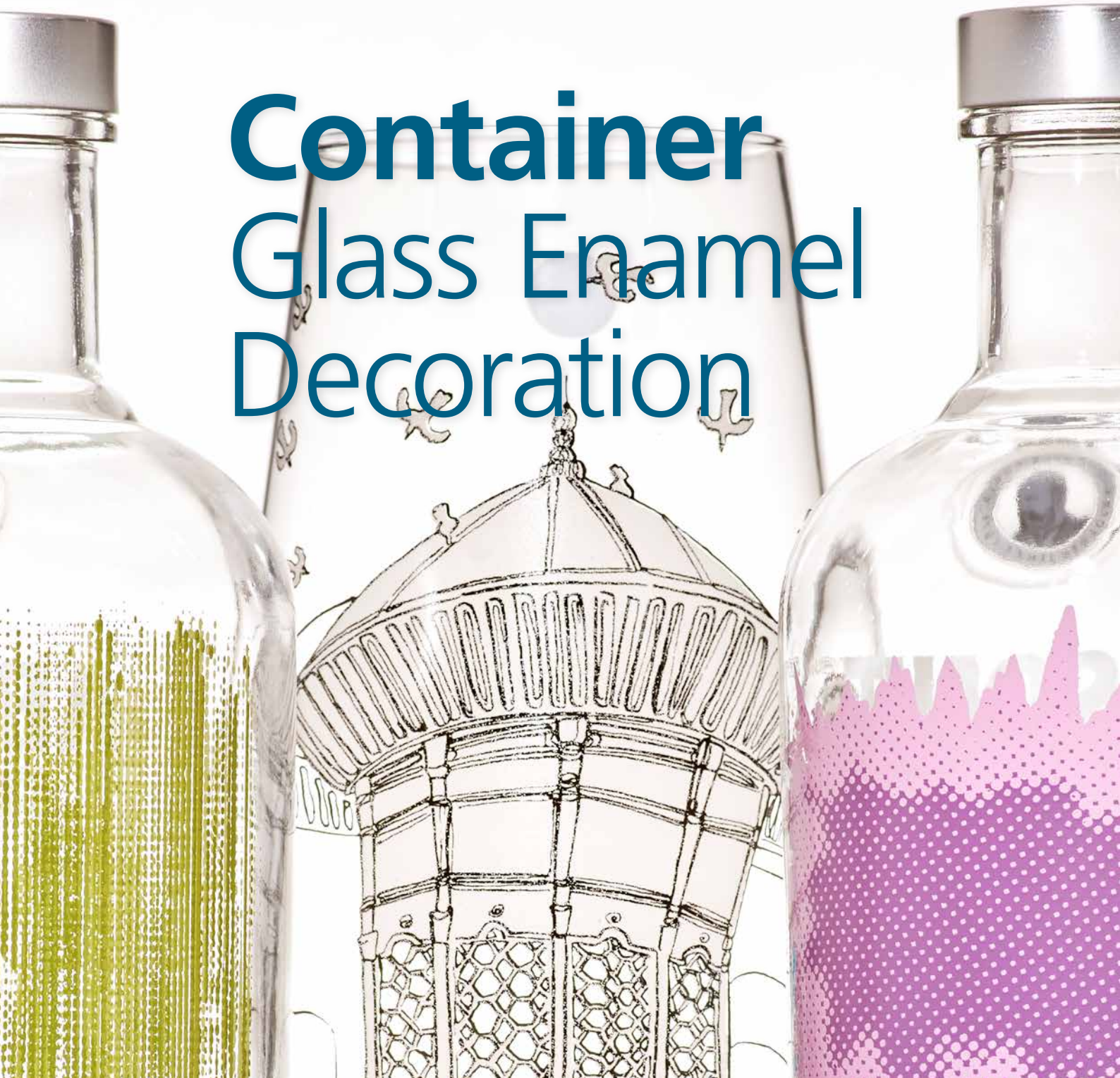


Technical Information



Container Glass Enamel Decoration



Ferro: enhancing life through superior materials performance

Headquartered in Mayfield Heights, Ohio, USA, Ferro Corporation 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.
- Ferro 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. Ferro 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

HGS02



Container Glass Enamel Decoration Systems-Overview

Ferro System

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



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- **Ferro Lead-Free Systems**

| Market Segment | Ferro System | Firing Temp (Deg. C) |
|------------------------------|--------------|----------------------|
| Multi-Trip Bottles | VNR | 620-650 |
| Single-Trip Bottles | VNS | 620-630 |
| Cosmetic and Perfume Bottles | VN | 580-600 |
| Tumblers and Tableware | NPR | 630-650 |
| Borosilicate Glass | VPS | 630-650 |

- **Ferro Lead-Containing Systems**

| Market Segment | Ferro System | Firing Temp (Deg. C) |
|---------------------------------|--------------|----------------------|
| Multi-Trip Bottles | VR | 600-630 |
| Semi-Resistant Cosmetic Bottles | VS | 580-600 |
| Borosilicate Glass | PR | 620-640 |
| Low-Firing Cosmetic Bottles | System 30 | 540-580 |

Heavy Metal and Lithium Content

Our heavy metal-free systems are in compliance
With Packaging and Packaging waste Directive
2004/12/EC and fulfill the following limits:

| | Pb | Pb+Cd* | Li |
|-------------------------------------|-----------|-----------|----------|
| VNR Plus multi-trip bottles* ** | < 100 ppm | < 100 ppm | < 30 ppm |
| VNS single-trip bottles* | < 100 ppm | < 100 ppm | < 30 ppm |
| VN cosmetic and perfume bottles* ** | < 100 ppm | < 100 ppm | |
| NPR tumbler & tableware* | < 100 ppm | < 100 ppm | |
| VPS borosilicate glass* | < 100 ppm | < 100 ppm | |

Our values are measured on our products themselves in dependence on the Packaging and Packaging waste Directive 2004/12/EC

* for those containing cadmium-free pigments

** Exceptions are the cobalt blue products (VNR 2403, VN 2301 and enamels containing even partially these two cobalt blues), which have a guaranteed Pb + Cd content of maximum 300 ppm.

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

Heavy Metal Content in Packaging

Latest legislation requires decorators to declare the content of heavy metals in their decorated articles.

To support you, based on the weight of the glass and the enamel deposited on the article, we can calculate the quantity of heavy metals and relate that to the total weight of the packaging, according to EU Packaging Directive 2004/12/EC.

REACH Update

Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is a European Union regulation which entered into force 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 have different data requirements for the registration. Companies planning to register a substance are members of consortia with the objective to organize data exchange, manage

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 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 highest priority for Ferro. Ferro REACH managers have checked the volumes of production and importation to decide which registrations are necessary. More than 200 substances have been registered by Ferro'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 substances may be subject to authorization. Substances which may be authorized in the future are listed on the candidate list or list of Substance of Very High Concern (SVHC). The presence of a SVHC substance is communicated to our customer in compliance with the REACH regulation. Ferro's policy is to manage any risks, so our research and development departments are continuously looking to replace these substances whenever possible.

System Test Specifications

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, Ferro 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 & 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 cm².

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. Troubleshooting Guide

The most commonly noticed defects are:

- **Bad aspect of Cd-containing reds and yellows**
Cadmium pigments are very sensitive to kiln atmosphere. Oxidizing 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 Systems

We offer 5 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
- Total Transfer Medium – used for total transfer process

Recommended Ferro Medium Systems

| Application Method | Product Reference | Medium Type | Properties |
|--------------------|-------------------|----------------|------------------------|
| Direct screening | MX 54 | Oil-based | Medium drying rate |
| | 80 392 | Oil-based | Fast drying rate |
| | MX 44.62 | Thermoplastic | Mainly for Pb-products |
| | MX 57 | Thermoplastic | Mainly for Pb-free |
| Spraying | 80 1022 | Water-friendly | Medium drying rate |
| | 80 1026 | Water-friendly | Long drying rate |
| Pad-printing | 80 4084 | Thermoplastic | Solid @RT |
| | 80 4085 | Thinner | Thinner for 80 4084 |
| Total-Transfer | 74-120 | Paste | Remains sticky @RT |

Generally the medium used is also used as the thinner.

Indirect Printing Process

Total Transfer and Pad Printing Process

These indirect printing application processes are used if the shape of the substrate is difficult and a simple screen print process can not be used, such as concave or convex surfaces such as plates.

Total Transfer Process

The advantage of the total transfer process in comparison to the Pad Printing process is the higher film thickness of the print which is achievable in one process step.

The print quality itself is lower than with the Pad Printing process.

Our specially developed medium 74-120 TT gives best properties that allow a very good transfer using the Total Transfer 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).

| | |
|---------------------------|-------------|
| Pasting ratio: | 10:4 – 10:6 |
| Screen temperature: | 70° - 80° C |
| TT-substrate temperature: | 40° - 45° C |
| Pad/ Pulp temperature: | 30° - 35° C |
| Glass temperature: | 20° - 25° C |

The temperature should decrease with each application step.

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.

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Please refer our Material Safety Data Sheet for safe handling and use of our products, prior to use.



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