Porcelain (Vitreous) Enamels and Industrial Enamelling Processes

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Abstract

Porcelain (Vitreous) Enamels and Industrial Enamelling Processes is a comprehensive book for the researcher, engineer and technician involved in the development and application of porcelain enamels in a wide range of systems. This volume, updated and expanded from the original Porcelain Enamels by A. I. Andrews in the USA, covers the scientific basis for glass formulation from the molecular level to raw material choices and their combinations to create useful materials for coating various metals. Properties of enamel (glass) systems are extensively discussed regarding thermal expansion, density, elasticity, thermal conductivity, colour, optical and appearance properties and other characteristics critical for successful development.

Metal choices and pre-treatments are reviewed in depth for steel, cast iron, stainless steels, various alloys and aluminium as well as the machinery and materials needed to accomplish these vital processes. Up-to-date information is included on metal chemistry, forming and welding technology.

Manufacturing of enamels is extensively covered from weighing, mixing, smelting and milling. Detailed information on smelters and mills is included highlighting developments since the advent of electrostatic dry powder enamel application. Application of enamels by producers of finished products is discussed for wet, dry and various two coat – one fire methodologies which have been developed in recent years.

The physical, chemical, mechanical, and electrical properties of enamelled products are extensively covered along with references to national standards worldwide. Appendices include various national standards, troubleshooting cause-and-effect diagrams, an Atlas of Enamel Defects with a wide range of visual illustrations, methodologies of fishscale testing, various technical data sheets and a glossary of enamelling terms.

This new book is a collaborator effort of many individuals associated with the enamelling industry throughout the world. It is a useful addition for academic institutions, research and development laboratories and manufacturing companies for reference and instruction.

Introduction

The goal of the current efforts of this new book is to disseminate porcelain (vitreous) enamel technology and increase the focus on its value and uniqueness. This new book builds on the 1961 publication Porcelain Enamels by A. I. Andrews with expanded sections to support scientific concepts in order improve their understanding. Of special note is the enhanced discussion of the chemistry of steel and adherence of porcelain (vitreous) enamels to aid those involved in industry and research regarding enamelling technology.

Porcelain enamels continue to be a remarkable coating for steel and other metals. During the last several decades, new formulations and methods have provided for commercially economical and desirable enamelled products. No nickel-no pickle ground coats have provided means of
meeting ecological directives and at the same time improving the efficiency of enamelling operations without regard the volume of production. Electrostatic powders and electrophoretic application have additionally remade the industry while reducing material, labour and production costs. Today, these new materials and processes are the norm and we look forward to new innovations.

**Porcelain (Vitreous) Enamels** provides an up-to-date and thorough compilation of materials, methods of smelting, application, firing and testing while providing fundamental understanding of the processes involved with better and larger details of porcelain enamel chemical and physical properties to enhance the value for many applications such as drinking water, solar energy and coatings on various metals and alloys. Key information on modern steels is provided as well as welding which is important for many sheet steel products. Over the last several decades, the manufacture of steel has been revolutionised by continuous casting which has changed the chemistry of steel and improved their quality.

New sources of information in the Appendices are included. They are

- Porcelain (Vitreous) Enamel Standards – This is a compilation of standards including ISO, EN, ASTM, UNI, DIN, BS and AFNOR. The appendix provided a comprehensive table of equivalents for rapid identification. Standardisation of testing will continue to be of key importance regarding enamels on metal and rationalisation of standards worldwide will improve their acceptance and promotion.
- Ishikawa’s Cause and Effect Diagrams and Atlas of Enamel and Enamelling Defects - This appendix provides an easy and rapid method of identifying many enamelling problems, their causes and possible remedies. The Atlas of Enamel and Enamelling Defects is an excellent visual aid, originally developed by the Institute of Vitreous Enamellers and augmented with some additional resources.
- Fishscale Measurement – Fishscaling has been a challenging problem for many years in the enamelling of various types of steel. New methods have been devised to characterize steels by direct testing and indirect methods such as permeation of hydrogen.
- Porcelain (Vitreous) Enamel Technical Data Sheet and Metrics and Metric Units Conversion Tables – Both metric and English units of measure have been used throughout the book. Some technician and researchers find that both units are meaningful and may be used in one locality or another. This appendix provides numerous important factors and measurements.
- Glossary of Enamelling Terms – Each technology has its own terminology and enamellers are not exception. A listing of many new and traditional terms is included in a definition format to aid in the understanding of the terms.
- Burner Technology - New specialised burners with integral heat exchangers are illustrated and their efficiencies compared.
Highlights of the Book and New Technology

Electrostatic Powders

Enamelling processes have evolved greatly in recent years, building on previous developments. A key new area is electrostatic application of enamels using powder spraying equipment. Modification of the surfaces of enamel frit particles has been accomplished by the use of a variety of reactive silicone compounds which react with the surface hydroxyls on the particles. This has allowed the development of high surface resistivity needed to hold an electrostatic charge.

Application of the electrostatic powders was successfully adapted from equipment developed for organic powders and modified to handle the abrasive nature of glass. Figure 1 illustrates the application of porcelain (vitreous) enamel powders. A wide variety of finish coats and ground coats are now routinely applied with this methodology. There are limitations on the colour of enamels which with wet methodology have pigments used for various colours. Due to the charge to mass ratio which is important with the electrostatic process, pigments tends to separate and selective deposit on points of high electrical potential such as edges and corners of target pieces.

![Figure 1 – Schematic of Powder Application System. Smalto Porcellanato, Figure 1-Smaltura elettrosttica a polveri:gli impianti, September-December 2000, page 159.](image)

Development of the equipment needed to efficient application and very high material utilisation occurred over a period of a couple of decades. Continuing improvements are being made by equipment manufacturers to continue the progress made to date. The electrostatic application process reduced the material usage, energy needed to apply the frit powder coating and less overall labour to achieve the same level of production as conventional wet processes.

The basic components are of a fluidized bed: venturi pump system, applicator (gun) with one or more high voltage antennas, an application cabin or booth, an overspray collection system with primary and secondary air filters, and a powder return apparatus for recycling overspray. An important feature of the electrostatic powders is their particle size distribution which needs to be controlled initially as a virgin powder and then as a mix of virgin and recycled powder to achieve steady state conditions as much as possible. The fluidization of the powder and its subsequent density can affect application performance. Cold (low temperature) powders will not fluidize well.
and hot powders will tend to over-fluidize. All these conditions affect the spraying performance as shown in Figure 2.

![Figure 2. Influence of Air Fluidisation and Fluidity on Spraying.](image)

Metal and Metal Preparation

Continuously cast steel which are generally aluminium killed are nearly universal and various grades have replaced traditional types such as cold-rolled, enamelling iron and low carbon steels. The performance of these new steels is as good as traditional types and the quality is better (cleaner metal chemistry). With the advent of new steels, new no nickel – no pickle (Liberty) ground coats have been commercialized. These enamels have been adapted to both wet and dry processes systems and have evolved into various two coat – one fire methodologies such as 2C-1F dry/dry, wet/dry and wet/wet which are now routinely practiced. The metal preparation processes have been able to shed the costly acid etching and nickel deposition stages. Some manufacturers utilize the traditional pickling systems and the “clean-only” process together. Again, labour and material usage has been reduced along with much lower effluents and pollution concerns. Equipment for metal preparation may be manual or automatic. With newer electronic controls systems, very efficient processing is possible.

Electrophoresis

Electrophoretic enamel application was initiated to achieve more uniform application and edge coverage on thin metal shapes. In the USA, early work was directed at developing small electrically insulated substrates for simple circuits including some radio applications. European work, primarily by Miele for appliances, directed their efforts at developing superior surfaces and corrosion protection on the edges of panels. The European systems were successfully adapted to large scale production and continue to be refined. A schematic diagram of the anodic process is shown in Figure 3.
Furnaces

The development of high temperature ceramic fibres lead to the development of low thermal mass furnaces. These furnaces have low weight construction and non-specialized foundations. In some instances, the furnaces are built in modules which can be easily shipped, assembled and if desired may be progressively enlarged as production warrants. Newer combustion systems for furnaces utilize very efficient heat exchangers built into the burners themselves. Various configurations of alloy tubes maximize the heat transfer areas and minimize exhaust temperatures.

Enamel Characterization

The fit of enamel on the metal substrate is of critical importance. Rapid methods of measuring the thermal expansion have been developed such as dilatometer systems. This methodology only requires an annealed bar as opposed to previous interferometer methods. The heating schedule and output are automatically controlled and recorded. Glass viscosity characterization has also been developed such as the sophisticated heating microscopes. These systems can automatically determine a variety of glass characteristics as well as obtaining visual references of the stages of melting as shown in Figure 4.
Advanced Microscopy

Microscopy has greatly improved with the development of better optical systems and imaging technology allowing rapid results which can be electronically conveyed to almost any location at any time. Sample preparation continues to require skilled handling of the materials but has been automated in some instances. With prepared samples, conventional and electron microscopy provides researchers and technicians with greatly enhanced understanding of enamelling problems. Scanning Electron Microscope (SEM) produces an image by probing the specimen, either enamel surface, cross-section element or other artefact, with a focused electron beam that is scanned across a rectangular area (raster scanning). 1 "At each point on the specimen the incident electron beam loses some energy, and the lost energy is converted into other forms, such as heat, emission of low-energy secondary electrons, light emission (cathodoluminescence) or x-ray emission. The display of the SEM maps the varying intensity of any of these signals into the image corresponding to the position of the beam on the specimen when the signal is generated. In the image in Figure 4, the image was constructed from signals produced by secondary electron detector the normal or conventional image mode in most SEM. 1

Energy Dispersive X-ray Spectroscopy “(EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is one of the variant of
XRF (X-ray Fluorescence). As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analysing x-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique structure allowing x-rays that are characteristic of an element’s atomic structure to be identified uniquely from each other.”

Figure 5 illustrates the output from an SEM/EDS scan of the defect illustrated in Figure 6. The combined use of SEM and EDS equipment has greatly enhanced the capabilities of enamellers to determine cause and effect of various types of enamelling problems both in manufacturing of enamel frits and production of various appliances.

Figure 5 - Two coat – one fire enamel interface showing possible surface contamination resulting in gas evolution and metal surface reaction material being drawn into the enamel layer. Courtesy Ferro Corporation, Dave Gnizak Microscopist.

Figure 6 - The elemental composition of specific areas of a micrograph is possible with the Energy Dispersive Spectroscopy associated with the Scanning Electron Microscope. Courtesy of Ferro Corporation, Dave Gnizak Microscopist.
Specialised Substrate Coatings

Since the late 1970’s, various applications of enamels have been introduced including solar panels, heat reflective surfaces and electronic substrates. The electronic substrates have allowed for the development of extremely rugged boards for applications requiring impact, vibration and heat resistance not found in other substrate materials.

The optical properties of porcelain enamels may be customized while retaining their base characteristics of mechanical and chemical durability. Solar panels are normally optimised for absorption. With porcelain enamels, a secondary coating may be applied pyrolytically which further enhances the absorption by creating a selective surface that reduces the emissivity with minimal interference with the absorption.

Glass Melting Furnaces

Smelting of glass has progress for many years and is now at a high level of efficiency. Large continuous furnaces, computer controlled, produce close to ton per hour quantities to exacting specifications. Similar formulations are run consecutively around the clock. Construction the smelters (furnaces) is with high temperature refractory brick. The floor of the smelter may be a composite cement refractory or highly resistant fused cast blocks to withstand the corrosive action of the molten glasses. Heating of the furnaces is typically with gas and oxygen or gas and air followed by exhaust control systems to minimize volatile gases and particles of material carried out by the movement of the combustion products.

Induction melting of metals has been well known for many decades, however, non-metallic materials have been melted by induction furnaces in more recent years including refractory oxides and glasses. An important advantage of induction melting is the possibility of melting without direct contact with any crucible or refractory surface. The use of a water cooled induction container with a “skull crucible” allows the manufacture of materials without unwanted contaminants. Electricity or electric charge is transferred by ionic conduction in non-metallic materials such as glasses and whereas they are insulators at room temperatures they become conductors at elevated temperatures. This change in conductivity with temperature is opposite that of metals. The room temperature high resistivity allows the formation of the skull crucible, that is, a solid wall which insulates the mass of molten material from the induction furnace walls as shown in Figure 7. To start the melting process, it is necessary to preheat the batch to allow the magnetic-electric field to continue the melting process.\(^2\)


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Figure 7 - Schematic Diagram of an Induction Furnace with Skull Crucible.