DOI 10.1007/s11106-016-9771-6
Powder Metallurgy and Metal Ceramics, Vol. 54, Nos. 11-12, March, 2016 (Russian Original Vol. 54, Nos. 11-12, Nov.-Dec., 2015)

REVISITING THE HISTORY OF MATERIALS SCIENCE

GLASS, GLAZE, AND ENAMEL OVER THE MILLENNIA. II. GLAZES AND ENAMELS

G. G. Gnesin[1]

UDC 661.1.232.8:031.1

The paper presents a historical evolution of compositions and applications of glazes on various ceramics (majolica, facing tile, glazed pottery, porcelain). The origin and development of artistic and industrial enameling processes for metals are described. The effect of additions in glazes and enamels on the color and transparency of decorative, artistic, and technical vitreous coatings on metallic and nonmetallic materials is exemplified by objects created in different historical epochs.

Keywords: *glaze, enamel, opacifier, frit, slurry, celadon, underglaze and overglaze mineral paints, artistic and technical enameling.*

This paper offers a historical overview of the origin and development of techniques for depositing vitreous coatings onto ceramic and metallic materials and methods for controlling their color and optical transparency and outlines the evolution of enamel and glaze applications.

Chronologically, silicate glazes are the most ancient variety of vitreous materials. Their technology is inseparably linked with the origin of ceramic crafts in Mesopotamia and Predynastic Egypt in 4,000–5,000 B.C. Since the first potteries were originally baked in bonfires at 600–800ºC, they had residual porosity making long storage of liquids impossible. To protect the porous ceramics against external impacts, fusible glazes made from a powdered mixture of quartz sand (SiO_2) and wood ash containing Na_2CO_3, K_2CO_3, and small amounts of $CaCO_3$ were originally used. The slurry mixture applied to a fired ceramic object fused at about 800ºC to form a vitreous shiny coating preventing the penetration of moisture into the surface. Another glazing process was developed in parallel. It involved preliminary fusion of all components together to obtain a vitreous semifinished product (frit), which was then ground and placed on the ceramics to be further fused. The glazes initially played a leak-proofing role, and similar primitive glazing process (slip glazing) has been preserved to this day in handicraft workshops. Natural impurities of copper and iron oxides made the glazes dark blue or pale blue. Table 1 shows compositions of two types of Ancient Egyptian dark blue (1) and pale greenish-blue (2) glazes.

The glazing technique was applied for the lining of building products. For example, the door to the burial chamber in Pharaoh Djoser's Step Pyramid (15th century B.C.) was decorated with faience tiles covered with a blue-green glaze produced, in all likelihood, in a dedicated workshop. Glazed lining was in wide use in Mesopotamia to decorate palaces and houses of worship. Excavations of ancient Babylon uncovered numerous gate

---

[1] Frantsevich Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, Ukraine; e-mail: geognesin@yandex.ua.

Translated from Poroshkovaya Metallurgiya, Vol. 54, Nos. 11–12 (506), pp. 144–152, 2015. Original article submitted March 16, 2015.

TABLE 1. Chemical Composition of Ancient Egyptian Glaze Charges [1]

Composition, %	SiO_2	Al_2O_3	FeO	CaO	MgO	CuO	K_2CO_3	Na_2CO_3	MnO
1	75.6	0.8	0.8	3.8	0.7	1.8	10.7	5.5	0.3
2	92.9	0.3	0.5	0.8	–	1.1	0.5	1.6	–

fragments of Goddess Ishtar's Temple (sixth century B.C.) decorated with multicolored glazed ceramic tiles composing the relief facade of this tremendous building. The glazed tiles of Babylon and Assyria were characterized by white, yellow, orange, green, and black ornamental motifs on a bright blue background.

Along with glazing of fired ceramics, vitreous coatings were applied to objects made of steatite, representing a dense natural mineral of magnesium hydrosilicate. Possessing fine-grained structure and low hardness (about one on the Mohs scale), steatite can be easily processed. Hence, it was used in Ancient Egypt to make fine objects of art and religious amulets, such as scarabs. Steatite hardens when fired and is, therefore, suitable for glazing.

Various civilizations of the Ancient World experimentally elaborated numerous glaze formulations for ceramic objects over two to three millennia, having not only the desired properties but also high artistic value. The artistic effect was achieved with mineral additions imparting desired color and specific optical properties (high reflectivity, opalescence, etc.) to glazes.

Table 2 shows chemical compositions, firing temperatures, and colors of glazes belonging to the most advanced civilizations of the Ancient World and Middle Ages (Egypt, Mesopotamia, Greece, and Asia Minor) [2].

Note that the appearance of glazes is due to not only their chemical composition but also their structure and the presence of unfused crystalline inclusions. The color palette of ancient glazes depended on impurities of some metals. For example, depending on the degree of oxidation, iron compounds made glazes from yellow and green to brown and black, manganese compounds from purple to brown, chromium ones from pink to green, cobalt from light blue to dark blue, copper from green to dark blue, and tin from pink to red.

The development of new glazes in the Middle Ages contributed to the invention of porcelain in China (sixth to seventh centuries) and the fabrication of multicolored ornamental ceramic tiles for architectural decoration in Muslim states [3]. The traditional medieval Chinese porcelains differ in composition and firing modes. Thus, in the Chinese green-blue glazes with iron oxide impurities, known as celadon in Europe and referred to the era of Song dynasty (960–1279), inclusions of quartz and anorthite scatter light and make ceramic objects bright and color-saturated owing to the rough (matte) surface formed in high-temperature firing (1300ºC). Depending on the content of metal oxides, the color of such glazes can vary from light green to dark green or blue-gray. The firing process involved thermal cycling leading to microcracks in the glaze and imparting unique beauty to the objects. Another not less popular style of Chinese porcelain owed to a combination of the colorless transparent glaze and dark blue underglaze mineral paint containing cobalt oxide. The flourishing of blue-and-white porcelain dates back to the early 12th century. In the mid-16th century, the Doucai ('contrasting colors') multicolored porcelain decoration technique became widespread. It combined underglaze cobalt outlines and overglaze mineral colors. The overglaze coatings are commonly nontransparent. They are called opaque or top paints because they overlap the ceramic base color. The Chinese achievements in porcelain decoration are extensively applied nowadays at enterprises fabricating both artistic and household serial objects.

Countries with a dominant Islamic culture widely used colored ceramic tiles covered with glazes or enamels to create complex ornamental surface decorations on buildings facades (arabesques). The best-known architectural buildings decorated with arabesques include the Mosque of Isfahan (Iran), the Registan Square ensemble, and the Guri Amir Mausoleum of Tamerlane in Samarkand (Uzbekistan). The flowering of decorative ceramic mosaics in religious Muslim buildings falls into the 14th–16th centuries.

The Renaissance (14th–16th centuries) was marked by the flourishing of fine arts reflected in novel enamel and glaze applications, including architectural decoration. Thus, the famous Florentine sculptor Luca della Robbia

TABLE 2. Chemical Compositions

Glaze (color)	Ceramic base	Firing temperature, ºC	Components, wt.%			
			SiO_2	Al_2O_3	Fe_2O_3	CaO
Fritted slip (opaque black)	Marl clay	900–1000	59.00	14.54	13.59	4.98
Alkaline with high copper content (translucent dark blue)	Quartz	800–1000	78.97	0.51	0.19	0.70
Alkaline clay (opaque dark blue)	Clay with high iron content	900–1000	51.46	10.10	4.35	8.93
Slip (opaque)	Clay with high iron content	850–1050	45.63	32.52	13.61	0.45
Lime (transparent olive)	China stone	1100–1200	60.40	12.80	1.25	17.20
Translucent red and blue	China stone	1200–1300	71.70	10.40	1.74	8.53
Translucent green-blue	China stone	1200–1250	67.00	13.60–16.20	1.60	7.20–10.13
With high iron content (opaque)	China stone with high iron content	1100–1200	60.11	19.33	7.89	5.99
Fritted underglaze (transparent)	–	1000–1100	63.10	0.93	0.40	1.20
Enamel with high lead content (red)	Porcelain	700–900	24.90	4.78	23.76	2.39

(1400–1482) invented the special composition of an opaque glaze (white and light blue enamels) containing SnO_2. He created numerous architectural items (lunettes, bas-reliefs, sculpture in the round) from majolica covered with his enamels. The works of Luca della Robbia and his nephew Andrea della Robbia were so popular that a manufactory was established in England in the late 19th century to make glazed and enameled sculptures and bas-reliefs in a Della Robbia style. The compositions and structures of Della Robbia glazes and enamels are under careful study in our days [4].

The French hydraulic engineer and potter Bernard Palissy (1509–1589) made an invaluable contribution to the development of colored ceramics covered with decorative glazes and enamels. He described his experiments on the creation of colored glazes and enamels, as well as compositions including Sn, Pb, Fe, Sb, and Cu oxides, sand, and soda, in his treatise ‘On the Potter’s Art, Its Utility, Enamels, and Fire’ (Paris, 1580) [5]. However, the treatise does not describe specific formulations, including the ratio of enamel components and firing modes. Nevertheless, ceramic workshops in Paris and Tours managed to reproduce and imitate Palissy’s techniques in the late 19th century.

Glazes and enamels have found application not only for the exterior aesthetic finishing of ceramics but also in the wide-scale production of sanitary earthenware. They are commonly single-color, white, light blue, or light green porousless shine glazed items, which are easy to clean and are chemically resistant.

An individual area in the technology of decorative vitreous coatings is associated with the development of jewelry enamels applied to a metallic substrate. The jewelry enamels are used for color decoration of metallic articles, primarily gold and silver jewelries. Archaeological surveys revealed that the origin of artistic metal enameling could be referred back to the heyday era of Minoan civilization, preceding the classical antiquity. Thus, of Ancient Colored Glazes [2]

Fluxes, wt.%						Impurities and pigments, wt.%			Total weight, %
MgO	Na_2O	K_2O	PbO	TiO_2	P_2O_5	Cl	CuO	MnO	
1.17	1.60	3.20	–	0.49	0.10	–	0.20	0.31	99.18
–	9.25	0.24	–	–	–	0.59	9.46	0.06	99.97
4.23	14.37	3.31	0.15	0.80	–	–	1.37	0.01	99.08
2.40	0.64	4.18	–	0.51	–	–	–	–	99.94
2.30	0.95	1.60	–	0.70	1.71	–	–	–	98.91
1.60	1.30	3.92	–	0.21	0.42	–	0.10	–	99.92
0.65	0.50	5.60	–	0.08	0.04	–	–	0.55	96.82
1.75	0.11	2.55	–	0.65	1.05	–	–	–	99.43
0.98	16.81	1.32	13.70	0.02	–	–	–	–	98.46
0.11	0.28	0.25	42.90	–	0.10	–	–	–	99.47

the oldest articles of precious metals decorated with colored glass date back to the 15th–16th centuries B.C. and were found in Cyprus and Mycenae. The desire to decorate gold and silver articles led to the creation of cloisonné technique, in which silver or gold wires were soldered to a gold base to add compartments to it and then the space was filled with powdered frit. The frit contained vitreous components and additions for the enamel to acquire desired color and other optical properties. After the frit was placed and dried, the enamel was fired in air at 750–850ºC and the vitreous base fused to dissolve coloring agents. The most common enamel paints in the antiquity and early Middle Ages were Cu, Fe, Cr, and Mn oxides derived from natural minerals. Enamels with additions of paints, such as $Na–Ca–SiO_2$, were used in Byzantine. The cloisonné technique was further developed in Medieval China (Beijing enamel) and Europe (Limoges enamel). In Limoges, a center of vitreous enamel was established to make reliquaries decorated with various enamels by the 12th century [6, 7].

Along with the cloisonné enameling, the champlevé technique was developed and was known as far back as in Hellenistic Egypt and Middle East in the fourth–third centuries B.C. In champlevé enameling, a metallic base was die struck to create a relief pattern whose hollows were filled with frit and further fired to fuse the enamel. This decoration technique for precious metals received further development in Byzantine and then extended to Georgia, Armenia, and Premongolian Rus. Ancient Rus jewelries decorated with cloisonné and champlevé enamels refer back to the 10th–12th centuries. In Rus they were called *finift* (from Greek *fingitis* meaning bright, shiny stone). The $K–Ca–SiO_2$ glass was the base for the Rus enamels. In that period, the largest artistic enameling centers were set up in Kiev, Chernigov, Galich, Vladimir, Ryazan, and Novgorod [8]. However, the experience and traditions of enamel art were lost after the Mongol invasion in 1237–1240, and their renaissance began only in the mid-15th century. The formulation of jewelry enamels was optimized in Europe, Byzantine, and Rus in those times. They mainly included the following components, %:

SiO_2	34–55
H_3BO_3	0–12.5
Na_2CO_3	3–8
K_2CO_3	1.5–11.0
Pb_3O_4	25–40
CaF_2	0–2.5
Na_3AlF_6	1–4
KNO_3	0–2
Oxide pigments	0.1–0.5

It should be noted that a variety of jewelry enamel formulations were developed in the Middle Ages and Modern Age, so the above data may substantially differ from other, widely used formulations. Nevertheless, silica SiO_2 introduced into the charge as quartz sand was the common enamel base. Besides SiO_2, additions of B_2O_3, P_2O_5, and PbO could be introduced to form, together with silica, borosilicate, phosphate, and lead glass, respectively. To decrease the melting point, fluxes were added to the enamels, such as $Na_2B_4O_7$, Na_2CO_3, $CaCO_3$, and Pb_3O_4. To homogenize the enamels and prepare the frit, the components were fused at 1000–1400ºC. Since they form optical transparent glass, opacifiers (SnO_2, TiO_2, CaF_2, and Na_3AlF_6) were used to produce opaque or opalescent enamels, creating nanostructured crystalline inclusions or gas bubbles in the glass that differed by refractive indices from the base.

Paints (pigments) give the final aesthetic appearance to jewelry enamels. Pigments for bulk coloring of enamels are divided into two types: ionic (commonly metal oxides) and colloidal. The first coloring type is determined by the charge of metal cations. Addition of metal oxides to obtain light blue enamels is an example of ionic coloring. The second coloring type is due to selective scattering of white light. Colloidal paints represent particles of some metals (Au, Ag, Cu) and sulfides 10–50 nm in size. Thus, transparent ruby enamels can be produced using additions of nanosized gold particles (Table 3).

Along with the paints shown in Table 3, enamels also include components that decrease the melt surface tension and the contact angle at the metal–melt interface. To improve the wettability, B_2O_3, PbO, K_2O, Na_2O, Li_2O, CaF_2, V_2O_5, MoO_3, and WO_3 are added to enamels. The adhesion between the metal and enamel in cold state is

TABLE 3. Coloring Additives for Medieval Jewelry Enamels

Enamel color	Paint	Coloring type
Yellow	CdS	Colloidal
	$Pb_2Sb_2O_7 + ZnO + Al_2O_3$	Same
	Sb_2O_5	Same
Brown	$Fe_3O_4 + ZnO + Cr_2O_3$	Ion-colloidal
	CdS + CdSe	Colloidal
	$KCrO_2$	Ionic
Red and orange	$PbO + Cr_2O_3$	Ion-colloidal
	Nanosized gold (to 0.03%)	Colloidal
Dark blue	CoO	Ionic
Shades of dark blue	$CoO + MnO + SnO_2 + Fe_2O_3$	Ion-colloidal
Light blue	$CuSO_4$	Ionic
Green and blue-green	$Cr_2O_3 + Al_2O_3 + CoO + Fe_2O_3$	Ion-colloidal
Red and purple	$Mn_2O_3 + MnO$	Ionic
Black	$Cr_2O_3 + CoO + Fe_2O_3 + NiO + MnO_2$	Colloidal

TABLE 4. Compositions of Chemically Resistant Coating Enamels for Steels

Components	Enamel		
	acid-resistant	highly acid-resistant	acid- and alkali-resistant
SiO_2	55–70	60–70	55–60
B_2O_3	2–7	4–5	0–4
Na_2O	13–20	15–20	10–20
K_2O	2–5	–	–
Li_2O	0–3	0–3	4–5
CaO	1–5	5–10	2–6
Al_2O_3	3–4	2–13	3–7
TiO_2	3–6	2–13	–
ZrO_2	–	–	13–18

determined by not only the above factors but also by the compatibility of the thermal expansion coefficients. Artistic enameling of precious metals in the 19th–20th centuries became one of the most expressive ways to ornament jewelries and decorations. This is exemplified by Faberge Easter eggs made in Russia and some decorations (for example, the USSR Red Star Order decorated with transparent ruby silver-based enamel).

In the 18th century, some enterprises in Germany, England, and Sweden tried out industrial enameling of cast iron and steel objects. The production of enameled cast iron cookware, as well as fireplace and stove parts, was arranged at the Lauchhammer Iron Works in 1785. As distinct from jewelry enamels, those on ferrous metals consist of two layers. Besides the base containing CaF_2, SiO_2, and B_2O_3, the first (precoating) layer includes CoO and NiO, required to strengthen the adhesion between the enamel and iron. The color varies from black to dark blue. In addition to the above components, the outer (coating) layer may contain opacifiers, determining the color of enameled objects and coating density: pyrophyllite, cryolite, zinc oxide, zirconium silicate (Table 4).

The most optimum compositions of precoating and coating enamels were developed and commercially introduced in a period from 1860 to 1900. In the 20th century, enamel compositions and technologies for their application onto copper and aluminum parts were developed. Special enamels with a firing temperature of 600–650°C were created for aluminum and 720–800°C for copper. Enamel coatings are placed using slurries or pastes based on dispersed frits, which are applied to metallic objects by spraying or immersing into slurries.

For ferrous metals, precoating enamels are fired at 800–900°C and coating ones at 750–850°C. Technical enameling is currently used in the production of various kitchen appliances and sanitary wares, as well as piping and parts for chemical and pharmaceutical applications when the surfaces need to be protected against corrosion and thermal effects [9, 10].

The following example would help to imagine the scale of commercial enameling: 89.4 thousand enameled cast iron and steel bathtubs were produced in Russia in 2010, and their import to Russia amounted to 277 t.

Therefore, the origin and history of ceramic glazing techniques and enameling technologies can serve as an example of century-old sustainable improvement of formulations and application of inorganic vitreous coatings on ceramics and metals.

REFERENCES

1. A. Lukas, *Ancient Egyptian Materials and Industries*, Edward Arnold, London (1934).
2. P. B. Vandiver, "Ancient glazes," *Sci. Am.*, **262**, No. 4, 106–113 (1990).
3. L. F. Akunova, *Technology for Producing and Decorating Art Ceramics* [in Russian], Vysshaya Shkola, Moscow (1984), p. 243.

4. K. Sakellariou, C. Miliani, A. Moressi, and M. Ombelli, “Spectroscopic investigation of yellow majolica glazes,” *J. Raman Spectrosc.*, **35**, 61–67 (2004).
5. J.-P. Porter, *Bernard Palissy: The Secret of Enamels* [in French], Pygmalion, Paris (2008), p. 237.
6. A. A. Puparev, *Art Enamel* [in Russian], Vsesouz. Kooperativ. Obyedinen. Izd., Moscow (1948), p. 82.
7. E. Brepohl, *Artistic Enameling* [in German], VEB Fachbuch Verlag, Leipzig (1983).
8. T. I. Makarova, *Cloisonné Enamels of Ancient Rus* [in Russian], Nauka, Moscow (1975), p. 136.
9. L. L. Bragina and A. P. Zubekhin (eds.), *Technology of Enamels and Protective Coatings* [in Russian], Iz. Nats. Tekh. Univ. Kharkov Politech. Inst., Kharkov (2003), p. 484.
10. A. A. Appen, *Temperature-Resistant Inorganic Coatings* [in Russian], Khimiya, Leningrad (1967), p. 240.