

## DEVELOPMENT OF ACID PROOF METALLIC LUSTER GLAZES IN MULTI COLOUR

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**ABSTRACT:** Various metals in small quantities, singly and in various combinations, were ground in ceramic frit. It was found that various colored lusters, transparent and opaque, could be developed under a fair degree of control of temperature from cones 010 to 1. After cooling to a dull red heat, the glazes were given a short reduction firing. Standard decorative processes were used with the luster glazes. Additional colors were produced by adding stains and metal oxides. Acid-resistant luster glazes were developed.

**Key words:** Acid resistant, metallic luster, glazes, multi color, firing temperature

### INTRODUCTION

Luster is produced by direct application of very thin layer of metallic paint on the surface of glazed ceramic which after firing at temperatures between 500 to 600°C in a reducing atmosphere results in the formation of a metallic like layer (Perez, et al., 2004, Pradell, et al., 2004).

Luster is a decorative finish in which drawings and patterns applied on the surface of medieval luxury, tin-glazed pottery shows a coppery, golden, and silver-like metallic shine. The most surprising and characteristic luster decoration is the presence of iridescent colors (red, green, blue, and violet). Different recipes allowed potters to obtain several colors, such as yellow, green, olive green, brown amber, chocolate, ruby red, and also several metallic sheens like copper, gold, and silver (Caiger, 1985).

There are two types of lusters.

- (i) “Superficial luster” It is obtained by mixing metallic compounds with a suitable organic reducing medium and applying them to the surface of the glazed ware, which is then fired in oxidizing environment at a low temperature.
- (ii) “Hard luster” It is produced by adding metallic colorants directly to the glaze batch, and the desired reflection and color quality may be obtained by atmosphere and temperature control.

The theory of producing both hard and soft lusters has been discussed by (Piccolpasso, 1976). Most of the available information relates to the soft or “on-glaze” luster, which lacks permanence and depth but is more consistent in performance and combines easily with regular overglaze practice. Despite technical difficulties, the subject of hard luster glazes has always tempted the ceramic artist.

Glass containing a high amount of copper has been used in the preparation of glazes for fine porcelain, stoneware and tiles, which are fired in rapid cycles (45

min) at a temperature of about 1220°C, and show high mechanical properties and has been classified as the most important commercial tiles product (Biffi, 1994).

Among decorative items, gold, silver, and platinum are commonly used, in spite of their high cost. These industrial products containing noble metals are suitable for “third fire” use because they are applied and fired on substrates, which are either glazed or vitreous, that have undergone other firing cycles previously. After firing, the films, which have thickness of a few micrometers and are formed by metals or metallic oxides, have a typically shiny and metallic appearance. It is possible to obtain this metallic effect using different special frits (Siligardi, et al., 2010).

A wide range of Cu to Ag ratio has been observed in the luster layers, ranging from pure silver to pure copper luster decorations, even in the same design. Their chemical composition is related to their color i.e yellow, green to brown for the silver-rich lusters or orange, red to crimson for the copper-rich lusters (Perez, et al., 2004).

Since metallic lusters are being imported and are expensive. So purpose of the study was to develop economical lusters, in quality comparable to imported lusters.

### MATERIALS AND METHODS

Lead, leadless and lead borosilicate glazes were developed and a few of them were selected for study depending upon physical and chemical properties which are presented in table 1.

Experimental study consists of following steps.

- i) Study of the relative importance of the various factors like (a) strength of colorant; (b) dispersion and stability, (c) method and thickness of application, (d) glaze composition, and (e) fringe factors such as rate, atmosphere and temperature to control the development of hard luster glazes

- ii) Establishment of a reliable control over transparency
- iii) Production of acid and wear-resistant effects.

The firing was arbitrarily limited from cones 010 to 1

Copper, bismuth and silver salts were used as metallic colorants in amounts ranging from 0.5 to 14% in various combinations. Before application, a check on the effect of solubility was made by precipitating the soluble colorants in the glaze. Little difference in color effect was observed after firing between the precipitated and the unprecipitated colorant.

The clay bodies were "white" earthenware bisque at cone 6 and "red" earthenware maturing at cone 1. Firing was conducted in a downdraft kiln with natural gas as fuel. Kiln was equipped with a draw-type damper and was so constructed that the air ports and wicket could be tightly sealed during the time of reduction. The volume of fuel was controlled by various sizes of adjustable nozzles. The air was controlled by the usual method of regulating the air intake at the burner and by the manipulation of the draw damper.

The metallic colorants were ball-milled with the glaze batch in the usual way, and the glazes were applied by spraying in varying thicknesses on bisque white earthenware and raw and bisque red earthenware. Two types of settings were tried but, in the early stages of the experiment, the open setting was abandoned in favor of a semi muffle arrangement consisting of punched tile saggars. This setting offered advantages in the elimination of kiln dirt and in the prevention of reoxidation of the glazes. The ware was placed carefully at a level in the kiln which insured a maximum contact with the incoming flames.

Two firing schedules were selected (i) An oxidizing atmosphere was used to the maturing temperature of the glaze, and the kiln was then sealed and allowed to cool to 700°C and reducing atmosphere for 25 to 30 minutes, rising temperature from 50° to 70°C. The kiln was cooled to 600°C and reduced for 15 minutes. ii) Oxidizing atmosphere to the maturing temperature of the glaze, normal cooling to 600°C and reducing for 6 minutes.

**Acid Tests:** Luster glaze effects produced from glazes Nos. 6 to 8 were given acid tests for tableware decorations as described by Koenig and Watts (1934). These treatments were as follows: (a) a 4% acetic acid solution at room temperature immersed for 24 hours; (b) a 3% HCl solution at room temperature immersed for 5 hours; and (c) a 1% Na<sub>2</sub>CO<sub>3</sub> solution at boiling temperature immersed for 30 minutes. An additional test of 1/5 N HNO<sub>3</sub> at room temperature immersed for 15 minutes.

## RESULTS AND DISCUSSION

Various compositions of the glazes used in this study are given in table 1. Copper, bismuth and silver salts were used as metallic colorants in amounts ranging from 0.5 to 14% in various combinations. A little difference in color effect was observed after firing between the precipitated and the unprecipitated colorant. It was found that in copper containing mixture, cinnabar acted as a reducing agent, which transformed tenorite (CuO) to Cuprite (Cu<sub>2</sub>O) however by the addition of sulphur to mixture, tenorite was not reduced to cuprite and copper sulfide was formed at temperatures between 300-500°C, and transformed to CuSO<sub>4</sub> and (CuO. CuSO<sub>4</sub>).

For the silver containing mixture, cinnabar completely inhibited the formation of silver metal. Silver sulfide sulfate was formed at temperatures between 250-500°C and decomposes to form Ag<sub>2</sub>SO<sub>3</sub> and Ag<sub>2</sub>S at temperatures between 500-600°C. The sulfur containing mixture, produced silver sulfide, Ag<sub>2</sub>S, between 200-500°C, but at temperatures between 500-600°C converted to silver metal and some silver sulfide sulfate (3Ag<sub>2</sub>S. Ag<sub>2</sub>SO<sub>4</sub>).

The mechanism involved the ion exchange between the paint and the glaze beneath. In order to this could take place, copper and silver ionic compounds must be formed. In fact, silver and copper ionic compounds were preferred to be exchanged either by Na<sup>+</sup> and/or K<sup>+</sup> ions in the glaze. Ion exchange reaction indicated the formation of these compounds within the temperature range typically ~500-600°C. This temperature was high enough to facilitate ion exchange and diffusion into the glaze but low enough to avoid glaze softening. Cinnabar transformed and decomposed at temperatures >350°C, and produced a sulphur rich locally reducing atmosphere. As a consequence, Cu<sup>2+</sup> was reduced to Cu<sup>+</sup> and copper and silver sulfides were formed at temperatures between 500-600°C. Due to the presence of mercury, the formation of silver metal was inhibited because an amalgam was formed that does not allow for its crystallization. Although sulfides were mainly covalent in nature, the electronic configuration of sulfur leads to the formation of more delocalized bonding systems than in oxides or silicates and complex non stoichiometric compounds (Molera, 2001).

The addition of elemental sulfur to the mixtures assisted the formation of copper and silver at a temperature of >500°C. At temperature >500°C copper oxidized and formed CuSO<sub>4</sub> and CuO. CuSO<sub>4</sub> and silver was transformed to metal silver. Therefore, the use of sulfur containing mixtures could be perfectly adequate for silver lusters because they were fired at low temperature as recorded in ancient documents (Caiger, 1985, Piccolpasso, 1976, Allan and A I Qasim, 1973, Porter, 2003).

In both cinnabar and sulfur containing mixtures, different reactions involving sulfur can enrich the reducing atmosphere with the formation of sulphure dioxide gas (SO<sub>2</sub>) directly in the luster layer, aiding the final reduction and formation of the metal nanoparticles.

**Strength of Colorant:** Heavy concentration of color produced opacity, heavy metallic effects and a general darkening of color. Low concentration tended towards greater transparency, more brilliant color, and higher luster. Silver nitrate in concentration from 0.5 to 2% produced yellow-to-gray colors. Bismuth subnitrate in concentration from 2 to 8% produced ware from gray-to-brown colors. When bismuth subnitrate was used in combination with silver nitrate, an increase was observed in reflecting properties and iridescence plus the coloring effect of bismuth. Copper produced the usual pink to red color and amounts from 1 to 2% which gave metallic copper effect. Rainbow and ruby effect was produced with silver, bismuth and copper, separately and in combination. The average amount of these metals used was silver 1%, bismuth 4%, and copper 1%.

Special attention is currently paid to sophisticated decoration of ornamental ceramics. This characteristic in fact was the most predominant feature of metallic luster. Depth and richness seems to be influenced by the extent of reduction and subsequent reoxidation. A glaze with high boric acid contents, as glaze No. 7, yielded mottled iridescent, opaque, and pearly lusters. Transparency and depth of light penetration was obtained by using lead and lead borosilicate glazes.

**Firing:** The best results seemed to occur when reduction, on cooling, coincided with the softening point of the glaze, which was a factor in preventing reoxidation on cooling. Strong reduction, followed by a tight seal against air, seemed to be essential. Luster effect may be

developed at a wide range of temperature after the glaze has been matured, but these effects can be retained on cooling only if re-oxidation of the glaze is prevented. When reduction occurred below the softening point of the glaze, the effect was more metallic and lacked durability. Tests showed that when low concentrations of metal were used it was best to begin reduction at a temperature as low as possible and to take special precaution against reoxidation.

**Decorative Techniques:** Starting transformation of color and reflectance occurred when luster glazes were applied in moderately thin coats over colored bodies, engobes, and under glazes and fired.

The palette of color possibilities may be broadened further by the introduction of small amounts of coloring oxides, such as cobalt, iron, nickel, chrome, and commercial stains, in conjunction with the metallic colorants.

When semi opaque and transparent luster glazes were used with overglazed and under glazed processes, interesting results were obtained. Unusual color effects were also noted when luster glazes were applied over previously fired high-temperature colored mat glazes. The same process permits decoration in contrasting color and texture.

Acid tests revealed that there was no change in the quality of the luster or in the texture of the glaze. The thickness of luster layer ranged between 400–1000 nm. The experiments indicated that the range of variation in hard luster effects may be controlled within the limits necessary for practical production of many types of ceramic ware. Because only a few of the decorative possibilities were touched in this experiment, future experiments along this line should offer many interesting results.

Table-1. Weight percentage of Glazes

Ingredients	Weight percentages							
	1	2	3	4	5	6	7	8
SiO <sub>2</sub>	59.4	52.6	49.18	52.17	67.27	44.4	55.0	55.2
Na <sub>2</sub> O	3.1	3.5	5.25	2.95	11.65	2.3	6.0	4.1
K <sub>2</sub> O	1.8	0	1.86	2.67	0.19	1.7	0	4.4
CaO	5.5	6.4	6.15	7.07	1.85	4.6	6.4	6.2
B <sub>2</sub> O <sub>3</sub>	3.8	7.4	8.24	7.07	10.85	9.3	13.7	11.0
Al <sub>2</sub> O <sub>3</sub>	5.5	4.8	10.47	9.97	8.19	5.9	4.5	8.2
PbO	21.0	25	18.90	18.09	0	15.3	0	0
ZnO	0	0	0	0	0	5.2	4.3	4.9
ZrO <sub>2</sub>	0	0	0	0	0	11.3	9.7	7.9
Softening point (°C)	880	880	1050	1020	960	820	820	850
Thermal expansion (10 <sup>-7</sup> in./in/°C)	24	27	59	59	59	27	25	27

**Conclusions:** The most important factor seems to be the establishment of complete reduction and prevention of

reoxidation on cooling. If these conditions prevail, luster effects could be developed in the range between 400–

1000 nm at any temperature consistent with the glaze composition and stability of the metal involved. The factors involving types and thicknesses of glazes and the concentration of metal could easily be standardized.

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## REFERENCES

- Allan, J. W and Abu'l-Qasim's Treatise on Ceramics. Iran XI: 111-120 (1973)
- Biffi, G. Fine Porcelain Stoneware Tiles: Technology, Production, Marketing. Gruppo Editoriale, Faenza Editrice, 16-38 (1994).
- Caiger, S. A. Lustre Pottery: Technique, Tradition and Innovation in Islam and the Western World. p 33, Faber and Faber, London, (1985).
- Koenig, C. J. and A. S. Watts. The Durability of Tableware Decorations. J. Am. Ceram. Soc., 17: 259-62 (1934).
- Molera, J., M. Mesquida, J. Pe'rez-Arantegui, T. Pradell, and M. Vendrell. Lustre Recipes from a Medieval Workshop of Paterna. Archaeometry, 43: 455-60 (2001).
- Perez, J., A. Larrea, J. Molera, T. Pradell, and M. Vendrell. Some Aspects of the Characterization of Decorations on Ceramic Glazes. Appl. Phys. A, 79: 235-239 (2004).
- Piccolpasso, C. Li Tre Libri dell'Arte del Vasaio. 1557 Edizioni all'Insegna del Giglio, Firenze, (1976).
- Porter, Y. Les Techniques du Luster Metallique d'apres le Jowhar-Name-ye Nezami (1196 AD). Proceedings of the Conference of Mediterranean Medieval Ceramics (Thessalonica, 1999) 427-436 Edited by Ch. Bakirtzis, La Caisse des Recettes Archeologiques, Athens, Greece, (2003).
- Pradell, T., J. Molera, M. Vendrell, J. Pe'rez-Arantegui, E. Pantos, M. Roberts, and M. DiMichiel. The Role of Cinnabar in Lustre Production. J. Am. Ceram. Soc., 87: 1018-1023 (2004).
- Siligardi, C., M. Montecchi, M. Montorsi, and L. Pasquali. Ceria-Containing Frit for Lustre in Modern Ceramic Glaze. J. Am. Ceram. Soc. 93: 2545-2550 (2010).