METALLIC ENAMELS OF HIGH GLOSS, SMOOTHNESS AND COLOR EFFECTS

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Metallic Enamels of High Gloss, Smoothness and Color Effects

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Abstract Alkali contents of porcelain enamel very often react with the surfaces of metallic pigments during firing at around 800 degrees C., which results in a poor color development. Therefore, a large amount of the pigments must be added to get a good color development, but it loses glossiness substantially.

We have considered how to produce excellent metallic appearance of high gloss, smoothness and color effects with the addition of a reasonably small amount of metallic pigments. The aspects considered are a) chemical compositions of enamel frit, b) selection of metallic pigments, c) milling formula to control surface waviness when sprayed and fired, d) selection of spray guns and application methods and e) firing conditions.

Conclusions Metallic surfaces with high gloss and color effects are obtained with the addition of a reasonably small amount of metallic pigments by improving chemical compositions of frit and milling formula and selection of the pigments. Surface waviness is controlled by adjusting spraying and firing conditions.

Key words Metallic pigments, Color effects, Glossiness, Spraying conditions, Firing conditions

Introduction

Conventional metallic enamels are inferior to metallic paints in appearance in terms of metallic effect, glossiness and surface smoothness. We have planned to develop the metallic enamels which can produce excellent metallic appearance of high gloss and color effects. In order to obtain the high gloss and color effects, firstly we have studied chemical compositions of enamel frit, particularly less reacting with pigments as well as selection of metallic pigments which produce a good color development.

Following examinations of frit and metallic pigment, we have studied application methods to improve surface smoothness. As a result, the development of metallic enamels of high gloss, smoothness and good color effects was successfully done.

Improvement of Frit

Alkali contents of porcelain enamel easily react with the surfaces of metallic pigments during firing over 800 degrees C., which results in a poor color development. Therefore, a large amount of the pigments must be added to get enough color development, but it loses glossiness after firing substantially. The frit newly developed can restrain the reaction with metallic pigments after firing and produce a good color development with the addition of much smaller amount of metallic pigments (one-tenth in wt%). This also improves the glossiness of enamel surface. Excellent metallic appearance can be obtained with this frit at the firing temperature below 820 degrees C..

Selection of Metallic Pigments

Four types of metallic pigments were prepared and enameled using a newly developed frit in the

same conditions. Brightness of each enamel surface after firing was observed by visual observation. Thermal changes were observed by DTA (Differential Thermal Analysis) to figure out the cause of variation of color effect.

Table 1 Firing results of metallic pigments

Type	Color effect	Average particle size (μ m)	Thermal change (heating up to 900 degrees C.)
Pigment A	good	90	Weight loss at around 750 degrees C.
Pigment B	poor	90	Transition point at around 580 degrees C., start melting at 860 degrees C.
Pigment C	excellent	90	No change
Pigment D	poor	30	Weight loss at around 270 degrees C., and then no change up to 900 degrees C.

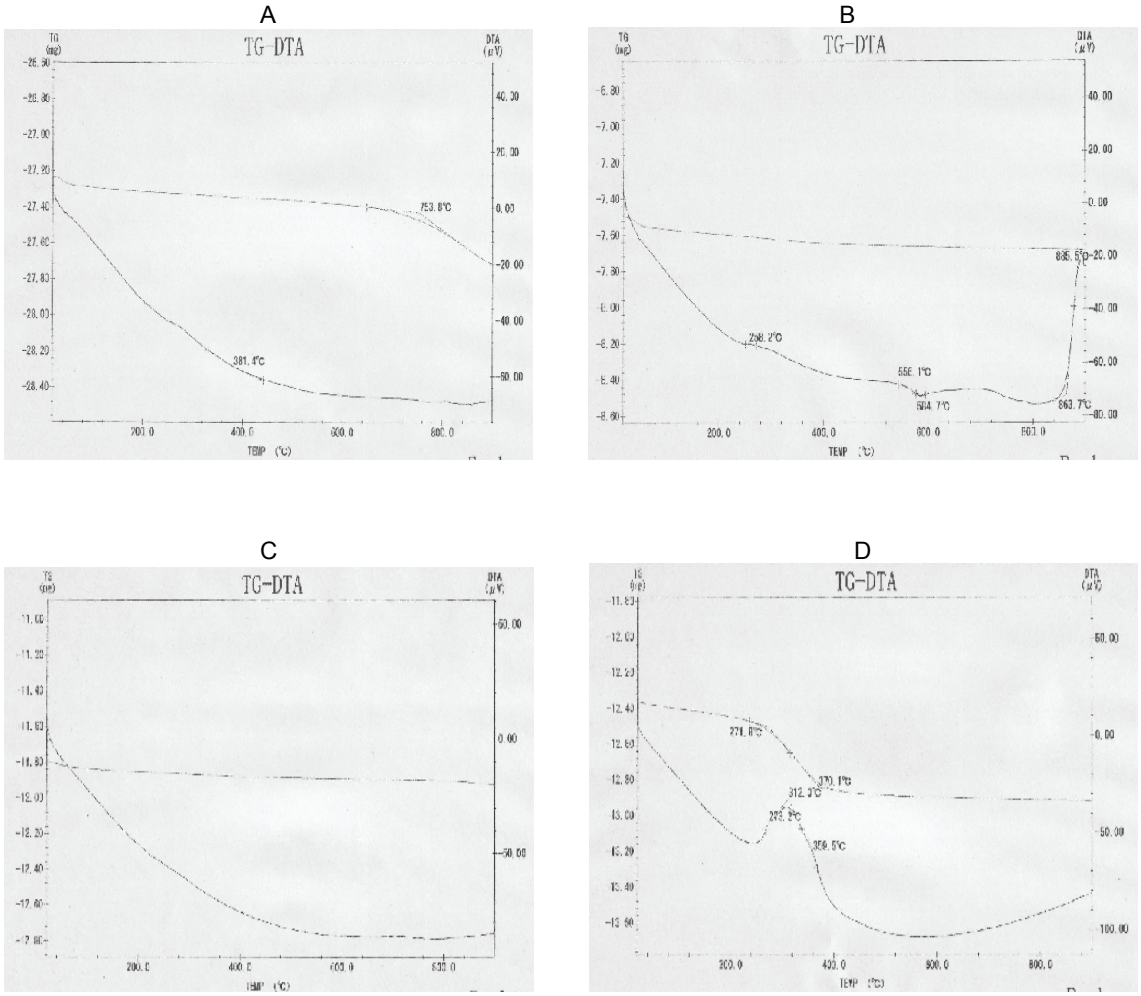


Fig. 1 Measurement results of metallic pigments by DTA

As a result, only pigment C has the excellent color effect and pigment B is next. According to the measurement results of DTA, only pigment C is stable to heat with no heat change up to 900 degrees C..

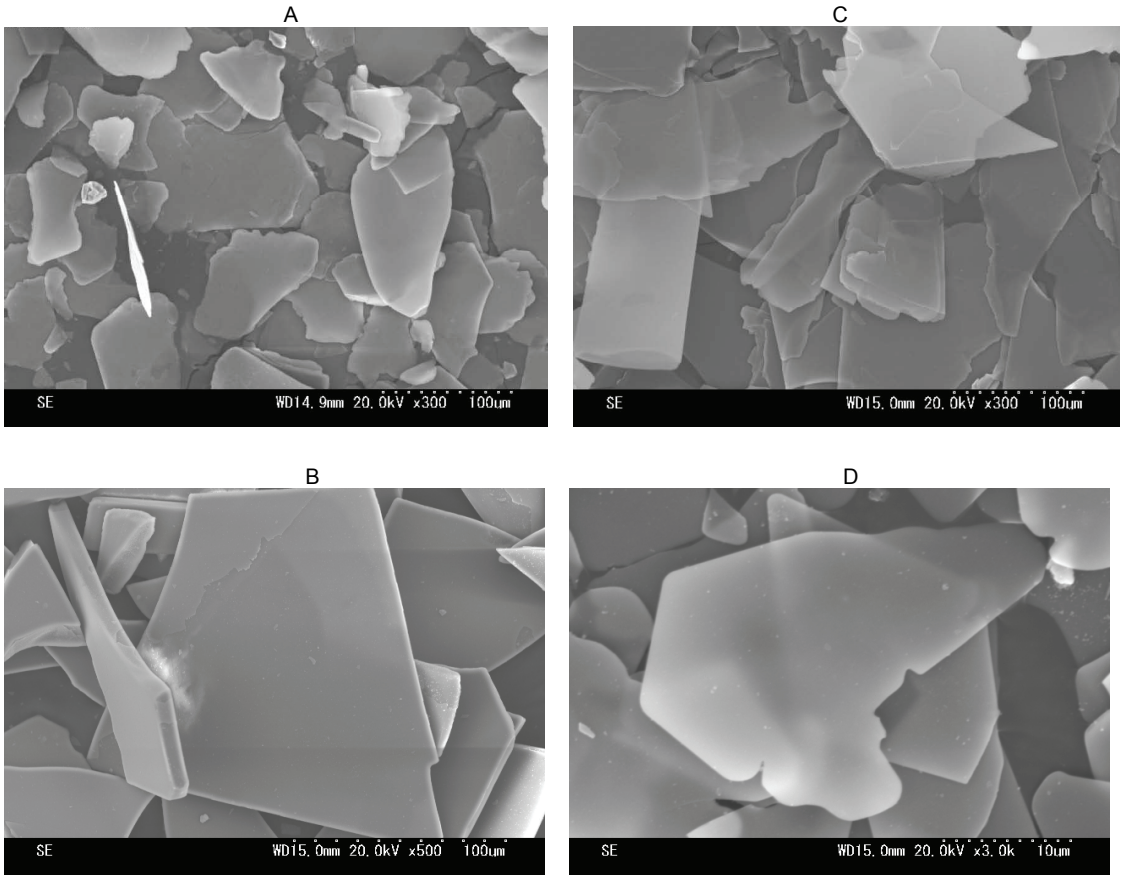


Fig. 2 Electron microscope pictures of pigments

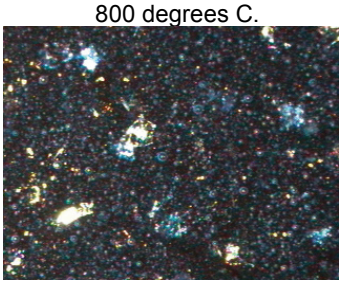
Shapes of the four pigments were observed by electron microscope. The shapes of the four pigments are similar in flake, and there is no significant difference. It is estimated that the thermal changes affected the color effects of A, B and D judging from the measurement results by DTA.

Differences of color effects by combinations of frit and metallic pigment
(observed by electron microscope of 200 magnifications)

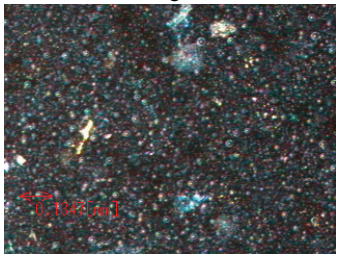
Color effects were examined using our conventional type of frit and newly developed frit, and pigment A and C

Conventional frit ant pigment C

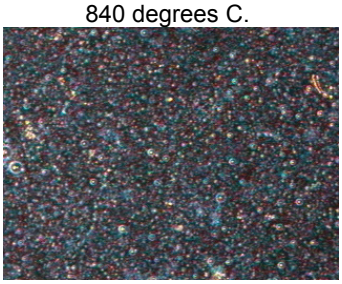
800 degrees C.



820 degrees C.

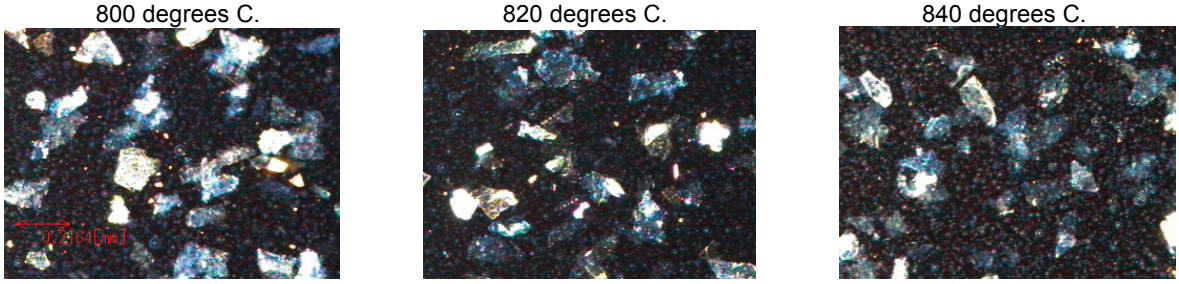


840 degrees C.



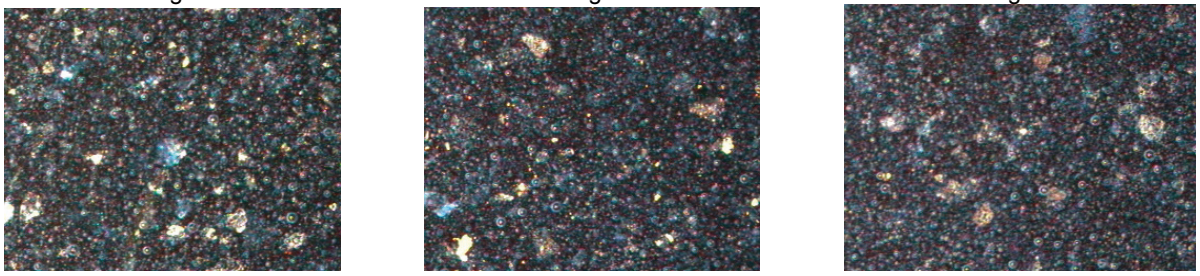
New frit and pigment C

800 degrees C. 820 degrees C. 840 degrees C.



Conventional frit and pigment A

800 degrees C. 820 degrees C. 840 degrees C



New frit and pigment A

800 degrees C. 820 degrees C. 840 degrees C

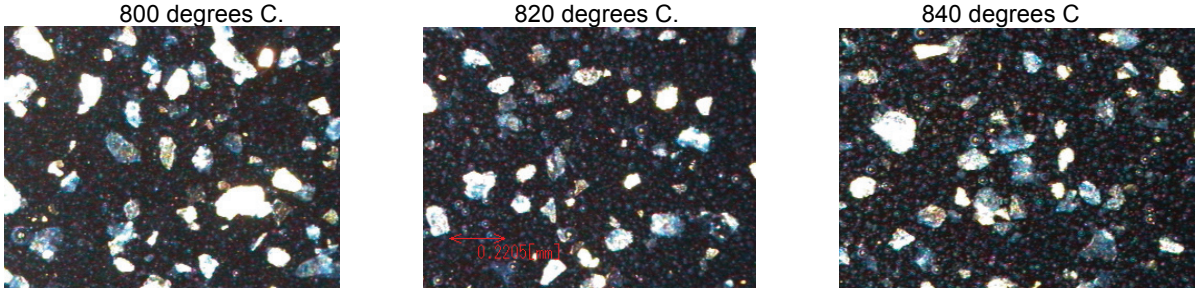


Fig. 4 Differences of color effects by combinations of frit and pigment

Table 2 Results of combinations

Combination	Results
Conventional frit and pigment C	△ some color effect, but not enough
New frit and pigment C	◎ excellent color effect
Conventional frit and pigment A	× poor color effect
New frit and pigment A	○ good color effect, but inferior to pigment C

Excellent color effect was obtained with the combination of new frit and pigment C at 800 and 820 degrees C.. The combination of new frit and pigment A also shows good results. It was confirmed that the new frit restrains the reaction with metallic pigments to a great extent.

Properties of newly developed frit

Coefficient of thermal expansion: 293x10-7/℃ (100-300℃) (FRIT)
Acid resistance (PEI citric acid test): AA (no mark)
Alkali resistance (10% sodium carbonate test): no mark

In developing frit, the following were studied subject to 2 coat application in consideration of how to meet three points, a) surface smoothness after firing, b) adaptability to various colors and c) high glossiness.

Milling formula

2 coat method is recommendable when using various metallic colors. The new frit was developed as top coat. Surface waviness often happens when sprayed or fired metallic enamels. To solve this problem, selection of suitable base coat and milling formulas were inspected for pastel and dark colors.

Example of milling formula of base coat for pastel colors

Frit A (low temperature type)	25
Frit B (middle temperature type)	75
Clay	0-5
Electrolytes	0.2-0.4
Pigments	as required

Example of milling formula of base coat for dark colors

Frit C	100
Clay	0-5
Electrolytes	0.4-0.6
Quartz	0-10
Pigments	as required

Example of milling formula of top coat

New frit	100
Clay	0-5
Electrolytes	0.4-0.6
Pigments	0-4
Metallic pigment	as required

For the pastel colors, a good surface smoothness was obtained according to this milling formula when coated at 100 μm thick even by direct-on application. Application of top coat further improves glossiness and surface smoothness.

Particle size of frit

While average particle size of frit is normally around 20 μm, it was ground to 10 μm . Finer particle size increased surface smoothness after firing. Milling formula was rearranged to protect aging of enamel slip.

Specific gravity and application weight of enamel slip

Good surface conditions were obtained at 1.60 to 1.63 of specific gravity and 15 to 18 g/150cm2 of application weight for both base coat and top coat. Specific gravity and application weight should be adjusted depending on temperature and moisture during operation.

Application methods

Coating tests were made only by manual spray application.
Type of spray gun: Low pressure atomization gun made by company D
Spraying amount: 200-300cc/min.
Air pressure: 0.5Mpa
Spraying pattern: 150mm

Distance from gun to workpiece: 300mm

Smooth surfaces were obtained with the above conditions. Fine atomization by low pressure gun produces good surface and was less affected by firing.

Workpieces were laid down and gun was operated in parallel to make even coating.

Coating thickness
Coating thickness of 80 to 120 μ m for base coat and 80 to 120 μ m for top coat are recommendable.

Firing conditions
2mm thick enameling grade sheet steel and a continuous furnace were used. Firing temperature and time were inspected.

Conditions:
Base coat: 820 degrees C. x 5.5 min. (in hot zone)
Top coat: 810 degrees C. x 4 min. (in hot zone)

Smooth surface and the best metallic color effect were obtained with the above conditions as per picture 5.

The left picture was taken diagonally and shows the surface sprayed and fired by conventional method. The surface is wavy.

The right picture was taken diagonally, too. The surface sprayed and fired by improved method is not wavy.

Comparison of fired surfaces

Surface by conventional method | Surface by improved method

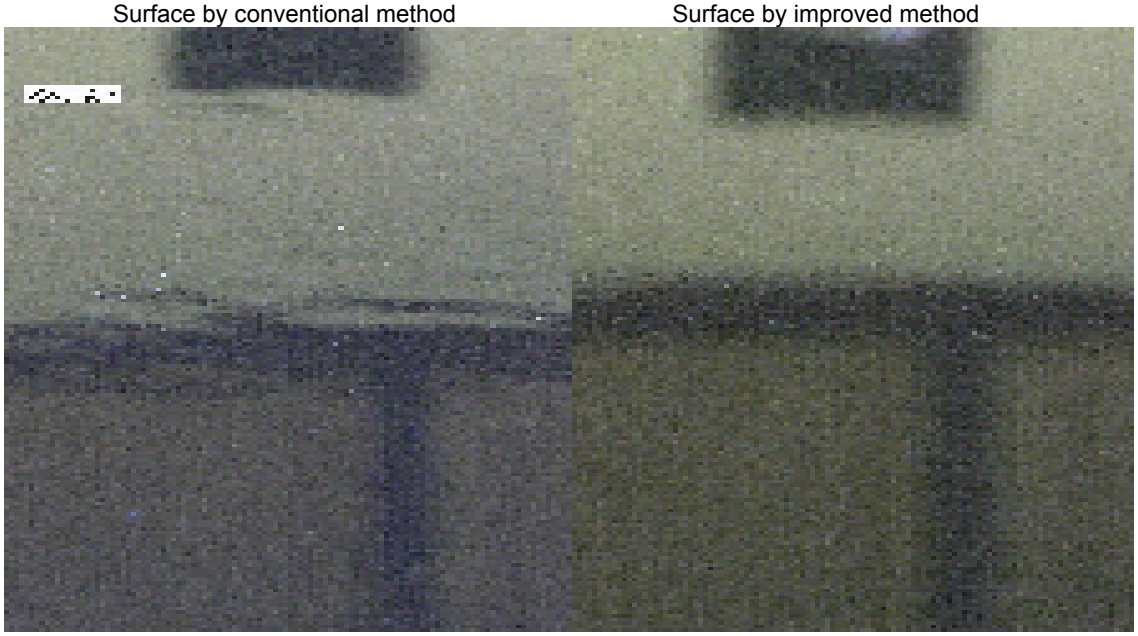


Fig. 5

Conclusions

In order to obtain excellent metallic and smooth surfaces with high gloss and color effects, a) development of new frit, b) selection of metallic pigment, c) modifications of milling formula and slip conditions of base coat and top coat and d) considering spraying and firing conditions were made. The following are the summary.

1) The properties of pigment C does not change at 900 degrees C. and is able to obtain stable light reflectance compared with pigment A, B and D.

2) Newly developed frit is specially formulated to restrain reaction with metallic pigments. Optimizing milling formulas ensure excellent metallic color effects at a firing temperature of 820 degrees C. or below.

3) Smooth surface can be obtained by modifying enamel frit, its particle size, application method, coating thickness and firing conditions.