Materials & Equipment/Whitewares

A Collection of Papers Presented at the
89th Annual Meeting
and the 1987 Fall Meeting
of the Materials & Equipment and
Whitewares Divisions

Cullen Hackler and John C. Meiman
Proceedings Committee

April 26-30, 1987
David L. Lawrence Convention Center
Pittsburgh, PA
and
September 23-26, 1987
French Lick Springs Resort
French Lick, IN

ISSN 0196-6219

Published by
The American Ceramic Society, Inc.
757 Brookside Plaza Drive
Westerville, OH 43081-6136
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Preface

This is the eighth volume of Ceramic Engineering and Science Proceedings to contain papers presented to the Materials & Equipment and Whitewares Divisions. Specifically included are papers from the 1987 Annual Meeting in Pittsburgh, Pennsylvania as well as papers from the 1987 Fall Meeting in French Lick, IN. Use of this publication continues to grow as it is proving to be a very fast and efficient way of disseminating the valuable information presented. It is our sincere hope that the proceedings will see increased interest by authors of technical papers to the benefit of the entire industry.

Direct contact with the individual authors is encouraged in case of any questions, etc. as there may be some inadvertent inaccuracies due to our efforts to publish quickly.

The Proceedings Committee for the Whitewares and Materials & Equipment Divisions wish to thank the authors, program chairmen and others, especially Neil Schattin, for their help in compiling the papers in this volume.

Cullen L. Hackler
John C. Meiman
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Whitewares and Materials & Equipment Divisions
Each issue of Ceramic Engineering and Science Proceedings includes a collection of technical articles in a general area of interest, such as glass, engineering ceramics, and refractories. These articles are of practical value for the ceramic industries. The issues are based on the proceedings of a conference. Both The American Ceramic Society, Inc., and non-Society conferences provide these technical articles. Each issue is organized by an editor who selects and edits material from the conference. Some issues may not be complete representations of the conference proceedings. There is no other review prior to publication.
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Selecting Ceramic Pigments

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Several factors must be considered in selecting a pigment or pigments for a specific application. These factors include the extent and tinctorial strength of the required palette, color uniformity requirements, costs, the compatibility of selected components, whether the pigment is to be used in masstone or letdown, the stability requirements during processing, and particle size requirements.

Introduction

There are several factors which must be considered in selecting a pigment or pigments for a specific ceramic application. The choice of application method determines the processing stability requirements, which for many applications are the most restrictive parameters to be faced. The extent and the purity of the required palette of colors affects the choice and the cost of the pigments. Pigment systems vary in their uniformity and reproducibility. The particle size distribution has two quite separate aspects: the mean size and the extent of coarse particles. Finally, the pigment is only one component of a system that may also include glaze or body, opacifiers, additives of one kind or another, and application media. The compatibility of these diverse components deserves serious attention.

Stability in Processing

A major limitation on the selection of a ceramic pigment is the processing conditions it must undergo during application, and subsequent processing of the ware. There are at least five separate steps in the processing of glazed ceramic ware where pigments can be added: as a body stain, as an engobe, as an underglaze color, as a colored glaze, or as an overglaze or glass color. Using a body stain refers to adding a pigment to the body formulation itself. The technique of applying engobes may be described as that of applying a ceramic pigment with a flux to the surface of an unfired body. Underglaze decorating is the application of color to a bisque body. In colored glazes, the pigment is dispersed in the glaze itself. Overglazes or glass colors are applied to the already formed and fired glaze.

If an engobe or body stain is used, it must be stable to the bisque fire, which is usually between cone 7 (1225 °C) and cone 11 (1300 °C). The engobe must also be stable to the corrosive nature of the flux used to adhere it to the body. Subsequently it must be stable to the glost fire while in contact with the molten glaze.

An underglaze color or a colored glaze must be stable to the glost fire, which is usually between cone 06 (1000 °C) and cone 4 (1200 °C). The pigments therein must be stable to corrosion by the molten glaze.

On the other hand, an overglaze or glass color need only be stable to the
decorating fire in which it is applied, which is usually cone 020 (625 °C) to cone 016 (775 °C). Under these conditions, the most severe requirement is stability to the molten flux used in their application. Very corrosive high PbO fluxes are very common in overglaze decorating.

Table I shows the firing stability for the various pigment systems in use today. The list of pigments is from the DCMA classification, with addition of cadmium pigments. Stability ranges from pigments, such as the various rutiles that can only be used at decorating temperatures in porcelain enamels or glass colors, to pigments that are stable to the most severe conditions. In some cases, there are formulation limitations which will be discussed below.

Thus, processing conditions affect the range and purity of colors obtainable. Yellow, green, blue, brown, and black are obtainable under all conditions, but red and orange are restricted to cone 04 or less.

Palette

In selecting the palette of colors to be used in an application, there are several considerations to be addressed. The limitations imposed by processing have already been discussed. In terms of colors possible, processing primarily limits the ability to obtain red and orange to firings less than cone 04.

A major consideration is the purity of color required. If a very pure color is needed, the choice of pigment to be used is greatly reduced. For example, if a moderately strong yellow is needed, a zirconia vanadium yellow may be satisfactory. But, if a very pure yellow is required, only a praseodymium-zircon yellow will do.

Some of these considerations are illustrated on Fig. 1, which attempts to relate to each other the colors which are currently available. Figure 1 expresses color in the uniform color space, or CIELAB chroma diagram. In this diagram, whites, grays and blacks are clustered near the origin, as they differ only in lightness and have essentially no chroma. A +a reading is a measure of red, a +b of yellow, a -a of green, and a -b of blue. Distance from the origin is an indicator of the purity of color of the pigment.

This chart also shows the colors obtainable with the major pigment families. At the bottom of the chart are the blues. Traditionally, the way to obtain blue is with cobalt. Both CoAl₂O₄ spinel and Co₃SiO₄ olivine are produced. The cobalt silicate involves the use of a considerably higher percentage of cobalt oxide than does the aluminate spinel, with only a modest increase in color intensity.

In the spinel system, it is possible to adjust the shade towards turquoise or green by additions of chromium oxide to replace alumina and zinc oxide to replace cobalt oxide.

The alternative avenue to turquoise blue is vanadium-doped zircon. These pigments are not quite as strong as the cobalt-bearing pigments, and are on the turquoise side of blue, but they have the excellent stability characteristic of zircon pigments.

Historically, green pigmentation was obtained with Cr₂O₃. This material, however, is only of limited stability. It reacts with any zinc oxide or tin oxide in the glaze. More satisfactory results are obtained if chromium is used as a constituent of a calcined spinel pigment. Zinc chromate has a color similar to Cr₂O₃. The cobalt chromate blue-green pigments are a continuum of colors from zinc chromate to cobalt aluminate, which was discussed above.
By using higher concentrations of chromium oxide and lower concentrations of cobalt oxide the greener pigments are obtained. Conversely, by lowering the chromium oxide, and raising the cobalt oxide, shades from blue-green to blue are obtained.

A special type of chromium containing green is the Victoria green garnet. This pigment gives a very beautiful bright green color, but is very transparent. Also, it is a very difficult color to make well, and it is very sensitive to glaze formulation.

There is a limit to the brilliance obtainable with chromium oxide. Brighter glazes can be obtained in systems containing two parts of a praseodymium-zircon yellow to one part vanadium-zircon blue.¹

Just as there are several possibilities for green colors, there are also a number of possibilities for preparing a yellow color.⁴ The zirconia-vanadium yellows⁹ are an economic solution when yellow of only moderate purity is required. A range from lemon yellow to orange yellow is possible. Tin-vanadium yellows¹⁰ have somewhat greater purity, and are of high stability. However, the price of tin-containing pigments has been high in recent years. The best tinting strength in oxide-based pigments is obtained with the praseodymium-doped zircon pigments. This pigment is similar in structure to the vanadium-zircon turquoise blue, and is used with that blue to make greens. When used alone, it gives a bright clean yellow of fairly good stability.

An orange-yellow or maple pigment for use at cone 010 or less is formed from chromium-doped rutile.¹¹ This material decomposes at about 1000°C, but is a useful pigment for lower temperature applications.

The strongest yellow is obtained with cadmium sulfide. However, as a non-oxide material, its stability in oxide-based glazes is very limited.

Brown pigments are found in a small region of color-space near +a = +b = 10. Most of these are chrome-iron-zinc browns.¹¹ Darker pigments with similar color can be produced using manganese oxides. A somewhat lighter and brighter brown, approaching a maple, is found in the chrome-iron-zinc-alumina system. These pigments are really crosses between chrome-iron-zinc browns and chrome-alumina pinks, and have the modest stability characteristic of the chrome-alumina pinks.

It is but a short stop in color space from brown to pink.⁴ Here we find three systems from which to choose. The iron-zircon pinks, or corals as they are sometimes called, are pigments of high stability, but are limited in purity of color. The chrome-alumina pinks have somewhat greater tinting strength, but they are considerably less stable in glazes.

The final system, and the only one to produce purple and maroon shades, is the chrome-tin pink. A purple shade is obtained from a small amount of chrome fired with tin oxide. The rose to maroon shades are obtained in chromium-doped sphene¹²—calcium-tin silicate. These materials are quite sensitive to the glaze composition in which they are placed.

For bright red or orange shades, the only choice is one of the cadmium sulfoselenides.⁴ The chart illustrates the excellent tinting strength of these materials. The color depends on the sulfur-to-selenium ratio. At 19.5% selenide an orange shade is obtained. At ratios of 1.7/1 to 1.3/1 a red is obtained. By 1/1 a maroon is obtained. Unfortunately, these non-oxide pigments have only limited stability in oxide glazes. Oxidation of the cadmium sulfide pigments yields colorless sulfates. Cone 06 is the top of the range for these sensitive materials.
Uniformity, Reproducibility

Most ceramic pigments are prepared by solid state reactions which approach equilibrium only with difficulty. Rapid, uniform and reproducible conversion to the desired pigment requires great care in production. In most cases, adjustment of each lot to standard, using toners, is required.

Certain pigments are inherently difficult to reproduce from lot-to-lot. The Victoria green garnet, the manganese-alumina pink corundum, and the chrome-tin pink sphen are noteworthy for their difficulty in making reproducible pigments. In the case of the chrome-tin pink, this difficulty is related to the simultaneous presence of some chrome-tin orchid cassiterite.

If a small amount (less than 5%) of a strong pigment is used as a component in a blend, it will be difficult to obtain sufficiently uniform mixing that specking is avoided. There is a natural economic tendency in making a light pastel color to use small amounts of strong pigments, since the pigment is usually the most expensive constituent of a glaze. This tendency must be resisted, particularly in the wall tile and sanitary ware industries, where large surfaces must have a uniform color. Particularly difficult in this regard is attempting to make a gray by mixing a black pigment with a white opacifier.

The solution to this problem is to use larger concentrations of a less intense pigment. For example, using a cobalt-nickel gray periclase instead of a black plus a white will give a more uniform color.

There are also pigments which are sensitive to details of the glaze application and firing procedures. With these pigments it may be difficult to maintain uniformity, even within a given lot of material. The Victoria green garnet is very sensitive to firing fluctuations and to the presence of any zinc oxide. The copper greens are so sensitive to glaze acidity and to firing conditions that they are used by artists to obtain one-of-a-kind effects. The cadmium sulfoselendides are sensitive to any conditions which promote oxidation of the pigment. The glaze must be free of any strong oxidizing agents, such as nitrates. By contrast, the glaze must also be free of any reducing agents which can react with the selenium in the pigment to produce black selenides. The gases in the kiln over the glaze can also produce this blackening.

With the exception of the zinc-iron chromite brown spinel, the chromium-containing greens, and the pigments based on zirconia or titania, most pigments impart little opacity to a glaze. There are applications in artware where low opacity is desired, to yield highlights, when applied over uneven surfaces. For most applications, however, uniformity of color is required. To obtain uniformity of color, variations in the surface color of the ceramic body must be excluded. This requires an opaque glaze. Opacity is achieved by additions of an opacifier, usually zircon.

Particle Size

Most calcined ceramic pigments are in the one to ten \( \mu \text{m} \) range in mean particle size, with no residue on a 325-mesh (44 \( \mu \text{m} \)) screen. The selection of an optimum particle size distribution is a compromise between several considerations. It is simply not true that the finest pigment is the best pigment.

In the first place, the tendency for the pigment to dissolve in a molten glaze during manufacture is a function of the pigment surface area per unit value exposed to the glaze, which in turn is inversely proportional to the particle size. Hence the finer the pigment, the greater the tendency to dissolve in the glaze. Dissolution is a particular problem in cobalt-containing pigments,
where it leads to the defect called cobalt bleeding. It aggravates the difficulty in using pigments like cadmium sulfoselenides which are sensitive to reaction with the glaze. Dissolution is particularly noticeable in pigments where the chromophore in solution is of different color than it is in the pigment—as in chrome-alumina pink spinel and chrome-tin pink sphene.

Agglomeration of the pigment, which prevents dispersion of that pigment in a glaze, is also a function of the surface area per unit volume, and hence inversely proportional to the particle size. Titania-based pigments are particularly susceptible to agglomeration. They are usually fluid energy milled before sale to minimize this problem.

On the other hand, the size of the largest pigment particles must be limited to prevent the particles causing an uneven surface. A common rule of thumb is that the maximum particle size should be less than one-tenth the coating thickness. For conventional glazes, this works out to about 20 \( \mu \text{m} \).

Fineness in a pigment is normally obtained by milling that pigment after preparation. Some pigments lose strength as they are milled. This behavior is to be expected for any doped pigment or mordant pigment, where milling exposes surfaces which have not reacted to produce the desired color. All of the zirconia and zircon pigments are in this class.

In a masstone, the color of a glaze is relatively insensitive to the pigment particle size. On the other hand, in a letdown, a finer pigment will usually give a stronger color. This result is due to improved dispersion of the pigment with the opacifier present in a letdown. This difference is illustrated on Fig. 2, which shows the effect of milling time on the lightness of a black pigment. In masstone there is no effect of milling time. In letdown, the lightness decreases significantly as the particle size is reduced by milling.

One further factor is the amount of milling the pigment will receive while the glaze it is used in is milled. The less the pigment is milled in glaze preparation, the finer it must be as supplied.

The conclusion is that the optimum particle size is the largest size that gives adequate dispersion and adequate strength in letdowns.

**Compatibility**

To be successfully used, a ceramic pigment must function as a component in an integral glaze for porcelain enamel system. Hence, it must be compatible with the other components—the glaze itself, the opacifier(s), and the other additives.

Pigment-opacifier compatibility consists mainly in matching elemental types, in order to reduce pigment solubility. Zircon opacifier should be used with all zirconia and zircon pigments. Titania opacifier should be used with titanium-containing pigments. Titania opacifier should be used with titanium-containing pigments. Pigments containing tin oxide, such as chrome-tin pinks and tin-vanadium yellows should be matched with at least some tin oxide opacifier.

There is a large variability in glaze-pigment interaction during firing. Some pigments, such as the zircon pigments, are relatively inert in conventional glazes. Other pigments are much more reactive. Moreover, some glaze constituents are more interactive than others.

Probably the most important glaze consideration is the presence of absence of \( \text{ZnO} \) in the glaze. There are several pigments which are not stable in the presence of \( \text{ZnO} \). These include the manganese-alumina pink corun-
dum, chromium green-black hematite, Victoria green garnet, chrome-tin orchid cassiterite, and chrome-tin pink sphene. On the other hand, the iron brown hematite, chrome-alumina pink spinel, iron-chromite brown spinel, zinc ferrite brown spinel, and zinc-iron chromite brown spinel require high ZnO concentration for adequate stability.

Calcium oxide concentration is important for a number of pigment systems. High concentrations of CaO are required for adequate stability of Victoria green garnet, and chrome-tin pink sphene. By contrast, CaO should be avoided when using chrome-alumina pink spinel, zinc ferrite brown spinel, and zinc-iron chromite brown spinel.

High alumina concentrations required for stability of chrome-alumina pink corundum, managanese-alumina pink corundum, chrome-alumina pink spinel, and zinc-iron chromite brown. Reactive ingredients such as PbO and B₂O₃ should be limited when using zirconium-vanadium yellow baddeleyite, chrome-alumina pink spinel, and the cadmium sulfoselenide pigments. The latter require addition of several percent of CdO to the glaze for adequate stability.

There is only one significant incompatibility between pigments. Pigments containing chromium (III) oxide are incompatible with pigments containing tin oxide. This incompatibility even extends to the sequential passage of ware through a kiln, as trapped volatiles from one can affect the other.

Conclusions

The selection of a pigment or pigments involves a balance between several, often conflicting, criteria. The further a pigment is from the glaze surface, the more durable it will be in service. Conversely, the earlier it is applied in the manufacturing process, the more severe are the conditions it must withstand in production.

The purity and chroma of the required colors affects the pigment choices available. When very pure colors are required, the number of pigment choices is severely restricted. In addition, pigment systems vary in their uniformity and reproducibility. When uniformity is important, pigments should be selected that are less sensitive to processing variables.

The pigment particle size must be fine enough that coarse particles are not visible in the coating, and that adequate dispersion is obtained in letdowns. However, excessive fineness will lead to increased solubility in the glaze, and to difficulties in dispersion.

Finally, the compatibility of the various glaze components—pigment, opacifier, glaze additives—must be considered. The calcium oxide and zinc oxide contents of the glaze, in particular, determine the stability of many pigments.

References