COLORANTS FOR CERAMICS

1. Introduction

Any product that depends on aesthetics for consideration for purchase and use will be improved by the use of color. Hence, many ceramic products, such as tile, sanitary ware, porcelain enameled appliances, tableware, and some structural clay products and glasses, contain colorants.

For both economic and technical reasons, the most effective way to impart color to a ceramic product is to apply a ceramic coating that contains the colorant. The most common coatings, glazes, and porcelain enamels are vitreous in nature. Hence, most applications for ceramic colorants involve the coloring of a vitreous material.

There are a number of ways to obtain color in a ceramic material (1). First, certain transition-metal ions can be melted into a glass or dispersed in a ceramic body when it is made. Although suitable for bulk ceramics, this method is rarely used in coatings because adequate tinting strength and purity of color cannot be obtained this way.

A second method to obtain color is to induce the precipitation of a colored crystal in a transparent matrix. Certain materials dissolve to some extent in a vitreous material at high temperatures, but when the temperature is reduced, the solubility is also reduced and precipitation occurs. This method is used to disperse nonoxide precipitates of gold, copper, or cadmium sulfoselenide in bulk glass. In coatings it is used for opacification, the production of an opaque white color. Normally, some or all of the opacifier added to the coating slip dissolves during the firing process and recrystallizes upon cooling. For oxide colors other than white, however, this method lacks the necessary control for reproducible results and is seldom used.

The third method to obtain color in a vitreous matrix is to disperse in that matrix an insoluble crystal or crystals that are colored. The color of the crystal is then imparted to the transparent matrix. This method is the one most commonly used to introduce color to vitreous coatings.

2. Colored Bodies and Glasses

The addition of oxides to ceramic bodies and to glasses to produce color has been known since antiquity (2). The use of iron and copper oxides predates recorded history. Cobalt was introduced into Chinese porcelain ~700 AD. Chromium compounds have been used since 1800 AD.

The colors obtained depend primarily on the oxidation state and coordination number of the coloring ion (3). Table 1 lists the solution colors of several ions in glass. All of these ions are transition metals; some rare-earth ions show similar effects. The electronic transitions within the partially filled *d* and *f* shells of these ions are of such frequency that they fall in that narrow band of frequencies from 400 to 700 nm, which constitutes the visible spectrum (4). Hence, they are suitable for producing color (qv).

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Table 1. **Solution Colors in Glass**

Ion	Number of *d* Electrons	Color
Ti^{3+}	1	blue-green
V^{3+}	2	gray
V^{4+}	1	blue
Cr^{3+}	3	dark green
Mn^{3+}	4	purple
Fe^{3+}	5	yellow-brown
Fe^{2+}	6	light blue or green
Co^{3+}	6	pink
Co^{2+}	7	dark blue
Ni^{2+}	8	gray
Cu^{2+}	9	light blue

Decolorizing is sometimes desirable (5). In the manufacture of glass, the presence of iron as an impurity cannot be completely avoided. Iron imparts an unacceptable dirty brown color to the glass. If the iron can be oxidized through the use of additives such as arsenic oxide [1327-53-3] (As_2O_3), cerium oxide [1306-38-3] (CeO_2), or manganese oxide [1313-13-9] (MnO_2), the discoloration can be diminished through chemical means. Alternatively, the effect of the iron can be negated through the addition of ingredients that themselves produce complementary colors in the glass. Materials such as selenium [22541-48-6], cobalt oxide [1308-06-1] (Co_3O_4), neodymium oxide [1313-97-9] (Nd_2O_3), and manganese oxide are used for this purpose. The addition of one of these materials produces a slightly darker, but more neutrally colored glass, which is more acceptable visually.

3. Precipitation Colors

Several colors in bulk glass can be produced by precipitation processes. One such technique involves developing a colloidal suspension in the glass matrix (5). Metals, such as gold, silver, and copper (or possibly Cu_2O), and nonoxide pigments, such as the cadmium sulfoselenides, produce strong colors when precipitated from a colloidal suspension in glass (Table 2).

To produce this color, the glass is melted, formed, and annealed as is usually done in making glass, which is followed by reheating to a temperature

Table 2. **Colloidal Precipitation Colors**

Crystal	CAS Registry number	Color
Au	[7440-57-5]	gold
Ag	[7440-22-4]	gray
Cu	[7440-50-8]	red
CdS	[1306-23-6]	yellow
Cd(S,Se)	[a]	red, orange

[a] Cadmium sulfoselenides (CdSSe) [11112-63-3], (Cd_2SSe) [12214-12-9].

where nuclei of the desired material are formed. The temperature is then adjusted to permit these nuclei to grow to an optimum size for the development of the particular color. This process is known as striking the color.

Most striking colors are obtained in glasses containing 10–20 wt% K_2O, 10–22 wt% ZnO, and 50–60 wt% silica. Calcium oxide (CaO) and B_2O_3 may also be present (6). To this batch is added 1–3 wt% CdS, CdSe, and/or CdTe. Melting must be under neutral or mildly reducing conditions. Otherwise, S, Se, and Te will be oxidized to SO_2, SeO_2, or TeO_2, which are colorless.

After casting, the glasses solidify to colorless glass. When reheated at 550–700°C, the glasses precipitate minute crystals of a cadmium sulfoselenide, which causes the absorption edge to move to longer wavelengths, producing colors from yellow to orange, to red, to maroon.

The color obtained is a function of both the composition and the particle size of the precipitated crystals. A redder color results from both increased selenium to sulfur ratio and from larger crystals, caused by a more severe heat treatment. Hence, it is possible to make, a series of color filter types from the same glass by controlled reheating.

A related but different type of colored glass is the ruby glass (6). Ruby glasses can be made in several base glass systems by adding to the batch 0.003–0.1 wt% of a noble metal salt, ie, copper(II) chloride [7447-39-4], silver nitrate [19582-44-6], or gold chloride [13453-07-1], together with a reducing agent such as stannous chloride or antimony oxide. When cooled from the melt, they are usually colorless or weakly colored. Reheating results in a more or less intense red for copper, yellow-brown for silver, and red for gold. The color comes from a colloidal dispersion of metal particles that have precipitated from the glass.

4. Opacification

Whiteness or opacity is introduced into ceramic coatings by the addition to the coating formulation of a substance that will disperse in the coating as discrete particles that scatter and reflect some of the incident light(7). To be effective as a scatterer, the discrete substance must have a refractive index that differs appreciably from that of the clear ceramic coating, because the greater the difference in index of refraction between the matrix and the scattering phase, the greater the degree of opacity. The refractive index of most glasses is 1.5–1.6, and therefore the refractive indexes of opacifiers must be either greater or less than this value. As a practical matter, opacifiers of high refractive index are used. Some possibilities include tin oxide [18282-10-5] (SnO_2), with $n_D = 2.04$, zirconium oxide [1314-23-4] (ZrO_2), with $n_D = 2.40$, zirconium silicate [10101-52-7] ($ZrSiO_4$), with $n_D = 1.85$, titanium oxide [13463-67-7] (TiO_2), with $n_D = 2.5$ for anatase [1317-70-0], and $n_D = 2.7$ for rutile [1317-80-2].

In glazes fired at temperatures $>1000°C$, zircon [14940-68-2] is the opacifier of choice (8). It has a solubility of $\sim 5\%$ in many glazes at high temperature, and 2–3% at room temperature. A customary mill addition would be 8–10% zircon. Thus most opacified glazes contain both zircon that was placed in the mill and went through the firing process unchanged, and zircon that dissolved in the molten glaze during firing but recrystallized on cooling.

The solubility of zircon in glazes is a function of the glaze composition (9). Zinc oxide (ZnO) lowers the solubility, promoting opacification where SrO increases solubility.

In porcelain enamels and in glazes firing under 1000°C, TiO_2 in the anatase crystal phase is the opacifying agent of choice (10,11). Because it has the highest refractive index, TiO_2 is the most effective opacifying agent. However, at temperatures of ~850°C, anatase inverts to rutile in silicate glasses. Once inverted to rutile, TiO_2 crystals are able to grow rapidly to sizes that are no longer effective for opacification. Moreover, because the absorption edge of rutile is very close to the visible, as the rutile particles grow the absorption edge extends into the visible range, leading to a pronounced cream color. Thus while TiO_2 is a very effective opacifier at lower temperatures, it cannot be used >1000°C.

The solubility of TiO_2 in molten silicates is ~8–10%. At room temperature this solubility is reduced to ~5%. Thus when using TiO_2 as an opacifier, substantial amounts, ~15%, must be used.

5. Ceramic Pigments

The principal method of coloration of ceramic coatings is dispersal of a ceramic pigment in a vitreous matrix. To be suitable as a ceramic pigment, a material must possess a number of properties (12) that fall in two categories: strength of pigmentation and stability. The first requirement is high tinting strength or intensity of color. It is also desirable that the color be pure and free of grayness or muddiness. Related to the intensity is the diversity of colors obtainable with similar and compatible materials, since many users blend two or more colors to obtain the final shade desired.

The other important property of a ceramic pigment is stability under the high temperatures and corrosive environments encountered in the firing of glazes. The rates of solution in the molten glass should be very low in spite of very fine particle sizes (~10 μm). Neither should gases be given off as a result of the contact of the ceramic pigment with the molten vitreous material.

Another desirable property for a ceramic color is a high refractive index. For example, valuable pigments are based on spinels [1302-67-6] ($n_D = 1.8$) and on zircon ($n_D = 1.9$), but no valuable pigments are based on apatite ($n_D = 1.6$), even though the lattice of apatite is as versatile for making ionic substitutions as that of spinel.

5.1. Manufacturing.

Although a number of different pigment systems exist, most are prepared by similar manufacturing methods. The first step in pigment manufacture is close control over the selection of raw materials. Most of these raw materials are metallic oxides or salts of the desired metals. Considerable differences in the required chemical purity are encountered, ranging from impure natural minerals to chemicals of industrial-grade purity. In pigment manufacture, purity does not always equal quality. Often less pure raw materials may prove superior in the production of a given pigment.

The raw materials are weighed and then thoroughly blended. The reaction forming the pigment crystal occurs in a high temperature calcining operation. The temperature may range from 500 to 1400°C depending on the particular system. Normally, air is the atmosphere of choice because the pigments must ultimately be stable in a molten oxide coating, so materials sensitive to oxygen have limited use. During the calcination process, any volatiles are driven off and the pigment crystal is developed in a sintering reaction. Some of these reactions occur in the solid state, but many involve a fluid-phase mineralizing pathway. Although a few large volume pigments may be made in rotary kilns, most pigments are placed in saggers of 22–45 kg (50–100 lb) capacity for the calcining operation.

Following calcination, the product may require milling to reduce particle size to that necessary for use. This size reduction may be carried out either wet or dry. If there are soluble by-products, a washing operation may also be required. It is almost always necessary to break up agglomerates by a process such as micronizing.

It has been found that there are several advantages to modification of pigments by addition to the calcined product of a small quantity of a dispersing agent (13).

5.2. Pigment Systems. Most of the crystals used for ceramic pigments are complex oxides, owing to the great stability of oxides in molten silicate glasses. Table 3 lists these materials. Blues, yellows, browns, pinks, blacks, and grays are available in high purity (14). Greens and purples are available in fair purity. However, the purity of red and orange is very poor. Therefore, the one significant exception to the use of oxides is the family of cadmium sulfoselenide red pigments. This family is used because the red and orange colors obtained cannot be obtained in oxide systems; thus it is necessary to sustain the difficulties of a nonoxide system.

Table 3 is arranged by crystal class (16). The crystal class of a given pigment is determined almost solely by the ratio of the ionic sizes of the cation and the anion and their respective valences. Hence, for any given stoichiometry and ionic size ratio, only one or two structures will be possible. In some classes (spinel, zircon), a wide range of colors is possible within the confines of that class. Pigments within a given class usually have excellent chemical and physical compatibility with each other. This compatability is important, as most applications involve the mixing of two or more pigments to achieve the desired shade.

Table 3. **Classification of Mixed-Metal Oxide Inorganic Pigments According to Crystal Class**[a]

Pigment name	CAS Registry number	Formula	DCMA number[b]
	Baddeleyite		
zirconium vanadium yellow baddeleyite	[68187-01-9]	$(Zr,V)O_2$	1-01-4
	Borate		
cobalt magnesium red-blue borate	[68608-93-5]	$(Co,Mg)B_2O_5$	2-02-1

Table 3 (*Continued*)

Pigment name	CAS Registry number	Formula	DCMA number[b]
Corundum–hematite			
chromium alumina pink corundum	[68187-27-9]	$(Al,Cr)_2O_3$	3-03-5
manganese alumina pink corundum	[68186-99-2]	$(Al,Mn)_2O_3$	3-04-5
chromium green-black hematite	[68909-79-5]	$(Cr,Fe)_2O_3$	3-05-3
iron brown hematite	[68187-35-9]	Fe_2O_3	3-06-7
Garnet			
victoria green garnet	[68553-01-5]	$3CaO \cdot Cr_2O_3 \cdot 3SiO_2$	4-07-3
Olivine			
cobalt silicate blue olivine	[68187-40-6]	Co_2SiO_4	5-08-2
nickel silicate green olivine	[68515-84-4]	Ni_2SiO_4	5-45-3
Periclase			
cobalt nickel gray periclase	[68186-89-0]	$(Co,Ni)O$	6-09-8
Phenacite			
cobalt zinc silicate blue phenacite	[68412-74-8]	$(Co,Zn)_2SiO_4$	7-10-2
Phosphate			
cobalt violet phosphate	[13455-36-2]	$Co_3(PO_4)_2$	8-11-1
cobalt lithium violet phosphate	[68610-13-9]	$CoLiPO_4$	8-12-1
Priderite			
nickel barium titanium primrose priderite	[68610-24-2]	$2NiO \cdot 3BaO \cdot 17TiO_2$	9-13-4
Pyrochlore			
lead antimonate yellow pyrochlore	[68187-20-2]	$Pb_2Sb_2O_7$	10-14-4
Rutile–cassiterite			
nickel antimony titanium yellowrutile	[71077-18-4]	$(Ti,Ni,Sb)O_2$	11-15-4
nickel niobium titanium yellow rutile	[68611-43-8]	$(Ti,Ni,Nb)O_2$	11-16-4
chromium antimony titanium buff rutile	[68186-90-3]	$(Ti,Cr,Sb)O_2$	11-17-6
chromium niobium titanium buff rutile	[68611-42-7]	$(Ti,Cr,Nb)O_2$	11-18-6
chromium tungsten titanium buff rutile	[68186-92-5]	$(Ti,Cr,W)O_2$	11-19-6
manganese antimony titanium buff rutile	[68412-38-4]	$(Ti,(Ti,Mn,Sb)O_2$	11-20-6
titanium vanadium antimony grayrutile	[68187-00-8]	$(Ti,V,Sb)O_2$	11-21-8
tin vanadium yellow cassiterite	[68186-93-6]	$(Sn,V)O_2$	11-22-4
chromium tin orchid cassiterite	[68187-53-1]	$(Sn,Cr)O_2$	11-23-5
tin antimony gray cassiterite	[68187-54-2]	$(Sn,Sb)O_2$	11-24-8

Table 3 (*Continued*)

Pigment name	CAS Registry number	Formula	DCMA number[b]
manganese chromium antimony titanium brown rutile	[69991-68-0]	$(Ti,Mn,Cr,Sb)O_2$	11-46-7
manganese niobium titanium brownrutile	[70248-09-8]	$(Ti,Mn,Nb)O_2$	11-47-7
Sphene			
chromium tin pink sphene	[68187-12-2]	$CaO \cdot SnO_2 \cdot SiO_2{:}Cr$	12-25-5
Spinel			
cobalt aluminate blue spinel	[68186-86-7]	$CoAl_2O_4$	13-26-2
cobalt tin blue-gray spinel	[68187-05-3]	Co_2SnO_4	13-27-2
cobalt zinc aluminate blue spinel	[68186-87-8]	$(Co,Zn)Al_2O_4$	13-28-2
cobalt chromite blue-green spinel	[68187-11-1]	$Co(Al,Cr)_2O_4$	13-29-2
cobalt chromite green spinel	[68187-49-5]	$CoCr_2O_4$	13-30-3
cobalt titanate green spinel	[68186-85-6]	Co_2TiO_4	13-31-3
chrome alumina pink spinel	[68201-65-0]	$Zn(Al,Cr)_2O_4$	13-32-5
iron chromite brown spinel	[68187-09-7]	$Fe(Fe,Cr)_2O_4$	13-33-7
iron titanium brown spinel	[68187-02-0]	Fe_2TiO_4	13-34-7
nickel ferrite brown spinel	[68187-10-0]	$NiFe_2O_4$	13-35-7
zinc ferrite brown spinel	[68187-51-9]	$(Zn,Fe)Fe_2O_4$	13-36-7
zinc iron chromite brown spinel	[68186-88-9]	$(Zn,Fe)(Fe,Cr)_2O_4$	13-37-7
copper chromite black spinel	[68186-91-4]	$CuCr_2O_4$	13-38-9
iron cobalt black spinel	[68187-50-8]	$(Fe,Co)Fe_2O_4$	13-39-9
iron cobalt chromite black spinel	[68186-97-0]	$(Co,Fe)(Fe,Cr)_2O_4$	13-40-9
manganese ferrite black spinel	[68186-94-7]	$(Fe,Mn)(Fe,Mn)_2O_4$	13-41-9
chromium iron manganese brownspinel	[68555-06-6]	$(Fe,Mn)\ (Fe,Cr,Mn)_2O_4$	13-48-7
cobalt tin alumina blue spinel	[68608-09-3]	$CoAl_2O_4$	13-49-2
chromium iron nickel black spinel	[71631-15-7]	$(Ni,Fe)(Cr,Fe)_2O_4$	13-50-9
chromium manganese zinc brown spinel	[71750-83-9]	$(Zn,Mn)Cr_2O_4$	13-51-7
Zircon			
zirconium vanadium blue zircon	[68186-95-8]	$(Zr,V)SiO_4$	14-42-2
zirconium praseodymium yellow zircon	[68187-15-5]	$(Zr,Pr)SiO_4$	14-43-4
zirconium iron coral zircon	[68187-13-3]	$(Zr,Fe)SiO_4$	14-44-5

[a] Refs. 1,13.

[b] Dry Color Manufacturers Association, Arlington, Va.

Red Pigments. There are no oxides that can be used to give a true red pigment that is stable to the firing of ceramic coatings. Hence, orange, red, and dark red colors are obtained by the use of cadmium sulfoselenide pigments (7,17–19). The cadmium sulfoselenides are a group of pigments based on solid solutions of cadmium selenide, cadmium sulfide, and/or zinc sulfide.

The synthetic pigment is produced by one of several related procedures. The best quality product is made by reaction of an aqueous solution of $CdSO_4$ or $CdCl_2$ with a solution of an alkaline metal sulfide or H_2S. Zn, Se, or Hg may be added to the CdS to produce shade variations. After precipitation, the color is filtered, washed, and calcined in an inert atmosphere at 500–600°C.

The colors come in a range of shades from primrose yellow through yellow, orange to red, and maroon. The primrose or light yellow color is produced by precipitating a small amount of ZnS with the CdS. The orange, red, and maroon shades are made by incorporating increasing amounts of selenium compounds with the CdS. An orange pigment is obtained at a CdS to CdSe ratio of ~4:1. A red pigment is obtained at a ratio of CdS/CdSe of 1.7:1. A deeper red is formed at a ratio of 1.3:1. A very deep red-maroon is manufactured at a ratio of 1:1.

These pigments require a glaze specially designed for their use. The glaze will contain only small amounts of PbO, B_2O_3, or other aggressive fluxes, because strong fluxes react with the selenium to form black lead selenide. The glaze should have a low alkali content. It should contain a few percent of CdO so that its chemical potential for Cd, relative to Cd in the pigment, is reduced. The glaze must also be free of strong oxidizing agents, such as nitrates, which hasten the breakdown of the cadmium sulfoselenide pigment.

The resistance of these materials to firing temperature is definitely limited. They can be fired to ~1000°C. Hence, they are limited to use in porcelain enamels and in low firing artware glazes.

These sulfoselenide pigments have good resistance to alkali solutions, but poor resistance to even dilute acids. Owing to the latter, together with the high toxicity of cadmium, cadmium sulfoselenide pigments should not be used in applications that will come in contact with food and drink. They must also be handled with great care to avoid the possibility of ingestion.

In an attempt to extend the firing range of these colors, the inclusion pigments (12,20) have been developed. In these pigments cadmium sulfoselenides are incorporated within a clear zircon lattice. The superior stability of zircon is thus imparted to the pigment. Colors from yellow to orange-red are available. Deep red is not available, and the purity of these colors is limited.

Pink and Purple Pigments. Although red is not available in oxide systems, pink and purple shades are obtained several ways. One such system is the chrome alumina pinks (19,21). Chrome alumina pinks are combinations of ZnO, Al_2O_3, and Cr_2O_3. Depending on the concentration of zinc, the crystal structure may be either spinel or corundum. The latter is analogous to the ruby.

In general, a ceramic coating formulated for use of a chrome alumina pink should be free of CaO, low in PbO and B_2O_3, and with a surplus of ZnO and Al_2O_3. Using an improper coating may lead to a brown instead of a pink. Sufficient ZnO must be in the coating to prevent the glaze from attacking the pigment and removing zinc from it. An excess of alumina prevents the molten coating from dissolving the pigment.

A related but somewhat stronger pink pigment is the manganese alumina pink (7,19). This composition is formulated from additions of manganese oxide and phosphate to alumina and produces a very pure clean pigment. It requires a zinc-free coating high in alumina. Unfortunately, this pigment cannot be made without creating some serious pollution problems and there is question as to its continued availability.

The most stable pink pigment is the iron-doped zircon system (12,19,22,23). This pigment is made by calcining a mixture of ZrO_2, SiO_2, and iron oxide at a stoichiometry to produce zircon. This pigment is sensitive to details of the manufacturing process, so one manufacturer's product may not duplicate another's (24,25). Color variations extend from pink to coral. The pigments are stable in all coating systems, but those without zinc are bluer in shade.

The chrome–tin system is the only family to produce purple and maroon shades, as well as pinks. The system can be defined as pigments that are produced by the calcination of mixtures of small amounts of chromium oxide with substantial amounts of tin oxide. In addition, most formulations contain substantial amounts of silica and calcium oxide.

The chemistry of these materials is complex (19,26). If one mixes $\sim$90% of tin oxide with small amounts of Cr_2O_3 and either CaO or CeO_2, together with B_2O_3 as a mineralizer, one obtains a purple or orchid shade. The crystal structure is cassiterite. This pigment is a solid solution of chromium oxide in tin oxide. Although this is not the crystal structure of most chrome–tin pinks, residual amounts are present in almost all cases. This residual amount of chromium-doped tin oxide gives most chrome tin pinks a gray or purple overtone.

Most chrome–tin pinks also contain substantial amounts of CaO and SiO_2. Only in the presence of these materials can pink, red, or maroon shades be obtained. Here, the crystal structure is tin sphene ($CaO{-}SnO_2{-}SiO_2$) with Cr_2O_3 dissolved as an impurity.

The color of this pigment depends on the ratio of Cr_2O_3 to tin oxide. With high chrome contents, the pigments are green. As the chrome is reduced, the color becomes purple at a Cr_2O_3/SnO_2 ratio of 1:15, red at a ratio of 1:17, maroon at a ratio of 1:20, and pink at a ratio of 1:25.

These pigments must be used in a coating low in ZnO and high in CaO. Some SnO_2 should be used as an opacifier, in order to increase the strength and stability of the pigment.

Gold purple, often called Purple of Cassius, is a tin oxide gel colored by finely divided gold (7). It has good coverage and brilliance in low temperature coatings such as porcelain enamels. It is a very expensive pigment, because of its difficult preparation as well as the price of gold.

Brown Pigments. The most important brown pigments used in ceramic coatings are the zinc iron chromite spinels (19,27,28). This pigment system produces a wide palette of tan and brown shades. It can be controlled with reasonable care to produce uniform, reproducible pigments. In this pigment, the Cr_2O_3 is found on the octahedral sites of the spinel structure; the ZnO is found on the tetrahedral sites and the iron oxide is distributed in such a way as to fulfill the stoichiometry of the structure. Consequently, adjustment of the formula does result in alteration of the shade. For example, minor additions of NiO to this system produce a dark chocolate brown. The presence or absence of iron on the tetrahedral site affects the yellowness of the shade. Because they are comparatively low in price, these pigments are the browns selected for most applications.

Two systems closely related to the zinc iron chromites have been developed to improve the stability and firing range of brown pigments (19). The first of these is the zinc iron chrome aluminate pigment. It is a hybrid of the zinc iron chromite brown and the chrome alumina pink. It produces warm and orange brown shades of improved firing stability. The pigment must be used in coatings high in ZnO and Al_2O_3, low in CaO.

The other related pigment is the chrome iron tin brown, often called a tin tan. It must always be used in a ZnO containing coating, since the pigment requires ZnO from the coating to react during the firing process to produce a zinc iron chromite pigment. This pigment is characterized by excellent stability at low concentrations. Thus it makes an excellent toner for tan and beige shades in blends with pink pigments.

The last brown pigment to be considered is the iron manganese brown, which is the deep brown associated with electrical porcelain insulators and with artware and bean pots. In many glazes, the presence of manganese will cause poor surface and unstable color. Hence, the use of this pigment is limited to dark colors on products where glaze surface quality requirements are modest.

Yellow Pigments. There are several systems for preparing a yellow ceramic pigment. Moreover, there are valid technical and economic reasons for the use of a particular yellow pigment in a given application (19). The pigments of greatest tinting strength, the lead antimonate yellows, cadmium sulfide, and the chrome titania maples, do not have adequate resistance to molten ceramic coatings. Thus other systems must be used if the firing temperature is $>1000^\circ C$.

Zirconia vanadia yellows are prepared by calcining ZrO_2 with small amounts of V_2O_5 (19,29,30). Small amounts of Fe_2O_3, with or without TiO_2, may be used to alter the shade from lemon yellow to orange yellow. In ceramic coatings, zirconia vanadia yellows are usually weaker than tin vanadium yellows and dirtier than praseodymium zircon yellows. However, they are economical pigments for use with a broad range of coatings firing at temperatures $>1000^\circ C$. They are brighter and stronger in glazes low in PbO and B_2O_3.

Tin vanadium yellows are prepared by introducing small amounts of vanadium oxide into the cassiterite structure of SnO_2(19,31). Tin vanadium yellows develop a strong color in all ceramic coating compositions. They are very opaque pigments, requiring little further opacification. The pigments are not stable under reducing conditions. They are incompatible with pigments containing Cr_2O_3. However, the primary deterrent to their use is the very high cost of the SnO_2, their principal component.

The praseodymium zircon pigments are formed by calcination of $\sim 5\%$ of praseodymium oxide with a stoichiometric zircon mixture of ZrO_2 and SiO_2 to yield a bright yellow pigment (12,19,31,32). The crystal structure is zircon. These pigments have excellent tinting strength in coatings fired to as high as $1280^\circ C$ (cone 10). They can be used in almost any ceramic coating, although preferably with zircon opacifiers. They are compatible with most other pigments, particularly other zircon and zirconia pigments.

For applications fired $<1000^\circ C$, the tinting strength of the lead antimonate pigment is unsurpassed, except by the cadmium sulfoselenides (19). These

Pb–Sb pigments are very clean and bright and have good covering power, requiring little or no opacifier. Their primary limitation is their instability above 1000°C, followed by volatilization of the Sb_2O_3. Substitutions of CeO_2, Al_2O_3, or SnO_2 are sometimes made for a portion of the Sb_2O_3 to improve stability, but these are just palliatives. Hence, their use is limited to coatings such as porcelain enamels, which fire at temperatures $<1000°C$. Moreover, such pigments are formulated with toxic materials, and great care is required in their use.

An orange-yellow pigment is formed when Cr_2O_3 is added together with Sb_2O_3 and TiO_2 to form a doped rutile (19,33). This material gives an orange yellow or maple shade useful at lower firing temperatures. Like the lead antimony yellows, this material also decomposes $\sim$1000°C. It has substantial use in enamels, where it is the basis for some of the more important appliance colors.

Cadmium sulfide yellow can be considered for the brightest low temperature applications (16,19). It is a very bright, clean orange yellow. Primrose yellow and light yellow shades are made by precipitating small amounts of ZnS with the CdS. All the limitations of the cadmium sulfoselenide reds discussed above apply to the cadmium sulfide yellow.

Green Pigments. Just as there are several alternative yellow pigments, there are several alternative green pigments (19,34). Formerly, the chromium ion was the basis for green pigments. Green Cr_2O_3 itself may be used in a few applications. This procedure, however, has several limitations. There is some tendency for pure Cr_2O_3 to fume and volatilize during firing of the coating, leading to absorption of chromium into the refractory lining of the furnace. Chromium oxide is incompatible with tin oxide, reacting to form a pink coloration. The coating must not contain ZnO, because ZnO in the coating reacts with Cr_2O_3 to produce an undesirable dirty brown color.

Higher quality results are obtained if chromium oxide is used as a constituent in a calcined pigment. One such system is the cobalt zinc alumina chromite used to produce blue-green pigments. These pigments are spinels in which varying amounts of cobalt and zinc appear in the tetrahedral sites and varying amounts of alumina and chromium oxide appear in the octahedral sites. By using higher concentrations of Cr_2O_3 and lower amounts of CoO greener pigments are obtained. Conversely, by lowering the amounts of Cr_2O_3 and raising the amount of CoO, shades from blue-green to blue are obtained. These pigments should only be used in strong masstones. In low concentrations they give an undesirable dirty gray color.

Victoria green is prepared by calcining silica and a dichromate with calcium carbonate to form the garnet $3CaO{-}Cr_2O_3{-}3SiO_2$. This pigment gives a transparent bright green color. It tends to blacken if applied too thinly. It is not satisfactory for opaque glazes or pastel shades because then it has a gray cast. It can be used only in zinc-free coatings with high CaO content, which is a difficult, costly pigment to manufacture correctly.

Because of all the difficulties with the use of chromium-containing pigments and because there is a definite limitation on the brilliance of green pigments made with chromium, many green ceramic glazes are now made with zircon pigments (12,19). The cleanest, most stable greens are obtained today by the use of blends of a zircon vanadium blue and a zircon praseodymium yellow. The bright green shades are obtained from a mixture of about two parts of the yellow pigment to one part of the blue pigment.

The final green to be discussed involves copper compounds for low firing-temperature applications. The use of copper is of little interest to most industrial manufacturers, but the colors obtained from them are of great interest to artists because of the many subtle shades that can be obtained. These subtle shade variations arise because the pH of the glaze used has a particular effect on the colors obtained. If the coating is acidic, a beautiful green color is developed; but if the coating is alkaline, a turquoise blue color results. The copper oxide dissolves in the coating producing a very transparent color. Copper oxide glazes are limited to 1000°C because of copper volatilization. Also, copper oxide renders all lead-containing glazes unsafe for use with food and drink (35).

Blue Pigments. The traditional way to obtain blue in a ceramic coating is with cobalt, which has been used as a solution color since antiquity (19,36). Today, cobalt may react with Al_2O_3 to produce the spinel $CoAl_2O_4$ or with silica to produce the olivine Co_2SiO_4. The silicate involves higher concentrations of cobalt, with only modestly stronger color. In porcelain enamels and glass colors, pigments based on cobalt continue to be fully satisfactory both for stability and for tinting strength. At the higher temperatures used for ceramic glazes, difficulties arise from partial solution of the pigment, and diffusion of cobalt oxide in the glaze, causing a defect called cobalt bleeding.

In glazes, the cobalt pigments have been largely replaced by pigments based on vanadium-doped zircon (12,19,37,38). These pigments are turquoise in shade and are less intense than the cobalt pigments. Therefore, they are not applicable when the greatest tinting strength is required or when a purple shade is called for. Where they are applicable they give vastly improved color stability.

The zircon vanadium blue pigment is made by calcining a mixture of zirconia, silica, and vanadia in the stoichiometry of zircon and in the presence of a mineralizer. Mineralizers, selected from various halides and silicohalides, facilitate the transport of the silica during the reaction forming the pigment (24). The strongest pigments are formed at the stoichiometry of zircon, using such mineralizers as will facilitate the various transport processes, incorporating the maximum amount of vanadium into the zircon structure.

5.3. Black Pigments. Black ceramic pigments are formed by calcination of several oxides to form the spinel structure (19,39,40). The formulation of black illustrates the flexibility of the spinel structure in incorporating various chemical entities. The divalent ion may be cobalt, manganese, nickel, iron, or copper. The trivalent ions may be iron, chromium, manganese, or aluminum. The selection of a particular black pigment depends somewhat on the specific coating material with which the pigment is to be used. Care must be taken to see that the pigment does not show a green, blue, or brown tint after firing. Of particular importance is the tendency of some glazes to attack the pigment and release cobalt. Thus in some cases it is desirable to use a cobalt-free pigment.

The prototype black is a cobalt iron chromite. In some systems, however, it will have a slight greenish tint. In zinc-containing glazes, a black with some nickel oxide would be recommended. For a black with a slightly bluish tint, a formula containing manganese and higher cobalt would be recommended. For a black with a brownish tint, a complex formula containing cobalt, iron, nickel, manganese, alumina, and chrome would be recommended.

When a cobalt-free system is needed, there are three possibilities. The copper chromite black pigment is a spinel, which is suitable for use in coatings firing below 1000°C, such as porcelain enamels. The chromium black hematite is an inexpensive system that is suitable for use in zinc-free coatings (41,42). If ZnO is present, it will react to form a brown color. For glazes firing >1000°C, and containing ZnO, the chromium iron nickel black spinel can be used (39,43). This pigment can be used in most glazes and on firing schedules as high as cone 10.

5.4. Gray Pigments.

It might be expected that the easiest way to obtain a gray pigment would be to dilute a black pigment with a white opacifier. However, it is very difficult to provide an even color, free of specking, with this technique. Usually, it is preferable to select a compound that has been formulated to give a gray color.

It is easiest to obtain a uniform gray color when a calcined pigment is used that is based on zirconia or zircon as a carrier for various ingredients of blacks such as Co, Ni, Fe, and Cr oxides (19). This pigment is called cobalt nickel gray periclase. For underglaze decorations it is possible to prepare a very beautiful deep gray color by dispersing antimony oxide in tin oxide. The limitation on the use of this material is the high cost of the SnO_2, which limits its use to special effects.

6. Economic Aspects

Owing to the limited market and the variety and complexity of the products, ceramic pigments are manufactured by specialist firms, not by the users. The principal producers are Ceramic Color and Chemical Corp., Englehard Corp., Ferro Corp., General Color and Chemical Corp., Mason Color and Chemical Corp., and Pemco Corp. Estimated annual production is ~2500–3000 metric tons. This figure does not include some of the same and similar products manufactured for use in non-ceramic applications. The costs of ceramic pigments range from \$10 to \$60/kg or higher, depending on the elemental composition and the required processing. The most expensive pigments are those containing gold and the cadmium sulfoselenides.

7. Health and Safety Factors

Properly handled, ceramic colorants should not cause unacceptable problems of health and safety. Preventive measures to avoid inhalation of fine particulate matter should invariably be used. Care should be taken to avoid ingestion of pigments by thorough washing before eating or smoking. Particular care should be taken in handling cadmium sulfoselenide pigments and lead antimonate pigments, which are highly toxic if ingested or inhaled (44).

When these pigments are used with lead-containing glazes, care should be exercised to use lead-safe glaze materials (see LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY).

8. Use of Pigments in Coatings

There are several additional factors that must be considered in selecting pigments for a specific coating application (44). These factors include processing stability requirements, pigment uniformity and reproducibility, particle size distribution, dispersibility, and compatibility of all materials to be used.

8.1. Processing Stability. A significant limitation on the selection of ceramic pigments is the set of processing conditions imposed during coating application and firing (44). An engobe or body stain must be stable to the bisque fire, usually between cone 7 (1225°C) and cone 11 (1300°C). An underglaze color, or a colored glaze, must be stable to the glost fire, usually between cone 06 (1000°C) and cone 4 (1200°C), and to corrosion by the molten glaze ingredients. An overglaze or glass color needs only to be stable to the decorating fire by which it is applied, usually between cone 020 (625°C) and cone 016 (775°). More important here is corrosion by the molten flux used in the application.

The stability of the various pigments is discussed above for those pigments with limited stability. Detailed information is available (44).

8.2. Uniformity and Reproducibility. For most ceramic pigments rapid, uniform, and reproducible conversion to the desired product requires great care in production (44). Adjustment of each lot to standard, using toners, is usually required. The Victoria green garnet, the manganese alumina pink corundum, and the chrome–tin pink sphene are noteworthy for their difficulty in making reproducible product.

If a small amount (<5% of the blend) of a strong pigment is used as a component in a blend, it will be difficult to obtain sufficiently uniform mixing to avoid specking. It is preferable to use larger concentrations of a less intense pigment.

Some pigments 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, the copper greens, and the cadmium sulfoselenides are particularly sensitive to these problems.

8.3. Particle Size. Most calcined ceramic pigments are in the 1–10-μm range in mean particle size, with no residue on a 325 mesh (44 μm) screen. The selection of an optimum particle size distribution is a compromise between considerations of dissolution rate, agglomeration of the pigment, loss of strength on milling, uneven surface smoothness, and pigment strength (44–47). The optimum particle size is the largest size that gives adequate dispersion and adequate strength in letdowns.

8.4. Dispersibility. Pigments modified with a dispersion additive take less time and energy to disperse in a coating (13,48). The equipment for blunging is simpler and less expensive than ball mills. Color correction is simplified and settling is minimized. Color strength in letdowns is often improved (46).

8.5. Compatibility. A ceramic pigment must function as a component in a glaze or porcelain enamel system. Hence, it must be compatible with the other components, ie, the glaze itself, the opacifier(s), and other additives (44). There is a large variability in glaze–pigment interaction during firing. Some pigments, such as the zircon compounds, are relatively inert in conventional glazes. Other pigments are much more reactive. In particular, it is important to prevent reaction of a pigment with a glaze component to produce a more stable pigment

(49). Hematite pigments react with divalent ions in the glaze to form spinels. Victoria Green garnet reacts with divalent ions to form spinels plus silicates.

Probably the most important glaze consideration is the presence or absence of ZnO in the glaze (19). The manganese alumina pink corundum, chromium, green–black hematite, Victoria green garnet, chrome–tin orchid cassiterite, and chrome–tin pink sphene are not stable in the presence of zinc oxide [1314-13-2], (ZnO). 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. High calcium oxide concentration is required for adequate stability of Victoria green garnet and chrome–tin pink sphene. Calcium oxide should be avoided when using chrome alumina pink spinel, zinc ferrite brown spinel, and zinc iron chromite brown spinel. Pigments containing chromium(III) oxide are incompatible with pigments containing tin oxide.

The presence or absence of PbO in a glaze affects some pigments (50). Victoria green and cobalt black pigments are stronger in a high PbO glaze. Zircon vanadium blue, zirconia vanadium yellow, and chrome–tin pink pigments are only suitable for low PbO or lead-free glazes. Mixed zircon greens, zircon iron pink, zinc iron chromite brown, and zirconia gray pigments are stronger in low PbO and lead-free glazes.

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