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MATERIALS AND METHODS USED IN THE MANUFACTURE OF ENAMELED CAST-IRON WARES

BY

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By Homer F. Staley

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INTRODUCTION

The enameling of metals is a relatively old art, but its general application to household and industrial articles represents a comparatively recent development. In the last few years the production of enameled cast-iron and sheet-steel wares has attained a position of considerable economic importance.

It is the purpose of this paper to deal with the materials and methods employed in the manufacture of enameled cast-iron ware. In order that more general information may be available regarding the raw materials used in the compounding of enamels, considerable attention is given to the sources and methods of preparation of these materials, as well as to their properties and effects when introduced into the enamel composition. Methods of calculating enamel formulas and examples of the compositions of enamels of various types are given. The defects in enamels, their causes, and the remedies to be employed in overcoming them are discussed from both the theoretical and practical standpoints. Manufacturing methods and equipment used in compounding the enamels, making and preparing the castings, and applying the enamels are also discussed.

This treatise deals with the enameling of cast iron by the dry, or American, process. In this method of manufacture, the thoroughly cleaned casting is painted with a suspension in water of powdered glass, clay, and other materials. This suspension is known as the ground coat. The casting is then heated until the ground coat is thoroughly fused, forming an extremely thin layer of transparent glass on the casting. The piece of ware is withdrawn from the furnace and immediately coated, by means of long-handled sieves, with a layer of opaque, white, powdered glass, known as the cover-coat enamel. Next, the casting is returned to the furnace for a couple of minutes during which the cover-coat enamel fuses to a smooth layer. Two such layers of cover coat are usually applied, giving a total thickness of from $\frac{1}{32}$ to $\frac{3}{32}$ of an inch. The treatise does not deal with the methods of enameling cast iron by the wet process, in which a relatively thin cover coat is applied to a thick and only partially fused opaque ground coat.

I. RAW MATERIALS—REFRACTORIES

In order to use his raw materials to the best advantage, the enamel maker should have some knowledge of the method of their manufacture, their physical and chemical properties, the impurities they are liable to contain, and their action in the enamel. Generally he has rather definite opinions in regard to the last point, based on his individual experience, but often his ideas in regard to the other points are very hazy indeed. It seems worth while, therefore, to gather from a great variety of sources the pertinent facts about enamel raw materials and to insert the compilation as one section of this treatise.

The materials used for making white enamels for cast iron may be classified as follows:

Refractories	Fluxes	Opacifying agents
Feldspars	Calcium carbonate	Tin oxide
Cornwall stone	Building lime	Antimony oxide
White mica	Dolomite	Sodium metantimonate
Cullet	Magnesium carbonate	Zirconium compounds
Quartz and other forms of silica	Barium carbonate and hydroxide	Titanium oxide
Clays	Soda ash	Spinels
	Sodium nitrate	Arsenic oxide
	Potassium carbonate	Fluorides
	Potassium nitrate	Bone ash and other phosphates
	Lead compounds	
	Zinc oxide	
	Borax and boric acid	
	Fluorides	

1. FELDSPARS

(*a*) PROPERTIES OF FELDSPARS.—The feldspars[1] are hard, crystalline minerals. Chemically they are compounds of silica and alumina with the bases potash, soda, and lime. The compositions of the important pure types are shown in Table 1.

TABLE 1.—Composition of Pure Feldspars

Trade names	Potash feldspars	Soda feldspar	Lime feldspar
Mineralological names	Orthoclase and microcline	Albite	Anorthite
Chemical formulas[1]	$KAlSi_3O_8$ or K_2O, Al_2O_3, $6SiO_2$	$NaAlSi_3O_8$ or Na_2O, Al_2O_3, $6SiO_2$	$CaAl_2Si_2O_8$ or CaO, Al_2O_3, $2SiO_2$
Silica (SiO_2)	64.7 per cent	68.8 per cent	43.3 per cent
Alumina (Al_2O_3)	18.4 per cent	19.4 per cent	36.6 per cent
Potassium oxide (K_2O)	16.9 per cent		
Sodium oxide (Na_2O)		11.8 per cent	
Calcium oxide (CaO)			20.1 per cent

Feldspars corresponding to these type formulas are seldom found, however. Two or more of these typical feldspars may be found mechanically mixed in the same deposit, or even intergrown in the same crystal. Also the commercial feldspars usually contain admixtures of other minerals as well.

Potash feldspar occurs in two mineral forms, orthoclase and microcline. Contrary to popular belief, microcline is the more common of these two. For practical purposes they may be regarded as identical, since they have the same chemical composition and are similar in most of their physical properties. Soda may partly replace potash in these feldspars. The color may be white, pearl gray, light yellow, light green, or any shade of red from pink to brick red. Potash feldspars break readily into angular fragments which show two distinct cleavage planes intersecting approximately at right angles. The surfaces of these cleavage planes have a brilliant, glossy luster. A third, less prominent, cleavage plane is sometimes noticeable. The hardness corresponds to 6 in Mohr's scale, so that the mineral can be scratched with a knife blade only with difficulty. The specific gravity varies from 2.54 to 2.56.

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[1] General references: Bastian, Edson S., Economic Geology of the Feldspar Deposits of the United States (Bull. 420, U. S. Geological Survey). Watts, A. S., Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region (Bull. 53, U. S. Bureau of Mines); also The Feldspars of the New England and North Appalachian States (Bull. 92, U. S. Bureau of Mines). Day, A. L., and Allen, E. T., The Isomorphism and Thermal Properties of the Feldspars (Publ. No. 31, Carnegie Inst. of Washington; also Am. Jour. of Sci., 4th ser., **19**, pp. 93–142). The Feldspars of Canada, Canadian Department of Mines.

Potash feldspars do not melt suddenly, as do many minerals and practically all metals, but undergo gradual fusion. In the geophysical laboratory of the Carnegie Institution,[2] it was found that powdered microcline started to sinter at 1000° C (1832° F), formed a solid cake at 1075° C (1965° F) and became a viscous glass at 1300° C (2375° F). The true melting point—i. e., the temperature at which the feldspar lost its crystalline character and became an amorphous glass—was determined to be about 1200° C (2200° F). When made up into cones and heated with Seger pyrometric cones, potash feldspar deforms along with Seger cone 9. The presence of soda feldspar lowers the fusion point, the most fusible mixture, 70 per cent albite—30 per cent microcline, deforming before cone 6.[3]

Pure soda feldspar, albite, is seldom found, part of the Na_2O usually being replaced by lime or potash and lime. Its color is usually white to pale green although it may be reddish or gray. It has a hardness of 6 and a specific gravity of 2.6. Two distinct cleavage planes are noticeable, but these intersect at an angle of 86° instead of 90° as in the case of potash feldspars. The surface of the most brilliant of the cleavage planes is marked by faint straight striations. Like the potash feldspars, albite fuses slowly to a viscous glass. The true melting point is between 1200° C (2200° F) and 1290° C (2350° F). When tested in comparison with Seger cones, albite deforms along with cone 7.

Lime feldspar, anorthite, is rare but there is a continuous series of lime-soda feldspars, known as plagioclases, ranging from pure albite at one end to anorthite at the other. The member of this series most commonly used in ceramic work is oligoclase, which has the following composition: Lime (CaO) 3 per cent, soda (Na_2O) 10 per cent, alumina (Al_2O_3,) 22.1 per cent, and silica (SiO_2) 64.9 per cent. In fact, most so-called soda feldspars approach more nearly to oligoclase in composition than they do to albite. The high-soda plagioclase feldspars conform closely in color, crystalline forms and physical properties to albite. The specific gravity increases with calcium content, and the true melting point is also raised. However, since lime tends to produce very fluid glasses, the fusion point is not raised until the lime content becomes quite high. High-lime feldspars are not used in ceramic work because they make very fluid, easily crystallizable glasses.

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[2] Day, A. L., and Allen, loc. cit., pp. 420–426.

[3] Watts, A. S., Bull. 92, U. S. Bureau of Mines, p. 35.

While the intensity of the color in fresh feldspar is no indication of the color which the fused feldspar will have, yet it is not true that dark feldspars fuse to as perfectly white glasses as do the colorless varieties. In general the feldspars that fuse to the most nearly colorless glasses are the pure white or colorless varieties, then come in order the pale salmon, cream, brown and buff, and finally the sea green and olive green varieties.[4] Even slight carelessness in separating colored impurities from the feldspar, or contamination during grinding may have far greater effect on the color of the fused feldspars than does the variation in tint of minerals themselves. Red feldspars are pink when ground, but the cream-colored and white feldspars are nearly pure white.

(*b*) OCCURRENCE OF FELDSPARS.—Feldspars are among the most widely distributed minerals. They occur as constituents of nearly all rocks and soils. In all soils and in most rocks, the feldspar is in too small grains and is too intimately associated with other minerals to be economically separated. Commercially valuable feldspars usually occur as constituents of igneous rocks of extremely coarse texture, known as pegmatites. These pegmatite masses may vary from bands a few inches wide to great masses half a mile wide and over a mile long. They seem to have been intruded as molten masses along fractures in the surrounding rock, and are, therefore, very irregular in form, although lenticular forms are commonly noted. When the pegmatite mass stands nearly vertical it is called a dike. When it approaches the horizontal position it is called a sill.

Pegmatites vary greatly in coarseness. Some are fairly fine grained while others contain single crystals 20 feet across.[5] It is in the fairly coarse-grained deposits only that the feldspar can be separated economically, and such deposits are rather rare. The texture of pegmatite is very irregular, a gigantic crystal being liable to occur in a mass of small ones.

Pegmatites usually contain the following minerals in addition to the feldspars: Quartz, muscovite (white mica), beryl, biotite (black mica), tourmaline, garnet, and magnetite. The proportions in which these minerals occur vary greatly in different deposits and even within a few feet in the same deposit. A deposit yielding good feldspar may change suddenly to a worthless mixture, high in quartz or iron-bearing minerals. A feldspar is rendered offgrade in color by the presence of only a few per cent

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[4] Watts, A. S., Bull. 92, U. S. Bureau of Mines, p. 23.

[5] Bastian, Edson S., Bull. 420, U. S. Geological Survey.

of ferruginous minerals. Feldspars containing considerable iron can be used in making enamels, but such feldspars are sold at lower prices than those low in iron. White mica and beryl do no particular harm, but are difficult to grind. Variation in the kinds of feldspar and the amount of quartz is a very serious problem, since these variations are quite common and affect the working properties of the mixtures made with the feldspar.

(*c*) MINING AND PREPARATION.—Most feldspar is quarried from open pits, although sometimes short tunnels are run from the pits. The material coming from the pits is broken and sorted by men known as "cobbers." The feldspar is then piled in the open for a few weeks in order that any adhering dirt may be washed away by rain.

The crude feldspar is hauled to the mill, then dried, if necessary, and either reduced to 1-inch size in an ordinary rock crusher or broken to about 4-inch size with hammers. An objection to the rock crusher is that considerable amounts of iron may be introduced into the feldspar. The coarse material is crushed to pass a 10-mesh sieve in a buhr-stone chaser mill. This mill consists of a large granite disk laid flat on which two large granite wheels, 5 or 6 feet in diameter and 12 to 18 inches thick, run in a circular path. It is a crude machine, but its use avoids contamination with metallic particles. From this machine the feldspar goes to ball mills or tube mills for fine grinding. From these it is bagged or sent to stock sheds, no sieving or bolting being practiced.

The large majority of feldspar deposits in this country are quartz-bearing pegmatites and the products from these quarries are graded as follows:

No. 1. Free from iron-bearing minerals, contains little white mica and not over 5 per cent quartz.

No. 2. Nearly free from iron-bearing minerals and white mica, may contain up to 15 or 20 per cent quartz. This grade is also known as "standard."

No. 3. Not carefully selected, contains higher percentages of iron-bearing minerals, white mica, and quartz.

In southeastern Pennsylvania and the neighboring parts of Maryland soda feldspar is mined from pegmatites that are free from quartz, the chief impurity being hornblende. This feldspar is graded according to its freedom from iron-bearing minerals as follows:

No. 1. Carefully selected, practically no impurities.

No. 2. Not so carefully selected, small amounts only of impurities.

No. 3. Not carefully selected, contains enough iron-bearing minerals to render it decidedly off color.

The No. 1 and No. 2 grades are generally ground in the fine grinding machines for 4 to 6 hours. The No. 3 grade is ground for only 2 to 3 hours. Bastin[6] found that the No. 1 and No. 2 grades of commercial feldspar were of a fineness that would permit 99 per cent to pass a 100-mesh sieve and 96 per cent to pass a 200-mesh. The No. 1 and No. 2 grades are sold to potters. The No. 3 and part of the No. 2 grade is sold to enamel and glass makers.

Published analyses of feldspars, and even those given out by feldspar dealers, are for the most part of little value to feldspar users, since they are generally made on hand-picked samples of pure rock. Of course in mining feldspar the producer gets a mixture of minerals. In fact, it is common practice to blend feldspar from different parts of the same deposit or from different deposits to produce as large an amount as possible of feldspar that is not too impure to be salable. In Table 2 are given some analyses of commercial ground feldspars. Of course the feldspars marketed from the same quarries the next month might be of different composition.

TABLE 2.—Analyses of Commercial Ground Feldspars

	I [a]	II [b]	III [c]	IV [d]	V [e]	VI [f]	VII [g]	VIII [g]
Silica (SiO_2)	76.37	65.87	65.73	69.05	69.45	65.50	68.20	71.07
Alumina (Al_2O_3)	[h] 13.87	[h] 19.10	[h] 19.28	1.40	16.76	21.17	17.17	16.23
Ferric oxide (Fe_2O_3)	....	....	....	.15	.20	.18	.66	.53
Lime (CaO)	.26	.20	.22	.12	.45	.87	.38	.43
Magnesia (MgO)	.00	....	....	....	.05	1.40	.26	.24
Potash (K_2O)	5.24	12.24	10.26	10.03	9.80	8.98	10.18	8.24
Soda (Na_2O)	3.74	2.56	4.08	2.97	2.60	1.00	2.60	2.98
Loss on ignition	.30	.64	.48	....	.28	.15	.59	.39

[a] Bull. 420, U. S. Geological Survey, p. 9. Ground feldspars, No. 3 grade, from near Bedford, N. Y. Analysis by Geo. Steiger, U. S. Geological Survey.

[b] Bull. 420, U. S. Geological Survey, p. 9. Ground feldspar, No. 1 grade, from Bedford, Ontario, Canada, Analysis by Geo. Steiger, U. S. Geological Survey.

[c] Bull. 420, U. S. Geological Survey, p. 24. Ground feldspar, No. 1 grade, from Auburn, Me. Analysis made of U. S. Geological Survey.

[d] Bull. 92, U. S. Bureau of Mines, p. 18. Pennsylvania potash feldspar. Ground commercial feldspar, 1910. Grade not stated; analysis made by D. J. Demorest.

[e] Trans. A. C. S., 16, pp. 88 and 212. Number 2 potash feldspar from near Bedford, N. Y.

[f] Trans. A. C. S. 16, p. 212. Soda feldspar.

[g] No. 1 grade Maine feldspar. Analyses by H. C. Evans, U. S. Bureau of Standards. These analyses show the extreme variations of five shipments received at the Bureau of Standards Clay Products Laboratory during the two years extending from the summer of 1915 to that of 1917.

[h] Including small amounts of iron oxide.

[6] Loc. cit.

The approximate mineral composition of these feldspars as calculated from the analyses are as shown in Table 3:

TABLE 3.—Mineral Composition of Commercial Ground Feldspars

	I	II	III	IV	V	VI	VII	VIII
Potash feldspar	30.58	72.28	60.60	59.32	58.70	6.0	60.22	48.80
Soda feldspar[a]	32.83	22.59	35.69	25.74	25.15	83.86	23.98	27.33
Quartz	34.37	3.84	2.22	10.29	16.15	10.14	11.97	19.49
Other constituents	1.93	1.86	1.50	4.65	....	....	3.87	4.48

[a] Including small amounts of lime feldspar.

It is evident from analyses I, V, and VIII that the free quartz in some commercial feldspars runs quite high. It is also shown by analyses III, VII, and VIII that the variation in the composition of the feldspar of a given grade and brand may be great.

The foregoing outline of the geological occurrence and the methods of winning and grinding feldspars is given to emphasize as much as possible a fact that is of great economic importance to enamel makers, namely, that commercial feldspar is a very changeable commodity. Not only is it liable to change from carload to carload but even from bag to bag. Yet enamel makers habitually buy their feldspar by brand names and assume that they are getting a definite product. Quite often they are satisfied to order simply by the name of the State from which the product is to come, as Maine feldspar or Connecticut feldspar, and let their purchasing agent or jobber secure the material at the lowest price. When it is realized that few enamelers, and still fewer purchasing agents, know that feldspar is sorted into three grades, and on the other hand that all feldspar producers think that No. 3 grade is entirely suitable for enameling purposes, it is evident that enamelers as a rule get a low grade and variable supply of feldspar.

(*d*) EFFECTS OF COMPOSITION OF FELDSPAR IN ENAMELS.—As to color, the variation in iron-bearing minerals has little detrimental effect. It is remarkable how little effect contamination of raw materials by iron has on the color of enamels. This is no doubt due to the volatilization of the iron as iron fluoride during the smelting of the enamel according to the following schematic reactions:

$$FeO + CaF_2 \rightarrow FeF_2 \text{ (gas)} + CaO$$

or

$$Fe_2O_3 + 3CaF_2 \rightarrow 2FeF_3 \text{ (gas)} + 3CaO$$

Of course we would have similar reactions if cryolite or any other fluoride were used. In fact, iron can be volatilized from enamels by the use of a chloride, sodium chloride (common salt), for instance, but this salt has a detrimental effect on the properties of the enamel.[7] Before the introduction of fluorides, ammonium chloride was a common constituent of enamel batches.

The variation in the amount of quartz in the feldspar has a very decided effect on enamels. It is true, as shown by Watts,[8] that an addition of 15 to 20 per cent of quartz to a feldspar raises the melting point but little. However, the action of such a mixture in an enamel would be altogether different from that of pure feldspar. The enamel would be more refractory and have a decided tendency to chip. Of course, on the other hand, if the enameler has been using feldspar high in quartz and the percentage is decreased, the enamel tends to craze.

Of equal importance is the variation in the relative amounts of potash feldspar and soda or lime-soda feldspar in the commercial feldspar brands. Increase of potash feldspar with corresponding decrease of soda or lime-soda feldspar tends to cause crazing, and the reverse variation to cause chipping. Variation in the relative amounts of potash and soda (or rather lime-soda) feldspars in the mix is the method used by some enamel makers for controlling crazing and chipping.

In No. 1 and No. 2 grades of feldspar the producers attempt to control the percentage amount of quartz within rather wide limits, but they do not attempt to control the variations in the relative amounts of the different feldspars present. In the No. 3 grade, which is the kind enamelers generally get, they do not attempt to control either. Since in American enameling practice feldspar generally constitutes 35 to 45 per cent of the melt, slight percentage variations in the composition of the feldspar used materially affect the properties of the enamels.

While a few enamelers have realized that they were having trouble from variations in their feldspar, they have not understood how to overcome this. Chemical analyses are tedious, expensive, and really of little service. An analysis may tell the enameler that a given carload of feldspar has a different composition from the one he has been using, but it will not tell him how to alter his mix to overcome this difference. If he is skilled in chemical calculations, he may compound a mix with the new

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[7] Bole, Geo. A., and House, R. M., Trans. A. C. S., 17, pp. 125–129.

[8] Bull. 53, U. S. Bureau of Mines, p. 26.

feldspar that has the same chemical composition as his old mix; but, owing to the differences in physical condition and chemical combination of the ingredients in the two mixes, the new and the old one are very likely to act differently on the ware.[9] This difference in action is due to variation in the approach to complete homogeniety by the two compositions in the rapid melting process employed in making the frits. Another possible cause of variation is difference in final composition of the two enamels due to greater losses by volatilization in one case than in the other.

The physical and mineralogical condition of the ingredients of an enamel have a decided bearing on the rate of attainment of homogeneity. In the extremely viscous fluids with which we are dealing, diffusion, or natural mingling of fluids, is very slow. Coarse particles of a mineral of high melting point may remain in the semifused glass for a long time before enough material that acts as a flux toward this mineral comes in contact with them to cause them to melt. Moreover, it is perfectly possible for globules of one melted mineral to lie suspended in another for many hours at elevated temperatures. In fact, some cases of opacity seem to be due to this very circumstance. Such mixtures are glass emulsions. Of course all emulsions are not opaque, as this property depends upon the optical characteristics of the liquids. Now the viscosity of a mixture of liquids in the form of an emulsion is not the same as if the mixture were homogeneous. In silicate mixtures it is generally greater.

All glasses pass more or less rapidly through this emulsion state, the degree of homogeneity obtained depending upon: (1) The size of the globules. This is dependent upon the fineness of grinding of materials used. (2) The rate of diffusion. This is dependent upon the viscosity of the minerals in the melt, and the amount of stirring given the enamel. For each mineral, viscosity is dependent upon the temperature. (3) Time. For a concrete illustration, we may take SiO_2. If we introduce this in the form of flint, we know that the finer the grinding—that is, the smaller the globules formed when the material fuses—the nearer the approach to homogeneity, and, therefore, the less the viscosity of our glass at a given stage in the melting. If we replace fine flint by sand and do not alter our melting procedure the resultant enamel will have a higher fusion point and will not be as near homogeneity. In fact, it will be possible to identify small particles

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[9] Staley, Homer F., Trans. A. C. S., 10, p. 114; 13, p. 676.

of partially-melted sand in the enamel on the ware. If we introduce SiO_2 by means of soda-lime feldspar, a mineral with less viscosity at given temperatures than flint, and therefore a more rapid rate of diffusion, we may obtain the same degree of maturity if the metal is ground less fine, or if the mixture is fired to a lower temperature, or for a shorter time.

For these reasons enamel makers find that the most satisfactory method of testing a new feldspar is to incorporate it in various proportions into trial mixes and to study the effect of these when applied to the ware. However, no enamel maker can afford to take the risk of introducing a practically new mix into his shop every time he gets a new shipment or new carload of feldspar. Moreover, as we have pointed out, from the very nature of its method of occurrence and preparation, the different parts of the same shipment of feldspar or even two adjacent bags may differ in composition.

The most practicable solution of the feldspar problem for enamel makers seems to be to adopt the methods that have been used by porcelain manufacturers for many years. These are as follows:

1. The purchase of feldspar of grade not poorer than No. 2 from reputable producers, and insistence that the material furnished be up to grade.
2. The use of at least two brands of feldspar in each mix, the amount of each brand used being taken from two different shipments.
3. Thorough testing in trial melts of each new shipment of feldspar to determine what change, if any, should be made in the mix to accommodate it to the new feldspar.

This method of blending feldspars reduces the effect of variation in any particular shipment to not over one-fourth what it would be if the shipment were used alone. Moreover, the variations of different shipments and brands tend to be averaged and so to neutralize one another. It should be noted that it is necessary not to start the use of more than one new shipment at a time.

There are two objections that enamel makers may make to this program: First, the extra cost of a higher grade of feldspar; second, the inconvenience of storing four to six shipments of the material. A good grade of feldspar will cost \$2 to \$3 per ton more than a poor grade. A ton of feldspar will make enamel to cover about \$3000 worth of ware. It is a very exceptional case where the use of high-grade feldspar of uniform quality will not cut the enameling-room loss by at least 1 per cent. Allowing a couple of dollars per ton for cost of storage and extra handling incident to the blending system, we can credit a profit of at least $25 per ton to the use of blended high-grade feldspars. In most cases the credit should be much more than this. The absolute necessity of maintaining a supply of feldspar of as uniform quality as possible can not be overemphasized. Feldspar is more variable in composition than any of the other ingredients used in enamels and the results of variation are, as we have tried to point out, disastrous. Probably more loss has been caused in the enameling business by variation of feldspar than by any one other factor.

Feldspar is a refractory ingredient in enamels owing to its content of alumina and silica. In cast-iron enameling practice, it is often the only refractory ingredient used, although sometimes flint or quartz is employed with it. It is looked upon as the foundation of the enamel, since it is used in larger amounts than any other ingredient. Increase of feldspar in an enamel makes it less fusible, increases opacity to a slight extent, tends to stop crazing and to cause chipping. Feldspar makes more opaque, richer-looking enamels that are not so liable to craze and chip than do quartz or flint when used as refractory ingredients.

A given percentage of potash feldspar will give an enamel that is more liable to craze and less liable to chip than will the same amount of soda feldspar, or rather the high-soda, lime-soda feldspar that is usually sold under the name of soda feldspar. This is due to the fact that the combined percentage of silica and alumina, the refractory ingredients, is lower in potash feldspar than in the usual commercial soda feldspars. Crazing and chipping can be controlled in many cases simply by varying the relative proportions of these two kinds of feldspar. When potash feldspar is to be substituted for soda feldspar without changing the fit of the enamel, a larger amount of it must be used. These are the usual relations, but of course an impure potash feldspar very high in quartz might cause chipping when substituted for a nearly pure soda feldspar.

Potassium gives more brilliant glasses than sodium; but the effect on luster of change in alkalies incident to change of feldspars is generally obscured by the more powerful influences of the large amounts of fluxes, opacifiers, etc., present in the enamel mix.

(*e*) TESTS FOR FELDSPAR.—As indicated before there are no simple chemical tests for the quality of feldspars. If a complete chemical analysis is wanted, it should be made by an experienced analyst, following the methods given by Hillebrand [10] with determination of the alkalies by the J. Lawrence Smith method. A quick qualitative and a fairly accurate quantitative examination can be made by a skilled microscopist following the methods described by McCaughey.[11] The enamel mixer will generally have to judge the quality of a shipment of feldspar by incorporating it into a trial melt.

It sometimes happens that a question arises as to whether a certain lot of material is feldspar or not. Feldspar is liable to be confused with some of the other white, gritty materials. These may be whiting, fluorspar, cryolite, or flint. Whiting gives a violent effervescence when treated with hydrochloric acid; feldspar is not affected. Fluorspar and cryolite give off pungent white fumes (poisonous) of hydrofluoric acid when heated with strong sulphuric acid in a platinum vessel; feldspar is not affected. A cone made from 90 per cent feldspar and 10 per cent fire clay will deform before Seger cone 10, while a similar cone made from flint and fire clay will not be affected until much higher temperatures are reached. Flint is generally much nearer pure white in color than feldspar. The particles of grit that can be washed out of feldspar are, when viewed under a good magnifying glass, generally oblong in shape and of dull luster, while those from flint are irregular or rounded and generally of brilliant luster.

2. CORNWALL STONE

In England, and to some extent in America, Cornwall stone, sometimes called Cornish stone or simply "stone," is used in place of feldspar. It is a pegmatite that has been partly decomposed by the action of gaseous compounds of fluorine. It consists largely of feldspar, silica, kaolin, and white mica, with a small percentage of fluorspar. It is rather variable in composition but generally contains 4 to 6 per cent of potassium oxide, 2 to 3.5 per cent sodium oxide, and 0.5 to 2 per cent calcium and magnesium oxides. The silica runs from 70 to 75 per cent, and alumina, 14 to 17 per cent. Analyses are given in Table 4.

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[10] Hillebrand, Bull. 422, U. S. Geol. Sur.

[11] McCaughey, Trans. Am. Cer. Soc., 15, pp. 381-387.

TABLE 4.—Analyses of Cornwall Stone

	I[a]	II[a]	III[b]
Silica (SiO_2)	72.28	73.18	72.21
Alumina	14.90	16.13	16.32
Iron oxide	.50	.52	....
Calcium oxide	1.66	.61	2.02
Magnesium oxide	.15	.14	.20
Potassium oxide	5.25	4.41	4.39
Sodium oxide	3.01	2.18	2.86
Fluorine	.88	.23	([c])
Phosphoric oxide	.53	.45	([c])
Water	.81	2.01	1.97

[a] Howe, J. A., Handbook to the Collection of Kaolin, China Clay, and China Stone in the Museum of Practical Geology. No. I represents the best "hard purple" grade and No. II the poorest "buff" grade.
[b] Coulter, L. B., Trans. A. C. S., 8, p. 357.
[c] Not determined.

Coulter found that when Cornwall stone was substituted for feldspar in glazes, keeping the chemical formula of the glaze uniform, the Cornwall stone glazes were slightly more fusible than the feldspar glazes. This was probably due to the presence of 2 or 3 per cent of fluorspar in Cornwall stone, a point apparently overlooked by Coulter. He also found that Cornwall stone substituted pound for pound for feldspar gave a less fusible glaze. Ashley claims[12] that the following mixture can be substituted for Cornwall stone: 11 per cent kaolin, 22 per cent quartz, and 67 per cent potash feldspar.

Over 75 000 tons of Cornwall stone are quarried in England each year, 35 000 of which are exported. It is brought to this country as ballast, but even with such cheap ocean freight rates costs more here than feldspar.

Pegmatites, coarse granites composed of mixtures of feldspar, quartz, and a little mica, are mined in Europe for use in place of feldspar. This material corresponds in composition to the No. 2 feldspar sold in this country.

3. WHITE MICA

The use of muscovite, white mica, in place of feldspar has been tried by Stull in an experimental way.[13] He found that when finely ground this material acts very much like feldspar, but that it is more refractory. Owing to the sheetlike form in which mica occurs, it is very difficult to grind fine. For this reason the white mica occurring with feldspar is generally broken off and discarded before the feldspar is sent to the mill.

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[12] Ashley, H. E., Trans. A. C. S., 12, p. 438.

[13] Trans. A. C. S., 4, p. 255.

4. CULLET

Cullet, scrap glass, is sometimes used as an ingredient of enamels. The only kind that can be had in any quantity is ordinary lime-soda glass such as is used for window glass and cheap bottles. It produces a slightly more fusible glass than the same amount of feldspar. It is difficult to get a supply of uniform composition or of approximate freedom from dirt and coloring matter. The average composition corresponds to Na_2O, CaO, $5SiO_2$, the raw batch for 100 pounds of such a mixture being 25 pounds of soda ash, 24 pounds whiting, and 72 pounds of quartz. It is safer and more economical to introduce the raw ingredients that go to make glass than to use questionable cullet.

5. QUARTZ AND OTHER FORMS OF SILICA

(*a*) Occurrence and Properties of Silica Minerals.—Quartz is crystalline silica, SiO_2. The crystals are commonly prismatic. The luster is vitreous, sometimes greasy, brilliant to nearly dull. Quartz has a conchoidal fracture like glass. The color varies widely; commonly it is colorless or white, but may be gray, pink, red, yellow, amethyst, green, blue, brown, or black. Some forms are translucent, while others are opaque.

Quartz, which occurs in massive beds of quartzite rock or silex, in small and large crystals in granites and many other igneous rocks, is the chief constituent of common sand and sandstones, and in fine grains is an important constituent of most soils.

Silica also occurs in amorphous or noncrystalline form. In this form it is translucent with a waxy to dull luster and varies in color from colorless or white to yellow, red, and dark brown. It breaks with a conchoidal fracture. It seems to have been deposited from aqueous solution and is found lining or filling cavities in rock and as lenticular masses in clay, coal, and limestone beds. Pebbles of it are common in the chalk deposits of England and in the gravel beds on the coast of France, Iceland, and other European countries. The common forms are known as flint or chert. These are dark colored and have a dull luster.

There are several varieties of hydrated oxide of silica. These are amorphous and the amount of chemically combined water they contain varies. Varieties are geyserite, deposited by hot springs or geysers; various kinds of opal; infusorial earth, also known as diatomaceous earth and kieselguhr, which consists of the siliceous casts of small sea plants.

Tripoli, as known in the United States, is the residue left by the solution of siliceous sandstones. It is generally nearly pure silica of very fine grain. It may be either crystalline or amorphous. When pure it makes an excellent form of flint.

Free silica is used in enamels in two forms, glassmakers' sand and potters' flint. Glass sand is prepared by crushing quartzite rock or nearly pure sandstone, which is usually calcined to facilitate the grinding. In a few places a nearly pure sand is used. The crushed sandstone and sand are commonly washed to remove impurities. A good glassmakers' sand will run over 99 per cent silica and less than 0.5 per cent iron oxide.

In England potters' flint is prepared from flint and chert pebbles occurring in the soft limestone or chalk beds and cliffs that are so common there. When calcined, these turn to a pure white, friable, easily ground mass. It is ground wet and usually delivered in a thin paste, known as ''slop flint.'' In this country ''flint'' is prepared by dry grinding in ball or tube mills, quartzite rock, sandstone, or sand. The flint prepared in this way is not as fine grained as the wet ground flint of England. If the mills are lined with wooden blocks, the flint is liable to contain splinters of wood and will not be as fine as that ground the same length of time in mills lined with quartz blocks.

Infusorial earth is generally more or less discolored by infiltrated mineral or organic matter. When burned it should become snowy white. It is the lightest form of silica known, because of the immense amount of pore space and the thinness of the casts. It is essentially amorphous and therefore more ready for chemical attack than crystalline forms. This, together with its extreme fineness and large surface area, renders it more easily incorporated into a melt than any other form of silica. It forms an ideal substitute for flint.

(*b*) EFFECT OF SILICA IN ENAMELS.—Silica is used in enamels in the same way that feldspars are, as a refractory ingredient. Increase of silica renders the enamel less fusible, more resistant to chemical attack and more liable to chip. Compared with feldspar as a refractory, silica makes less opaque enamels and seemingly more brittle ones; that is, the enamels are more prone to chip and craze. For making ground coats, glassmakers' sand is more satisfactory than flint. Some German authorities even claim that too fine grinding of sand or flint causes ''decay'' of the enamel, although they do not explain what they mean by the term.[14] For making cover enamels, fine-ground flint is better than sand. Complete fusion of the enamel is more readily obtained and the enamel is more opaque. When sand is used, the unfused granules show up in the finished ware as small white specks. These specks, which are of different composition than the bulk of the enamel, form centers for lines of stress that sometimes result in minute crazes. It has been found in practice that the temperature range between the point at which the ground coats melt and that at which they begin to volatilize or "burn off" is greater in sand coats than in flint coats.

(*c*) Tests of Silica.—A residue of 2 per cent on a 100-mesh or more than 5 per cent on a 120-mesh sieve should not be found in a good grade of flint. In composition it should correspond to good glassmakers' sand.

The chemical tests for silica are very simple. It is insoluble in all acids except hydrofluoric. A small quantity of finely ground silicia warmed in a platinum crucible with an excess of hydrofluoric acid will be completely volatilized as silicon-tetrafluoride (poisonous). Methods of distinguishing flint from the other white gritty enameling materials have been given under feldspar.

(*d*) Substitution of Flint for Feldspar.—In making an enamel of given fusibility only about two-thirds as much flint can be used as feldspar. Although flint is of about the same price as feldspar, its use as a substitute raises the percentage of expensive fluxes and opacifiers in the enamel and so increases the cost per pound of the finished enamel.

Example: Assume in an enamel—

600 pounds, melted fluxes and opacifier, at $0.08	$48.00
400 pounds feldspar, at $0.005	2.00
1000 pounds	50.00

$\frac{\$50.00}{1000}=\$0.05$ per pound.

If 267 pounds of flint are substituted for the feldspar, the amounts and values are—

600 pounds, melted fluxes and opacifier, at $0.08	$48.00
267 pounds flint, at $0.005	1.33
867 pounds	49.33

$\frac{\$49.33}{867}=\$0.057$ per pound.

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[14] Grünwald, J., Raw Materials of the Enameling Industry, p. 17.

6. CLAYS

(*a*) ORIGIN AND CLASSIFICATION.—Clays are more or less heterogenous mixtures of minerals containing hydrated silicate of alumina. Plastic when wet, they retain shape on drying and burn to a hard mass. The hydrated silicate of alumina that is the basis of most clays is kaolinite, Al_2O_3, $2SiO_2$, $2H_2O$,[15] but several other minerals containing these oxides in various proportions may form clays.

All clays are of secondary origin; that is, formed by the alteration of other rocks. Clays vary in composition and properties according to the rocks from which they were formed, their mode of formation, the amount and method of transportation undergone, the amount of contamination during transportation, and the conditions to which they have been subject in the positions in which they are now found.[16]

All clays originate ultimately from igneous rocks. Most clays have been formed from these by the processes called weathering; the combined action of alterations of heat and cold, freezing and thawing, attack by carbon dioxide (CO_2) and other gases in the air, and the solvent action of percolating waters. In some cases the decomposition has been due to the action of gases that have penetrated the rock. This process is spoken of as pneumatolysis. Cornwall stone, extensively used in England, seems to owe its formation to the action of gaseous compounds of fluorine on feldspar. As a general thing the clays formed by weathering are more plastic than those formed by pneumatolysis.

When formed from igneous rocks, such as feldspar, granites, etc., in the place in which they are now found, clays are said to be *primary*. If formed from iron-free rocks and not contaminated by iron-bearing waters after formation, they will be white burning. Some white-burning clays owe their origin to iron-bearing rocks, the iron having been removed by percolating waters. If the mass is composed of only partly decomposed rock, it is known as *china stone*. Such material is not plastic enough to be used for the purposes for which clay is employed. If the rock is completely decomposed, the material is known as *kaolin*. Kaolins are fairly plastic but contain a large amount of angular fragments, fine white sand, and mica, derived from the parent rock. Kaolins are therefore always washed to free them from these impurities before they come on the market. The kaolins of this country

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[15] Silica (SiO_2) 46.3 per cent, alumina (Al_2O_3) 39.8 per cent, water (H_2O) 13.9 per cent.

[16] In classification of clays we have followed, with variations, Edward Orton, jr., A Chart Showing the Principal Types of Clay Deposits.

come mostly from North and South Carolina. A few deposits are being opened in western States.

Clays which contain iron are red burning. Partially decomposed red-burning rock has no value. Entirely decomposed red-burning primary clays can be used for crude products only.

When clays have been transported after formation they are called *secondary*. The transportation may have been performed by wind, ice, or water. *Wind-blown clays* are known as loess. They are red burning, sandy, not very plastic and therefore not suitable for enameling or other high-grade ceramic work. The *clays transported by ice* in the form of glaciers contain a large variety of sizes and kinds of mineral impurities. They are generally high in lime and are red burning. The coarse-textured varieties are worthless for any fine ceramic work. Occasionally deposits of glacial clay have been reworked by water and second depositions made of very fine-grained clay. These are often very fusible and burn to a dark color. Such deposits, known as slip clays, may be used in making colored glazes and enamels. Examples are the famous Albany slip, Rowley slip, Michigan slip, etc.

The *clays transported by water* may have been deposited from running water or from quiet water. Those deposited from running water are too sandy for ceramic products. Those deposited from quiet water will be fine grained and may be divided into into white burning, buff burning, and red burning.

The fine-grained, white-burning clays are divided according to plasticity into secondary kaolins and ball clays. The secondary kaolins have good plasticity and are quite refractory, not vitrifying until temperatures around 1400° C (2550° F) are reached. They are light colored in the raw state and comparatively free from organic and oily matter. Examples are Georgia kaolin and Florida kaolin. The ball clays are of extreme plasticity and vitrify at about 1250° C (2280° F). They are dark colored in the raw state, and frequently contain organic and oily matter. The ball clays mined in this country usually come from Tennessee and Kentucky. Some ball clays are imported from England.

The buff-burning clays must be divided into two classes, calcareous, buff-burning clays, and fire clays. The calcareous clays are high in both iron and lime, and the only reason they burn buff instead of red is that the lime and iron form a combination with the other constituents of the clay that burns to a buff color. They are fusible, extremely variable in composition, and can be used for crude products only.

Fire clays are low in iron and comparatively low in other fluxes and consequently fuse at high temperatures only. They are divided according to physical condition into flint and plastic fire clays. The flint clays are hard and rocklike and have a conchoidal fracture. They become slightly plastic only after weathering, or long continued grinding in water. According to fusibility they are divided into No. 1 flint fire clay and No. 2 flint fire clay. The No. 1 clay is highly refractory and valuable for making fire-clay goods; the No. 2 clay is less refractory and is of little value for any purpose. The plastic fire clays are soft and earthy and have good plasticity. They may or may not contain oily and bituminous matter. According to fusibility they are divided into refractory bond clays and vitrifying or No. 2 plastic fire clays. The bond clays are used largely as a binder for No. 1 flint clay and grog in making fire-clay goods. Certain grades are used as floating agents in enamels; in other words, as a means for keeping ground enamel glass in suspension in water. The No. 2 plastic fire clays are used in making stoneware, sewer pipe, buff paving and face brick.

The fine-grained, red-burning secondary clays form the great bulk of clays in the world. According to structure they are divided into soft clays, or simply clays, and shales. In composition the various deposits vary widely. Usually some one mineral component dominates the behavior of the clay or shale in burning and furnishes a qualifying adjective for its identification. Thus we speak of ferruginous, micaceous, calcareous, siliceous, etc., shales and clays. Any deposits of these shales and clays may or may not contain oily and bituminous matter. For the most part the soft clays have been deposited in recent times in lakes, swamps, and shallow estuaries. They are therefore generally of small extent and apt to be variable in composition. The shales, on the other hand, were laid down in the beds of ancient oceans and are of vast extent. They are therefore more liable to run uniform in composition, especially in lateral extension of the various layers. In digging vertically through a shale bed we often find abrupt changes in composition.

It happens sometimes that clay is deposited with some other mineral, and later this mineral is dissolved away, leaving a pocket of residual clay. These clays are very variable in composition.

(*b*) USE OF CLAY IN ENAMELS.—Clay may be used in enamels in two different ways: First, as a refractory ingredient in the glass; second, as a floating agent in ground-coat and wet-coat enamels. The use of a clay as a refractory ingredient would depend first on an ample supply of uniform quality. Second, if the enamel were to be white the clay must be white burning or buff burning. For colored enamels an iron-bearing clay would be satisfactory. Ample supplies of uniform quality of light-burning clays can be had among the primary kaolins, secondary kaolins, ball clays, and fire clays. Among red-burning clays certain strata of shale of uniform quality extend over great areas. The question is really only one of quality of enamel and cost.

As far as quality of enamel is concerned, compared to feldspar and flint as a refractory, clay makes a more opaque enamel and when used in small amounts gives an equally good finish. It has a decidedly greater effect in making the enamel less fusible, and for this reason with a given amount of fluxing ingredients only about half as much clay can be used as feldspar. With most formulas the enamel becomes dull in luster when clay is substituted for feldspar in amounts that bring in over 10 per cent of clay in the enamel. Since by substituting clay for feldspar in the proportion of one part of clay to two of feldspar the proportion of expensive fluxes and opacifiers is raised, the cost per pound of the finished enamel is increased. In feldspar enamels the reduction that can be made in the amount of opacifier due to the presence of the clay usually does not compensate for this increased cost. In high-flint enamels the amount of clay that can be used is greater and the effect of clay on opacity is more marked. Clay can be used to advantage in such enamels, but it would probably be more satisfactory to convert the enamel into the feldspar type and avoid the use of clay, and of flint, as much as possible.

The other use for clay in enamels is as a floating agent for ground coats and wet-cover coats. The requirements of a suitable clay for this use are as follows: (1) An ample supply of uniform quality; (2) for white enamels, that the clay be white or buff burning; (3) high plasticity; (4) freedom from granules of carbonates, sulphides, and sulphates; (5) freedom from discoloring particles; (6) freedom from oily matter.

The first two requirements are the same as for clays to be used in enamel glass. That the clay be highly plastic ("rich," "fat," "sticky") is desirable in order that as little of it as possible need be used, especially in cover coats. Raw clay tends to diminish the luster of an enamel very materially if the amount used runs above a few per cent. Carbonates, sulphides, and sulphates give off gases during the burning of the enamel. Large bubbles of these gases cause blisters in the enamel. If the oxide left behind is calcium oxide or magnesium oxide, the granule will not be taken into solution in the short heat treatment incident to baking the enamel. If, in the course of time, moisture works through the metal, or through pinholes or crazes in the enamel, these oxides will hydrate (in the same manner as quick lime) and swell, spalling off the enamel above them.

Particles commonly found in clays that may cause discoloration in a white enamel, if the clay is used raw, are granules of iron sulphide (FeS_2, iron pyrites) and carbonate ($FeCO_3$) roots, stems, and other particles of vegetable matter, particles of coal, lignite, and other forms of fossilized carbonaceous matter. In addition the clay may be contaminated with metallic, mineral, or carbonaceous matter during the processes of winning, shipping, and preparation. Freedom from oily matter is very important. The presence of this in a clay used for floating enamel makes the enamel "run" or slip off the metal in a very erratic manner when attempt is made to float it evenly on the ware. It is to be noted that we do not list refractoriness as a necessity in clays for this use. The only reason refractory clays are commonly used is that a clay that is pure enough to meet the requirements we have listed is liable to be found only in the nearly pure or refractory classes of clays.

These various requirements reduce the clays suitable for this purpose to a very few, indeed. The first two exclude, in general, all clays except kaolins, ball clays, fire clays, and, for colored enamels and ground coats, shales. The third excludes all but secondary kaolins, ball clays, plastic fire clays, and plastic shales. The last three requirements exclude most ball clays and plastic fire clays and shales. This leaves as available secondary kaolins, exceptional ball clays, a few plastic fire clays, and, for ground coats and colored enamels, rare shales. Of course a very exceptional deposit of plastic soft clay or glacial slip clay that would meet the above specifications might be found, but it is not probable. As far as all of the other requirements are concerned, the secondary kaolins are the most suitable of available American clays, but unfortunately they are not sufficiently plastic to meet fully the third requirement.

So difficult has it been to find a clay entirely suitable for floating enamels that, up to the time of the beginning of the European war, only a few clays were used for this purpose. These were high-grade, washed, plastic fire clays found in Germany and

Austria and shipped all over the world. The most famous of these was the Vallendar clay from the Coblentz district in Germany. Since that time several American clays have been noted as being suitable. Florida kaolin, Tennessee ball clay (Porter No. 11), Kentucky ball clay, washed, plastic kaolin from Anna, Ill., and mixtures of these have all been used commercially. The only objection to the Florida kaolin is that it is not quite plastic enough.

(*c*) PURIFICATION OF CLAYS.—Any clay can be freed from coarse granules of impurities by washing. This consists of blunging the clay to a thin slip, allowing the granules to settle, floating off and collecting the fine particles. When large quantities of clay are to be washed under the direction of a trained technical man, the floating off of the clay particles and settling of impurities can be facilitated by the use of chemicals.[17] Small amounts of alkalies—for instance, sodium-hydroxide—added to a blunged slip of a given consistency will make it much thinner. In this thin slip the fine clay particles will float and the coarser impurities and larger grains of clay will settle. After the purified slip has been tapped off, the clay can be made to settle more rapidly by the addition of a small amount of any inorganic acid, such as hydrochloric acid. This peculiar action of small amounts of chemical reagents on clay in suspension is due to the fact that some of the particles of clay are so extremely small as to be in what is called the colloidal state. Clay particles in the colloidal state are deflocculated, that is, separated into individual grains which float readily, in dilute solutions of alkaline salts, and are coagulated, or gathered into spongy masses which tend to settle, in dilute solutions of acids. The addition of salts in the washing of clays is practicable only with nearly pure clays. With impure clays the amounts of reagents needed are so large that they have an injurious effect on the plasticity of the washed clay.

When the washing is done in the enameling plant, it is not necessary to dry the clay. The amount of clay in a given volume of slip can be determined by drying and weighing a small sample. Of course new determinations must be made from time to time on account of unavoidable evaporation of water from the slip. It is necessary to stir the slip to uniform consistency before taking each sample and also before removing any slip for use. Unless considerable care is taken to secure the proper weight of clay in slip form, it is safer to dry the slip. This is not much trouble

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[17] A. V. Bleininger, Bureau of Standards Technical Paper No. 51.

or expense in a factory with as much waste heat as is to be found in the usual enameling plant.

In European enameling plants it is customary to soak clay for several days and then to boil it. The fermentation during the soaking and boiling does away with a good deal of organic and oily matter in clay. In fact a considerable amount of oily matter, lignite, particles of wood, etc., can be skimmed off the top of the boiling suspension with many clays. This is especially the case with ball clays.

By careful washing and purification by means of boiling, many plastic American clays can be made suitable for floating enamels. In this as in every other stage of manufacture the tendency of American manufacturers is to avoid first small expense and painstaking care. The result is that some plants are using improperly prepared clays and in consequence are suffering considerable loss in the quality of their finished ware.

II. RAW MATERIALS—FLUXES

1. CALCIUM CARBONATE

Carbonate of calcium, $CaCO_3$, occurs in various forms and is an important constituent of the earth 's crust. It occurs as limestone, marble, chalk, calcite, marl, and dolomite. The prepared forms of calcium carbonate are known as whiting, Paris white, English cliff stone, etc. With the exception of dolomite, these are all the same, and if pure yield 56 per cent calcium oxide and 44 per cent carbon dioxide when they are heated to bright redness.

Limestones, of the nondolomitic type, run from 80 to 99 per cent calcium carbonate; percentages of 90 to 96 per cent are common. They are liable to be contaminated with clay or silica. Some are badly stained by iron oxide. Only the purest forms should be used in making whiting.

Marble is crystalline limestone. It is generally supposed to be limestone that has been metamorphosed, hardened and caused to crystalize, by heat and pressure. Its purity varies as much as that of the better grades of limestone. The white variety is the only kind suitable for ceramic work. It is no more valuable for this use than a pure grade of limestone.

Chalk is formed from the shells of microscopic animals. It is soft and amorphous, easily pulverized, and generally very fine grained.

Marl is a soft mudlike chalk formed in fresh water. If dried and pulverized it makes a form of calcium carbonate very readily taken into solution in glassy magmas on account of its soft amorphous structure.

Calcite, or calcspar, as it is sometimes called, is a crystalline form of calcium carbonate, which differs from marble in that it is transparent. It may contain several per cent of impurities, and is no more valuable for ceramic work than limestone of equal purity.

Paris white was originally, and in England is still, a washed and purified form of chalk. English cliff stone and whiting were other grades of chalk. In America, at the present time, practically all whiting is made from ground limestone. The ground product is separated according to fineness of grain into the following grades, the coarsest grained being named first: Paris white, commercial whiting, American Paris white, English cliff stone Paris white. Special potters whiting is ground limestone of no standard fineness and varies with each manufacturer.

Calcium carbonate is always used in the pulverized form, whiting, in enamels. It is a high-temperature flux; that is, it does not exert its fluxing action except at high temperatures. It is refractory in comparison with the fluxes used in making enamels. It really affects the fusibility of the enamel but little and can be used in amounts up to 5 per cent simply to make bulk. Its use for this purpose is dangerous, however, for if on application to the metal the enamel is heated quite hot, the lime may begin to exert its fluxing action. When it does begin to act as a flux, its action is very severe and may make the enamel on the hot pieces a great deal more fluid and difficult to manage during the enameling operations than that on the pieces not heated so strongly. Such erratic behavior is pretty sure to produce disastrous results.

Calcium carbonate is added to some antimony-bearing enamels for the sake of the effect it has on opacity and color. This will be discussed later, but we may say here that a certain calcium content seems to be desirable in producing opaque white enamels with the use of antimony compounds and opacifiers.

Enamels high in any calcium compound seem to be lacking in strength and elasticity. The range of workable conditions is greatly narrowed. With a slight variation of composition of enamel, character of castings, or heat treatment, either crazing or chipping will result. The workmen commonly describe such an enamel by the word "rotten." Calcium oxide, as compared with lead oxide, makes enamels less ductile when hot and less flexible when cold.

Whiting should be nearly pure white in color and ground so fine that no grit can be felt with the fingers. It should not leave a residue of more than 5 per cent when dissolved in dilute hydrochloric acid. The solution will take place with violent effervescence of colorless and ordorless carbon dioxide gas CO_2. (Test for carbonates.) The impurities are usually clay and sand, but sometimes calium sulphate is present. This is a very objectionable impurity since it produces blisters in the enamel; whiting containning it should not be used.

2. BUILDING LIME

It is possible to use a pure grade of building lime (calcium oxide, CaO) in place of whiting. This practice is quite common in glass making. The chief objections to this are the fact that there is discomfort attending the handling of quicklime, and the fact that lime, if allowed to stand, takes up water from the atmosphere, and slakes. Thus it is difficult to be sure that a uniform amount of lime, the ingredient that is stable in the fire, is added ($Ca\ (OH)_2 + \text{heat} = CaO + H_2O$ (steam)). This difficulty could not be obviated by using slaked lime, for slaked lime takes up carbonic acid gas from the atmosphere, turning to calcium carbonate. Unless the lime can be had fresh from limekilns as it is to be used, it is safer to use some form of whiting. Of course building lime acts in the same way in enamels as whiting, since both yield calcium oxide upon heating.

Building lime should correspond in purity to whiting. It is a white powder that slakes with considerable heat when put in water. It has a characteristic caustic taste.

3. DOLOMITE

Dolomite is a very common form of limestone found in numerous places. When pure it contains 56 per cent calcium carbonate and 44 per cent magnesium carbonate. When heated to redness it gives 53.4 per cent calcium and magnesium oxides and 46.6 per cent carbon dioxide gas. Like high-calcium limestone, many dolomites contain clay and silica as chief impurities and frequently are stained by iron oxide.

Dolomitic whiting begins to act as a flux at a slightly lower temperature than high-calcium whiting, and its fluxing action proceeds at a more regular rate. It is, therefore, more satisfactory for use as a flux than high-calcium whiting, but is not as commonly used. In making common lime-soda glass, such as is used for window glass and cheap bottles, it has been found that the use of dolomitic limestone and lime gives glass that is not so liable to be devitrified (rendered dull by minute crystals) as high-calcium limestone and lime. This is due to the fact that when dolomitic limestone is used in place of high-calcium limestone, the percentage of calcium compounds in the glass is not so high, therefore they are not so liable to be thrown out of solution as crystals.

The action of dolomite in enamels is similar to that of high-calcium limestones. It is seldom used.

Dolomitic whiting should correspond to high-calcium whiting in fineness of grinding and purity. It will give all the tests for calcium carbonate and in addition a strong test for magnesium.

4. MAGNESIUM CARBONATE

Magnesium carbonate, $MgCO_3$, was formerly imported into this country from Austria. It is now mined on a large scale in California. The ore is called magnesite and is extensively used for making highly refractory brick, magnesite brick, and for making pipe covering and other forms of heat insulators. As it comes to enamel makers, magnesium carbonate is a pure white, exceedingly light, fluffy material, hard to manage in the raw enamel batch. On heating to redness it gives 48 per cent magnesium oxide (MgO) and 52 per cent carbon dioxide gas, CO_2. It is generally quite pure.

The action of magnesium carbonate in enamels is similar to that of calcium carbonate. It acts as a refractory until high temperatures are reached; it then acts as a flux but not so violently as calcium carbonate. It is recommended in old enamel receipts for stopping crazing. This is due to its refractory nature at low temperatures. There is no advantage in using magnesium carbonate in well proportioned enamel formulas.

5. BARIUM CARBONATE AND HYDROXIDE

Barium carbonate, $BaCO_3$, is available in an impure form as the natural mineral, witherite, and in a pure artificial form as precipitated barium carbonate. The latter form is the one used by enamel makers. On heating to bright redness barium carbonate gives 77.7 per cent barium oxide, BaO, and 22.3 per cent carbon dioxide gas CO_2.

Barium hydroxide, $Ba(OH)_2$, can be used in place of the carbonate if the price per unit of barium oxide is not greater. This chemical, when heated, yields 89.5 per cent oxide, and 10.5 per cent water.

The starting point in the manufacture of barium carbonate, as of all other manufactured barium chemicals, is barium sulphate or barytes.[18] Of this mineral over 100 000 tons a year are mined in the United States. Before 1914 all manufactured barium chemicals were imported. In 1915 over 9000 tons of these were made in this country.

In making barium carbonate the sulphate is reduced to sulphide by heating it with coal and a little common salt. The soluble sulphide is extracted with hot water and barium carbonate precipitated by adding sodium carbonate. Sodium sulphide, a marketable commodity, is obtained as a by-product.[19]

Precipitated barium carbonate can be made also by pouring a solution of barium chloride into an excess of a hot solution of ammonium carbonate.[20]

Precipitated barium carbonate is a dense cream-white powder. It is almost insoluble in water, but dissolves readily, with effervescence of carbon dioxide, in hydrochloric acid. Its melting point is 980° C (1796° F). It is liable to contain sulphur compounds, and in that made by the last described process chloride may be present.

Barium hydroxide occurs as a white powder, which is slightly soluble in cold water and very soluble in hot water. The solution is strongly alkaline. Barium hydroxide prepared by dry methods conforms to the formula, $Ba(OH)_2$, 89.5 per cent BaO and 10.5 per cent H_2O, but that prepared in the wet way usually has the formula, $Ba(OH)_2.8H_2O$, which gives 48.6 per cent BaO and 51.4 per cent H_2O. It may contain sulphur or chlorine compounds.

Barium oxide is a powerful flux in enamels. In moderate amounts it produces enamels with especially high luster; larger amounts produce a greasy finish. If used in too large amounts, the compounds formed by it with other elements are prone to separate out in minute crystals and so give dull finish to the enamels. This is especially likely to happen if the enamel is also high in calcium oxide. Barium oxide may be used in amounts

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[18] Some enamel makers call barium carbonate "barytes." This is both incorrect and dangerous, for if the error should lead to the introduction of barium sulphate into the enamel, the latter would be ruined.

[19] Mineral Resources of the United States, 1915. Barium.

[20] Roscoe and Schorlemmer, Chemistry, **2**, p. 665.

up to 8 per cent of the melted weight of the enamel,[21] depending on the composition as a whole. It is similar to lead oxide in increasing the density, brilliance, and coefficient of expansion of enamels, but gives enamels of less strength and elasticity than those made with lead oxide.

6. SODA ASH

Soda ash (Na_2CO_3) is made in this country by three methods, the Leblanc, the ammonia, and the cryolite processes. In the first two, common salt is the raw material; in the last, cryolite.

(*a*) LEBLANC SODA PROCESS.—The oldest method of making soda ash on a commercial scale was devised by Nicolas Leblanc in France about 1791. Common salt is heated with sulphuric acid and converted to salt cake, sodium sulphate (Na_2SO_4). By heating a mixture of salt cake, ground limestone, and powdered coal, and leaching the resultant mass, an impure solution of sodium carbonate is secured. This is evaporated and the residue calcined to produce cream-colored or light-brown soda ash. This is purified by resolution, treatment with bleaching powder, decantation, evaporation, and calcination.

Good Leblanc soda ash is white or pale yellow. It contains usually other salts of soda, such as a little caustic soda, traces of sulphides and sulphates, some chloride and sulphate, and not more than 1 per cent of insoluble matter.

(*b*) AMMONIA SODA PROCESS.—More than one-half the soda ash used in the world is made by the ammonia soda process. This is sometimes known as the Solvay process because Ernest Solvay, a Belgian, was highly instrumental in putting it on a commercial basis about 1865, although it had been discovered by others 30 years before that time. Its chief advantage lies in the purity of the product.

Ammonia vapor is led into very concentrated salt solution, which has been purified from iron, silica, magnesia, etc. Carbon dioxide is allowed to bubble up through the solution, and sodium bicarbonate is precipitated, since it is not soluble in cold ammoniacal salt solution. The precipitated sodium bicarbonate is filtered, washed with water to remove as much of the sodium and ammonium chlorides as possible, and is then calcined to obtain anhydrous sodium carbonate, which may contain a little chloride as impurity.

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[21] The use of larger amounts, as suggested by F. H. Riddle (Trans. A. C. S., 9, p. 659), is not common in factory practice.

(*c*) CRYOLITE SODA PROCESS.—Soda ash is made from cryolite according to a process used by one firm in this country. The raw material is a double fluoride of sodium and aluminum. The only deposit of any importance known at present is in southern Greenland. The ground cryolite is mixed with powdered limestone and calcined at red heat. The residue is lixiviated with water, a solution of sodium aluminate being formed and insoluble calcium fluoride being left. The sodium aluminate solution is filtered off and impregnated with carbon dioxide gas. Hydrated alumina is precipitated and sodium carbonate remains in solution. The solution is evaporated and calcined, a high grade of soda ash being obtained.

(*d*) PROPERTIES AND EFFECT OF SODA ASH IN ENAMELS.—Soda ash is a white granular powder with an alkaline reaction and taste. It is slightly hygroscopic and so is inclined to form hard lumps if stored in a damp place. It dissolves readily in both hot and cold water with evolution of heat to form a strongly alkaline solution. It gives a violent effervescence of carbon dioxide gas when dissolved in dilute acids. It melts at 850° C (1562° F) and in the smelting tank yields 58 per cent sodium oxide (Na_2O) and 42 per cent carbon dioxide gas. Sodium oxide is a powerful flux in enamels, being equal pound for pound to lead oxide. Compared to lead oxide it makes enamels that are more liable to craze or shiver but which have a harder surface. Sodium oxide has a very decided effect in increasing the coefficient of expansion of enamels, and likewise in decreasing their strength and elasticity.

Compared to potash it gives enamels that are less brilliant but which remain soft or ductile for a longer time after being melted. When used in large amounts it gives dull-finish enamels, due to the separation in crystalline form of sodium compounds. The amount of sodium oxide that can be introduced as soda ash depends on the amount of other sodium salts used. In general the total amount of free sodium oxide (not present in feldspar or cryolite) should not exceed 10 per cent of the melted weight of the enamel.

(*e*) HYDRATED SODIUM CARBONATE.—Soda crystals or sal soda (Na_2CO_3, $10H_2O$) is made by dissolving soda ash in hot water, allowing all impurities to settle, drawing off the clarified liquor, and allowing the sodium carbonate to crystallize. The crystals are nearly pure but quite bulky for the weight of Na_2CO_3, as they contain 63 per cent water of crystallization. It takes 2.7 pounds to equal 1 pound of soda ash. The action of the sodium oxide derived from the hydrated carbonate is the same as that from soda ash.

7. SODIUM NITRATE

Sodium nitrate, Chile saltpeter, $NaNO_3$, is found in large quantities in desert regions near the eastern border of Chili. The deposit averages about 5 feet in depth, 2 miles in width, and is over 200 miles long. The crude nitrate, which contains 20 to 60 per cent $NaNO_3$, lies near the surface and is usually covered by rock débris cemented together by gypsum and salt. The ore is boiled with water, and the solution is run off and allowed to crystallize. The crystals are raked into piles and allowed to drain or are put through a centrifuge. They are then allowed to dry in the sun, bagged and shipped as crude Chile saltpeter, containing 94 to 98 per cent $NaNO_3$.

Crude sodium nitrate is colored cream or brown by mud and other impurities. At one time a certain factory received a shipment of several carloads which contained balls of organic matter about three-fourth inch in diameter. These balls were a deep indigo blue in color, and the color from these stained the surrounding niter. Enamel made from this niter was of a blue cast. The importers of the niter were unable to explain the origin of this discoloring matter. They recrystallized this niter, and although the purified salt had a light blue cast it did not discolor the enamel.

(*a*) PURIFICATION OF NITER.—Refined nitrate of soda usually costs about $40 a ton more than the crude. The recrystallization is really a very simple process, and a quality suitable for enameling purposes can be prepared at comparatively small expense. All that in necessary is a tank for boiling the niter and a couple of tanks for cooling and crystallization. For small production, scrap enameled iron bathtubs make satisfactory tanks. The crystallizing tanks should be provided with crosspieces from which thin iron rods extend down into the solution. The largest and purest crystals grow on these rods. The crude niter is boiled with water in the boiling tank, and the solution allowed to stand until the mud and other dirt have settled close to the bottom. The clear supernatant solution, which will be still warm, is then tapped off into the crystallization tanks. The crystals which form on the rods and sides of these tanks as the solution cools are dried and used as refined niter. The fine crystals in the bottom of the tank, which will usually be discolored by dirt, and the remaining liquor are returned to the boiling tank. More water and crude niter are added and the process is repeated.

After a while the residue in the tank will be so great as to interfere with securing a large yield of clean niter. It is then boiled three times with water, without the addition of crude niter, and the final residue is thrown away. Using one scrap enameled iron bathtub as a boiling tank and two as crystallization tanks, the author was able to refine 1000 pounds of crude nitrate of soda per day with the labor of one man working half time on that job. The fuel for boiling the niter solution cost 50 cents per day, and the drying was done with waste heat. The total cost did not reach $5 per ton.

The amount of insoluble impurities in crude nitrate of soda should not exceed 5 per cent. Recrystallization of this crude nitrate to entirely soluble nitrate is recommended. This refined nitrate is liable to contain small amounts of chloride and sulphate of sodium, but generally the percentage will be so small as to be negligible. Nitrate of soda is slightly deliquescent; that is, takes up water from the air and becomes damp. Therefore it is unpleasant to handle, and in working to exact chemical composition, allowance must be made for the moisture. With the amounts of nitrate of soda ordinarily used in enamel batches, 2 to 3 per cent, this moisture is of no importance.

(*b*) Effect of Sodium Nitrate in Enamels.—In the smelting tank sodium nitrate yields 36.5 per cent sodium oxide and 63.5 per cent of a group of oxidizing gases. The sodium oxide acts in the same way as sodium oxide from other salts. The oxidizing gases prevent the reduction of lead, tin, and other metallic oxides to the state of metal during the smelting process. The amount of nitrate it is necessary to use depends on the composition of the melt and the condition of the fire in the smelting tank. Ordinarily 2 or 3 per cent of the raw batch of enamel is nitrate of soda. In oxide of antimony enamels the percentage of sodium nitrate used is about double this.

8. POTASSIUM CARBONATE AND NITRATE

Potassium carbonate is made from potassium chloride by the Leblanc process, in the same way as soda ash is made from sodium chloride. The ammonia process can not be used, since potassium bicarbonate is soluble in ammoniacal solutions of KCl and does not precipitate. There are few known deposits of potassium salts of importance in the world. The immense one at Stassfurt, Germany, is the most prominent. Up to the breaking out of the European war this was the source of practically all potassium salts. Recently the production of potassium salts from the ashes of seaweeds found in the Pacific Ocean, from certain lake brines, and from the flue dust of cement works and blast furnaces has become actually or potentially important. Small amounts of potassium carbonate and other potassium salts are obtained from wood ashes, residues from beet-sugar molasses manufacture, and from wool scourings.

Potassium carbonate occurs as a white granular powder, which has a strongly alkaline reaction and a salty and slightly caustic taste. It is extremely hygroscopic and when exposed to the air soon forms an oily liquid. It is very soluble in both cold and hot water. Potassium chloride is a common impurity. The melting point of potassium carbonate is 880°C (1615° F). When heated to red heat it gives 68 per cent potassium oxide, K_2O, and 32 per cent carbon dioxide gas, CO_2.

The action of potassium oxide in enamels is similar to that of sodium oxide. It increases the coefficient of expansion, and decreases strength and elasticity. On account of the last two properties it tends to produce brittle enamels that have not a wide range of "fit" on the castings. Therefore enamels high in potassium oxide tend to craze or shiver, according to conditions. Compared to sodium oxide it produces enamels of a harder and more brilliant surface. Owing to the great difference in cost potassium carbonate has been almost entirely replaced in enamel making by soda ash.

Potassium nitrate is made by treating hot concentrated solutions of potassium chloride with sodium nitrate.

$$NaNO_3 + KCl = NaCl + KNO_3$$

As the solution cools, the sodium chloride, being less soluble than the potassium nitrate, separates in crystals; first and as much as possible is "fished" out. The nitrate then crystallizes and is washed and recrystallized to free it from salt. If it contains any magnesium chloride, it will become wet on exposure to the atmosphere, since magnesium chloride is deliquescent. However, the presence of this impurity is rare. In the melting tank it yields 46.6 per cent potassium oxide and 53.4 per cent of oxidizing gases.

The action of potassium nitrate is similar to that of sodium nitrate and for the sake of economy has been replaced quite generally by sodium nitrate. Owing to the fact that it seldom becomes damp on exposure to air, it is still preferred by some enamel mixers to sodium nitrate.

9. LEAD COMPOUNDS

(*a*) RED LEAD.—Red lead, Pb_3O_4, also known as minium, is made by oxidizing metallic lead. Ordinarily it is made in two steps. In the first step the lead is made into massicot, PbO, by heating in a reverberatory furnace to just above the melting point of lead, but below the melting point of massicot. The crude massicot is raked off and cooled. It is yellow in color and much of it contains particles of metallic lead. It is finely ground, levigated, and then heated with frequent stirring to a dull red heat in a reverberatory or muffle furnace with ample access of air. In about 48 hours enough of the lead oxide has been converted to red lead to give the color demanded by the trade. On heating it breaks down to 98 per cent lead oxide and 2 per cent oxygen. Red lead may be adulterated with red iron ore, barium sulphate, and even brick dust. Red lead will be completely dissolved in warm dilute nitric acid to which a little sugar has been added. The impurities named will remain undissolved.

(*b*) LITHARGE AND MASSICOT.—Litharge and massicot are chemically the same, both being lead oxide, PbO; but they differ physically and in their method of preparation. Litharge is bright yellow and is prepared by oxidizing metallic lead at temperatures at which the PbO formed melts. Massicot is lighter yellow and is made by oxidizing metallic lead at temperatures below the melting point of lead oxide. Litharge is simply melted massicot. Both these forms of lead oxide are liable to contain particles of metallic lead unless carefully levigated.

(*c*) WHITE LEAD.—White lead is a basic carbonate of lead, the theoretical formula being $2PbCO_3.Pb(OH)_2$; but the proportions of carbonate and hydroxide vary widely in commercial brands of white lead. This chemical is made by three processes, the Dutch, the German, and the French.

In the Dutch process, earthenware pots which are about 8 inches high and each of which contains a shelf are used. In the bottom of the pot is placed a small amount of acetic acid and on the shelf a coil of thin sheet lead. In filling a shed or "stack" there is first put in a layer of moist tanbark, then a layer of pots, and next a layer of large lead gratings. About 6 inches above this a floor is laid in and on this a new series of layers is started. These alternate layers of tanbark, pots, etc., are continued until the stack is 15 to 20 feet high. The fermentation of the tanbark heats the acid in the pots to a point at which it is volatilized and attacks the metallic lead, forming basic lead acetate. The carbon dioxide gas given off at the same time by the fermenting tanbark converts the basic acetate into basic carbonate of lead, and sets free the acetic acid to attack more lead. In about three months, the stack is torn down and the wholly or partially decomposed lead is ground and seived. Any metallic lead is flattened by the grinding process and so retained on the seives. The white lead passing through the seive is ground wet in buhrstone mills and is then levigated.

The German or chamber process is an attempt to produce artificially the conditions existing inside the Dutch "stack." Sheet lead is hung in a heated room and acetic acid and carbon dioxide vapors are introduced. The corrosion takes five weeks only in this process; but it is much more difficult to control than the Dutch process, and the quantity and quality of output is subject to variation. The reactions are the same as those in the Dutch process.

In the French process a clear solution of lead acetate is made by dissolving litharge in acetic acid. White lead is precipitated from this by leading in carbon dioxide gas. There are several patented modifications of this method, among which may be mentioned Carter's process. In this method granulated lead is wet with acetic acid and treated in revolving drums with carbon dioxide.

White lead is frequently adulterated with barytes (barium sulphate), lead sulphate, or whiting. A pure white lead should dissolve completely in chemically pure nitric acid. Common nitric acid will not give a clear solution since it contains sulphuric acid. On being heated white lead gives about 85 per cent lead oxide and 15 per cent water and carbon dioxide.

(*d*) EFFECT OF LEAD OXIDE IN ENAMELS.—Lead oxide is used in enamels as a flux. It has the advantage over all the other fluxing oxides, except boric oxide, that it can be added in very large amounts without causing dull finish by the separation of its compounds in crystalline form. It produces enamels of great brilliancy and, in the absence of antimony oxide, of a pure white to cream tint. Used in amounts of over 10 per cent with antimony compounds it produces canary-yellow enamels.

Lead oxide shares with zinc oxide and barium oxide the properties of increasing the strength and elasticity of enamels without at the same time causing the coefficient of contraction to vary widely from that of cast iron. Since lead oxide is the only one of these three that can be used in large amounts in the type of enamels used in this country, it has the general reputation of giving enamels good mechanical properties. It is said to furnish "give and take" and elasticity to the enamel. As one old enameler expressively stated, "lead oxide makes the enamel able to go around the corners."

In attempting to make leadless enamels, it has been found, as in leadless glazes, that the substitution of other oxides produced enamels of more restricted working range. They were more likely to craze or shiver with slight changes in composition of the enamel, or of the iron in the castings, or even with the manner of heating. In making enamels for cast iron in this country lead oxide is highly valued, but in Europe its use seems to be disparaged.[22] It must be remembered, however, that in Europe much higher percentages of boric oxide are used than it is customary to use here.

10. ZINC OXIDE

(*a*) Occurrence and Preparation.—Zinc is found in ores as the sulphide (blende), the carbonate (smithsonite), the hydrated and anhydrous silicate (hemimorphite and willemite), the oxide (zincite), and a complex oxide of zinc, iron, and manganese (franklinite).

The ores containing sulphur are roasted at a low heat to eliminate the sulphur, and the carbonate and hydrated ores are generally calcined to volatilize carbon dioxide and water. The pulverized ore is mixed with coal or coke and roasted in fire-clay retorts. Metallic zinc passes off as a vapor and is condensed to the metal in air-cooled, fire-clay condensers. It is refined by remelting in reverberatory furnaces.

Zinc oxide can be made in two ways, from the ore direct and from the refined metal. The cheapest way is not to condense the vapors of metallic zinc obtained by the process just described, but to allow them to come in contact with hot air. The hot vapors burn readily to voluminous white clouds of zinc oxide. These are collected and at the same time sized in a series of settling chambers followed by coarsely woven, large, cotton bags. The coarsest grained and most impure zinc oxide is deposited in the first settling chamber; the finest and purest in the last of the bags. This method does not give entirely pure zinc oxide with most ores. Cadmium in the ore will be volatilized with the zinc and will give the oxide a brown color. The oxide is also subject to contamination by lead and iron oxides.

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[22] Grünwald, J., Stahl u. Eisen, 30, p. 1204.

In making zinc oxide from the metal the process is the same except that the hot vapors of metallic zinc are obtained by heating refined metal. Oxide prepared in this way is known as Florence zinc oxide and is more nearly pure than most zinc oxide made directly from the ore.

Florence zinc oxide is sold in three grades, white seal, green seal, and red seal, the finest grained and most nearly pure being named first. The cheaper brands of zinc oxides, mostly made direct from the ore, are sold under brand names selected by individual producers such as "potters selected, XX," etc. The white seal zinc oxide is pure white in color, but the other brands show increasing depth of yellow tint as the grade decreases. This difference in tint is emphasized if samples of the various grades are heated in closed unglazed earthenware cups. In making cast-iron enamels, however, the author has not been able to detect any difference in the effect of a moderate-priced zinc oxide and the most expensive brands. This experience has been confirmed by others.[23] Nevertheless, some enamel makers claim that it is necessary to use the better grades in their compositions.

When heated, zinc oxide becomes lemon yellow, but loses this color again as it cools. It dissolves readily in acids. The solutions have a metallic taste and are more or less poisonous.

(*b*) EFFECT OF ZINC OXIDE IN ENAMELS.—Zinc oxide is a valuable flux in enamels. In small amounts, 3 or 4 per cent, it is equal to lead oxide, pound for pound in fluxing power; but in larger amounts it is slightly less active, or possibly it would be more accurate to say that the difference in fluxing power becomes more noticeable. Zinc oxide has been shown to have a decidedly favorable influence on the strength and elasticity of glasses. Compared with other fluxes, it has an intermediate effect on the coefficient of expansion. Some of the most satisfactory enamel formulas used in this country call for 7 to 9 per cent of zinc oxide. In enamels low in lead it is especially desirable. The amount of zinc oxide that can be used is limited by the fact that when present in large amounts it tends to separate in fine crystalline combinations, producing a dull finish.

11. BORAX AND BORIC ACID.

(*a*) OCCURENCE AND PREPARATION.—Boron is found in many mineral combinations. The chief of these are: Boric acid vapor in volcanic steam, native borax (tinkal), magnesium borate

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[23] Ashley, H. E., Trans. A. C. S., 12, pp. 446, 459.

(boracite), calcium borate (borocalcite, colmanite), and double borate of sodium and calcium (boronatrocalcite). California furnishes about 50000 tons of boron ores a year; Chile about 40000 tons; Turkey 14000 tons; Peru, Bolivia, and Italy about 2000 tons each; Argentina about 1000 tons; Tibet about 300 tons, and Germany 150 tons.[24]

In Tuscany, boric acid, $B(OH)_3$ or $B_2O_3.3H_2O$, occurs as vapor in the steam arising from volcanic fissures. The steam is passed through water which absorbs the boric acid. The solution is evaporated, and the boric acid crystals which separate are purified somewhat by recrystallization. The boric acid produced in this way is known as "flaky" or Tuscany boric acid and is generally yellow in color and quite impure. Below are given two analyses made on samples taken from the stock of an American factory.[25]

Composition	I	II
	Per cent	Per cent
Boric acid	80.76	82.46
Silica	.71	.87
Alumina and iron oxide	.33	.28
Lime	.85	1.40
Sulphuric anhydride	9.32	8.46
Alkalies	2.59	2.08
Ammonium oxide	4.23	3.75
	98.79	99.30

As stated by Ashley,[26] the composition of brown Tuscany boric acid may be roughly expressed as 70 per cent pure boric acid, 15 per cent borax, and 15 per cent volatile matter and objectionable sulphates.

Boric acid is made from the borax and calcium borate found in California and Nevada, the calcium borate found in Chile, and the magnesium borate found in the Stassfurt salt deposits in Germany. In each case the boric acid is produced by decomposing the borate with hydrochloric or sulphuric acid. The following reaction is typical:

$$CaB_4O_7.6H_2O + H_2SO_4 + H_2O = CaSO_4.2H_2O + 2B_2O_3.3H_2O.$$

The boric acid prepared in these ways is usually quite pure.

When pure, boric acid forms pearly white, laminated crystals which are very slightly soluble in cold water but readily soluble in hot water. When heated to 100° C (212° F) it loses 1 molecule

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[24] Mineral Resources, U. S., 1914. [25] Aashley, H. E., Trans. A. C. S., 12, p. 447. [26] Ibid., p. 448.

of water, at 140° C (284° F) another, and at red heat becomes anhydrous. Care must be taken not to store it in a hot place. It contains 56.4 per cent boric oxide and 43.6 per cent water.

Borax is prepared from calcium and magnesium borates by a double decomposition reaction with sodium carbonate, according to the following typical reaction:

$$CaB_4O_7.6H_2O + Na_2CO_3 + 4H_2O = CaCO_3 + Na_2B_4O_7.10H_2O.$$

Borax crystallizes from its solutions in two forms, prismatic or common borax, $Na_2B_4O_7.10H_2O$ or $Na_2O.2B_2O_3.10H_2O$, and jeweler's or octahedral borax $Na_2B_4O_7.5H_2O$. The common or prismatic borax is the kind usually sold for enameling purposes. Octahedral borax separates from concentrated solutions at temperatures above 56° C (133° F) and common borax separates at temperatures below that point. By controlling the concentration and temperature, either type of crystal can be made at the will of the operator. In making common borax the hot solution is filtered to get rid of the slime of calcium carbonate and insoluble materials in the original chemicals, so diluted that no crystals will separate above the temperature of 56° C, and allowed to crystallize very slowly in large heat-insulated tanks. In buying common borax there is little danger that it will contain any appreciable amount of the octahedral variety, since the borax manufacturer would lose money by furnishing a product richer in boron than the grade being paid for.

The prismatic borax manufactured in this country is quite pure. It effloresces in air very slightly, to the extent that the crystals are whitened at the edges, but for practical purposes may be considered permanent in air at moderate temperatures. Care must be taken, however, that it is not stored close to a furnace or in any other hot place, for when heated it loses part of its water of crystallization. The borax used in Europe must contain traces of deliquescent salts as impurities, for Grünwald states [27] that it is so deliquescent that it must be stored in tight boxes in order to avoid errors in weighing the enamel mixes. In the melt ordinary borax yields 16.2 per cent sodium oxide, 36.6 per cent boric oxide, and 47.2 per cent water.

(*b*) EFFECTS OF BORAX AND BORIC ACID IN ENAMELS.—Both boric acid and borax act as fluxes in enamels. The soda in borax has the same effect as soda introduced as carbonate or nitrate. The boric oxide (B_2O_3) in boric acid and borax act as a strong flux,

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[27] Grünwald, J., Raw Materials of the Enamel Industry, p. 69.

and at the same time reduces the coefficient of expansion of the enamel. Other things being equal, therefore, increase of boric oxide tends to stop crazing and to cause chipping. It is the only fluxing oxide that has this property. It has a favorable influence on the strength and elasticity of enamels. Boric oxide tends to produce glasses that are viscous at low temperatures; and therefore increase of it, even to a large percentage, not only does not result in crystallization of its compounds, but hinders the crystallization of other easily crystallizable compounds. High boric oxide is the chief dependence of the enamel mixer in preventing the dull finish due to devitrification (crystallization) of fusible enamels low in lead.

Borax is cheaper per unit weight of B_2O_3 in this country than boric acid, on account of the greater expense of manufacture of the latter. In all formulas calling for pure boric acid, borax may be used without altering the properties of the enamel, provided a reduction is made in the soda ash corresponding to the sodium oxide brought in by the borax. The proper proportions are: 100 pounds of borax equal 68.5 pounds of boric acid and 28 pounds soda ash. In most cases it will be sufficiently accurate to say 70 pounds of boric acid and 30 pounds of soda ash. In substituting borax for brown Tuscany boric acid, it is necessary to remember the usual composition of this as given above.

12. FLUORSPAR

(*a*) SOURCES OF FLUORSPAR.—Calcium fluoride, CaF_2, is known as fluorspar, owing to its content of fluorine. It has been imported into this country for some time from England, being gathered up from old dump heaps of abandoned lead mines. This imported fluorspar is generally quite impure, containing considerable silica, iron, and even some lead compounds.

Large quantities of very pure fluorspar are found in southern Illinois and western Kentucky. It varies in color from pure water white, through pink and yellow to deep purple. The coloring matter is not objectionable, being in this class of fluorspar nothing more than minute quantities of hydrocarbons. The purest grade of fluorspar runs over 98 per cent calcium fluoride and is sold for the manufacture of hydrofluoric acid. The next grade contains 85 to 98 per cent calcium fluoride and is the grade generally sold for enamel making. Large quantities of this grade in lump form are sold for use as a flux in steel manufacture. In making enamels it is not advisable to use fluorspar running below 94 or 95 per cent calcium fluoride, since silica, the chief impurity, has a hardening effect on the enamel and so detracts from the fluxing power of the fluorspar. Below are given the compositions of two No. 2 brands of American fluorspar.

Composition	I	II
	Per cent	Per cent
Calcium fluoride	90 and over	96 to 98
Carbonate of lime	3.50 to 4.09	1 to 2.5
Silica	to 4.00	1 to 1.5
Alumina	0.50 to 1	Trace.

(*b*) FLUORSPAR AS A FLUX.—Fluorspar is a very powerful flux, owing to the fact that the lime is in chemical combination with an element that is stable in the melt and because it contains a high percentage of the very active flux, fluorine. Fluorspar has also the valuable property of making glass and enamels semiopaque. It is largely used in making opal glass. An enamel mix high in fluorspar, or other fluorides, requires less high-priced opacifiers to render it fully opaque than a mix low in fluorides. Fluorspar, like most strong fluxes, tends to produce crazing in enamels. When used in large amounts it tends to produce enamels that seem to be deficient in strength and elasticity. This is probably due in part to the calcium content of the mineral, as we note the same thing with other forms of calcium.

The use of fluorspar is avoided by European enamel manufacturers[28] but it is commonly used, with or without cryolite, by American enamel makers. As long as the fluorspar does not exceed 10 per cent of the melted wieght of the enamel, and no other fluorides are used, there is no marked effect on the working properties. When the percentage approaches 15 per cent, the enamels are very brittle and moreover are liable to have a dull greasy finish. However, an enamel containing 15 per cent of cryolite will also be brittle. If other fluorides are used with fluorspar, this ingredient must be reduced by a corresponding amount.

(*c*) FLUORSPAR AS AN OPACIFIER.—The opacifying power of fluorspar and all other fluorides depends largely on the length of time the enamel is in the smelting furnace. If the smelting is done rapidly and the enamel is tapped out of the furnace as soon as bubbling ceases, the greatest opacifying effect is obtained from fluorides. It has been found that in this case most of the fluorine

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[28] Grünwald, Julius, Enameling on Iron and Steel, p. 7.

remains in the enamel. As the heating of the enamel is prolonged from this point on, the opacifying effect produced by fluorine gradually decreases and at last with prolonged heating at high temperatures, if no other opacifiers are present in the enamel, the glass becomes perfectly transparent.[29] Analyses of such glasses show that practically all the fluorine and a considerable amount of silica have been volatilized. The reaction is supposed to be:

$$2CaF_2 + SiO_2 = 2CaO + SiF_4$$

Many theories have been put forward as to the manner in which fluorides cause opacity.[30] It has been held that the opacity is due to gaseous compounds of fluorine inclosed in the enamel on cooling;[31] the crystallization of silica or other compounds, not fluorides, which is aided by the great fluidity given the glass by the fluxing action of fluorides;[32] precipitated alumina, all fluorine being volatilized;[33] bubbles;[34] sodium fluoride;[35] and aluminum fluoride.[36]

It would be possible to add still another explanation to the above list, namely, that the opacity is due to globules of melted fluoride or globules high in fluoride that have not combined with the rest of the enamel. This explanation is based on the principle of producing opacity by the refraction of light through a mixture of transparent particles of two different indices of refraction. This principle is fully explained by Schott.[37] Most of these proposed explanations are purely speculative. We know only that as the fluorine is volatilized from the enamel the opacifying effect produced by the fluoride decreases.

In regard to the effect of the various fluorides, we find it to be about the same with all if the melting period is very short, but that as it is prolonged the effect of fluorspar decreases rapidly and that of cryolite less rapidly. Sodium silicofluoride occupies an intermediate position.

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[29] Meyer and Havas, Chem. Ytg. 758; 1909. Landrum, R. D., Trans. A. C. S., **14**, p. 544. Voght, G., 6th Int. Congress of Applied Chem., London, 1909.

[30] Shaw, J. B., Trans. A. C. S., **14**, p. 577. Grunwald, Julius, Raw Materials of the Enameling Industry, p. 86.

[31] Encquist, Erik, Chem. Engineering, **10**, p. 54.

[32] Beurath, Die Pol. J., **192**, p. 239.

[33] Grunwald, loc. cit.

[34] Landrum, R. D., Trans. A. C. S., **16**, p. 579.

[35] Riedel, Chem. Ytg., p. 1305; 1909.

[36] Vondracek, Sprechsaal, pp. 584 and 589; 1909.

[37] Hovestadt, H., Jena Glass, p. 397.

13. CRYOLITE

(*a*) OCCURRENCE AND PREPARATION.—Cryolite is a double fluoride of sodium and aluminum. Its chemical formula is Na_3AlF_6 or $3NaF.AlF_3$, which corresponds to 32.79 per cent sodium, 12.85 per cent aluminum, and 54.36 per cent fluorine. It occurs as a brittle crystalline mineral, ranging in color from pure white through pink and yellow to black. The color disappears on heating. Cryolite melts at about 1000° C (1800° F).

Practically the whole commercial supply of cryolite comes from Ivigtut in southwestern Greenland. A great lense of the material, 500 feet long by 200 feet wide by over 150 feet deep, has been quarried there since 1850. The chief impurity is quartz, but there may be small amounts of iron oxide, and sulphides of zinc, iron, copper, and lead. The crude material is shipped to Copenhagen, where it is hand-cobbed, crushed, and separated into various sizes and grades. The purest grade is sold for the manufacture of aluminum. This contains less than 0.2 per cent of quartz. The grade sold for enamel and glass-making purposes may contain 1 to 4 per cent of silica, 0.3 per cent iron, and traces of lead, copper, and zinc. It comes on the market as a rather coarsely ground white powder.

Cryolite is prepared artificially by adding common salt to alumina dissolved in hydrofluoric acid. When properly prepared, this material conforms in composition to natural cryolite and contains even less impurities than the natural mineral. However, it may be adulterated with other substances, such as soda ash, fluorspar, and zinc oxide. Sometimes sodium silicofluoride, or mixtures containing this, are marketed under the name of artificial cryolite. This may contain up to 35 per cent quartz as an adulteration.

A mixture of artificial cryolite with precipitated silica can be prepared by adding alumina and sodium carbonate to a hot solution of sodium silicofluoride.[38] The equation given for the reaction is:

$$2Na_2SiF_6 + Al_2O_3 + Na_2CO_3 = 2Na_3AlF_6 + CO_2 + 2SiO_2$$

Of course the same product could be obtained by adding alumina and soda ash to the solution of hydrofluosilic acid obtained from the absorption towers of fertilizer plants. (See sodium silicofluoride.) This mixture is claimed to be entirely suitable for enameling purposes, and there is no reason why it should not

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[38] French patent 408134.

be used, since many enamels contain cryolite and all contain silica. Of course the price paid for it should depend on the cryolite content, since the silica is of comparatively little value.

(*b*) EFFECT OF CRYOLITE IN ENAMELS.—Cryolite is probably the strongest flux used in enamel making. One pound of cryolite is approximately equal in fluxing power to two pounds of lead oxide. It has a decided effect in raising the coefficient of expansion of enamels. On account of this, it is liable to cause crazing when added to an enamel mix or substituted for other fluxes in enamels, unless corresponding reduction in the other fluxes or increase in refractories is made at the same time. When no other fluorides are used, cryolite may constitute 15 per cent of the melted weight of an enamel for cast iron. As this limit is approached the enamel becomes rather brittle[39] and 10 or 12 per cent is a safer limit.

Besides acting as a flux, cryolite has the well-known property of imparting to enamels a milky opacity, which greatly reduces the amount of more expensive opacifiers that must be employed. The effect of cryolite on opacity does not decrease so rapidly with continued smelting of the enamel as in the case of flourspar.

14. SODIUM SILICOFLUORIDE

Sodium silicofluoride has the formula Na_2SiF_6 and is the sodium salt of hydrofluosilicic acid. In recent years it has been prepared in large quantities in Europe and to some extent in this country as a by-product of the manufacture of phosphate fertilizers.

Most phosphate rock contains several per cent of fluorspar and considerable silica and silicates. When the rock is treated with sulphuric acid in the manufacture of fertilizer, the fluorine of the fluorspar unites with some of the silica present and silicon tetrafluoride, SiF_4 is driven out as a gas. Since this gas is injurious to the health of men and animals, in most locations it must be taken care of. The usual procedure is to absorb it in water in spray chambers. When dissolved in water, this gas gives a precipitate of pure white gelatinous hydrated silica leaving hydrofluosilicic acid in solution. This solution is run off from the precipitated silica and treated with common salt, when sodium silicofluoride is precipitated and hydrochloric acid remains in solution. Sodium silicofluoride prepared in this way must be washed very thoroughly to free it from chlorides, if it is to be

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[39] That cryolite makes enamel brittle has been disputed by R. D. Landrum. (Trans. A. C. S., 14, p. 543).

used for enameling purposes. To avoid this washing some firms precipitate with soda ash.

Since this chemical is sometimes adulterated with inert and less valuable materials, a simple method of analysis is of importance. Grünwald recommends[40] dissolving the sample in hot water and titrating with 2N caustic soda. The amount of sodium silicofluoride present is calculated according to the equation:

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O.$$

The commercial brands usually contain 90 to 95 per cent of silicofluoride, the rest being chiefly silica.

The action of sodium silicofluoride in enamels is very similar to that of cryolite. It acts as a strong flux and opacifier and tends to produce crazing. Its opacifying effect decreases on continued heating of the enamel in the melting tank more rapidly than that of cryolite but not so rapidly as that of fluorspar.

15. BARIUM FLUORIDE

Barium fluoride (BaF_2) is made as a by-product in the manufacture of hydrogen peroxide from barium peroxide. A limited amount comes on the market as a coarse white powder. It melts at 1280° C (2335° F). Its action is similar to that of cryolite rather than that of fluorspar. It has a strong opacifying effect and does not have the injurious effect on the strength of enamels that fluorspar has. It also has no effect on the color of antimony-bearing enamels. As a flux it is about equal, pound for pound, to fluorspar.

III. RAW MATERIALS—OPACIFYING AGENTS

1. THEORY OF OPACIFYING AGENTS

Opacifying agents in enamels are divided, according to their effectiveness, into true opacifiers and accessory opacifiers. The true opacifiers used alone are capable of making enamels completely opaque, while the accessory opacifiers are used along with one or more of the true opacifiers as minor aids in producing opacity. The true opacifiers include oxides or other compounds of tin, zirconium, titanium, antimony and arsenic, and calcined spinels. The only important accessory opacifiers in use at the present time are the various fluorides. Bone ash and other phosphates are used as accessory opacifiers to a limited extent.

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[40] Grünwald, Julius, Enameling on Iron and Steel, p. 10.

With the exception of the spinels, the substances used as true opacifiers are oxides or other compounds of elements lying close to tin oxide in the periodic arrangement of the elements. Chemically the oxides of this group of elements, which includes tin, zirconium, titanium, antimony and arsenic, are characterized by their chemical inertness, possessing neither strong basic nor acidic qualities. Therefore they do not readily form chemical compounds and do not readily go into solution in the enamel glass. The spinels, when calcined at high temperatures, are also chemically inert and not readily soluble in molten enamels. We may say, then, that one characteristic of the true opacifiers is that they are comparatively insoluble in enamels.

Contrary to popular belief, the true opacifiers in enamels are not opaque. Viewed under the microscope in thin section, tin oxide, titanium oxide, zirconium oxide, zirconium silicate, antimony oxide, sodium metantimonate, arsenic oxide, and the spinels are all transparent. These substances do not, therefore, make enamels opaque simply by forming suspensions of opaque material in the enamel glass.

They are characterized by high indices of refraction, much higher than that of the enamel glass in which they are suspended. This, together with their insolubility and fine state of division, is probably the explanation of their opacifying power. Schott and Herschkowitz pointed out in 1901 [41] that opal glass could be produced by the diffusion of light produced by perfectly transparent particles having a different index of refraction from the material in which they are imbedded. Fritz Haber [42] extended the theory definitely to the opacity of enamels.

The theory is that the light striking the particles with indices of refraction different from that of the glass in which they are embedded is deflected in various directions. Since with a finely divided opacifier there are multitudes of these particles in each small section of the enamel and they are embedded in the glass at all sorts of angles, the diffusion of the light is so great that the enamel becomes opaque white.

2. TIN OXIDE

The chief ore of tin is cassiterite, or tin stone. This is impure, natural tin dioxide, SnO_2. The principal sources of supply are the Malay Peninsula and East Indies, Bolivia, and Cornwall,

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[41] Jour. f. Gasbeleuchtung und Wasserversorgung, 1901, No. 26; also Jena Glass, p. 397.

[42] Jour. Soc. Chem. Ind., 33, p. 49; 1914.

England. While the native ore is largely tin dioxide, the form used in enamel making, it is too impure to be used directly. It is first reduced to pig tin and then reconverted to tin dioxide.

(*a*) METHOD OF MANUFACTURE.—For making pig tin the ore is crushed, washed to remove rock and earthy matter, and then roasted to drive off sulphur and arsenic. It is then washed again to remove sulphate of copper and oxide of iron in the form of light powder, and reduced with coal in a shaft or reverberatory furnace. The tin is remelted on a sloping hearth at a low temperature, and the pure metal flows away from the compounds of iron and arsenic.

Tin forms two oxides, stannous oxide or tin monoxide, SnO; and stannic oxide, tin dioxide, SnO_2. Stannous oxide is black and a very objectionable impurity in tin dioxide that is to be used for making white enamels. Stannic oxide or dioxide, when pure, is white in color, and the most valuable opacifying agent known to enamel makers.

Formerly tin dioxide was made by the wet process. This consisted of treating metallic tin with concentrated nitric acid, washing and levigating the insoluble hydrated oxide of tin (metastannic acid) formed, and igniting it at a bright red heat. This method produced a very pure, dense oxide of tin. It is still used for producing small amounts of tin oxide for special purposes, but is too expensive to compete with the dry methods for quantity production.

The common method of making tin oxide is the so-called dry method. This consists in oxidizing metallic tin at a bright red heat. The process is usually conducted in a reverberatory furnace, the molten metal being "rabbled" or stirred with a rake constantly. As fast as the oxide forms on the surface it is raked off. This crude oxide is ground and sized, usually by air-flotation methods, only the finest particles being put on the market. The flotation method of sizing also separates any particles of metallic tin. Care must be taken that the air and tin are both hot before they come in contact, for if any oxidation takes place at low temperatures, black monoxide will be formed. If this lies in the furnace in contact with hot air, it will be readily converted to dioxide; but three is always danger that some black monoxide will be taken out with the dioxide. It is not possible to separate the monoxide by flotation methods since it has about the same specific gravity as the dioxide.

Many types of furnaces have been proposed for preparing tin oxide, most of these being characterized by some device for preheating the air to be used for oxidizing the tin. Among others may be mentioned those of Foersterling and of Wasserman and Jaeger. Foersterling employs a reverberatory furnace using for combustion and oxidation air that has been preheated by being drawn through the hot walls of the furnace.[43] Considerable amounts of tin oxide of good quality are made in this country by the use of this furnace. Wasserman and Jaeger blow heated air through melted tin lying in a muffle connected with settling chambers. The oxide of tin is carried to these chambers as fast as it is formed. This process was patented in 1885.[44]

Tin oxide is also made in this country by injecting hot granulated tin or tin vapor into furnaces through which hot air is being forced.[45] The tin oxidizes so rapidly that it actually burns to fumes of oxide of tin. The fumes are collected and at the same time sized in collecting chambers followed by large bags.

In recent years considerable tin oxide has been prepared from recovered tin; that is, tin dissolved from tin plate scrap. Owing to the difficulties introduced by grease and other impurities, only clean scrap tin plate from various industries has been utilized successfully for recovery purposes up to the present time. The solvent used is perfectly dry chlorine gas. Gaseous tin tetrachloride is formed and condensed by passage through cooled pipe coils. Oxide of tin can be made from the stannic chloride by precipitating hydrated stannic oxide by means of an alkali, washing and igniting to form stannic oxide. By another process metallic tin is produced from the stannic chloride and stannic oxide is made from this by the dry method. Enamel makers have been inclined to avoid the use of tin oxide made from recovered tin, but large amounts have been sold and used in this country for making high-grade enamels, often without the user knowing the source of the oxide.

(*b*) CHARACTERISTICS OF TIN OXIDES.—There is a difference in the opacifying power and tint of cast-iron enamels produced by various brands of tin oxide on the market. Some grades give enamels of a certain opacity when 10 per cent less oxide is used than of other grades. In using certain brands there is a decided tendency for the enamels to be cream in tint, while other brands

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[43] U. S. patents Nos. 780984 and 880873.

[44] German patent 34653, Kl 12.

[45] One form of apparatus is described in U. S. patents Nos. 813785 and 813786, issued to L. Fink-Huguenot.

give blue or greenish tints. These differences are noticeable even when both brands have been made by modifications of the dry process. The cause of this differcnce is diffcult to determine, since, when quantitative chemical analyses are made, the analyst almost invariably reports practically pure tin dioxide. However, he may be in error in this, for the usual method of procedure in quantitative work is to get all the tin compounds present into some soluble form, to determine the amount of tin in the solution, and to calculate the amount of tin dioxide to which this is equivalent. Of course in this method of working all tin monoxide and even metallic tin are reported as tin dioxide.

However, some brands that give inferior opacity in cast-iron enamels produce beautiful, dense sheet steel enamels when added at the mill. This would seem to indicate that the poor showing of these brands when smelted in cast-iron enamels is due to solution of part of the tin oxide during the smelting process. The fact that the tin oxide acting in this way is invariably very fine grained strengthens this hypothesis. The opacity produced by these brands is materially increased by reducing the amount of alkalies, sodium and potassium oxides, in the enamels. These oxides tend to produce translucent sodium and potassium stannates.

Metallic tin and coarse granules of other impurties can be separated by repeated washing and decantation. Ten grams of the oxide are put into a large beaker and stirred up with water. After being allowed to stand for 10 seconds, all the freely floating suspension is poured or decanted off, the sludge of heavier particles being left in the bottom of the beaker. More water is added and the process repeated until the supernatant liquid becomes clear within 10 seconds after cessation of stirring. In the bottom of the beaker will be found coarse granules, the nature of which can generally be determined by examination with a good magnifying glass and by simple qualitative chemical tests. The coarse impurities separated in this way usually consist of pellets of metallic tin; coarse granules of tin oxide, which usually contain a pellet of metallic tin in their center; particles of iron from the machinery used in preparing the oxide; and granules of fire brick from the furnaces used in making the oxide.

Aside from differences in amount of impurities, there is a physical difference in tin oxides. The oxide prepared by the old wet method is very dense, a given sized package weighing more than twice as much as one containing tin oxide prepared by the dry method. This seems to be simply a difference in the compactness with which the grains of the two kinds of oxide can be packed together, and not a difference in the specific weight or density of the particles of tin oxide themselves. Dense oxide of tin can be substituted pound for pound in place of oxide of tin made by the dry process without producing any noticable difference in the opacity of the enamels. In fact there is likely to be less difference between a good brand of wet process tin oxide and a good brand of dry process oxide than between a good and a poor brand of dry-process tin oxide.

Tin dioxide is an amorphous white powder, insoluble in water and most concentrated acids, but soluble in concentrated sulphuric acid. It is not volatile and fuses only at a very high temperature. On heating it becomes yellow, then brown. Fused with sodium carbonate or hydroxide, it forms a transparent mass, sodium stannate.

3. ANTIMONY OXIDE

The chief ore of antimony is the trisulphide, Sb_2S_3, known as stibnite or needle antimony. This is a gray mineral made up of long slender needles. The chief sources of supply are China, Bolivia, and Hungary. Beginning with 1915, considerable antimony has been produced in the western United States. Metallic antimony is made from this ore by roasting it in air to drive out the sulphur and form the tetroxide and then reducing this to the metal by roasting it with carbon. It may also be obtained by heating the sulphide with iron.

There are three oxides of antimony, the trioxide, Sb_2O_3, the tetroxide, Sb_2O_4, and the pentoxide Sb_2O_5. The trioxide is obtained by roasting metallic antimony with a restricted supply of air and collecting the volatile oxide in settling chambers, or by dissolving the metal in dilute nitric acid. It is creamy white in color. The tetroxide is obtained by roasting stibnite with plenty of air. When pure it is white in color, but some commercial brands are light gray, owing to the presence of fine, dust-like particles of stibnite. A product of lighter color and one more nearly pure is obtained by heating metallic antimony with plenty of air. A tetroxide of good quality is also obtained when the trioxide is heated in air. The pentoxide is a yellow amorphous powder obtained by heating antimonic acid. Antimonic acid is made by vigorous oxidation of metallic antimony with nitric acid. Both the trioxide and pentoxide pass into the tetroxide when heated to redness.

The chief impurities found in antimony oxides are pellets or granules of antimony sulphide, in oxides made direct from the ore, and granules of metallic antimony in those made by oxidizing the metal with nitric acid. Both of these impurities can be detected by washing and decanting the oxides in the manner described under tin oxide.

Oxide of antimony produces yellow enamels when used in compositions high in lead oxide. For producing white enamels, therefore, it must be used in compositions containing not over 10 per cent of lead oxide. In addition to control of the lead content, the calcium content and also the method of melting the enamels must be carefully controlled. These factors will be discussed under antimony enamel compositions.

4. SODIUM METANTIMONATE

Sodium metantimonate is sold under various trade names such as "leukonin" and "substitute". By the original method of Rickmann[46] it is made by fusing a mixture of antimony oxide, sodium hydroxide, and sodium nitrate with a considerable amount of some inert substance such as sodium chloride, sulphate, or carbonate. The action of the inert flux medium is claimed to be purely mechanical, preventing the fusing together of the antimonate. It has been found[47] that a satisfactory grade of sodium antimonate can be made without the use of this flux medium. In either case, after the fusion the melt is cooled and lixiviated thoroughly with water. Great care must be taken to remove the last traces of chlorides and sulphates. Insufficient washing of the metantimonate is liable to cause an efflorescence of fine white crystalline masses on the ware covered with enamel made from the impure antimonate. Sodium metantimonate is a voluminous white powder having, when pure, the formula $NaSbO_3$ or Na_2O, Sb_2O_5, which calls for 84 per cent oxide of antimony. As sold in this country the sodium metantimonate content varies from 84 to 97 per cent. Some brands seem to be adulterated with kaolin.

Sodium metantimonate must be used in the same sort of compositions as oxide of antimony. These compositions will be discussed under sodium antimonate enamels.

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[46] German patent No. 134744, Aug. 14, 1901.

[47] Weimer, U. S. patent No. 932839, Aug. 31, 1909; Rickmann, German patent No. 244880, Aug. 26, 1911.

5. ZIRCONIUM COMPOUNDS

Zirconium is found occuring naturally as zirconium silicate, $ZrSiO_4$, and zirconium dioxide, ZrO_2. The chief source of supply is Brazil. Pure zirconium oxide is made by fusing the crude ore with sodium bisulphate and precipitating the zirconium from the neutralized aqueous solution by aniline sulphate. It is a voluminous white powder, insoluble in most acids, even hydrofluoric, but dissolves when heated in a mixture of two parts sulphuric acid and one part of water.

For a given opacity it is necessary to use slightly larger amounts of zirconium oxide than of tin oxide. The enamels produced are of a slightly yellow tint and a little more refractory than tin oxide enamels made from the same formula. Up to the present time the high cost of zirconium oxide has precluded its extensive use.

The treatment of zirconium silicate for the production of an opacifier has become of importance. The natural silicate does not act as a strong opacifying agent, probably because it is impossible to grind it fine enough. However, when the silicate is fused with sodium compounds a finely divided white powder is formed, which makes a very satisfactory opacifying agent.[48] During the process of fusion and lixiviation part of the silica is removed and about 4 per cent of sodium oxide and 10 per cent of water are taken up. The varying percentage of titanium dioxide carried by the original zirconium silicate is retained. The improvement in opacifying power is probably due to greater fineness of grain rather than to any chemical change. This material has been sold to a limited extent in this country, under the trade name "terrar". It is necessary to use a slightly larger percentage of it than of tin oxide in order to produce enamels of the same density.

6. TITANIUM OXIDE

Titanium oxide, TiO_2, is found native in three crystalline forms as the minerals rutile, anatase, and brookite. The minerals are always colored brown or black by iron oxide. The separation of this iron was quite a problem for a long time since TiO_2 and Fe_2O_3 react similarly to most chemical reagents. Methods of doing this economically have been found in the last few years, and now pure white TiO_2 is available for opacifying purposes at moderate prices. One of the most satisfactory methods of freeing iron-bearing titanium oxide from iron oxide is to conduct chlorine

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[48] The use of this material has been developed by the Vereiniste Chemsische Fabriken, Landau, Kreidl, Heller & Co. (See French patents Nos. 429665, 450288, and 463623.)

vapors over the impure titanium dioxide heated to redness. The iron is entirely volatilized as iron trichloride, leaving snow-white titanium dioxide. It is very similar to silicon dioxide in its action, readily forming titanates when fused with alkali carbonates, unless it has been strongly ignited.

When titanium oxide is substituted for tin oxide, it gives yellowish enamels that are more refractory than the tin oxide bearing glasses. This is due to the fact that titanium oxide is slightly soluble in enamels, and any that goes into solution acts similarly to silica, rendering the enamels more refractory and more liable to chip. As a substitute for tin oxide it has the advantage over antimony compounds that it is nonpoisonous. The use of barium and calcium titanates has also been proposed.[49]

7. SPINELS

The spinels are insoluble aluminates. The use of these as opacifiers is an old idea, but it is only recently that they have been seriously considered.[50] Zinc spinel ($ZnOAl_2O_3$) and magnesium spinel ($MgOAl_2O_3$) are the most promising. When artificial spinels of these compositions are calcined at extremely high temperatures so as to be practically insoluble in molten enamels they make satisfactory opacifying agents. Most of the spinels put on the market so far have not been rendered sufficiently insoluble and therefore have partially dissolved in the enamel. This has reduced their opacifying power and at the same time raised the fusion point of the enamels quite materially. They produce pure white enamels of high gloss and are both cheap and nonpoisonous. The use of spinels as opacifiers has many desirable features, but at present must be considered to be in the experimental stage.

8. ARSENIC OXIDE

White oxide of arsenic, As_2O_3, was formerly used as an opacifying agent. Its use has been abandoned by all progressive enamel makers, first, because it is a deadly poison and, second, because it causes minute pinholes in the enamels and consequently gives poor luster, when used in amounts sufficient to give good opacity. A very small amount of arsenic oxide improves the luster of most enamels and glasses, but the use of any amount is dangerous to the health of the men who make the enamel and apply it to the ware. Oxide of arsenic enamels may be recognized by their bluish translucent border.

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[49] English patent No. 12583.

[50] Mayer, M., and Havas, B., U. S. patent No. 1104266, 1914; Heilman, E., English patent No. 26498, 1914.

9. FLUORIDES

The action of fluorides as accessory opacifiers has been discussed under fluorspar among the fluxes. Since molten fluorides are not readily mixable with or soluble in enamel glasses, it is probable that the opacity is due to globules of melted fluorides, or glass high in fluorides, which have a different index of refraction from the body of the glass in which they are suspended. If this is the case, the opacity is produced in the same way as that brought about by the true opacifiers.

10. BONE ASH AND OTHER PHOSPHATES

The phosphates are even less soluble in molten glasses than the fluorides. As the phosphoric acid radical is driven out, and the bases with which it is combined go into solution, the opacity disappears. It seems very likely that the opacity brought about by the phosphates is produced in the same way as that due to fluorides.

Bone ash is made, as the name implies, by burning bones. It is composed of about 80 per cent calcium phosphate $Ca_3(PO_4)_2$, the remainder being magnesium phosphate, calcium carbonate, and calcium fluoride. It is generally light gray in color due to traces of carbon left in the burning. Impure calcium phosphate in combination with calcium fluoride occurs in vast quantities as apatite, the mineral from which phosphate fertilizers are made. As far as can be learned this mineral has been found too impure to use directly in enamel.

Nearly pure, precipitated calcium phosphate is produced by adding sodium phosphate to a solution of calcium chloride. This salt is pure white in color, but may contain traces of calcium chloride. Calcium phosphate is soluble in many salt solutions, such as those of sodium chloride and sodium nitrate. It is readily soluble in all strong acids.

Bone ash and precipitated calcium phosphate have long been known to have some opacifying power in enamels. However, when enough of either is used to have any marked effect in making enamels opaque, it causes dull luster by producing minute pinholes, especially on vertical surfaces. This is no doubt due to the volatilization of phosphorus pentoxide (P_2O_5). Both materials produce enamels that chip and blister readily if not carefully manipulated. One or two per cent of one or the other is the most that can be used satisfactorily in enamels for cast iron. They are used to a slight extent as accessory opacifiers.

Many attempts have been made to use, by patented methods, bone ash, precipitated calcium phosphate, and other phosphates as opacifying agents in enamels.[51] Hermsdorf and Wagner [52] use a mixture of two enamels, one containing phosphoric acid and the other calcium in some form other than the phosphate. In another patent,[53] it is proposed to use barium or strontium phosphate in place of calcium phosphate. Wagner [54] proposes the use of a rather infusible enamel which contains calcium phosphate with an easily fusible one which contains no phosphate. Traines [55] melts alkaline phosphates with fluorspar to produce an opacifying medium. He also suggests [56] the substitution of alkaline phosphates wholly or partially for cryolite and borax in the enamel and the elimination of alkaline earths. Knospel [57] goes to the other extreme and, in enamels depending on calcium phosphate for opacity, replaces potassium carbonate by barium compounds. In addition to calcium, sodium, and strontium phosphates and phosphoric acid, the use of lead and barium phosphates have been proposed at various times.

Notwithstanding these various attempts to develop methods of employing phosphates as opacifiers in enamels, they have never had any extended use. The fundamental difficulty seems to be that the opacity is dependent on the presence of the phosphoric acid radical and this is volatile at high temperatures in melts containing silica or silicates. Just as sulphuric acid will replace and drive out of combination hydrochloric acid at ordinary temperatures, so silicic acid replaces and drives out phosphoric acid at high temperatures.

IV. ENAMEL-MAKING DEPARTMENT

The enamel-making department, usually known as the "mill room," comprises facilities for storing, weighing, and mixing raw chemicals, furnaces for melting the enamels, enamel dryers, and mills for grinding and sifting the enamel.

1. STORING, WEIGHING, AND MIXING RAW MATERIALS

The relative arrangement of these various parts can, of course, be varied at will. A commonly used and convenient arrangement is a three-story building with the melting furnaces at one side or

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[51] Grunwald, Julius, Raw Materials of the Enamel Industry, p. 128.
[52] German patent No. 166672.
[53] German patent No. 186423.
[54] German patent No. 179440.
[55] United States patent No. 589544.
[56] German patent No. 81754.
[57] German patent No. 133943.

end. The crude raw materials are stored on the third floor. There they are sifted by mechanical riddles and are then fed into chutes leading to bins on the second floor. The sifting not only removes any nails, pieces of twine, etc., that may have gotten into the raw materials, but also serves to break up the lumps that commonly form in powdered chemicals. The absence of lumps greatly facilitates the fusion of the enamel to a homogeneous glass.

On the second floor the batches are weighed and mixed. In one arrangement the bins are built in a long row with their bottoms a few feet above the floor level. A set of scales on wheels runs on a track in front of this row of bins. The chemicals can be scraped by a hoe as desired from the various bins. Gravity feed of the powdered chemicals into the weighing box has not proved successful. Part of the time they stick and do not feed at all, and the rest of the time they come down with a rush. This system eliminates all shoveling, but entails considerable moving of the scales and partially completed mix back and forth. In another system, the bins are arranged in a circle around the scales. The chemicals can be scraped into the weighing box by means of a hoe and troughs, but often are simply shoveled in. Multiple-beam scales, weighing at least six ingredients with a single setting, are commonly used.

The mixing of the raw batch should be very thorough. With small batches this is often done by "cutting" the completed mix with shovels. Care should be taken to see that each shovelful of the mix is actually turned over in each of at least three cuttings. After this the whole mix should be run through as fine a riddle as possible. With large batches mechanical mixers of various types are employed. In general it may be said that batch mixers are more satisfactory than continuous ones; and that the drum type, in which the whole mix is thrown over and over, is better than the trough type, in which mixing blades travel through the batch lying in a stationary container. In continuous mixers, the portion fed into the machine first comes out first; therefore, the batch as a whole is never blended. When dependence is placed on mixing blades in a stationary trough or a fixed container of other shape, a layer next to the shell is not mixed in with the rest.

A simple and efficient batch mixer of the drum type consists of a ball mill without any balls. A lining is not necessary. If desired, three or four stout bars may be inserted midway between the circumference and axis and extending from one end of the mill to the other. These are not necessary; neither are shelves to carry the mix up the sides of the mill. If a batch not filling the mill over two-thirds full is run at a proper speed for five minutes in a plain ball mill without balls, it will be found to be very thoroughly mixed.

A convenient location for the mixer is below the floor level of the weighing floor, but above the level of the top of the melting furnaces. If not more than three furnaces are to be fed from one mixer and these are built close together, the material may be dumped into a stationary hopper and fed into the top of the furnaces by spouts. The angle of the feed spouts with the horizontal should be at least 60°. When the material is to be carried a greater distance, a hopper-bottomed car or lorry running over the tops of the furnaces is convenient. The sides of this hopper should also form an angle of at least 60° with the horizontal. It is too hot on top of a furnace to permit dislodging material that sticks in a hopper or spout.

2. MELTING THE ENAMEL

(*a*) MELTING FURNACES.—The furnaces used for melting enamel are of the reverberatory type. They are similar to the ordinary potter's frit kiln[58] but are larger; some hold over 2 tons of melted enamel. They are simply large boxes with inclined bottoms and low arched roofs. The raw material is fed in batches at the top, or side, and drawn off periodically from a tap hole on one side. Many efforts have been made to operate melting furnaces continuously, but up to the present time without much success. The heat is obtained from a flame passing across the kiln just beneath the roof. Various attempts have been made to build frit kilns that would be heated from below without contact of the combustion gases with the frit, but no material has been found that will transmit the heat readily and yet resist the intense corroding action of the molten frit.

In Fig. 1 are shown drawings of a frit furnace used in several plants. It will be noticed that the arch of this furnace does not drop down as it approaches the end away from the fire. A dropping arch is more expensive to build than a straight one, and proper approach of the flame to the melt can be obtained by regulation of the height of the arch as a whole, the slope of the floor, and the outlet of the chimney. In another type of furnace

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[58] Mayer, Ernest, Trans. A. C. S., 2, p. 196.

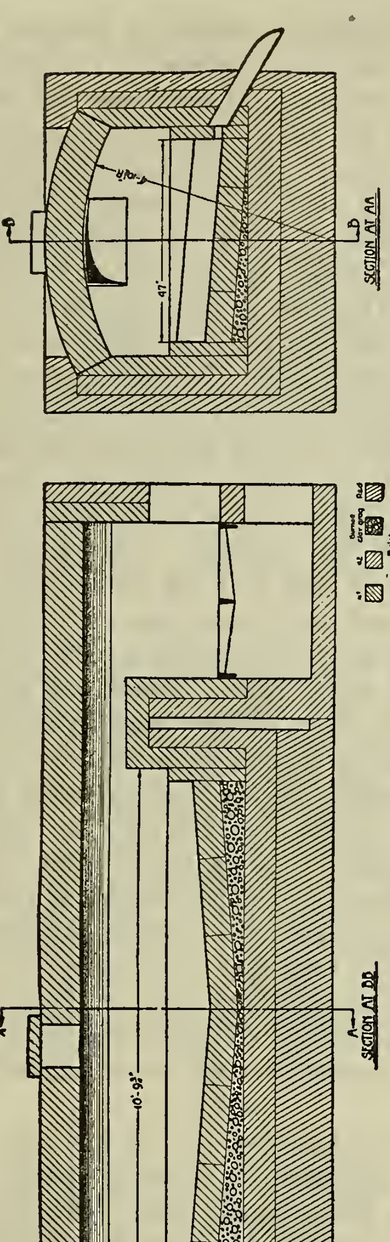

FIG. 1.—*Enamel-melting furnace*

the position of the melting chamber is reversed from that shown in these drawings, the flame traveling across the short dimension. In that type the extraction of heat from the flame is not quite as complete as in the case where the flame travels lengthwise of the melting chamber. Where the furnaces are used with oil or gas for fuel part of the fire box is bricked up and a checkerwork of fire brick is placed on top of the brick filling.

In some cases a second melting chamber for melting ground-coat glass has been built on to the cold end or side of the enamel melting chamber, the idea being to utilize some of the heat that ordinarily goes up the chimney for melting the ground-coat glass. These have not proved very successful, mainly because the heat obtained is not sufficient to do much melting, and supplementary burners have to be installed. When the bridge wall between the two melting chambers is not built hollow, the glass from one tank works through into the other. The melting tank for ground coat should be built like that for the cover coat, but may be smaller. For ground-coat glasses that are to be drawn while viscous, the tap hole may be left about 4 inches square and stopped up by a couple of wedge brick. Sometimes ground-coat glass is melted simply to a very viscous mass in scrap sinks, placed in the hottest part of an enameling furnace for 18 to 24 hours.

For melting enamels, natural gas, producer gas, or oil should be used for fuel. When coal and coke are used too much dust and ash are deposited on the melting enamel. Whatever kind of fuel is used, the flame should be thoroughly oxidizing; that is, a blue flame free from smoke and incandescent carbon which makes a yellow flame. The least fuel is used when the draft is so regulated that the tip of the flame reaches just across the furnace. A shorter flame means that too much air is being used for economy and a longer one means that the stack instead of the enamel is being heated.

(*b*) The Melting Process.—After the raw enamel batch is put into the melting tank, it is pushed back against the walls in every direction from the tap hole. This is done because the deepest part of the melting tank is at the tap hole, and if the top of the charge is made level it is difficult to melt the material deep down near the tap hole. In the course of one to four hours, depending on the size of the batch, the melting is finished. The amount of stirring that should be done during the melting depends on the uniformity of the mixing of the raw batch, the type of furnace, and the kind of enamel. The finer the grain of the materials composing the batch and the more uniformly they are blended, the less the necessity for stirring. If a furnace of large capacity compared to the size of the batch is used, so that the material can be spread out in a thin layer, stirring is not so necessary. Using thoroughly blended batches and large-capacity furnaces, the author seldom found it necessary to stir tin enamels. In order to get uniform color in antimony enamels the mix must nearly always be stirred toward the end of the melting period.

The objection to stirring enamels, aside from the small amount of labor involved, is contamination of the melt with iron from the stirring rods. It has been found that cheap tool-steel rods give less scale than rod irons. The enamel adhering to the rods should never be broken off into the tank used for holding good enamel. If the rods are chilled in a separate barrel of water, the dirty enamel may be saved and remelted with a new batch. In order to avoid stirring of the enamel one company, which makes steel tanks, goes to the length of melting the enamel in what is virtually a large rocking ladle.

Tin enamels are nearly always tapped off within a few minutes after bubbling ceases. It was formerly held that this was necessary in order to prevent the enamel from overheating and becoming contaminated with metallic lead and tin. With better control over and understanding of our fires, we find that this reduction was not due to overheating but to reducing conditions in the flame and combustion gases used for melting. With a good clear blue flame a tin enamel may be heated for hours after bubbling ceases without changing color. As explained in another section, the tint of antimony enamels varies greatly with the amount of heating which they undergo. All enamels which depend partly on fluorides, especially fluorspar for opacity, become less opaque on continued heating.

3. DRYERS

The enamel is tapped out into a large tank into which a supply of cold water, amply sufficient to chill it, is running, and is then taken to the dryers. One type of enamel dryer consists of a large revolving iron drum with a fire beneath it. A certain amount of fine iron scale is ground off this drum into each batch of enamel. In other cases the enamel is dried in thick layers in large pans heated by waste gases from a furnace or melting tank or by a separate fire. The enamel must be stirred in order to get it dried in a reasonable length of time and to prevent it from sticking to the pans, which become quite hot.

Still another method is to spread the enamel in thin layers in pans placed on racks in large drying cupboards. These are generally heated by gas. No stirring is necessary, and there is little contamination of the enamel, but the amount of room devoted to drying must be large. Rotary dryers have been built, which are lined with porcelain blocks and have projecting shelves made by inserting rows of deeper porcelain blocks. These are heated by blowing hot air through them. They must be made quite large compared to their capacity, for if the blast of air traveling through them is strong it blows out all the fine particles of enamel.

4. GRINDING MACHINERY

Ball mills are used almost universally for grinding enamel. Porcelain brick are nearly always used for lining. Formerly flint pebbles were used for grinding, but in late years the use of hard-burned porcelain balls has largely superseded them. Any particles ground off the balls show up less in the enamel than similar particles from the dark flint pebbles, and when a good grade of porcelain is used the balls wear less than the pebbles. While very hard and resistant to abrasion, the pebbles are brittle, and are often destroyed by splitting. The balls are worn down by abrasion a little more rapidly than the pebbles, but seldom split. Mills of from 250 pounds to 3000 pounds capacity per charge are used. The size is largely a matter of choice, as some of the largest plants use the smallest mills. Often large and small mills will be used in the same plant. Some enamel makers claim that with small mills there is less contamination of the enamel by abrasion of the linings and balls; but this is largely a matter of proper regulation of the charge and speed of the mill. Large mills require less labor for a given capacity.

In a few cases continuous ball mills, or tube mills, have been used. These have not proved very satisfactory, mainly because the output is small compared to the amount of power used and the money invested in the machines. The charge in a tube mill does not more than half fill the machine, while in ball mills the charge usually fills the machine to 75 per cent of its capacity. Hence the charge in the ball mills is more nearly balanced on the center of gravity of the machine and at the same time is larger, which results in a greater output for a given amount of power and volume capacity of mills.

Whatever type or size of mill is used, great care should be taken to see that no metal is exposed to abrasion. This is most likely to occur around the door frames. The resulting contamination of the glass causes black specks, which are especially noticeable in antimony enamels. Care should also be taken to prevent contamination of the enamel by grease and dirt from pulleys, belts, and bearings. The wear on linings and balls will be lessened and the contamination from that source greatly reduced if arrangements are made to empty ball mills while they are running at a very slow speed.

Cover enamels are ground dry to a fineness such that they will pass a 60-mesh sieve. Ground-coat enamels usually are ground wet to extreme fineness.

5. SCREENS

In a few plants the enamel is not really screened in the mill room, but is simply shoveled through a coarse riddle to take out lumps of enamel and small pieces of mill lining and stones. It has been found that the small amount of coarse material in the enamel powder seriously interferes with the speed of application of the enamel, and at most plants all enamel is screened in the mill room. The screen wire used is commonly about 10 meshes finer than that used in the dredges; that is, the sieves used in applying the enamel to the castings.

Various types of screens are used, revolving screens probably being the most common. In order to get the enamel powder through these they must be jarred. Formerly this was commonly done by an iron hammer hitting on a ring of iron knobs encircling the center of the screen. With the introduction of antimony enamels, it was found that the contamination of the enamel by specks of metal from these knobs and the hammer was very noticeable. The use of rawhide hammers reduced the dirt somewhat and changed the specks from iron specks to carbon specks, produced by particles of rawhide. Various expedients have been employed to overcome this trouble with revolving screens, the most practicable of which seems to be the placing of the beater ring and hammer at one end of the screen frame beyond the screening area. This eliminates the dirt but cuts down the capacity of the screen, since the jarring action is greatly reduced.

Another screen is of the reciprocating type. A flat screen is hung from a frame by wire cables and made to move back and forth by a short-stroke air motor such as is used for foundry riddles. Such a screen is clean and well suited to plants of moderate capacity. To keep down dust, it may be inclosed in a cabinet, the motor being placed on the outside. Of course the air motor may be replaced by a belt-driven eccentric or any other mechanical device that will give a reciprocating motion.

A sifter adapted from the flour-mill industry has a combined rotary and sliding movement. An oblong screen is set in a box with a solid bottom. One end of this box runs on rollers, while the other end, which is slightly higher, is supported by a ball and socket joint on the end of a pin set eccentrically on a horizontally running wheel. The sifter is operated by power applied by an adjustable friction drive. As the pulley revolves, the upper end of the box takes a rotary motion while the lower end runs back and forth on the rollers. The horizontal pulley, and of course the upper end of the box, make about 230 revolutions a minute. The enamel passing through the screen slides down the inclined bottom of the box and out through a chute at the lower end. The coarse material passes out through a similar chute at the lower end of the screen. Since all wearing surfaces in this machine are below the floor of the box in which the enamel is sifted and caught, there is no contamination of the enamel powder from that source. The capacity of this screen, as well as the sliding screen previously described, may be materially increased by attaching to the screen frame a compressed air vibrator, such as is used for vibrating molds in foundries.

V. CALCULATION OF ENAMEL FORMULAS

1. METHODS OF EXPRESSING FORMULAS

In order to compare a number of enamel formulas they must be reduced to some common form. The most commonly used forms are: Percentage amounts of raw materials, calculated percentage amounts of melted materials, and empirical chemical formulas.

The use of percentage amounts of raw materials is essentially the same as the use of a raw batch of a given weight. It is the simplest of all methods, has been used for hundreds of years by men who were able to get results, and is still used. When the number of ingredients is small, and the variations to be made are not large, the system works fairly well. When the reverse of these conditions is encountered and especially when the amount of volatile matter varies, the difficulties of drawing accurate conclusions as to the effect of variation in percentage amounts of raw batch become great.

Below are given the raw batches, in parts per thousand raw, of two enamels.

Enamel II:	
Potash feldspar	334
Sodium nitrate	24
Boric acid	179
Borax	195
Zinc oxide	102
Cryolite	98
Tin oxide	68
	1000

Enamel V:	
Potash feldspar	334
Sodium nitrate	22
Soda ash	44
Borax	147
Barium carbonate	66
Zinc oxide	55
Red lead	154
Fluorspar	106
Tin oxide	75
	1000

According to these formulas enamel II contains the same amount of feldspar as enamel V and less fluoride and tin oxide. By reference to the section on tin enamel compositions, where these two formulas are given in percentage of melted materials, we find that in the melted batches enamel II contains more feldspar than enamel V and practically the same amounts of fluoride and tin oxide. A 1000-pound raw batch of enamel II will yield approximately 814 pounds of enamel, while a 1000-pound raw batch of enamel V will yield approximately 890 pounds of enamel. In each case there will be a small reduction, amounting to from 2 to 4 per cent, due to mechanical loss in handling.

In the use of calculated percentage amounts of melted materials the size of the raw batch varies, but the amount of enamel produced per batch remains constant. This system has several advantages. First, melting tanks, dryers, mills, etc., can always be worked to full capacity. Second, the cost per pound of the enamel can be determined directly from the cost of the raw batch. Third, the relations of the various ingredients in the enamel are not obscured by the presence of variable amounts of volatile ingredients. Fourth, minerals such as feldspar and fluorspar can be treated as such and not be distributed into various oxides as is the case when empirical formulas are used. The physical condition of the raw materials and the state of aggregation of the various elements entering into an enamel batch have a decided effect on the properties of the enamel.[59]

Empirical chemical formulas are derived from the calculated analyses of the melted enamels. They are expressed in terms of so-called chemical molecules. They are much used in glaze work

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[59] Grünwald, Julius, The Technology of Iron Enameling and Tinning, p. 21. Staley, Homer F., Trans. A. C. S., **10**, p. 114.

and to some extent in enameling. Those who use them claim that various ratios in the formulas are important.[60]

In this treatise we have given enamel formulas in three forms: Raw batch for 1000 pounds melted enamel, calulated percentage composition of the melted enamel, and empirical chemical formulas. Since the calculations employed in deriving these various forms from a batch recipe are rather involved and not well known to some enamel makers, we will give as a typical example the complete figure for enamel VI.[61]

2. EXAMPLE OF CALCULATION

The first step is to obtain the calculated melted weight of the batch recipe. In the section on raw materials the percentage composition and the volatile parts of the various raw materials have been given. The melted weights are obtained by multiplying the raw weight by the fractional part not volatile. In the absence of chemical analyses, all materials are considered pure. For cast-iron enamel formulas no fluorine is supposed to be lost. The volatile radicals are carbon dioxide from carbonates, water of chemical combination in various materials, and nitrogen pentoxide (N_2O_5) from nitrates.

The factory recipe for the enamel is shown in (1). From (2) we find that the calculated melted weight from this raw batch is 666 pounds. Since we want a raw batch that will give 1000 pounds melted, we divide 1000 by 666 in order to get a factor by which each quantity in (1) must be multiplied. Our factor is $\frac{1000}{666} = 1.5$, and the products are shown in (3).

In obtaining the percentage composition, melted, the first step is to divide the values given in (3) by 10, so as to obtain the raw batch for 100 pounds melted. This gives column (4). The amount of each material present in (4) is then multiplied by the fractional part each of the nonvolatile ingredients constitutes of the whole. These factors are, of course, obtained by dividing the percentages by 100. The products are shown in (5).

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[60] Landrum, R. D., Trans. A. C. S., 14, p. 493; Grünwald, Julius, The Technology of Iron Enameling and Tinning, p. 46. In a later publication, Raw Materials of the Enameling Industry, p. 206, Grünwald states that the use of percentage weights is better and more usual.

[61] For ceramic calculations in general, see Trans. A. C. S., 2; Jackson, W., Ceramic Calculations; Grünwald, Julius, Technology of Iron Enameling and Tinning, Chapter X.

Factory recipe	(1)		Factor		(2) Melted weights	(3) Raw batch for 1000 pounds melted	(4) Raw batch for 100 pounds melted		Factor		(5) Percentage composition melted	
Potash feldspar...	255	×	1.0	=	255.0	380	38.0	×	[a]0.647	=	24.58	silica
								×	.184	=	7.00	alumina
								×	.169	=	6.42	potassium oxide
Soda ash.........	20	×	.58	=	11.6	30	3.0	×	.580	=	1.74	
Sodium nitrate...	20	×	.365	=	7.3	30	3.0	×	.365	=	1.09	6.31 sodium oxide
Borax............	144	×	.53	=	76.0	215	21.5	×	.162	=	3.48	
								×	.366	=	7.87	boric oxide
Barium carbonate	33	×	.777	=	23.3	50	5.0	×	.777	=	3.88	barium oxide
Zinc oxide........	70	×	1.0	=	70.0	105	10.5	×	1.00	=	10.50	zinc oxide
Red lead..........	112	×	.98	=	110.0	168	16.8	×	.98	=	16.50	lead oxide
Fluorspar.........	33	×	1.0	=	33.0	50	5.0	×	1.0	=	5.00	calcium fluoride
Cryolite...........	20	×	1.0	=	20.0	30	3.0	×	[a].60	=	1.80	sodium fluoride
								×	.40	=	1.20	aluminum fluoride
Tin oxide.........	60	×	1.0	=	60.0	90	9.0	×	1.0	=	9.00	tin oxide
	767				666.2	1148	114.8				100.06	

Percentage composition, melted	(5)		Molecular weights		(6) Parts of molecules		(7) Parts of molecules		Factor		(8) Parts of molecules RO = 1.00
Silica..............	24.58	÷	60	=	0.410 SiO_2	K_2O...	0.068	×	2.066	=	0.140
Alumina...........	7.00	÷	102	=	.069 Al_2O_3	Na_2O..	.123	×	2.066	=	.254
Potassium oxide....	6.42	÷	94	=	.068 K_2O	CaO...	.064	×	2.066	=	.132
Sodium oxide.......	6.31	÷	62	=	.102 Na_2O	BaO...	.025	×	2.066	=	.052
Boric oxide.........	7.87	÷	70	=	.112 B_2O_3	ZnO...	.130	×	2.066	=	.269
Barium oxide.......	3.88	÷	153.5	=	.025 BaO	PbO...	.074	×	2.066	=	.153
Zinc oxide..........	10.50	÷	81	=	.130 ZnO		.484	×	2.066	=	1.000
Lead oxide.........	16.50	÷	223	=	.074 PbO	Al_2O_3..	.076	×	2.066	=	.157
Calcium fluoride...	5.00	÷	78	=	.064 $CaF_2 = \begin{cases} 0.064 CaO \\ 0.064 F_2 \end{cases}$	SiO_2... F_2......	.410 .106	× ×	2.066 2.066	= =	.847 .219
Sodium fluoride....	1.80	÷	84	=	.021 $Na_2F_2 = \begin{cases} 0.021 Na_2O \\ 0.021 F_2 \end{cases}$	SnO_2..	.060	×	2.066	=	.124
Aluminum fluoride	1.20	÷	168	=	.007 $Al_2F_6 = \begin{cases} 0.007 Al_2O_3 \\ 0.021 F_2 \end{cases}$						
Tin oxide..........	9.00	÷	150.5	=	.060 SnO_2						

[a] Little is gained by splitting feldspar and cryolite up into their constituent radicals. In factory work it is quite common to use 1.00 as the factors for these minerals and to call the results melted feldspar and cryolite.

The first step in obtaining the molecular formulas from the percentage composition is to divide[62] the percentage amount by the so-called molecular weights.[63] This gives us the list of parts of

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[62] Tables to facilitate this division are to be found in Quantitative Classification of Igneous Rocks, by Cross, Iddings, Pirsson, and Washington.

[63] The use of this term is simply a matter of custom. In this case the formula of a compound merely shows the proportions in which the elements are combined. (See Staley, H. F., Trans. A. C. S., 13 pp. 123, 133, and 147.)

molecules shown in (6). The results obtained in (6) are rearranged, like quantities being added together, and all RO oxides—that is, those containing only one oxygen—being placed in convenient order for adding. This gives us the arrangement in (7). Since the sum of the RO molecular fractions must be unity in the final formula, we divide 1 by 0.484 in order to get a factor, 2.066, by which each quantity in (7) must be multiplied. This multiplication gives us column (8). (The same result would, of course, be obtained by dividing each of the quantities by 0.484.)

In writing the empirical chemical formulas the oxides and radicals are divided into groups. The RO oxides make the first group, the trioxides that are not acids make the second, and the acid oxides and radicals make the third. Arranging the data in (7) in this manner, we obtain the following empirical chemical formula:

$$\left.\begin{array}{ll} 0.140 & K_2O \\ 0.254 & Na_2O \\ 0.132 & CaO \\ 0.052 & BaO \\ 0.269 & ZnO \\ 0.153 & PbO \end{array}\right\} 0.157\ Al_2O_3 \left\{\begin{array}{ll} 0.847 & SiO_2 \\ 0.231 & B_2O_3 \\ 0.219 & F_2 \\ 0.124 & SnO_2 \end{array}\right.$$

$$\overline{1.000}$$

In addition to the molecular weights used in this example, the following may be useful in deriving enamel formulas:

Magnesium oxide, MgO	40	Titanium oxide, TiO_2	80
Antimony trioxide, Sb_2O_3	288	Cobalt oxide, CoO	75
Antimony pentoxide, Sb_2O_5	320	Barium fluoride, BaF_2	175
Zirconium oxide, ZrO_2	123	Silicon fluoride, SiF_4	104

3. THE FLINT EQUIVALENT

It is quite difficult to estimate the comparative fusibility of a series of enamel formulas, whether these are given in the form of raw batch, percentage composition, or empirical chemical formulas. When only one refractory ingredient is used some idea can be obtained by observing the percentage this constitutes of the melted enamel. For this reason, in giving cover coat enamels we have employed formulas calling for potash feldspar as the only refractory. It is impossible to do this in ground coat enamels, for clay, flint, and feldspar must be taken into consideration.

By practical trial the writer has determined that in cast-iron enamels potash feldspar, flint, and clay can be substituted for one another, without changing the fusibility of the enamel, in the ratio of 100 feldspar: 66⅔ flint: 40 clay.[64] By assuming that flint is substituted in these ratios for all the clay and feldspar found in each of the ground coat formulas given in this paper and then again reducing the batch to 1000 pounds, melted, we obtain a number which indicates the pounds of flint that would have been used for 1000 pounds of ground coat, melted, if the only refractory employed had been flint. We have called this number the "flint equivalent" of the formula. The flint equivalent of a ground coat is a fair index of its refractoriness, for variation in the amount of flint used has such a decided effect that the influence of variations commonly found in the relative amounts of the various fluxing oxides can be neglected.

VI. GROUND COAT ENAMEL COMPOSITIONS

The function of a ground coat enamel is to act as a bond between the cover enamel and the iron and also to protect the iron from oxidizing while being heated to the temperature at which the cover enamel fuses. Statements are sometimes found in enameling literature that a ground coat is not necessary for powdered enamels for cast iron.[65] While it is sometimes possible to enamel a trial piece without the use of a ground coat, the percentage of good pieces obtained in this way is very small and the process is not a commercially feasible one. At the present time the use of some sort of ground coat is universally practiced in enameling cast iron in this country. Ground coats consist of suspensions in water of powdered frit (or glass) and various powdered raw materials. To these are added small amounts of certain chemicals, known as flotation agents, the function of which is to aid in keeping the solids in suspension.

1. MATERIALS USED IN FRITS

The materials commonly used in making the frits are flint or sand, feldspar, borax, red lead, and sodium nitrate. Flint and feldspar are the refractory ingredients of the enamel and supply the silica essential to the production of a permanent glass. Flint or sand is often used alone as the refractory, especially in older formulas, but many recipes call for the use of some feldspar in addition. Borax is the flux used in largest quantity on account of the well-known ability of boric oxide to dissolve iron oxide as well as other oxides. A ground coat glass high in boric oxide

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[64] Trans. A. C. S., 13, pp. 505 and 534.

[65] Holdcroft, H., Jour. Soc. Chem. Ind., 29, p. 123.

readily dissolves any small amounts of iron oxide present on the surface of the iron. Lead oxide is used because its compounds melt at low temperatures to produce fluid glasses and also glasses of good mechanical strength when cold. The small amount of sodium nitrate used is employed for the sake of the oxidizing effect of the nitrate radical which prevents reduction of the lead in fritting and the absorption of injurious sulphur gases by the glass during the fritting process. Small amounts of other fluxes, such as fluorspar, cryolite, barium oxide, and soda ash, are sometimes used, but these perform no distinctive service and most enamel frits are made from the above list of materials. Small amounts of magnesium carbonate and magnesium sulphate are sometimes used in enamel frits on the assumption that they aid the adhesion of the ground coat to the iron.[66] Cobalt oxide in very small amounts is used in many enamel frits for the same reason.

2. RAW MATERIALS IN GROUND COATS

For raw material to be added at the mill, clay is universally used on account of its ability to cause the enamel composition as a whole to float. It also acts as a refractory ingredient and in some cases is the only raw refractory used. Flint and feldspar are also occasionally used as raw refractories. Magnesium carbonate, magnesium sulphate, borax, lime water, ammonia, etc., in small amounts, are used to help float the enamel. Sometimes a little cobalt oxide is added raw, in cases where it has not been convenient to melt it into the frit.

3. COBALT OXIDE IN GROUND COATS

As to the function and value of cobalt oxide in ground coats for cast iron, we can only say that these are debatable questions. After a rather careful investigation of the subject Coe came to the conclusion that "the use of cobalt in a ground coat for cast-iron enamels is of doubtful value.[67]" On the other hand, makers of sheet-steel enamels in general claim they can not make a satisfactory ground coat without the use of cobalt oxide or some metallic oxide substitute for it. They are rather at a loss to account for the remarkable effects they claim for the very small amounts of cobalt oxide used, and put forth various fanciful and unproved theories to explain the phenomena.[68]

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[66] Randau, Paul, Enamels and Enameling, p. 126.

[67] Trans. A. C. S., 13, p. 545.

[68] Landrum, R. D., Trans. A. C. S., 14, pp. 756–763.

It is certain that cobalt oxide is not essential to the production of a satisfactory ground coat for cast iron, since many excellent coats contain no cobalt. On the other hand, so many factors enter into the production of satisfactory enameled iron ware that it is very difficult to determine the effect of cobalt oxide in the ground coat. The result is that many enamelers use cobalt oxide in their ground coats because they feel that it does no harm and possibly does some good. The cost of the cobalt oxide, compared to the value of the ware produced, is so small that they can not afford to risk leaving it out of the composition.

4. FLOTATION OF ENAMELS

As demonstrated by Ernest Mayer for glazes,[69] the settling of enamel suspensions is due to excessive alkalinity of the enamel solution. Mayer divides the vehicles used for flotation purposes into those that act physically and those whose action is chemical. In the first group are clay, sirup, gum arabic, dextrine, milk, and blood. The two latter soon curdle and make quite thick suspensions. In the chemical group are various acid substances such as boric acid, vinegar, hydrochloric and sulphuric acids, which reduce the alkalinity by neutralizing part of the alkali. A more effective group of chemicals are those which neutralize part of the alkalinity and at the same time produce a flocculent precipitate. The most commonly used of these are magnesium sulphate and magnesium chloride.

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4$$
$$MgCl_2 + 2NaOH = Mg(OH)_2 + 2NaCl$$

It is a noteworthy fact that none of these chemical vehicles has any appreciable effect unless clay is present. It would seem, then, that the effect of these reagents is to coagulate the clay and thus render it capable of floating the enamel. By the addition of acid substances the enamel suspension would be rendered acid or faintly alkaline, which conditions are favorable to coagulation. By the addition of magnesium salts, the alkalinity would be reduced, a flocculent precipitate, $Mg(OH)_2$, formed and a coagulating salt, sodium sulphate or chloride, would be left in solution. Ammonium carbonate is a very effective coagulant, while borax acts as a coagulant or deflocculent, according to conditions. All of the other chemicals used for floating enamels are capable of flocculating clay under the proper

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[69] Trans. A. C. S., 11, p. 369.

conditions and we have every reason for thinking this is their mode of action.[70]

As pointed out by Mayer, according to theory it is a mistake to introduce a sulphate, such as magnesium sulphate, into a ground coat on account of the danger of sulphur blisters. However, magnesium sulphate is the most commonly used vehicle, excepting clay, and apparently the small amounts employed do no harm. Grünwald[71] recommends magnesium oxide (calcined magnesium carbonate) and ammonium carbonate as being chemically harmless. Magnesium oxide and carbonate, as also calcium oxide, hydroxide (milk of lime) and carbonate, are liable to cause serious trouble if they happen to be deposited on the ware in large granules. These granules will not be melted into the ground coat or enamel but burn to particles of quicklime (CaO or MgO). In the course of several months some of these will hydrate, presumably by moisture working through the porous iron with which they are in contact, and expand. This causes the enamel above them to break off in little cone-shaped spalls. This danger is not an imaginary one, for $20,000 worth of ware in one stock room has been ruined in this manner. For this reason, it is preferable not to use insoluble forms of magnesium or calcium as vehicles.

These so-called vehicles may be added when the ground coat is put into the mill, but the more common practice is to add clay only before grinding and to add the others to measured quantities of the coat just before use. When vehicles other than clay are used the consistency of a ground coat varies greatly with age.

5. TYPES OF GROUND COATS

(*a*) SINTERED GROUND COATS.—Formerly it was the practice to use very refractory ground masses that were simply sintered onto the iron but not fused to a glass. The object was to produce a porcelain-like coating on the metal, over which the cover enamel would act as a glaze. This type of ground coat is still used for wet-coat enamels on cast iron, but for powdered enamels it has been almost entirely superseded by thin glossy ground coats.

The basis of these sintered ground coats was a frit made from flint and borax, or flint, feldspar, and borax, with small amounts of lead or sodium oxides. To this frit were added at the mill clay and flint, or clay and feldspar, in sufficient quantity to make the

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[70] Ashley, H. E., Technical Control of the Colloidal Matter in Clays, Technologic Papers of the Bureau of Standards No. 23, pp. 74-102.

[71] Sprechsaal, **43**, p. 594.

mass so refractory that it would sinter, but not fuse, in the enameling oven. Magnesium oxide or sulphate was used to aid in floating the enamel. The coat was supposed to be fired until it could not be rubbed off with the fingers and until the individual grains appeared rounded when examined with a good hand glass.[72] Ground-coat I is a composition of this type that has been used in this country for wet-coat enamels. Further examples can be found in Randau.[73]

(*b*) GLASSY GROUND COATS.—In the use of glassy ground coats, enamel makers have broken away from the idea of analogy between enameling cast iron and glazing porcelain and have attempted to produce glasses that would give them the maximum adhesion between the enamel and the metal. A good ground coat of this class should melt at dull red heat in order to protect the iron from oxidation; should be able to dissolve any oxides or foreign matter on the surface of the metal; should be sufficiently fluid to run, in part, into the minute pores of the metal so as to produce a good bond; and should not blister or volatilize ("burn off") until temperatures above those commonly employed in enameling are reached.[74]

The most simple and oldest type of glassy ground coat consists of a refractory frit, high in sand or flint and generally containing cobalt, to which only enough clay to float it is added at the mill. Ground coats II and III are typical examples, showing the range of lead oxide and borax commonly encountered in this type of ground coat. The variations in cobalt oxide also reach about the normal limits. High-borax ground coats are more popular than those high in lead oxide, so formulas approaching II are in more common use than those similar to III.

With the general adoption of feldspar cover enamels in late years, it is quite natural that feldspar should have been introduced into ground-coat frits. It has not replaced flint and sand entirely as in many cover enamels, for a formula for a ground-coat enamel calling for neither flint nor sand is unusual.

With the introduction of frit kilns it became inconvenient to melt cobalt into the ground-coat frit, for then the kiln could not be used for white or other colored enamels. Consequently, in some modern formulas, we find cobalt oxide as an addition to be made at the mill. Ground coat IV is a typical formula containing feldspar in the frit and calling for cobalt to be added at the mill.

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[72] Randau, Paul, Enamels and Enameling, 2d English ed., pp. 120 and 148.

[73] Randau, loc. cit., pp. 124–125.

[74] Compare Coe, J. H., Trans. A. C. S., 13, p. 531.

It was but natural that from time to time enamel mixers should make the experiment of blending two ground coats. In some cases the results were so satisfactory that the use of a formula calling for the blending of two ground coats became established in factory practice. According to the results obtained by J. H. Coe,[75] in some cases blends of two ground coats of about the same heat range will give coats of longer heat range than is given by either coat alone. Ground coat V is a typical formula of this kind. Incidentally, it calls for magnesium carbonate as a raw addition.

In the four glassy ground-coat formulas already given, the frits themselves are quite refractory and comprise the bulk of the coat. The raw material consists essentially of only enough clay to float the enamel. In late years, with the rather general use of frit kilns for smelting ground-coat frits, the use of formulas calling for more fusible frits and larger amounts of refractory raw additions has been adopted in a number of plants. Ground-coat VI is typical of a number of formulas in use calling for large amounts of clay as a raw refractory. One advantage of this type of formula is that the use of chemical "vehicles" for floating the coat can be avoided.

The use of clay alone as the raw refractory, where the amount to be added is large, is not as common as the employment of a small or moderate amount of clay as a floating agent and the addition of either flint or feldspar, or both of these, as refractories. Ground coat VII is a formula calling for clay, flint, and feldspar as raw additions. In this formula two frits are blended which, of course, give the same effect as blending two ground coats. This ground is more fusible than the preceding, since it is used with a soft enamel for light castings.

Ground coat I is quite refractory and has a high "flint equivalent." Ground coat VII is quite fusible and has a correspondingly low flint equivalent. Ground coats II to VI are supposed to be suited to general lines of enameled iron wares; and it is remarkable how nearly uniform are the "flint equivalents" of these five recipes, which are gathered from various sources.

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[75] Trans. A. C. S., 13, pp. 531-549.

Ground Coat I

Material	Batch for 1000 pounds		Composition	Per cent
	Raw	Melted		
Frit:				
Flint	350		Silica	77.83
Borax	185		Alumina	7.16
Sodium nitrate	35		Sodium oxide	4 28
Red lead	41		Boric oxide	6.77
	611	500	Lead oxide	4.00
Additions:				100.04
Flint	345	345		
Clay	180	155		
	1136	1000		

Flint equivalent, 869.

Empirical chemical formula:

$$\left.\begin{array}{r} 0.785\ Na_2O \\ \underline{.215}\ PbO \\ 1.000 \end{array}\right\} 0.807\ Al_2O_3 \left\{ \begin{array}{l} 14.743\ SiO_2 \\ 1.103\ B_2O_3 \end{array}\right.$$

Ground Coat II

Material	Batch for 1000 pounds		Composition	Per cent.
	Raw	Melted		
Frit:			Silica	70.28
Flint	675.0		Alumina	2.39
Borax	390.0		Sodium oxide	7.60
Sodium nitrate	35.0		Boric oxide	14.27
Red lead	52.5		Lead oxide	5.15
Cobalt oxide	3.0		Cobalt oxide	.30
	1155.5	948.0		99.99
Addition: Clay	60.0	52.0		
	1215.5	1000.0		

Flint equivalent, 736.

Empirical chemical formula:

$$\left.\begin{array}{r} 0.810\ Na_2O \\ .165\ PbO \\ \underline{.025}\ CoO \\ 1.000 \end{array}\right\} 0.158\ Al_2O_3 \left\{ \begin{array}{l} 7.705\ SiO_2 \\ 1.342\ B_2O_3 \end{array}\right.$$

Ground Coat III

Material	Batch for 1000 pounds		Composition	Per cent
	Raw	Melted		
Frit:			Silica	70.36
Flint	680		Alumina	2.03
Borax	170		Sodium oxide	4.575
Sodium nitrate	50		Boric oxide	6.26
Red lead	170		Lead oxide	16.66
Cobalt oxide	.85		Cobalt oxide	.085
	1071	956		99.97
Addition: Clay	51	44		
	1122	1000		

Flint equivalent, 735.

Empirical chemical formula:

$$\left.\begin{array}{r}0.448\ Na_2O\\ .485\ PbO\\ \underline{.067\ CoO}\\ 1{,}000\end{array}\right\}0.121\ Al_2O_3\left\{\begin{array}{l}7.102\ SiO_2\\ 0.539\ B_2O_3\end{array}\right.$$

Ground Coat IV

Material	Batch for 1000 pounds		Composition	Per cent
	Raw	Melted		
Frit:			Silica	58.30
Sand	275		Alumina	10.27
Potash feldspar	435		Potassium oxide	7.35
Borax	375		Sodium oxide	6.07
Red lead	41		Boric oxide	13.72
			Lead oxide	4.00
	1126	948	Cobalt oxide	.30
Additions:				
Clay	57	49		100.01
Cobalt oxide	3	3		
	1186	1000		

Flint equivalent, 733.

Empirical chemical formula:

$$\left.\begin{array}{r}0.392\ K_2O\\ .493\ Na_2O\\ .095\ PbO\\ \underline{.020\ CoO}\\ 1.000\end{array}\right\}0.507\ Al_2O_3\left\{\begin{array}{l}4.884\ SiO_2\\ .985\ B_2O_3\end{array}\right.$$

Ground Coat V

Material	Blue ground coat; batch for 1000 pounds.		White ground coat; batch for 1000 pounds.		Composition	Per cent
	Raw	Melted	Raw	Melted		
Frit:					Silica	67.82
Sand	685.0		395.0		Alumina	3.80
Potash feldspar			315.0		Potassium oxide	1.77
Borax	335.0		335.0		Sodium oxide	6.66
Sodium nitrate	30.0		30.0		Boric oxide	12.13
Red lead	85.0		60.0		Lead oxide	7.50
Cobalt	2.7				Magnesium oxide	.14
	1138.0	958.0	1135.0	958.0	Cobalt oxide	.18
Additions:						100.00
Clay	48.0	41.0	48.0	41.0		
Magnesium carbonate	3.0	1.5	3.0	1.5		
	1189.0	1000.5	1186.0	1000.5		

Flint equivalent, white enamel, 734. Flint equivalent, blue enamel, 730.

The final ground coat is made by taking two parts of blue ground coat and one part of white ground coat. This gives a flint equivalent of 733.

Empirical chemical formula:

$$\left.\begin{array}{rl} 0.115 & K_2O \\ .646 & Na_2O \\ .021 & MgO \\ .203 & PbO \\ \underline{.015} & CoO \\ 1.000 & \end{array}\right\} 0.224\ Al_2O_3 \left\}\begin{array}{l} 6.827\ SiO_2 \\ 1.033\ B_2O_3 \end{array}\right.$$

Ground Coat VI

Material	Batch for 1000 pounds		Composition	Per cent
	Raw	Melted		
Frit:			Silica	48.00
Sand	200		Alumina	16.61
Feldspar	200		Potassium oxide	3.38
Borax	390		Sodium oxide	7.42
Sodium nitrate	30		Boric oxide	14.27
Red lead	100		Lead oxide	9.80
Magnesium carbonate	10		Magnesium oxide	.48
			Cobalt oxide	.10
	930	720		
Additions:				100.06
Clay	325	279		
Cobalt oxide	1	1		
	1256	1000		

Flint equivalent, 732.

Empirical chemical formula:

$$\left.\begin{array}{r} 0.167\ K_2O \\ .553\ Na_2O \\ .056\ MgO \\ .219\ PbO \\ \underline{.005}\ CoO \\ 1.000 \end{array}\right\} 0.758\ Al_2O_3 \left\{\begin{array}{l} 3.72\ SiO_2 \\ .95\ B_2O_3 \end{array}\right.$$

Ground Coat VII

Material	Batch for 1000 pounds		Composition	Per cent
	Raw	Melted		
Frit I:			Silica	50.63
Potash feldspar	300		Alumina	10.71
Borax	115		Potassium oxide	7.10
Sodium nitrate	20		Sodium oxide	4.36
Red lead	125		Boric oxide	6.95
		490	Lead oxide	20.30
Frit II:				
Flint	125			100.05
Borax	75			
Sodium nitrate	15			
Red lead	82			
		250		
Additions:				
Clay	75	65		
Flint	75	75		
Feldspar	120	120		
	1127	1000		

Flint equivalent, 658.

Empirical chemical formula:

$$\left.\begin{array}{r} 0.31\ K_2O \\ .29\ Na_2O \\ \underline{.40}\ PbO \\ 1.00 \end{array}\right\} 0.428\ Al_2O_3 \left\{\begin{array}{l} 3.444\ SiO_2 \\ .404\ B_2O_3 \end{array}\right.$$

VII. TIN ENAMEL COMPOSITIONS

1. BASIS OF CLASSIFICATION

The tin enamel compositions for cast iron in common use have, for the most part, been developed in factory practice through long years of patient cut-and-try experiments by men who had little knowledge of chemistry and less of physics to guide them. In recent years a few ceramic engineers have entered this field and have materially reduced the cost of the enamels in use. This reduction in cost, however, has consisted mainly in substituting cheap forms of chemicals for more expensive forms and eliminating a few expensive ingredients of little value. The general types of enamels had been too thoroughly worked out in practice to permit any radical innovations. The fact that these types have stood the test of time and are really a "survival of the fittest" is in itself proof that they must conform, at least roughly, to the laws of physics and chemistry applicable to enamel compositions.

Many factors determine the availability of an enamel, such as fusibility, luster, coefficient of expansion, strength, elasticity, color, hardness, and resistance to chemical agents. Enamel compositions might be classified according to the relations of composition to any one of these factors, but the most obvious relation is that of composition to luster, as dependent on the ability of the enamel to remain glassy and not devitrify during working and cooling. Of course, all the other factors have a modifying effect in determining the actual compositions used. In fact, any enamel composition is a compromise.

As stated under the discussion of luster, boric oxide and lead oxide are the only fluxing oxides that can be present in enamels in large amounts without causing devitrification. The amount of the other fluxing oxides that can be added without causing devitrification is so small that it is practically impossible to make a satisfactory enamel for cast iron unless the sum of these two oxides is above a certain minimum. Boric oxide is always used, and tin-bearing enamel compositions fall into three general types: (1) leadless enamels, (2) low-lead enamels, (3) high-lead enamels. Of course it is understood that the following compositions are for powdered enamels to be applied to cast iron.

2. THE LEADLESS TYPE

The leadless type of enamel has been developed in Germany. It is characterized by very high boric oxide. Since the enamel is so high in boric oxide it would have a very low coefficient of expansion and would therefore tend to chip, other factors, such as strength and elasticity, being equal, if this were not corrected in the rest of the composition. Therefore the German enamels high in boric oxide are high in sodium oxide and cryolite, both of which have a very decided tendency to raise the coefficient of expansion of enamels. Since boric oxide has a favorable effect on the strength and elasticity of enamels, the unfavorable effect of a large amount of sodium oxide on these properties is counterbalanced. On account of the solvent action of glasses high in sodium oxide on tin oxide, the amount of the latter substance is high compared to American practice.

Enamel I is a formula of this type, published by Dr. Julius Grünwald,[76] who has written extensively on German enameling practice. Clay is seldom used in making enamel melts in America, and the amount of tin oxide in Grünwald's formula would be considered excessive. A formula such as enamel II conforms more nearly to American ideas of what a leadless enamel high in boric oxide should be.[77]

3. THE LOW-LEAD TYPE

Since lead oxide is present in considerable amounts in the low-lead type of composition, the boric oxide can be lower than in the prevoius type without danger of devitrification taking place. The lead oxide generally runs under 10 per cent and the boric oxide over 8 per cent. In American practice considerable zinc oxide is generally used in this type of enamel. Enamel III is an old formula for this type of enamel and enamel IV is a modern derivative of the same formula.

4. THE HIGH-LEAD TYPE

In the high-lead type of enamel the lead oxide runs from 16 to 25 per cent of the melted weight of the enamel. Since the lead oxide is so high the boric oxide can be low, around 6 per cent of the melted weight, as in enamel V, without danger of devitrification. However, on account of considerations of strength and elasticity, the boric oxide is often kept as high as 8 per cent in high-lead enamels, as in enamels VI and VII. The amounts of the other fluxing oxides vary widely, but that of any one seldom exceeds 10 per cent. This is the type of powdered enamel for cast iron most commonly used in this country, and many formulas might be given, but enamels V, VI, and VII are typical.

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[76] Stahl and Eisen, 30, p. 1204.

[77] Staley, H. F., and Fisher, G. P., Trans. A. C. S., 15, p. 626.

Enamel I

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
Potash feldspar	340.0	Silica	24.46
Clay	55.0	Alumina	8.44
Sodium nitrate	5.5	Potassium oxide	5.66
Soda ash	21.0	Sodium oxide	10.41
Borax	555.0	Boric oxide	20.33
Cryolite	110.0	Aluminum fluoride	4.40
Fluorspar	5.5	Sodium fluoride	6.60
Ammonium carbonate	8.0	Calcium fluoride	.55
Magnesium carbonate	5.5	Magnesium oxide	.26
Tin oxide	188.6	Tin oxide	18.86
	1294.1		99.97

Empirical chemical formula:

$$\left.\begin{array}{r}0.188\ K_2O\\ .773\ Na_2O\\ .021\ CaO\\ .018\ MgO\end{array}\right\}\ 0.332\ Al_2O_3\ \left\{\begin{array}{l}1.255\ SiO_2\\ .890\ B_2O_3\\ .519\ F_2\\ .383\ SnO_2\end{array}\right.$$

$$\overline{1.000}$$

Enamel II

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
Potash feldspar	410	Potash feldspar:	
Sodium nitrate	30	Silica	26.5
Borax	240	Alumina	7.5
Boric acid	220	Potassium oxide	7.0
Zinc oxide	125	Sodium oxide	5.0
Cryolite	120	Boric oxide	21.2
Tin oxide	83	Zinc oxide	12.5
		Aluminum fluoride	4.8
	1228	Sodium fluoride	7.2
		Tin oxide	8.3
			100.0

Empirical chemical formula:

$$\left.\begin{array}{r}0.187\ K_2O\\ .423\ Na_2O\\ .390\ ZnO\end{array}\right\}\ 0.260\ Al_2O_3\ \left\{\begin{array}{l}1.118\ SiO_2\\ .766\ B_2O_3\\ .436\ F_2\\ .140\ SnO_2\end{array}\right.$$

$$\overline{1.000}$$

Enamel III

Raw batch, for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
Potash feldspar	380	Silica	26.08
Quartz	15	Alumina	7.00
Potassium nitrate	60	Potassium oxide	11.22
Potassium carbonate	30	Sodium oxide	5.38
Soda ash	30	Boric oxide	8.23
Borax	225	Zinc oxide	10.80
Zinc oxide	108	Lead oxide	8.00
Red lead	82	Aluminum fluoride	.40
Cryolite	10	Sodium fluoride	2.36
Sodium silico fluoride	40	Silicon fluoride	2.24
Fluorspar	85	Calcium fluoride	8.50
Ammonium carbonate	1	Manganese oxide	.10
Manganese dioxide	1	Arsenic oxide	.60
Arsenic oxide	6	Tin oxide	9.20
Tin oxide	92		
	1165		100.11

Empirical chemical formula:

$$\left.\begin{array}{r l} 0.230 & K_2O \\ .222 & Na_2O \\ .212 & CaO \\ .258 & ZnO \\ .076 & PbO \\ .002 & MnO \\ \hline 1.000 & \end{array}\right\}\ 0.138\ Al_2O_3 \left\{\begin{array}{r l} 0.882 & SiO_2 \\ .229 & B_2O_3 \\ .356 & F_2 \\ .118 & SnO_2 \end{array}\right.$$

Enamel IV

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
		Potash feldspar:	
Potash feldspar	400	Silica	25.88
Soda ash	90	Alumina	7.36
Sodium nitrate	30	Potassium oxide	6.76
Borax	225	Sodium oxide	9.95
Zinc oxide	108	Boric oxide	8.23
Red lead	94	Zinc oxide	10.80
Cryolite	40	Lead oxide	9.20
Fluorspar	85	Aluminum fluoride	1.60
Tin oxide	94	Sodium fluoride	2.40
		Calcium fluoride	8.50
	1166	Tin oxide	9.40
			100.08

Empirical chemical formula:

$$\left.\begin{array}{r}0.130\ K_2O\\ .345\ Na_2O\\ .200\ CaO\\ .244\ ZnO\\ .081\ PbO\\ \hline 1.000\end{array}\right\}\ 0.150\ Al_2O_3\ \left\{\begin{array}{l}0.790\ SiO_2\\ .216\ B_2O_3\\ 266\ F_2\\ .114\ SnO_2\end{array}\right.$$

Enamel V

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
		Potash feldspar:	
		Silica	24.58
Potash feldspar	380	Alumina	7.00
Soda ash	50	Potassium oxide	6.42
Sodium nitrate	25	Sodium oxide	6.50
Borax	165	Boric oxide	6.04
Barium carbonate	75	Barium oxide	5.83
Zinc oxide	60	Zinc oxide	6.00
Red lead	175	Lead oxide	17.10
Fluorspar	120	Calcium fluoride	12.00
Tin oxide	85	Tin oxide	8.50
	1135		99.97

Empirical chemical formula:

$$\left.\begin{array}{r}0.130\ K_2O\\ .201\ Na_2O\\ .073\ BaO\\ .295\ CaO\\ .142\ ZnO\\ .159\ PbO\\ \hline 1.000\end{array}\right\}\ 0.132\ Al_2O_3\ \left\{\begin{array}{l}0.785\ SiO_2\\ .155\ B_2O_3\\ .295\ F_2\\ .107\ SnO_2\end{array}\right.$$

Enamel VI

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
		Potash feldspar:	
Potash feldspar	380	Silica	24.58
Soda ash	30	Alumina	7.00
Sodium nitrate	30	Potassium oxide	6.42
Borax	215	Sodium oxide	6.31
Barium carbonate	50	Boric oxide	7.87
Zinc oxide	105	Barium oxide	3.88
Red lead	168	Zinc oxide	10.50
Fluorspar	50	Lead oxide	16.50
Cryolite	30	Calcium fluoride	5.00
Tin oxide	90	Sodium fluoride	1.80
		Aluminum fluoride	1.20
	1148	Tin oxide	9.00
			100.06

Empirical chemical formula:

$$\left.\begin{array}{l} 0.140\ K_2O \\ .294\ Na_2O \\ .052\ BaO \\ .132\ CaO \\ .269\ ZnO \\ .153\ PbO \\ \hline 1.000 \end{array}\right\} 0.157\ Al_2O_3 \left\{\begin{array}{l} 0.847\ SiO_2 \\ .231\ B_2O_3 \\ .218\ F_2 \\ .124\ SnO_2 \end{array}\right.$$

Enamel VII

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Material	Pounds	Composition	Per cent
		Potash feldspar:	
Potash feldspar	380	Silica	24.58
Soda ash	30	Alumina	7.00
Sodium nitrate	30	Potassium oxide	6.42
Borax	215	Sodium oxide	6.31
Barium carbonate	50	Boric oxide	7.87
Zinc oxide	50	Barium oxide	3.88
Red lead	255	Zinc oxide	5.00
Fluorspar	50	Lead oxide	25.00
Tin oxide	90	Calcium fluoride	5.00
		Tin oxide	9.00
	1150		100.06

Empirical chemical formula:

$$\left.\begin{array}{l} 0.153\ K_2O \\ .230\ Na_2O \\ .059\ BaO \\ .145\ CaO \\ .140\ ZnO \\ .273\ PbO \\ \hline 1.000 \end{array}\right\} 0.156\ Al_2O_3 \left\{\begin{array}{l} 0.920\ SiO_2 \\ .253\ B_2O_3 \\ .144\ F_2 \\ .135\ SnO_2 \end{array}\right.$$

VIII. ANTIMONY ENAMEL COMPOSITIONS

That compounds of antimony could be used with some success as opacifying agents in enamels has been known for a very long time. However, only during the last 10 or 15 years have they been employed on a large scale in commercial operations. The many difficulties involved in the use of antimony compounds are the obvious reasons for their failure to come into general favor earlier. The constantly rising price of tin oxide and the growth in the technical ability of enamel makers are the causes for their more general employment during the last few years.

1. CONTROL OF COLOR

One of the great difficulties in the use of antimony compounds in enamels is the wide variation in colors, or rather tints, encountered. These vary from light tan or yellow through cream, a fair white, light green, and light blue to a decided robin-egg blue. The hue and tint obtained depends on the composition of the enamel and the heat treatment given it during melting.

(*a*) Effect of Composition.—It is well known that antimony enamels containing large amounts of lead give a yellow color. For instance, a beautiful lemon-colored enamel was obtained from the following composition, which is a tin-bearing enamel formula with oxide of antimony substituted for tin oxide:[78]

Potash feldspar	410
Borax	240
Cryolite	120
Sodium nitrate	27
Red lead	255
Antimony oxide	80
	1132=1000 melted

Entire elimination of lead oxide from antimony enamels is not desirable, however, for leadless enamels are not satisfactory in working properties. They craze and chip with seemingly no provocation, do not stand patching well, and they are not as opaque as enamels with the same amount of opacifier which contain lead. This latter defect is probably due to the fact that lead-bearing enamels are heavier than leadless ones, and therefore the opacifier is less diffused in the lead-bearing enamels. For these reasons many enamelers prefer to use as much lead in their antimony enamels as is consistent with a satisfactory color; and by experiment it has been found that enamels of fair color can be made containing considerable amounts of lead oxide. In amounts up to 10 per cent, lead oxide tends to impart a very faint yellow cast to the enamels. The tint is persistent, not altering with heat treatment. This color may be so combined with some other color, generally blue, that both are practically neutralized, or the proportions of the two colorants may be such that a light green color is produced.

If commercial antimony oxide and boric acid are melted together, a translucent brown glass is produced. The source of the color is unknown; it may be due to sulphur impurities since commercial oxide of antimony may contain one per cent of sulphur as antimony sulphide. If this glass is used as a component of

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[78] Staley, H. F., and Fisher, G. P., Trans. A. C. S., 15, p. 626.

an enamel, an opaque, white enamel is produced. All antimony enamels are of a decided tan during the first stages of the smelting process, and the depth of this color increases as the boric oxide increases. This tan color of the enamels is thought to be due to the same causes that produce the brown color in antimony oxide—boric acid mixtures. As the smelting continues this color gradually fades. However, if the amount of boric oxide is large, and no neutralizing color is present, the enamel may not become a good white unless the smelting is continued for a long time at high temperatures. In such cases the opacity of the enamel is reduced, because of the gradual solution of the opacifying agent. For this reason it is desirable to introduce some ingredient that will form a color to neutralize the last traces of tan or yellow. Cobalt oxide and manganese dioxide are sometimes used for this purpose, but generally the neutralization is accomplished, consciously or unwittingly, by the introduction of some form of calcium as explained below.

During the winter of 1912–13, the writer, with the aid of Samuel Rusoff, made a rather extended study of the effect of variation in composition of antimony enamels on the tints produced. Very much to our surprise, we definitely established the fact that calcium, introduced either as the carbonate of fluoride, had a decided effect on the hue of the enamel, always tending to produce blue tints. These tints seemed to be peculiar to antimony enamels, since they do not occur when tin oxide is used as the opacifier. By systematic elimination of the various ingredients commonly used in enamels we were able to determine that the coloring matter was due to some combination of antimony oxide, boric oxide, calcium and fluorine.[79] The intensity of the color increases with concentration of calcium compounds and with duration of heat treatment.

In practical enamel making, the only one of these four materials—i. e., antimony oxide, boric oxide, calcium and fluorine—that can be eliminated is calcium. The writer has found that under a given set of conditions, the tendency for oxide of antimony enamels to turn blue was lessened when the calcium in the mix was reduced. This means the partial replacement of whiting or fluorspar by other fluxes. It is generally necessary to use cryolite to take the place of part of the fluorspar.

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[79] Staley, Homer F., Antimony Compounds as Opacifiers in Enamels, Trans. A. C. S., 17, pp. 173–189.

When enamelers of cast iron first began experimenting with oxide of antimony enamels they found that the use of oxide of antimony and oxide of tin together in a raw batch produced blue tints. Since nearly all of the tin-bearing formulas used in this country for cast iron contain calcium in some form, it is not certain whether this is a new color phenomenon or is due simply to an intensification of the blue color produced by calcium. On the other hand, it has been found possible to blend antimony and tin enamels after melting, without producing tints other than those expected from the enamels used in the mixture. The mixing must be done thoroughly or an unpleasant mottled effect is produced.

(*b*) Effect of Heat Treatment.—As stated above, antimony enamels are all tan colored in the first stages of the burn, and this color decreases in intensity as the smelting progresses. Enamels containing lead oxide have a yellow color component which is not affected by heat treatment. Calcium produces a blue color, which increases in intensity with duration of the smelting process. The result of this combination of color effects is as follows: If a sample is drawn in the early stages of the smelting and cooled, it will be found to be a light tan if lead oxide is absent, and to be a tan enlivened by a mixture of yellow if lead oxide was used in the batch. As the heating progresses, the tan color will gradually fade, but the yellow, due to lead oxide, persists. If calcium is present in the composition, the blue color it produces is either not developed during the early stages of the burn, or is masked by the decided tan color. After long continued smelting, in the absence of both lead and calcium, the enamel gives a good white, but one of inferior opacity. If lead is present and calcium is absent, the white obtained will have a yellow tint, the intensity of which will depend on the amount of lead present. If calcium is present, the blue color developed thereby increases in intensity as the smelting proceeds and tends to neutralize the tan and yellow colors, which produces whites or tints of green. Finally, blue becomes the predominant color, and gives enamels that range in hue from a faint greenish blue to a pronounced robin-egg blue.

The whites secured by neutralization of the tan and yellow tints by blue are more opaque than those secured by eliminating the tan color by long-continued smelting, since the neutralization takes place at a comparatively early stage in the smelting; therefore there is much less opportunity for solution of the opacifying agent in the glass. Since all antimony enamels are tan at the beginning of smelting, the problem of producing a good opaque white enamel is so to control the proportions of lead oxide and calcium (or cobalt) oxide that the tan and yellow colors are neutralized by the blue, thereby producing a good white when the enamel is first thoroughly smelted. When it is remembered that any change in the composition of the enamel has a decided effect not only on the color, but on gloss, working properties, fit of the enamel to the iron, and durability of the finished ware, it is obvious that the problem is not a simple one.

2. DARK SPECKS

The second difficulty encountered in the use of antimony enamels is that dark specks are likely to appear, either near or at the surface of the enamel. These vary from the size of a pinhead down to microscopic size. Of course, even a few of the larger-sized specks disqualify a large piece of ware for sale as a high-grade fixture. The occurrence of the specks is quite erratic, varying widely in different batches of enamel made from the same formula and from the same raw materials.

(*a*) Cause.—The source of these specks has been attributed to many causes, mainly to impurities in one or other of the raw materials. Many attemps have been made by various enamelers to get rid of the specks by changing the composition of the enamel, or by securing raw materials from a new source. Owing to the spasmodic occurrence of the specks, some of these attempts seemed at first to be successful; but soon the specks would return, as numerous as ever. In fact, it is really surprising how much dirt can be incorporated into the raw batch of an enamel without noticeably affecting the appearance of the finished ware. Sometimes scrap enamel that contains enough sand, iron scale, etc., to render it decidedly gray in color will make, when remelted, cleaner ware than enamels made at the same time entirely from selected raw materials. Except in cases where external contamination by dirt was evident, the writer has never seen any specks of the kind under discussion in enamel frits before grinding. Equally significant is the fact the specks do not occur in carefully conducted laboratory experiments. In making several hundred laboratory melts with commercial materials, these specks were never found in trial pieces.

In examining under the microscope the specks in the antimony enamels from quite a number of different firms, it has been found that fully 90 per cent of the specks could be divided into two groups. The first class consisted of black globular masses which were hollow, and often contained small particles of carbon. Evidently these were caused by the carbonization of small particles of combustible material while the enamel was being melted on the ware. The specks in the second class were solid particles, either black or brownish black surrounded by a reddish-brown ring. These particles were decidedly magnetic, and when subjected to chemical test always showed the presence of iron. There is, therefore, no question but that they were due to contamination of the enamel with particles of metallic iron or the magnetic oxide of iron.

The cause, then, of the great majority of the dark specks in antimony enamels seems to lie in contamination of the enamel with external dirt after smelting. The particles causing the carbon spots may be small particles of wood from quenching tanks, mill covers, sieves, storage boxes, etc. On the other hand, they may be small specks of belt dressing or grease from the machinery used in the mill rooms and enameling rooms. The particles of iron and metallic oxide may come from the driers, mills, mechanical sifters, etc., or from the outside of the casting being enameled. In examination of the enamel powder from several plants, several or all of these foreign substances were invariably found.

The objection that is always raised by manufacturers to the above analysis of the cause of the dark specks is that the specks do not appear in tin enamels made in the same manner and with the same equipment. The answer is that it can be easily demonstrated that the tin enamels contain exactly the same kind of particles and just as many of them. The difference is that the specks do not show up as prominently in the tin enamels. In the first place, tin enamels are as a rule more opaque than antimony enamels, and hence any specks not actually at the surface of the ware are better hidden than in antimony enamels. In the second place, and much more important, is the fact that owing to differences in composition, the antimony enamels have a much stronger slagging action on the foreign particles, and the discoloration caused by the foreign particles spreads much further. The discoloration caused by a speck of foreign material in a tin enamel is practically the size of the particle. The discoloration caused by a similar particle in an antimony enamel may be six or eight times as large as the particle.

(*b*) REMEDY.—The obvious way to decrease the dark specks in antimony enamels is to use great care to keep them as free as possible from contamination. This is more easily said than done, however. In the first place, it is hard for even the man who makes the enamel to realize that the one essential requirement is absolute cleanliness. He is very likely to spend his energies in futile attempts to get rid of the dark specks by altering his formula or by securing some of his raw materials from new sources. Even more difficult is it to gain the confidence of the various workmen who handle the enamel, and without their hearty cooperation such a program will be more or less of a failure. In most cases, material decrease in the amount of contamination means more labor and changes in equipment, and consequently expenditure of considerable money. The men who hold the purse strings are liable to maintain that the equipment and labor that always gave fairly clean tin enamels should be equally satisfactory for antimony enamels.

Moreover, a new conception of cleanliness must be instilled into the minds of all connected with the making and handling of the enamels. In most plants, the making and handling of the tin enamels are conducted in a manner that is fairly clean, as cleanliness goes in factories. To make a marked improvement in these long-established shop methods means that every man concerned must make a distinct and sustained effort.

Antimony enamels have been in use longer in Germany than in this country. The cleanest antimony enamel the writer has seen was made by a German manufacturer who said that, after several years of strenuous effort, he had been able to inspire his shop organization with a general enthusiasm for cleanliness, and the result had been the production of antimony enamels practically free from black specks.

3. SODIUM METANTIMONATE ENAMEL COMPOSITIONS

Sodium metantimonate has been employed extensively in this country during late years as an opacifying agent for enamels for cast iron. The compositions used may be divided into three types, namely, the leadless, the low lead, and the medium lead.

(*a*) THE LEADLESS TYPE.—In Germany leadless enamels in which sodium metantimonate is the opacifier have been derived from the leadless tin enamels, similar to tin enamel I, very high in boric oxide and containing only one or two other fluxes. In this country, however, leadless enamels containing sodium metantimonate have been derived from the complicated formulas in use for tin enamels by substitution of other fluxes for lead oxide. This has resulted in complicated formulas rather high in boric oxide and generally high in zinc oxide. Boric oxide is increased as lead oxide is decreased because, when used in large amounts, it not only does not itself crystallize but it makes the enamel more viscous and thus prevents the crystallization of other compounds that may have been used partially to replace lead oxide.

The zinc oxide is raised as the lead oxide is decreased in order to maintain the strength and elasticity of the enamel. By using a complicated formula the amount of each of the other fluxing oxides is kept low, so that tendency for their compounds to crystallize and cause dull luster is lessened. Enamel VIII is a typical composition.

(*b*) THE LOW LEAD TYPE.—The low lead type of composition contains 3 to 5 per cent of lead oxide; the boric oxide and zinc oxides are usually a little lower than in the leadless type. The amount of each of the other fluxing oxides is kept low. Enamel IX is a typical example. In this the percentage of sodium oxide is approaching the danger limit as far as luster of the enamel is concerned. Its use would be safer if 50 pounds of borax were substituted for the 45 pounds of soda ash. This would give boric oxide and sodium oxide contents like those in enamel VIII.

(*c*) THE MEDIUM LEAD TYPE.—In the medium lead type of composition the lead oxide runs between 5 and 12 per cent. The boric oxide is slightly lower than in the previous type, but still higher than in high-lead, tin enamels, and the percentage of each of the other fluxing oxides is kept low. Enamels X and XI are typical compositions. It will be noted that in enamel XI no calcium carbonate, but a larger amount of fluorspar than in the other compositions is used. Thus the calcium content is maintained at the proper point to give good color and opacity.

4. OXIDE OF ANTIMONY ENAMEL COMPOSITIONS

The essential difference between sodium metantimonate enamel compositions and those in which oxide of antimony is used as the chief opacifier is that the latter contain much larger amounts of sodium nitrate. Corresponding reduction is made in other sodium compounds so that the total sodium oxide content remains about the same. This larger nitrate content may mean that the oxide of antimony is converted into sodium metantimonate (Na_2O, Sb_2O_5) or simply into antimony pentoxide (Sb_2O_5). Incidentally, the oxide of antimony enamels, which the writer has found in actual use in factories, contain considerable cryolite; therefore the percentage amount of oxide of antimony can be lower than in the case of sodium antimonate compositions containing little or no cryolite.

These compositions can be divided into the same three types as sodium antimonate enamels, the characteristics of each type being practically the same as before. Enamel XII is typical of the leadless type, enamel XIII of the low lead types, and enamels XIV and XV of the medium lead type.[80]

Enamel VIII

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	390	Potash feldspar:	
Sodium nitrate	35	Silica	25.23
Borax	350	Alumina	7.18
Barium carbonate	80	Potassium oxide	6.59
Zinc oxide	140	Sodium oxide	8.94
Calcium carbonate	30	Boric oxide	12.81
Fluorspar	73	Barium oxide	6.21
Sodium antimonate	120	Zinc oxide	14.00
		Calcium oxide	1.68
	1218	Calcium fluoride	7.30
		Antimony oxide	10.00
			99.94

Empirical chemical formula:

$$\left.\begin{array}{r} 0.127\ K_2O \\ .263\ Na_2O \\ .072\ BaO \\ .225\ CaO \\ .313\ ZnO \\ \hline 1.000 \end{array}\right\}\ 0.129\ Al_2O_3 \left\{\begin{array}{l} 0.761\ SiO_2 \\ .332\ B_2O_3 \\ .170\ F_2 \\ .063\ Sb_2O_5 \end{array}\right.$$

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[80] Compare Brown, R. E., Trans. A. C. S., 14, pp. 740–755. Staley, H. F., Trans. A. C. S., 17, pp. 173–189.

Enamel IX

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	390	Potash feldspar:	
Soda ash	45	Silica	25.23
Sodium nitrate	35	Alumina	7.18
Borax	300	Potassium oxide	6.59
Barium carbonate	80	Sodium oxide	10.75
Zinc oxide	110	Boric oxide	11.00
Red lead	31	Barium oxide	6.21
Calcium carbonate	30	Zinc oxide	11.00
Fluorspar	73	Lead oxide	3.00
Sodium antimonate	120	Calcium oxide	1.68
		Calcium fluoride	7.30
	1214	Antimony oxide	10.00
			99.94

Empirical chemical formula:

$$\left.\begin{array}{l} 0.125\ K_2O \\ .311\ Na_2O \\ .072\ BaO \\ .223\ CaO \\ .244\ ZnO \\ .025\ PbO \\ \hline 1.000 \end{array}\right\}\ 0.127\ Al_2O_3 \left\{\begin{array}{l} 0.754\ SiO_2 \\ .282\ B_2O_3 \\ .169\ F_2 \\ .063\ Sb_2O_5 \end{array}\right.$$

Enamel X

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	390	Potash feldspar:	
Soda ash	55	Silica	25.23
Sodium nitrate	35	Alumina	7.18
Borax	250	Potassium oxide	6.59
Barium carbonate	70	Sodium oxide	10.52
Zinc oxide	85	Boric oxide	9.15
Red lead	85	Barium oxide	5.44
Calcium carbonate	30	Zinc oxide	8.50
Calcium fluoride	73	Lead oxide	8.40
Sodium antimonate	120	Calcium oxide	1.68
		Calcium fluoride	7.30
	1193	Antimony oxide	10.00
			99.99

Empirical chemical formula:

$$\left.\begin{array}{r}0.128\ K_2O\\ .310\ Na_2O\\ .066\ BaO\\ .228\ CaO\\ .193\ ZnO\\ .075\ PbO\end{array}\right\}\ 0.130\ Al_2O_3\ \left\{\begin{array}{r}0.777\ SiO_2\\ .240\ B_2O_3\\ .173\ F_2\\ .064\ Sb_2O_5\end{array}\right.$$

$$\overline{1.000}$$

Enamel XI

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	375	Potash feldspar:	
Soda ash	25	Silica	24.26
Sodium nitrate	25	Alumina	6.90
Borax	275	Potassium oxide	6.34
Barium carbonate	100	Sodium oxide	8.57
Zinc oxide	70	Boric oxide	10.06
Red lead	102	Barium oxide	7.77
Fluorspar	100	Zinc oxide	7.00
Sodium antimonate	110	Lead oxide	10.00
	1182	Calcium fluoride	10.00
		Antimony oxide	9.24
			100.14

Empirical chemical formula:

$$\left.\begin{array}{r}0.129\ K_2O\\ .267\ Na_2O\\ .100\ BaO\\ .246\ CaO\\ .166\ ZnO\\ .092\ PbO\end{array}\right\}\ 0.131\ Al_2O_3\ \left\{\begin{array}{r}0.777\ SiO_2\\ .277\ B_2O_3\\ .246\ F_2\\ .062\ Sb_2O_5\end{array}\right.$$

$$\overline{1.000}$$

Enamel XII

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	410	Potash feldspar:	
Sodium nitrate	70	Silica	26.53
Borax	350	Alumina	7.54
Barium carbonate	80	Potassium oxide	6.93
Zinc oxide	140	Sodium oxide	8.22
Calcium carbonate	30	Boric oxide	12.81
Fluorspar	60	Barium oxide	6.20
Cryolite	40	Zinc oxide	14.00
Antimony oxide	60	Calcium oxide	1.68
		Calcium fluoride	6.00
	1240	Aluminum fluoride	1.60
		Sodium fluoride	2.40
		Antimony oxide	6.00
			99.91

Empirical chemical formula:

$$\left.\begin{array}{r} 0.132\ K_2O \\ .288\ Na_2O \\ .073\ BaO \\ .194\ CaO \\ .313\ ZnO \\ \hline 1.000 \end{array}\right\} 0.150Al_2O_3 \left\{\begin{array}{l} 0.801\ SiO_2 \\ .332\ B_2O_3 \\ .238\ F_2 \\ .038\ Sb_2O_5 \end{array}\right.$$

Enamel XIII

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	410	Potash feldspar:	
Soda ash	25	Silica	26.53
Sodium nitrate	70	Alumina	7.54
Borax	300	Potassium oxide	6.93
Barium carbonate	75	Sodium oxide	8.86
Zinc oxide	100	Boric oxide	11.00
Red lead	46	Barium oxide	5.83
Calcium carbonate	30	Zinc oxide	10.00
Fluorspar	73	Lead oxide	4.50
Cryolite	40	Calcium oxide	1.68
Antimony oxide	60	Calcium fluoride	7.30
	1229	Aluminum fluoride	1.60
		Sodium fluoride	2.40
		Antimony oxide	6.00
			100.17

Empirical chemical formula:

$$\left.\begin{array}{l} 0.133\ K_2O \\ .310\ Na_2O \\ .069\ BaO \\ .227\ CaO \\ .224\ ZnO \\ .037\ PbO \\ \hline 1.000 \end{array}\right\} 0.151\ Al_2O_3 \left\{\begin{array}{l} 0.803\ SiO_2 \\ .287\ B_2O_3 \\ .269\ F_2 \\ .038\ Sb_2O_5 \end{array}\right.$$

Enamel XIV

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	**Pounds**	**Composition**	**Per cent**
Potash feldspar	410	Potash feldspar:	
Soda ash	30	Silica	26.53
Sodium nitrate	90	Alumina	7.54
Borax	240	Potassium oxide	6.93
Barium carbonate	80	Sodium oxide	8.91
Zinc oxide	100	Boric oxide	8.78
Red lead	82	Barium oxide	6.21
Calcium carbonate	30	Zinc oxide	10.00
Fluorspar	45	Lead oxide	8.00
Cryolite	45	Calcium oxide	1.68
Antimony oxide	64	Calcium fluoride	4.50
		Aluminum fluoride	1.80
	1216	Sodium fluoride	2.70
		Antimony oxide	6.40
			99.98

Empirical chemical formula:

$$\left.\begin{array}{l} 0.135\ K_2O \\ .328\ Na_2O \\ .074\ BaO \\ .163\ CaO \\ .228\ ZnO \\ .072\ PbO \\ \hline 1.000 \end{array}\right\} 0.157\ Al_2O_3 \left\{\begin{array}{l} 0.818\ SiO_2 \\ .231\ B_2O_3 \\ .188\ F_2 \\ .041\ Sb_2O_5 \end{array}\right.$$

Enamel XV

Raw batch for 1000 pounds, melted		Calculated percentage composition, melted	
Materials	Pounds	Composition	Per cent
Potash feldspar	400	Potash feldspar:	
Soda ash	20	Silica	25.88
Sodium nitrate	75	Alumina	7.36
Borax	230	Potassium oxide	6.76
Barium carbonate	80	Sodium oxide	7.62
Zinc oxide	92	Boric oxide	8.42
Red lead	117	Barium oxide	6.21
Calcium carbonate	25	Zinc oxide	9.20
Fluorspar	55	Lead oxide	11.50
Cryolite	45	Calcium oxide	1.40
Antimony oxide	58	Calcium fluoride	5.50
	1197	Aluminum fluoride	1.80
		Sodium fluoride	2.70
		Antimony oxide	5.80
			100.15

Empirical chemical formula:

$$\left.\begin{array}{l} 0.133\ K_2O \\ .293\ Na_2O \\ .075\ BaO \\ .180\ CaO \\ .214\ ZnO \\ .105\ PbO \\ \hline 1.000 \end{array}\right| \quad 0.158\ Al_2O_3 \quad \left|\begin{array}{l} 0.808\ SiO_2 \\ .225\ B_2O_3 \\ .216\ F_2 \\ .038\ Sb_2O_5 \end{array}\right.$$

IX. LUSTER OF ENAMELS

1. CRYSTALLIZATION

When melted, glasses are true solutions, corresponding in all respects to solutions of salts and water at ordinary temperatures. When these molten solutions are cooled, we would expect them to turn gradually to a mass of crystals, just as an aqueous solution of salts does if the temperature to which it is cooled is sufficiently low. The only difference is that the glassy solutions should crystallize at higher temperatures. The temperatures at which glasses would become completely crystallized if sufficient time were allowed vary from 550° C (1000° F) to 1100° C (2000° F), yet in practice they are cooled and exist permanently at atmospheric temperatures without any crystallization taking place. In this condition they are still true solutions, differing from aqueous solutions only in being so viscous that they are rigid. All bright-finish enamels, glasses, and glazes may be regarded then as undercooled liquids. The tumblers from which we drink are in a sense just as truly liquids as the water they contain.

Of course if the constituents of a glass crystallize, the surface becomes mat instead of bright. Since bright-finish enamels are the type desired for enameling cast iron, the enamel maker must so compound his enamels that they will not crystallize when subjected to the normal working and cooling conditions of enameling shops. Fortunately the sudden cooling to which enameled-iron ware is subjected is not favorable to crystallization. On the other hand, the working temperature is so low that the glass is easily saturated by the compounds formed in the molten magma by some of the oxides used. Just as a hot, saturated, aqueous, salt solution tends to become supersaturated and to deposit crystals of the salt on cooling, just so does a hot, saturated, glass or enamel solution tend to deposit crystals when it is cooled.

(a) EFFECT OF VISCOSITY.—The most simple method of overcoming the tendency to crystallize is to make the enamel viscous at the temperatures at which crystallization takes place. In even a moderately viscous liquid it takes considerable time for crystallization to start, and the rate of growth is slow. Since enameled ironware is cooled so rapidly, sufficient time is not given in the cooling process for appreciable formation of crystals in a viscous enamel unless the tendency for deposition of crystals is very great.

Silica alone melts to a very viscous glass, and, in general, addition of silica to any melt increases viscosity. Silicates high in silica also melt to viscous glasses. If silica (flint, sand) or feldspar (a high-silica compound) is added to an enamel, the glass is rendered more viscous at all temperatures, and the tendency to become dull from crystallization is lessened. Since the working temperature of the enamel is raised by this procedure, this method has but slight application in controlling the viscosity for enamels that must mature at temperatures rather rigidly fixed by shop practice and working conditions.

Boric oxide alone forms a very viscous glass at low temperatures; but, as shown by the writer,[81] the viscosity decreases rapidly as the temperature rises. The glass was found to be three times as viscous at 750° C (1382° F) as it was at 1000° C (1832° F). The first temperature approximates that at which crystalliza-

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[81] The Viscosity of Molten Glasses, Original Communications, Eighth International Congress of Applied Chemistry, 5, p. 127.

tion takes place in enamels, and the second is near the maturing temperature of most enamels for cast iron. The borate glasses of any given base resemble silicate glasses in behavior and become more viscous as the percentage of boric oxide increases. The following results were obtained for barium-oxide and boric-oxide glasses:

Per cent B_2O_3	Per cent BaO	Relative viscosity at the same temperature	Per cent B_2O_3	Per cent BaO	Relative viscosity at the same temperature
20	80	3.05	35	65	3.52
25	75	3.18	40	60	3.70
30	70	3.35	45	55	4.02

The viscosity of borate glasses decreases with rise of temperature in the same general way as that of fused boric oxide, but not so rapidly. The effect of increasing the boric oxide in cast-iron enamels is to increase the viscosity at temperatures at which crystallization is liable to take place, and thus to decrease the tendency to matness. Its effect differs from that of silica in that the maturing temperature is not raised, and in the case of many enamels, actually lowered.

Kaolin (china clay) has a very decided tendency to raise the viscosity of enamels but is not much used in America, although found in some German formulas. Any material which does not fuse or go into solution in the enamel, such as most metallic oxides added as opacifiers, makes the enamel more viscous. Decrease of any of the fluxing oxides, except boric oxide, makes the enamel more viscous. Therefore viscosity may be increased by decreasing any of these. Decrease of fluorides has the same effect.

(*b*) EFFECT OF CONCENTRATIONS.—With the exception of boric oxide, all the materials in enamel compositions known as fluxes—that is, the oxides of lead, zinc, sodium, potassium, calcium, barium, magnesium, and the various fluorides—tend to form compounds which are easily crystallizable. Lead oxide differs from the others in that its compounds, when melted alone, do not crystallize until very low temperatures are reached. Lead silicates do not crystallize until temperatures of 750° C (1382° F) or lower are reached,[82] and lead borates have even lower crystallization temperatures. Since normal enamel compositions are too viscous at low temperatures to allow crystallization to take place, lead compounds do not crystallize from enamel glasses. Therefore lead oxide shares with boric oxide the distinction of being a flux

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[82] Cooper, Shaw, and Loomis, Am. Chem. Jour., p. 461; 1909.

yet not producing mat finish when present in the enamel composition in large amounts.

Of course the tendency for any compound to separate in the crystalline form from a cooling glass is decreased by decreasing the amount of the compound in the glass. Therefore the amount of each of the fluxes, except boric oxide and lead oxide, should be kept low. This means that as the total amount of these crystal-forming fluxes increases a greater variety must be used.

The effect of concentration of various fluxing oxides is shown by the following series of enamels. As the basis of the series, the following batch was taken:

Materials	Parts raw	Melted percentages, calculated
Potash feldspar	41.0	26.5 silica 7.5 alumina 7.0 potassium oxide
Borax	24.6	9.0 boric oxide
Sodium nitrate	2.7	4.0 1.0 sodium oxide
Cryolite	12.0	4.8 aluminum fluoride 7.2 sodium fluoride
Tin oxide	8.0	8.0 tin oxide
		75.0 constant 25.0 variable
		100.0

The composition of the 25 per cent variable part and the luster of the resultant enamels is indicated in Table 5.

Table 5.—Effect of Composition of Enamels on Luster

Number	Na_2O from soda ash	BaO from barium carbonate	CaO from calcium carbonate	ZnO from zinc oxide	PbO from red lead	B_2O_3 from boric acid	Luster
1	25						Mat
2		25					Semimat
3			25				Not melted
4				25			Mat
5					25		Bright
6						25	Do.
7	12.5	12.5					Semimat
8	12.5			12.5			Mat
9	12.5					12.5	Semimat
10		12.5		12.5			Do.
11		12.5				12.5	Bright
12				12.5		12.5	Do.
13	8.33	8.33		8.33			Oily
14		8.33		8.33		8.33	Bright
15	5.00	8.33		8.33	3.33		Do.
16	5.00	8.33		8.33		3.33	Do.

(*c*) ENAMELING TECHNIQUE.—Any necessity for prolonging the enameling operation that involves partial cooling and reheating of the enamel after the coat is matured furnishes favorable opportunity for the development of crystallization and dull finish. Therefore, considerable care must be taken to avoid all necessity for patching by having castings in the best possible shape for enameling before the operation commences, and by employing the most skillful workmen to apply the enamel.

2. SULPHUR COMPOUNDS

It is well known that sulphur compounds in an enamel tend to separate on the surface in featherlike crystals, causing a diminution of luster. While this may be due to sulphur in the enamel materials—and the presence of sulphur in these should be avoided—it is not probable that enamel compositions made from the grade of chemicals commonly employed contain enough sulphur to cause the trouble. Seger has shown that a glass can contain 2 to 4 per cent of sulphur trioxide and still be perfectly clear.[83] It is interesting to note that when Seger made a melt from sodium carbonate, barium sulphate and silica, the glass gall which separated when an excess of sulphur was present consisted of sodium sulphate and not barium sulphate as might be expected from the strong affinity of barium for sulphur at low temperatures. In fact glass gall from common glasses ordinarily consists largely of sodium sulphate. Mellor records experiments in which ordinary pottery glazes were found to dissolve comparatively large amounts of various sulphates, such as those of barium, calcium, lead, sodium, and potassium, without showing any ill effects.[84] An experienced enamel mixer states that he once had a separation of sodium sulphate in the form of glass gall in considerable amount from an enamel batch in the melting tank. In grinding this batch he mixed the glass gall with the good glass and got satisfactory ware from the mixture. Mellor believes that the feathering of pottery glazes by sulphur is due to the saturation of a surface film of the glaze by sulphur in the kiln atmosphere. This is probably the case in enamels, also, for it occurs most frequently when a sulphur-bearing fuel is used for heating the enameling furnaces. A number of enameling plants experienced difficulty from sulphur feathering when they changed from the use of natural gas to bituminous coal. The trouble is much less common when well-

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[83] Collected Writings of Herman A. Seger, American Ceramic Society, p. 646.

[84] Mellor, J. W., Clay and Pottery Industries, I, p. 63.

ventilated muffles are used than when the air currents in these are sluggish. Cracks in the floor of the muffle which allow products of combustion to leak in are apt to produce sulphured ware. Open-arch or semimuffle kilns are prone to produce ware of poor gloss unless a strong draft is used so as to keep the flame hugging the roof of the furnace.

Sometimes quicklime is placed around the inside of the muffle against the walls, in the hope that the quicklime will absorb the sulphur. This is generally not very effective. In the first place, it is only rarely that the sulphur-bearing fumes pass through or over the quicklime unless it is placed directly over a crack or hole. The lime does not attract the sulphur from the kiln atmosphere as a whole. In the second place, if sulphur-bearing fumes do come in contact with the lime, this soon becomes saturated and should be replaced much more often than is the common practice. One per cent of volatile sulphur in a ton of coal will give 40 pounds of sulphur dioxide or 50 pounds of sulphur trioxide, either of which will neutralize 35 pounds of quicklime if brought into intimate contact with it. Sometimes it pays to pile quicklime over a temporary patch in the floor of a muffle, but even then the lime should be changed daily.

3. INDEX OF REFRACTION

Aside from the question of glasses being dulled by the presence of crystals or sulphur compounds on their surface, the brillance of the glasses themselves will vary. The brilliance of a glass is measured by its refraction of light; the higher the index of refraction, the more brilliant the glass. In any one class of glasses the greater the density of the glass the higher is the index of refraction.[85] Since lead oxide, barium oxide, and zinc oxide tend to produce very heavy glasses, they also produce glasses of great brilliancy. Potassium oxide makes more brilliant glasses than sodium oxide, and substitution of boric oxide for silica makes more brilliant glasses, although the density of the glass is lowered slightly. High flint enamels are generally more brilliant than those in which feldspar is the only refractory.

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[85] Hovestadt, H., Jena Glass, pp. 388-393.

X. CRAZING IN ENAMELS

1. PRACTICAL CONTROL OF GENERAL CRAZING

Sometimes a large proportion of the ware made in a plant "crazes," or develops fine cracks, and "shivers," or chips off the ware. This general crazing or shivering is usually much more easily remedied than the trouble arising in single patterns or shapes to be discussed later. Nevertheless, the chemical and physical principles involved are rather complex, and it is desirable that the treatment of such cases be fully set forth, together with as much of an explanation for them as we can reach.[86]

It must be understood that in this discussion we are dealing with enamels applied by the American process, by which a thick coat of opaque glass is sifted dry on to a thoroughly fused and extremely thin ground coat. It is not intended to discuss the problems as they appear in enamels applied by the wet process in which a relatively thin cover coat is applied to a thick, and only partially fused, opaque ground coat.

(*a*) SEGER'S RULES.—Any discussion of the control of crazing must go back to the work of Seger and his well-known rules for correcting the defects of fritted glazes by altering their composition which are as follows:[87]

> I. On the Occurrence of Crazing: (*a*) By an increase of the silica content and decrease of the fluxes; raising the alumina at the same time, if this is necessary to prevent devitrification. With an increase of the silica and also the alumina content, an elevation of the melting point of the glaze takes place.
>
> (*b*) By an increase of the boric acid at the expense of the silica (in chemically equivalent amounts), leaving the other ingredients of the glaze unaltered. By this, a lowering of the melting point of the glaze is accomplished.
>
> (*c*) By substitution of one of the fluxes with a high equivalent weight (and, therefore giving a glaze with a low percentage of silica) by one having a lower equivalent weight (and, therefore, giving a glaze with a higher percentage of silica). An elevation of the melting point of the glaze is coincident with this change.
>
> II. On the Occurence of Shivering, Cracking of the Edges, etc.: Reverse the above rules.

The wording of the rules will be mystifying to most enamel workers. They are not accustomed to talking about "equivalent weights." This language is due to the custom, established by Seger, of recasting the composition of glazes into certain chemical units for purposes of calculation and comparison (see section on calculation of enamel formulas).

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[86] Staley, Homer F., Trans. A. C. S., 14, pp. 516–545.

[87] The Collected Writings of H. A. Seger, American Ceramic Society, p. 581.

Rules *A* and *C* can be combined and made to read, practically in the words of Seger, as follows: *On the occurrence of crazing, increase the percentage of silica, or silica and alumina, thus rendering the glaze more infusible.* This rule is well known to all enamel workers, and, in fact, to the majority of enameling plant workmen. It is common parlance around an enameling room to say "If the enamel crazes, harden it; if it shivers, soften it." [88]

Application to Enameling Practice.—This simple statement of Seger's rules *A* and *C* found in the "harden or soften" rule of the enameling shop is usually applied in cases of general crazing, or shivering. In many cases it is effective. The actual variation in the enamel batch differs widely among enamel workers. Red lead is most often used as a variant. Variation in the amount of fluorspar or cryolite is sometimes used. We know of one enamel maker who for several years successfully controlled crazing and shivering of this kind by varying soda ash. In our own experience, we have varied red lead, fluorspar, cryolite, barium carbonate, soda ash, borax, glassmakers' sand, flint, and feldspar.

Probably the safest ingredient to vary is feldspar. Since this is present in such a large amount in the batch, a moderate variation does not make a radical change in the general make-up of the enamel. Thus there is little danger of loss of luster, tendency to blister, change in tint, loss of opacity, etc. We thus deduce the following practical rule for shop practice.

Rule I: When general crazing occurs in a fusible enamel, increase the feldspar. When general shivering occurs in a refractory enamel, decrease the feldspar.

Seger's rule *B* states that crazing may be reduced by increase of the boric acid at the expense of the silica, and that a lowering of the fusing point of the glaze accompanies this change. In the terms of enamel makers, this means that crazing may be reduced by substituting boric acid for flint in the proportion of 124 parts of raw boric acid for 60 parts of flint. The validity of this rule as a cure for crazing in glazes has been called in question by Purdy and Fox [89] and others. The effectiveness of this rule for application in curing all cases of general crazing has been questioned by the writer.[90] If a soft enamel crazes, substitution of boric acid for flint will not cure the crazing. However, we sometimes find

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[88] "Harden" is used by enamelers in the sense of "render more infusible." "Soften" is used in the sense of "render more fusible."

[89] Trans. Amer. Cer. Soc., 9, p. 177.

[90] Ibid., 10, p. 120.

general crazing in hard enamels in which any attempt to cure the crazing by application of Seger's rules *A* and *C*, either in their complex form as used by some clayworkers or in their simplified form as used by enamel makers, results only in making the crazing worse. This treatment may go so far as to render the enamel too hard to be workable without decreasing the crazing. As has been demonstrated, this is due in many cases to the fact that the enamel is too hard for the ground coat.

When crazing occurs in a refractory enamel, we have found that a modified form of Seger's rule *B*, consisting of increase of boric oxide without decreasing silica, is the safest plan to follow. Boric oxide may be increased by simply putting in hydrous boric acid. In case it is desired to increase boric oxide by putting in borax, a reduction may be made in the soda ash in order that the sodium in the enamel may not be raised. The addition of 38 pounds of borax and the removal of 10.5 pounds of soda ash will have the same effect as the addition of 25 pounds of raw boric acid. This gives us all the advantage of a decrease in coefficient of expansion if the crazing should happen to be due, in part, to high coefficient of expansion in the enamel, and at the same time gives a more fusible enamel which is better suited to the ground coat. This leads to the following rule for shop practice:

Rule II: When general crazing occurs in a refractory enamel, increase boric oxide.

(*b*) RELATION OF FUSIBILITY OF THE GROUND COAT TO THAT OF THE ENAMEL.—As was stated above, general crazing sometimes seems to be due to a lack of conformity between the fusibility of the ground coat and that of the enamel, such lack of conformity resulting in poor adhesion between the enamel and the iron. We have known cases where an enamel that was giving good results crazed or shivered when applied over a ground coat that had given good results with another enamel. In fact, in extreme cases, both crazing and shivering would occur even on the same piece of ware. In these cases the trouble was remedied by changing the fusibility of either the enamel or the ground coat.

This lack of conformity may, of course, take two forms: First, the enamel may be too refractory for the ground coat. In this case, if the enamel is properly fused, the ground coat is simply burned to a cinder under the enamel and the bond between the enamel and iron is destroyed. If the ware is fired only until the ground coat is at its best strength, the enamel coat is not only rough but immature and consequently liable to craze. Second, the enamel may be too fusible for the ground coat. In this case the enamel matures before the ground coat has become fluid enough to take a proper hold on the iron, and consequently no firm bond between the enamel and iron is ever formed. The obvious remedy is to bring the maturing point of the enamel and the temperature range at which the ground coat is at its best closer together. Since at most plants either the enamel or ground coat will have a fusibility suited to the general working conditions of the enameling room, the remedy will consist of an alteration of the fusibility of the other coat. Incidentally, we might say that in some cases it would probably be advisable to secure a ground coat with a longer temperature range. This may be summarized in the following rule for shop practice:

Rule III: In all cases of general crazing or shivering, and especially in cases where these defects occur together, bring the fusibility of the ground coat and enamel into proper conformity.

(*c*) Advantages of a Thin and Uniform Coat of Enamel.—It has been the experience of the writer, working in several shops and with many different enamels, that the thinner and more uniform the enamel coat the less likely it was either to craze or shiver. As far as it has been possible to ascertain, this has been the experience of all enamel makers. This gives us another rule for shop practice.

Rule IV: Apply the enamel to the ware in as thin and as uniform a coat as possible.

(*d*) Variations in Strength and Elasticity of Enamels.—Various enamels of the same fusibility show minor differences in their tendency to craze and to shiver. In some cases increase in the percentage of a certain fluxing material at the expense of another fluxing material, in such proportions as to keep the fusibility of the enamel the same, always tends to reduce crazing and to produce chipping. The writer has found this true of boric oxide. In other cases increase in the percentage of a certain ingredient, keeping the fusibility the same, tends to accentuate the defect in fit to which the given enamel is subject. If the enamel tends to craze, the change makes the crazing worse; if it tends to shiver, the substitution increases the shivering. We believe that the alkali oxides and the fluorides have this tendency. In still other cases the substitution of a certain ingredient for others, keeping the fusibility the same, minimizes the fault of fit to which the enamel is subject. The use of lead oxide and of zinc oxide has, according to the observation of the writer, this effect when substituted for other fluxing materials. Zinc oxide, however, must be used with caution, for it forms compounds that are easily crystallized. When this occurs the enamel loses not only strength but also loses its luster.

2. CAUSES OF GENERAL CRAZING

(*a*) Physical Principles Involved.—Crazing and chipping consist of the rupturing of the enamel, the rupture being in different directions in the two cases. A solid becomes ruptured only by the application of a stress. We need then to consider the possible causes of stress. Since no stress can exist in the enamel while it is in the fused condition, all stresses must be introduced subsequent to that stage of the work.

Stresses may be introduced by external or internal forces. Stresses produced by external forces, such as those made by clamps or resulting from blows, are causes of stress in certain pieces of enameled ware; but they are not operative in the making of the large majority of pieces. They must be considered as a cause of crazing in special pieces, but not of general crazing.

Internal forces can result only from the tendency of the solid materials to expand or contract. Expansion and contraction may occur in the metal or in the enamel. They may result from changes of phase, i. e., development of bodies with new properties, or from thermal expansion. An important change of phase in cast iron is the formation of oxides of silicon and other elements, which results in permanent expansion or growth of castings. The separation of graphite which failed to separate at the recalescence temperature, 700° C (1690° F), due to rapid cooling of the casting when made, may be a factor in some cases. This must be considered as a possible cause of stress in cases of general crazing. Phase changes in the enamel would occur if it crystallized, but this is to be avoided in any case. The production of gas bubbles in the enamel might be included here for the sake of completeness, although the stresses produced by the gas itself are probably quite insignificant, however deleterious the bubbles may be for other reasons.

Thermal expansion (the term may be used to include contraction, which is negative expansion) may introduce stresses as the result of inequality of temperature or difference of the expansion coefficients of different parts of the structure. The expansion or contraction of a structure with temperature uniformity and with equal expansion coefficients in all parts and without phase change can produce absolutely no stress. Inequality of temperature is the important factor in producing stress in certain castings and is probably a contributory cause of stress in all cases of crazing. Difference of expansion must be considered as a possible cause of stress in cases of general crazing.

The accompanying chart summarizes the above and shows that the three possible causes of stress in cases of general crazing are: Growth due to the formation of oxides, inequality of temperature, and inequality of expansion coefficients.

Causes of stress	External forces	Operative in crazing in certain castings, but not in cases of general crazing		
	Internal forces	Change of dimensions with change of phase	In iron, growth due to formation of oxides	A possible cause of stress in general crazing
			In enamel, crystallization	Avoided
		Change of dimensions without change of phase (thermal expansion)	Inequality of temperature	Main cause of stress in crazing in certain castings and probably a contributory cause in all cases of crazing.
			Inequality of expansion coefficients	A possible cause of stress in general crazing

Whether the stress operating will cause the enamel to rupture will depend upon the magnitude of the stress, the form and thickness of the enamel coating, the breaking strength of the enamel, its elasticity, and its adhesion to the iron.

It is obvious that, even when the general nature of the phenomena as presented above are known, it may be very difficult to learn the precise causes of a particular defect or to find the best remedy. This is no reason why the available facts should not be presented, in order that the knowledge may be used when possible and may form the basis of developments in the work.

(*b*). GROWTH OF CAST IRON AS A FACTOR IN CAUSING STRESS.—Whenever a piece of cast iron is heated above 650° C (1200° F) in contact with air and cooled again, it is found to have undergone a permanent expansion or growth.[91] This is attributed to conversion of part of the elemental silicon and iron into oxides and the conversion of combined carbon into the graphite form, the oxidation of silicon being the most important factor. The size of the piece is increased approximately in proportion to the amount of silicon present. The amount of growth depends on the composition of the iron, the thickness and method of manufacture of the casting, and the temperature and duration of heating. In any one plant these factors are not apt to

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[91] Rugan, H. F., and Carpenter, H. C. H., Journal of the Iron and Steel Institute, 80, II, pp. 29–143, 1909. Carpenter, H. C. H., 83, I, pp. 196–248, 1911.

vary greatly, but the variation in two plants may be marked. The increase of size is most noticeable the first time the iron is heated after it is cast, as the amount of growth with successive heatings is small.

When a "green"or unannealed casting is enameled, the amount of contraction the iron should undergo in cooling is lessened by the growth taking place while the iron is at temperatures above 650° C. Therefore the iron will be fitted by an enamel with a low coefficient of expansion. If the casting is annealed and then enameled, the contraction in cooling will not be offset by any material growth, therefore will be greater than in the case of a green casting, and will necessitate the use of an enamel with a relatively high coefficient of expansion. The total contraction undergone by the casting in cooling through a given temperature range will depend on its coefficient of expansion and on the changes in volume due to growth of the casting.

Failure to take cognizance of the effect of oxidation results in stresses occuring in the enamel that may cause chipping or crazing. Chipping of reenameled pieces in shops in which annealing is not practiced is notorious, and it has often been noticed that there is a general tendency for annealed pieces to chip when only part of the output of a facotry is being annealed. It has also been observed that when a shop changes from the use of green castings to annealed ones, without changing enamel, chipping is apt to occur, and, in case of the reversed change, crazing

(*c*). INEQUALITY OF TEMPERATURE.—It is practically impossible to have every part of a piece of enameled iron at exactly the same temperature when it starts to cool; and it is altogether impossible in the accepted manner of manufacture to cool every part at exactly the same rate. Therefore in the cooling of any piece of enameled ware, strains are set up due to lack of uniform cooling. From our knowledge of the effect of such strains on the strength of unannealed glass, we must conclude that these strains must be very severe. If a sheet of glass the size and shape of the enamel coating on a bathtub, for instance, were cooled in the same manner that the enamel coatings are customarily cooled, it would be destroyed by the strains due to unequal cooling and the relative concentration of these strains at certain places by warping. That the enamel coating is not destroyed in the same way is due to its attachment to the iron which prevents excessive warping and also holds together the various parts of the coating.

These strains due to unequal cooling are known to be the cause of crazing in the case of certain castings. They are probably a contributory cause of stress in all cases of crazing.

(*d*). INEQUALITY OF EXPANSION COEFFICIENTS.—Among enamel makers and ceramists in general there has been a tendency to consider crazing and shivering as due simply to a difference in coefficients of thermal expansion of the enamel and body, and to lose sight of the other factors involved. It is to be noted that, although Seger did more than any other man to establish this theory of crazing in the minds of ceramists, he never did any experimental work to prove the validity of the theory. That his rules *A* and *C*, given above, work in glazes and enamels in the majority of cases of general crazing or shivering there can be no question. Rule *B* has been found to work in glazes only under certain conditions, and the same holds true in enamels, as has been shown. That these rules are a direct means of varying the coefficient of expansion is far from being established.

Winkelman and Schott[92] determined the actual thermal coefficient of expansion of 30 different glasses. They have published the following coefficients, by which the percentages of the constituent oxides of a glass are to be multiplied in order to obtain, by addition, ten million times the value of the cubical expansion of the glass per degree centigrade.

Na_2O	10.0	BaO	3.0
K_2O	8.5	ZnO	1.8
CaO	5.0	SiO_2	.8
Al_2O_3	5.0	B_2O_3	.1
PbO	3.0	MgO	.1

Mayer and Havas[93] have done a vast amount of valuable work in measuring the coefficients of expansion of enamels. These experiments confirm the values of Winkelman and Schott within 2 per cent, except that for PbO which they make 4.2. In addition they have found values for enamels containing opacifiers as follows:

Na_3AlF_6	7.4	TiO_2	4.1
NaF	7.4	Fe_2O_3	4.0
ThO_2	6.3	NiO	4.0
Cr_2O_3	5.1	Sb_2O5	3.6
BeO	4.7	CaF_2	2.5
CoO	4.4	MnO_2	2.2
AlF_3	4.4	CuO	2.2
CeO_2	4.2	ZnO	2.1
PbO	4.2	SnO_2	2.0

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[92] Ann. d. Phys. v. Chem., 51, p. 735, and "Jena Glass," by Hovestadt, p. 217.

[93] Sprechsaal, 42, p. 497; 44, pp. 188, 207, 220.

They found the coefficient of expansion of enamels for sheet steel to average around 0.0000300 and that of the steel used in making enamel sheet steel wares to average around 0.0000400. They, therefore, believe that the enamel on enameled sheet steel utensils is under considerable compression. This opinion is verified by the well-known fact that the enamel on this sort of ware seldom crazes but is rather prone to shiver. Mayer and Havas believe that, owing to the limitations on variation in composition of this type of enamel fixed by practical consideration of manufacture and necessary properties in the furnished ware, it is not possible to produce an enamel for sheet steel with a coefficient much higher than 75 per cent of that of the steel. They conclude that success in making this type of ware must depend on care in manufacture, and especially on producing ware with a thin coat of enamel and one of uniform thickness in order that the elasticity of the enamel may be developed to the highest degree.

The relations between chemical composition and physical properties of enamels and glasses have never been carefully studied. The coefficients given here and also in subdivisions 3, 4, and 5 of this section are open to question on account of the small number of compositions investigated. Furthermore, it is not to be taken for granted that these physical constants are strictly linear functions of the percentages of the constituent oxides. It must be remembered also that the various coefficients are likely to change with temperature. These coefficients are given because they are the best available and because they have proved to have practical value when used advisedly.

Using the factors of Mayer and Havas, the following values are calculated representing 10 000 000 times the value of the cubical expansion of twelve tin-bearing enamels for cast iron which have been actually used in factories:

I	310	VII	298
II	317	VIII	290
III	317	IX	296
IV	327	X	292
V	319	XI	292
VI	319	XII	311

The cubical coefficient of expansion of cast iron, when multiplied by 10 000 000, has been found to be close to 310. It will be seen that the coefficient of the enamels varies around that of cast iron. This may explain how an enamel on cast iron may develop either crazing or shivering, while sheet enamels do not craze. Using a number of these enamels on the same cast iron, the writer has not noticed any particular tendency for the enamels with high coefficients to craze or for those with low coefficients to shiver.

It is of interest to note in this connection that Purdy and Potts[94] measured the coefficient of expansion of a large number of porcelain bodies which were then all glazed with the same glaze. It was found that the crazing which appeared bore no direct relation to the coefficient of contraction of the porcelain body.

In considering the relation between expansion coefficients and crazings, it should be remembered that the magnitude of the stresses that result from difference of expansion coefficient will depend not only upon that difference but also upon the solidifying temperature of the enamel. Another consideration is that the expansion coefficient of a sample of the enamel may not be the same as that of the enamel on the metal, for the two coats of enamel probably flux together somewhat, although in American practice the ground coat is so thin that this action must have slight effect on the comparatively thick cover coat. Also the ground coat probably dissolves some iron oxide from the iron, and most expansion coefficients change with the temperature. Moreover, all the change in the dimensions of glass resulting from a change in temperature does not always occur at the same time that the temperature changes, but may continue slowly for months or even years. This may account for crazing or chipping occurring a long time after the ware has been made.

Some of the means used in enameling shop practice for overcoming crazing tend, according to the coefficients listed here, to reduce the coefficient of expansion of the enamel. Instances of this are increasing silica or boric oxide. On the other hand, increasing the percentage of sodium or lead oxides in order to overcome crazing in a refractory enamel increases the coefficient of expansion of the enamel, for these oxides have coefficients higher than the average enamel.

As explained in the discussion of the growth of the cast iron, the total contraction undergone by an iron casting during cooling through a given temperature range depends on the coefficient of expansion and on the change in volume due to growth of the casting at temperatures above 650° C. While the growth of the casting due to oxidation is taking place, a change must also be occurring in the coefficient of expansion. It would be rather futile to expect to produce an enamel whose coefficient of expansion would be the same at all temperatures as that of such an

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[94] Trans. A. C. S., 13, p. 431.

erratic substance as cast iron. All we can hope to do is make an enamel whose rate and total amount of contraction in cooling from the temperature of incipient rigidity will vary so little from those of the castings that either the stresses can be overcome by the strength and elasticity of the enamel, or if rupture does occur it can be repaired in later stages of the cooling.

The repair of crazes occurring in early stages of the cooling by the forcing together of the surfaces of the rupture during the later stages is a very common phenomenon in the enameling of cast iron. If a large piece of enameled cast iron is examined carefully while it is still too hot to be touched, it is very probable that it will be found to be crazed. Yet in most cases if the same piece is examined after it is cooled to atmospheric temperatures, these crazes will have disappeared. Some experienced enameling shop foremen claim that all pieces of enameled cast iron are crazed when hot. For this reason it is the general practice in most enameling shops to avoid the handling of the enamel surface while it is warm for fear that dirt will be rubbed into crazes and leave a line which will be considered an indication of a craze even though the fracture may be entirely healed during the further cooling of the piece. The production of crazes during cooling is accompanied by small sharp reports, or "pings," as the workmen call them. The workmen can tell by the loudness of the "pings" when a small or large craze is being produced and can judge whether or not the crazes will be liable to be healed when the piece is entirely cool.

(*e*) EFFECT OF FORM AND THICKNESS OF ENAMEL COATING.—The form of an enamel coating has a decided influence in determining whether rupture will be produced by a given amount of stress. As an illustration, it may be called to mind that enamel in the shape of a convexly curved layer is able to withstand much less compression than the same enamel could resist if it were in a flat sheet. Such cases are more or less intimately tied up with the design of certain castings and will be treated in the section devoted to crazing on special castings.

As has been stated before, it is common knowledge in enameling shop practice that a thin coating of enamel is less prone to chip or craze than a thick layer of the same enamel. This is due to the tendency of all solids to be more elastic and to withstand bending and warping better when in thin sheets than when in thick ones.

When enamel is applied to metal that is many times thicker than the enamel, any differential contraction extends or compresses the enamel by an amount which is almost independent of its thickness so long as there is no warping. Warping may be produced, however, by the differential expansion in amount increasing with the thickness of the enamel, by the application of external forces, and especially, by inequality of temperature in cooling. When warping occurs the strains in the enamel will not be uniformly distributed but will be concentrated to a considerable degree at certain places, and their magnitude where they are greatest will increase with the thickness of the enamel, possibly producing rupture.

(*f*) BREAKING STRENGTH OF GLASSES.—The crushing strength of glasses has never been carefully studied, but it is known that the crushing strength is many times greater than the tensile strength. When there is a tendency for enamels to chip, the enamel may be subjected to considerable compression, but it is very doubtful whether failure due to actual crushing of the glass ever occurs. Study of the surfaces of fracture of chips and the location of these on the castings leads to the conclusion that such failures are due to shears in which the tensile strength and elasticity of the glass are the factors that fail.

The relation of composition of 17 glasses to their tensile strength was studied by Winkelmann and Schott. They give [95] the following factors by which the percentage of the constituent oxides of a glass are to be multiplied in order to obtain, by addition, the tensile strength of the glass in kilograms per square millimeter.

(CaO	0.20)	B_2O_3	0.065	PbO	0.025
ZnO	.15	BaO	.05	Na_2O	.02
SiO_2	.09	Al_2O_3	.05	K_2O	.01

Uncertainty attaches to the position of CaO in the list, owing to the small proportion of this oxide contained in the glasses tested. This uncertainty is strengthened by the general reputation of lime for producing "weak" glasses.[96] The position of zinc oxide close to the top of the list and of the alkalies at the bottom is noteworthy.

(*g*) ELASTICITY OF GLASSES.—Winkelmann and Schott also investigated the relation of composition to elasticity of 19 different kinds of glass. They give [97] the following factors by which the

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[95] Hovestadt, Jena Glass, p. 149.

[96] Landrum, R. D., Trans. A. C. S., 14, p. 542.

[97] Hovestadt, Jena Glass, p. 159.

percentages of the different oxides in the glasses studied were to be multiplied in order to obtain, by addition, Young's modulus of elasticity for the glass in kilograms per square millimeter.

ZnO	15	SiO_2	65	CaO	100
B_2O_3	20	K_2O	71	Na_2O	100
PbO	47	BaO	100	Al_2O_3	160

This modulus represents the force which would be required to stretch a substance, of unit length and unit cross section to two units in length, if the relation between the applied load and the deformation remained constant. Since a low value for Young's modulus means that the substance is easily stretched, the oxides having low factors tend to produce easily extensible glasses. It is significant that zinc oxide, boric oxide, and lead oxide come at the head of the list.

(*h*) ABILITY OF GLASSES TO STRETCH.—By dividing the factors for tensile strength by those for Young's modulus, values are obtained showing the relative effect of equal percentages of the various oxides on the amount the glass can stretch without rupture. (This is on the assumption that the elastic limit and the rupturing point of the glasses are practically the same, which is probably the case.)

ZnO	$\frac{0.15}{15}=0.01000$	BaO	$\frac{0.05}{100}=0.00050$
B_2O_3	$\frac{0.065}{20}=.00325$	Al_2O_3	$\frac{0.05}{160}=.00031$
SiO_2	$\frac{0.09}{65}=.00138$	Na_2O	$\frac{0.02}{100}=.00020$
PbO	$\frac{0.025}{47}=.00053$	K_2O	$\frac{0.01}{71}=.00014$

These last figures are especially interesting, since they combine the tensile strength factors and those for elasticity (or stretch) into one set of figures. While the values given here are open to some question, on account of the small number of glasses studied, the order of the oxides in this last set of factors agrees qualitatively with practical experience in enameling. In enamels of given fusibility those high in zinc oxide, boric oxide, and lead oxide give less trouble from crazing and shivering than those high in alkalies. Along with the alkalies the writer would put fluorspar and cryolite. In the language of practical enamelers those high in the three oxides first mentioned have more "give and take" than the others, and can be used on a greater variety of castings and under more varied conditions of working and heating.

Barium oxide occupies an intermediate position, according to the experience of the writer, as it does in this list.

(*i*) INFLUENCE OF DEGREE OF ATTACHMENT OF ENAMEL TO IRON.—It is found in practice that tendency to craze and to shiver are decreased by proper attachment of the enamel to the iron. If the union between the two substances is not continuous each part of the enamel between two points of attachment has to bear the strain due to the overcontraction or expansion of the strip of enamel between these two points of attachment. The greater the distance between two points of attachment, the greater the strain each part of the strip has to bear and the greater the danger of rupture in the weakest part.

In some instances the point of attachment breaks instead of the enamel, thus giving a larger strip free of attachment to the iron with each part of the strip bearing a correspondingly heavier strain. This goes on until finally, if the enamel has the greater coefficient, a large fracture develops with the enamel on either side of the fracture not attached to the iron. In enameling shop vernacular such fractures are known as "lifts," because the enamel seems to have been raised or lifted free from the iron. The result of this action is scaling off of a large piece of enamel.

(*j*) SUMMARY OF CAUSES OF GENERAL CRAZING.—The possible causes of stress to be considered in cases of general crazing are growth of the iron in the casting while hot, inequality of temperature, and inequality of expansion coefficients of iron and enamel. Whether the stress will produce crazing (or its converse shivering) depends on the magnitude of the stress, the thickness of the enamel coating, the breaking strength of the enamel, the elasticity of the enamel, and its adhesion to the iron.

3. CRAZING DUE TO SPECIAL CAUSES

Much more common than the occurrence of general crazing is the occurrence of crazing or shivering in ware made over a certain pattern, or on castings made by a certain molder, or in ware that has been enameled by certain workmen. Obviously, such phenomena are not due primarily to the composition of the enamel but to special causes.

It is well to call attention to the fact that, just as the causes of special crazing may be auxiliary agents in bringing about general crazing, a tendency toward general crazing or shivering may be an auxiliary cause of special crazing or shivering. The two classes of causes, working together, may cause a rupture that would not appear if only one were operative. Therefore, a rule to be applied in all cases of special crazing or shivering is to minimize as much as possible the tendency to general crazing or shivering.

(*a*) THICK SPOTS IN THE CASTING.—*Effects.*—A thick spot in the casting has two effects: First, the thicker portion does not heat up as readily as the rest of the casting, consequently the ground coat is not properly fused on this spot by the time it is at its best strength on the rest of the casting. The result is a poor bond between the iron and enamel on the heavy spot. If the piece is fired until the ground coat is properly fused on the heavy spots, there is danger that the ground coat on the rest of the casting will be overfired. The result is a lack of proper attachment between the enamel and iron on the thinner portions of the casting. Second, the thick spots do not cool down as rapidly as the rest of the casting. Therefore, the enamel over the thick spot continues to contract and set after the surrounding enamel is rigid. The result is that this part of the enamel is under special stress and strain, which may be augmented by warping.

The defect due to a heavy spot depends upon the location of the heavy portion and the heat treatment given the casting. The heavy portion may consist of an iron bead on the edge of the casting or of a heavy portion at a convexly curved part of the casting. If the ground coat is not properly matured on these portions, there will be a tendency for chipping (shivering) to take place. When the casting is heated until the ground coat on the heavy portion is properly matured and the ground coat on the thinner portions of the casting is heated beyond its best strength, the enamel over these thinner portions tends to develop "lifting." A "lift" is as has been explained, a large distinct crack occurring in an area of enamel that lacks proper attachment to the iron.

In case the heavy portion is at a concave curve or in a flat surface and the ground coat over it is not properly fused, there is a tendency for fine crazing to occur. If the bond made by the ground coat is very defective, lifting may result. In case the piece is heated until the ground coat is properly fused over the heavy portions, there is the possibility that the ground coat on the thinner portions will be over-heated and that the bond between the enamel and iron at these areas thus will be rendered defective. In this case, the tendency is for the enamel on these areas to develop the defect to which it is subject, crazing or shivering as the case may be. When the bond is very defective, there may be lifting or scaling of the enamel in large flakes. Moreover, crazing may occur at the border of the heavy portion, owing to the contraction and setting of the enamel in this area after the surrounding enamel has become rigid.

Thus, we see that a heavy spot in the casting may cause either crazing or shivering. It may also cause "lifting" and in extreme cases may induce the development of crazing and shivering in the same piece.

Remedies.—(1) Reduce the thickness of the metal as much as possible. At one time beads were supposed to be a necessary ornament for every lavatory. In late years beads have been removed from lines, with much improvement in the beauty of the ware and a decided decrease in the amount of defective ware. Thick spots in casting are often due to slipshod methods in pattern making. This is inexcusable, even from the standpoint of economy. The use of a defective pattern in an enameling plant is one of the most extravagant ways of wasting money that can be devised. One of the characteristic differences, noted in visiting various plants, is that the successful plants invariably have good patterns and the unsuccessful ones generally have poor ones. All patterns should be filed to templates, not only on the larger surfaces but also in corners, on rims, etc. Of course, not all parts of a pattern should be of the same thickness, but it is possible to know just how thick each part is.

Especial care should be taken in the design of parts where it is necessary to have a double thickness of metal, as at the overflow channel of a lavatory. We have broken castings and found that because of carelessness in the design of core boxes, there was a thickness of five-eighths of an inch of metal between the overflow channel and the bowl of a lavatory. Is it any wonder that bowls made over that pattern had been giving trouble in the enameling room? Or is it any wonder that firms which habitually use patterns as grossly defective in one way or another as this are not able to compete with more alert concerns? Many of the collars around openings can be dispensed with easily, and others can be made much lighter where they lap over the body of the casting than is the custom in some shops. At a certain plant, considerable trouble was experienced from crazing around the outlet of roll-rim sinks of a certain size. On examination it was found that the collar of the bell was three-eighths of an inch thick and lapped over the bottom of the sink for 1⅛ inches. When the pattern was altered so that the collar was only a scant quarter of an inch thick and lapped over only one-half inch, the crazing immediately disappeared. Many other instances of the advantages gained by simple alterations in the thickness of parts of a pattern might be quoted.

(2) Turn and chill the piece while the ground coat is being fused. This is a trick of manipulation in use at most plants. It consists in removing the piece from the furnace when it has reached a dull red heat, allowing it to cool for a minute or two, then putting it back in the furnace in the reverse position from the one originally occupied. While the heavy spots heat up more slowly than the thinner portions, they also lose more slowly the heat they have gained. The chilling allows the piece to go back into the furnace with the heavy spots considerably higher in temperature than the thinner spots. Thus, there is a chance that the ground coat on the heavy spots will fuse at the same time that the ground coat on the rest of the casting does. The turning is, of course, in the interest of even heating of the casting.

(3) Put a more fusible ground coat on the heavy spot. The object of this is obviously to attempt to have it fuse down at the temperature at which the regular ground coat is at its best strength on the rest of the casting.

(4) Provide a ground coat that has a long heat range; that is, one that fuses at a low temperature and is still good at a high temperature. Such a ground coat will stand large inequalities of temperature in various parts of the casting. The procedure in obtaining such a ground coat is indicated in another section of this paper.

(5) Provide an enamel of high elasticity and great strength. How this can be done has been indicated in a general way. The main points to be observed are to have the enamel of proper composition and to apply it in a thin and uniform coat.

(*b*) THIN SPOTS IN THE CASTING.—Thin spots are obviously the reverse of thick spots, and the effects and remedies have been sufficiently indicated in the preceding section. The only variation in the remedies would be to endeavor to make the thin spots thicker and to apply a more refractory ground coat on the thin spot than on the rest of the casting. Chilling, a good ground coat, and a strong elastic enamel are just as serviceable in the case of thin spots as in that of heavy spots.

(*c*) SHARPLY CONVEX CURVES AND PROJECTING CORNERS.—*Effects*.—It is well known, as a matter of experience, that chipping is liable to occur on sharp projecting corners and sharply convex curved portions of a piece of ware. This is probably due, in part, in many cases, to the fact that such portions are apt to be especially thick, owing to the difficulty of properly filing the reverse surface in the pattern and of properly molding it in the casting. In addition to this, if the iron tends to contract more than the enamel, thereby compressing the enamel longitudinally, the enamel can resist much less compression when in the form of a curved sheet on a convex surface than when flat.

Remedies.—(1) Avoid sharp corners and make all convex curves with radii as large as possible.

(2) See that the reverse sides of convexly curved portions of patterns are properly hollowed out. See that such portions are properly molded.

(*d*) SHARPLY CONCAVE CURVES.—*Effects.*—Just as there is a tendency for enamel to fly off at a tangent to a convex curve, there is a tendency for enamel to be crushed on a sharply concave curved portion of a casting. As the casting cools, the angle of the concave curve becomes more acute, and the enamel must adjust itself to this sharper angle. This tendency, however, seldom manifests itself in a rupture for the simple reason that the power of enamel to resist such a strain is very great. The resistance of a glass to crushing is very high; as shown by Winkleman and Schott,[98] 10 to 20 times as great as its power to resist tension.

A sharply concave portion of a casting is frequently a cause of defect in the enamel for an entirely different reason. Owing to the method of applying the enamel by sifting it on as a dry powder, it is very difficult to cover the area around a sharply concave curve without getting an extra heavy coat of enamel in this portion or corner. This is especially true if the sharp curve or corner comes at the bottom of a straight area, such, for instance, as at the bottom of the straight back in a D-shaped lavatory bowl. The defect due to a heavy spot of enamel will be discussed in the next section, but sharply concave curves and corners constitute a special cause for the production of such spots.

Remedies.—(1) Eliminate, as far as possible, sharply concave curves in the casting. At different times, the writer has seen a large number of patterns altered so as to increase the radii of sharply concave curves on the surface. In all cases the tendency to crazing in these parts was greatly decreased and in most disappeared altogether.

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[98] Hovestadt, Jena Glass, p. 151.

(2) Apply the various rules for avoiding rolls given in the next case.

(*e*) ROLLS.—*Effects.*—A "roll" is a heavy accumulation of enamel on the surface of a casting. The difference between a roll and a simple thick spot of enamel is that a roll shows some evidence of flow. Practically all excessively thick spots of enamel, such as those that form in corners, become rolls. In addition to this, rolls may be caused by excessive flow in enamel on a straight or a slightly curved surface.

The effect of a roll is to produce a tendency toward crazing, either in the roll or in the enamel close around it. When the ware is cooling the roll remains hot longer than the thinner coat of enamel surrounding it. The result is that the enamel constituting the roll is contracting after the surrounding enamel has become rigid. Strains are thus set up that cause the crazing and lifting.

Remedies.—(1) Alter the pattern as directed under 5 so as to reduce the tendency for enamel to lodge in hollows and corners.

(2) Use finely ground enamel. When the enamel is coarse, it does not fuse and adhere readily on being applied to the casting, but part of it drops down and accumulates in piles, especially in corners and hollows.

(3) Use fairly fusible enamel. The purpose of this is to have the enamel adhere readily.

(4) Have the workmen use mechanically agitated sieves and take especial care in the application and heat treatment of enamel on castings in which rolls tend to form. The surface to which the enamel is being applied should be as nearly horizontal as possible. The enamel should be applied in as uniform a coat as possible and as soon as the enamel ceases to adhere well, application should be stopped. In heating, the ware should not become so hot that there is any large amount of flow in the enamel. In order to minimize the tendency for the formation of rolls, it is required to have the enamel applied in a coat so nearly uniform that it is not necessary to have any appreciable flow in the enamel while the ware is in the furnace. Such application is not readily obtained by use of sieves agitated by hand, but is easily obtained by the use of mechanically agitated sieves.

(*f*) BEADS OF ENAMEL.—*Effects.*—"Beads" are small rolls around the edge of an enameled surface. They are caused by the pressing up of the enamel into a roll when a workman tries to cut off the part of the enamel that has flowed down over the edge of the casting. They are especially prone to form if the trimming is done after the enamel has started to become rigid. Beads are very liable to chip off, since the enamel in then is not only of different thickness from the adjacent enamels, but more especially because the enamel in the beads has been thrown into a condition of strain by the process of trimming. These stresses very frequently do not manifest themselves as chips until some time, often months, after the piece has been made.

Remedies.—(1) Apply the enamel as thinly as possible at the edges of the piece. This is best done by putting very little enamel on the edge during the application of the first coat of enamel and only a light coat during the application of the last coat to the whole piece.

(2) If possible, do not heat the ware to such a point that the enamel flows down over the edge. This implies that the enamel should be applied to the whole casting in the manner described under the discussion of rolls.

(3) If the trimming is to be done at all, let it be done quickly while the enamel is still soft. It should be done with a good tool and with the blade of the tool making an acute angle with the enameled surface. This gives a clean, slanting cut, while any attempt to trim with the blade held perpendicular to the surface of the enamel results in more or less beading.

(*g*) STRESSES DUE TO APPARENT WARPING AND BENDING.—*Effects.*—Many castings, especially those of thin section and long, slender shape, show considerable warping and buckling on cooling, after the iron is black and the enamel has become fairly rigid. Of course, this has a tendency to set up strains between the enamel and iron and in the enamel itself. Such castings are especially common in plants manufacturing specialties. These strains must always tend to produce crazing or shivering and in aggravated cases produce actual rupture between the enamel and iron.

Remedies.—(1) Strengthen the sections by the use of iron ribs on the back, etc., so that the tendency to warping and buckling is minimized.

(2) Use a good ground coat and a strong elastic enamel.

(*h*) STRESSES DUE TO EXTERIOR MECHANICAL RESTRAINT.—*Effects.*—In making certain styles of castings, especially those for sectional work, it is very important that they conform to a certain shape. The expedient of cooling these castings in forms or clamps is sometimes used. This procedure may so interfere with the normal contraction of the iron and enamel as to set up strains that may cause crazing or shivering. As a case in point, we may quote the following: At a certain plant some rectangular sections about 24 by 48 inches in size were being made. It was necessary that the sides of these be perfectly straight, since the sections were to be bolted together and a good butt joint was required. It was found that when the castings came from the enameling furnace the sides were curved inward to a slight extent. When they were cooled in the ordinary way this curvature was still apparent in the cold pieces. To obviate this difficulty a heavy viselike arrangement was constructed, in which the castings were clamped while still hot and allowed to cool there. This straightened out the sides and produced a slight bulge at the ends of the piece. The deformation of the ends was immaterial, but it was found that this procedure caused the enamel to develop minute crazes at each corner of the section. It was concluded that when the castings were cooled in the vise the ends, which took the stress, were acting like compressed springs. When the clamp was removed the ends of the casting expanded and caused the enamel to craze. Acting on this thought, it was decided to put the castings in the clamp, compress them strongly while the iron was still hot and the enamel still plastic, and then immediately to remove the clamps. When this was done it was found that the ends were bulged slightly more than before, that the sides were straight, and that crazing was absent.

Another type of stress due to external constraint that enameled iron frequently has to undergo is that caused when a piece of ware, slightly out of shape, has to be drawn into place by bolts when being set up. This, of course, occurs most frequently in sectional ware.

Remedies.—(1) If possible, so fashion the patterns that the castings will not have to endure external stress either in cooling or when being put in place.

(2) If stress is to be applied, it should be applied while the iron is still hot and soft and the enamel is plastic.

(3) Use a fusible ground coat and a fusible enamel so that the casting will not have to be heated to a very high temperature in the enameling process and so will have little tendency to warp or deform.

(*i*) UNEQUAL COOLING.—*Effects.*—It sometimes happens that crazing or shivering occurs, in certain shaped patterns, for which there is no apparent cause. The defects are not amenable to any of the various treatments already suggested, but disappear when certain alterations are made in the pattern. For this reason we can not but think that the defect is due to strains in the enamel or between the enamel and iron caused by unequal cooling, due to some peculiarity in the pattern the significance of which we do not realize. This type of crazing is the most difficult to deal with, for it gives no indication of its cause. We are compelled to depend only on experience and systematic alteration of the pattern. For instance, we have found that, given two sinks of exactly the same size, shape, and thickness, with the exception that one has its outlet near one side or end and the other has its outlet at the center, the latter sink will have decidedly less tendency to develop crazing around the bell than the other. Again, we have found that a kitchen sink with a well-rounded bottom is less liable to develop crazing than one with a bottom that is nearly flat. Why these things are so, we can only conjecture. They are merely matters of experience. Similar cases might be multiplied if space permitted. The treatment of each case of crazing or shivering of this sort is a special problem.

Remedies.—(1) Apply all the rules for general or special crazing that are applicable.

(2) Depend on experience and systematic alteration of the pattern.

(*j*) SUMMARY OF CRAZING DUE TO SPECIAL CAUSES.—Crazing in special parts of patterns or in special patterns may be due to a large variety of causes and to various combinations of these causes. Likewise, the means of control must be many and varied so as to suit each special case.

There is no one panacea for crazing in enamels on cast iron. Efficiency in its control depends upon a thorough understanding of the chemical and physical factors involved and on wide experience.

XI. PINHOLES AND BLISTERS IN ENAMELS

1. CASTING HOLES

Pinholes and blisters in enamel are, of course, closely related. A pinhole is simply the hole left by the bursting of a blister. Usually the hole is more or less filled by flow of the enamel subsequent to the breaking of the blister. Therefore, the way to aviod pinholes is to avoid blisters. These may be due to many causes, of which the most common will be discussed.

Minute holes in the surface of the casting are a common cause of large blisters. These holes are generally due to little balls of slag. Sometimes they are due to spattering of drops of molten iron at the beginning of the pouring of the casting. When a sharp steel punch is driven into the hole, the orifice will be found to be much larger below than at the surface of the casting. When a piece containing such a hole is enameled, the air in the hole expands because of the heat and pushes out the enamel covering it into a large blister.

The formation of such holes should be avoided as much as possible by using fluid iron, which will allow the slag to come to the top and to be skimmed off, and by exercising care in pouring the casting. Any holes formed in the surface of the enamel should be punched open and filled with some "plugging mixture."

For plugging casting holes, various substances have been used. The so-called "casting cements" and "iron filler" cements, sold for patching defective castings in the foundry, flux into the enamel causing blisters and slag spots. Chalk has been used but is not at all satisfactory, for it burns to quicklime and, gradually taking up moisture from the air through the pores of the iron, swells and pushes off the enamel above it. Clay shrinks in drying and burning and is liable to float up into the cover enamel. Moreover, it is porous and has an expansion and contraction with heat entirely different from that of the enamel and cast iron. Hence the enamel is liable to craze in the course of time over a hole plugged with clay. Sometimes very small holes are plugged with ground coat. This is satisfactory provided it does not cause a blister during the enameling process, which it sometimes does. The most satisfactory plugging compositions used by the writer are made from a mixture of ground coat slip, clay slip, and ground flint. The proportions of the two slips depend on the refractoriness of the ground coat. Generally they are used in about equal amounts. Enough dry flint is kneaded in to produce a stiff mud. This should be worked into balls and thoroughly dried. For use, it is simply made stiffly plastic again with water. In this mixture the clay renders the mass plastic when wet and coherent when dry; the large amount of flint causes the mass to swell a little rather than to shrink during burning, and the ground coat causes the material to burn to a hard, dense mass.

2. IMPROPERLY CLEANED IRON

Blisters may be caused by scale and dirt left on the iron by insufficient sand blasting and cleaning. The interaction of these substances with the ground coat enamel causes gases to be given off which cause blisters. The remedy is, of course, better cleaning. Grease and oil, from the machinery used in the cleaning room, dropping onto the surface of a casting will cause blisters when this is enameled unless completely removed. If the spot is small it will generally suffice to wash it thoroughly with a rag quite wet with gasoline. When the spots are large the piece should be "burned out," or annealed, and reblasted. Perspiration from the hands of workmen is liable to cause blisters because of the soluble salts it contains and its pronounced tendency to cause rusting. Pieces on which perspiration marks are plainly visible should be burned out and reblasted.

3. DIRTY IRON

Even when the surface of a casting is clean, blisters may be caused by rust in the pores of the iron. This rust may form before or after the piece is sand blasted. It will form in a couple of days if a piece is allowed to stand in a cool place after sand blasting. Such pieces should be burned out and reblasted.

Blisters may be caused by what the enamelers call "dirty iron"; that is, iron from which there is an excrescence of black foamy matter when it is heated. In many cases this dirt is simply rust, but in other cases it occurs in castings fresh from the foundry and thoroughly blasted. In such occurrences the dirt may be due to minute particles of slag in the iron or to large crystals of graphite which have separated in the solidification of a very high carbon iron. The use of foundry facings also produces dirty iron. Such pieces should be burned out and reblasted. The cause of the trouble should be discovered and corrected.

Where the ground coat is defective in spots only, recourse may be had to preliminary baking of the ground coat. This consists in baking on the ground coat, allowing the piece to cool, rubbing off the spot of defective coat, applying fresh ground coat to the spot, reheating the piece and proceeding to enamel it. The practice of preliminary baking will reduce the blisters, whether they occur in spots or not, that are due to most of the causes connected with the casting or ground coat.

4. IMPROPERLY HEATED GROUND COAT

It is necessary for the ground coat to be heated to a temperature at least as high as that which will be used during the application of the enamel. During the baking of the ground coat onto the casting various chemical reactions take place between the constituents of the ground coat and of the iron, which result in the evolution of gases. As long as the temperature is being raised these gases will continue to be given off. If, during the baking of the cover coats, the temperature is raised above the highest point reached in the baking of the ground coat the evolution of these gases will cause the cover coat to puff up into a spongy mass.

On the other hand, melted ground coat, like any other liquid, tends to volatilize and rise up in blisters when a certain temperature is reached. It is folly to attempt to enamel over a blistered ground coat, for the result will be ware that is either blistered or "lifted," or both. Therefore the ground coat must not be heated to too high a temperature. Sulphates or other substances giving off gases at high temperatures are also causes of blistering of this kind.

If a casting contains thick and thin spots, there will be a tendency for the ground coat to be underheated in the thick spots when the rest of the casting is at the right temperature, and to be overheated on the thin spots when the remainder of the casting is properly heated. This difficulty can be overcome to a certain extent by "chilling" and turning the piece. Chilling the piece consists of withdrawing it from the furnace for a couple of minutes when partially heated and then putting it back to complete the heating. Thin spots gain heat more rapidly than thick ones, but during the chilling the thick spots retain more heat than the thin ones, so that the final heating results in a more uniformly heated piece than if resort had not been made to chilling. Of course, turning the piece is in favor of uniform heating.

5. IMPROPER THICKNESS OF GROUND COAT

If the layer of ground coat is too thin, it burns, at a comparatively low temperature, to a dry cinder owing to the loss of part of the glass by vaporization and supersaturation of the remainder with iron and other elements dissolved from the surface of the casting. When enamel is applied to such an overburned ground coat, the result is generally lifting instead of blistering, but the blisters are sometimes formed by interaction of the cover enamel with the cinder and iron beneath it. If too thick, the ground coat may blister, on account of the inability of the gases given off at the surface of contact of ground coat and casting to find their way through the thick layer of glass above them. In this case the gases may cause blisters in the ground coat or simply small bubbles. However, when the cover coat is being baked these bubbles of gas tend to work out of the ground coat and to cause blisters in the cover coat. If the ground coat is damp when the piece is put into the furnace, blisters will be formed by the sudden generation of steam.

6. DEFECTS DUE TO ENAMEL COMPOSITION

In the same manner as the ground coat, the cover coat enamel tends to volatilize and rise up in blisters when overheated. Moreover, certain ingredients sometimes used in cover coats give off gases when strongly heated in enamel compositions. Among these are bone ash and arsenic oxide. These do not produce large isolated blisters, as in the case of casting holes, but a multitude of little pimples and very small pinholes. An enamel high in fluorine will show the pinholes but not the pimples. Of course, if the enamel contains sulphates or absorbs sulphur gases from the furnace atmosphere, we may have blisters due to sulphur. Contamination of the enamel powder by particles of organic matter, such as splinters of wood or drops of oil or grease, will also cause blisters.

XII. MAKING THE CASTINGS

Foundry practice in the making of castings that are to be enameled differs from ordinary foundry practice only as it is necessary to produce castings of certain characteristics to meet the requirements of enameling-room practice. The chief of these requirements are: The avoidance of sharp curves and corners in the castings; control of the thickness of various parts so that the castings will heat and cool during enameling without warping and cracking, and without causing the enamel to blister, craze or chip; the elimination of "facings" on all surfaces that are to be enameled.

1. PATTERNS

Since most patterns are to be used many times, metal patterns are the general rule. Iron is commonly employed, although for small work white metal and aluminum patterns are sometimes used. A lead pattern is made first and from this one or more metal patterns are made by ordinary pattern room practice.[99]

If the piece is to be made by hand, the pattern consists of one piece, which, with the necessary allowance for shrinkage of the iron during cooling, is a duplicate of the desired casting. For

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[99] Detailed information, profusely illustrated, in regard to the making of patterns for enameled cast-iron sanitary ware and the mechanical equipment in general of one type of plant for the manufacture of such ware is given in a series of articles by Dillan Underhill in Foundry, 34, 35, and 36. Brief reference is made to the raw materials and chemistry of enameling.

machine-made ware, the pattern is made in two parts, one for the outer surface of the casting and the other for the inner surface. Each of these parts may consist of several pieces, some of them being movable.

For small ware the patterns are made so that the castings, in general, will have a thickness of from one-eighth to three-sixteenths of an inch, while for tubs and other large pieces the general thickness is about one-fourth of an inch. In order to keep the pieces from warping and cracking in the sand and in the enameling ovens, the patterns are so constructed that the castings will thicken rather abruptly at the edges. Thus, the body of a flat-rimmed kitchen sink will be one-eighth inch thick and the rim three-sixteenths; the body of a roll-rimmed sink will be three-sixteenths and the rim will thicken toward the outer edge to one-fourth inch; the body of a bathtub will be one-fourth inch thick and the rim will be five-sixteenths inch or even three-eighths inch thick at the outer edge. Sometimes the bottom or other parts of the castings are made heavier than the rest.

It has been found in practice that certain arrangements of parts in castings work better in the enameling room than others. It is better not to have the outlet of a sink too close to one side or end; oval basins in lavatories give much less loss from crazing than D-shaped bowls; heavy bells on sinks and heavy collars on the outlets of bathtubs should be avoided. After a pattern has been put into use it is often found that all the castings made from it tend to develop a certain defect when enameled. It is then necessary to alter this pattern, changing the shape of certain parts or making it thicker or thinner in certain places. In order to make a metal pattern thicker it is customary to put on a brass patch.

Except at the points where there is an object in having the casting thicker, great care is taken to have the pattern made so that the castings will be of uniform thickness and as thin as is consistent with good foundry and enameling practice. This is in the interest of low cost of production of castings. Often 5,000 to 10,000 castings a year are made from a single pattern, and 10 per cent reduction in the weight of these amounts to quite a sum in the cost of metal alone. Especial care is taken to see that the reverse sides of sharply convex surfaces, such as roll-rims, are properly hollowed out. Failure to do this causes waste of metal in the foundry and loss in the enameling processes.

In order to avoid chipping of enamel on sharply convex surfaces and accumulation of enamel in rolls in sharply concave surfaces, all corners are made as rounding as is consistent with good form and the use to which the piece is to be put. The use of beads for scrollwork and other similar ornamentation is avoided both on the score of difficulty in enameling and good taste. A well-designed piece of enameled ironware depends for its appeal to the sense of the beautiful on color, texture, good lines, and proper proportions.

2. FOUNDRY PRACTICE

(*a*) Mold Facings.—The only essential difference between making castings for enameling and castings for other purposes is that the use of sea coal, plumbago, soapstone, and other facings should be avoided on all surfaces that are to be enameled. In order to prevent confusion, the use of these materials is generally avoided altogether. It is possible to enamel surfaces on which facings have been used, but it is necessary to preheat or "burn out" such castings, and even then they are liable to cause blisters, chipping, and crazing during the enameling operations.

(*b*) Molding Machines.—The castings are made in the foundry either by hand or by machine methods. Practically all pieces that are made in large numbers are manufactured on some sort of molding machine. For small ware, almost every variety of molding machine is employed. Hand squeezer, power squeezer, jolt or jarring, stripping plate, roll over, power draft, etc., types of machine are all used. In addition various combinations of the principles involved in these different types are employed. Owing to the large variety of shapes and sizes of pieces made, different types of machine are found best suited to certain kinds of castings. The selection can be made by any well-informed foundry superintendent.

A few bathtubs are still made by hand, two men making four to six tubs in a day. Wooden flasks are commonly used for that class of work and small jib cranes for handling the flasks, shaking out, etc. Most tubs are made on molding machines. The machine used for making bathtub molds really consists of two machines, one of which makes the drag and the other the cope of the tub mold. Since bathtubs are always cast upside down and the parting line of the mold is at, or very near, the outer edge of the rim, the drag forms the inside of the tub and the top of the rim, while the cope forms the outside of the tub to the outer edge of the rim. The two machines are exactly similiar in type and can be described best as power-draft machines, although they do not conform strictly to any of the common types of molding machines.[100]

Two different types of flasks are in use for making the drag mold. One type contains a spider and is used without a bottom board; the other is an open flask and calls for the use of a bottom board.

The spider in the first type of flask is essentially a deep hollow oval section held in place by narrow fins extending inward from all parts of the shallow flask sides. In making the drag, the pattern is placed, of course, with the opening, corresponding to the inside of the tub, up. The flask is fitted on to this by means of guide pins which engage in holes in the pattern, and is clamped fast. The oval section of the spider extends down into the opening of the tub nearly to the bottom. The mold is then rammed up by means of small air rammers, most of the oval section being left hollow. The entire mold is then lifted into the air by a power hoist and trunnions at each end of the pattern, turned over, and set down again a few feet away. By means of four pins, located near the corners of the pattern and operated by cams that are geared together, the pattern is raised about one-half inch from the mold. The cams are operated by a hand lever; but from this point on the pattern is raised and carried back to the molding station by a power hoist attached to a trolley or crane. The drag mold is then carried to the place where the cope mold is to be placed on it.

In using the plain flask the tub is made in exactly the same way, except that the mold is rammed up solid with sand and a bottom board is clamped on before the pattern is turned over. Instead of small air rammers, a very large rammer with a head 10 or 12 inches in diameter is used. This rammer is built and operated like a steam hammer, each blow being under the control of the operator. Molds can be made very rapidly by this method.

For making cope molds two types of flask outfit are used also. One consists of a plain, deep, cheek flask and a shallow-rimmed cope flask, which also constitutes a pouring box. The other consists of a single flask, with a depth corresponding to that of the two flasks in the previous set, and a separate light pouring box. Since tubs are nearly always poured from the rim, both

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[100] For illustration see Underhill, Dillan, Foundry, 35, p. 10. For similar machines used in Germany see Irresberger, C., Stahl und Eisen, 30, pp. 579–585.

types of flask have four projecting bags for the accommodation of pouring holes.

The cope is made with the surface corresponding to the outside of the tub up. Around this is placed the cheek flask, which leaves a few inches between the sides of the pattern and flask. The position of the flask is fixed by four holes in the flask and four pins attached to the pattern or machine. The positions of these holes and pins are located by the same template used for locating the corresponding ones on the drag flask and machine. After the cheek flask has been rammed up by means of air rammers, the cope flask or pouring box, as the case may be, according to the type of flask used, is clamped on and the mold finished. The mold is then lifted off the pattern by cams and power hoist as in the case of the drag mold. It is closed with the use of a power hoist, proper fit being insured by the guide pins extending up from the drag flask and the holes in the cheek flask.

(*c*) METHODS OF HANDLING MOLDS.—Two systems of handling flasks and molds are in use—the crane system and the track system. It is not necessarily the case, but it actually happens, that the crane system is used for moderately intensive systems of working, in which 25 to 35 tubs are made from a mold in a shift, and the track system is used for a very intensive system, in which about 75 molds are made from a pattern in a shift.

The general layout of a tub foundry operated by the crane system is as follows. (See Fig. 2.) The building is long and narrow, with a high roof. In the center and at one side are two cupolas and in front of each of these are several shallow basins in which the tubs are placed to be poured.

Between the two sets of pouring pits is a mechanical shake-out apparatus and sand-tempering apparatus. Extending down along the walls of the foundry are the molding stations. In each end is storage space for extra patterns and flasks. Overhead is a traveling crane equipment, fitted with at least two, and sometimes three, cranes. A bucket elevator raises the sand from the shake-out pits to large reciprocating conveyors, working on the principle of a hoe, which feed it, thoroughly tempered, into the individual sand bins at the various molding stations. The space between the rows of molding stations, in each end of the shops, is used for the storage of finished molds if necessary.

With the crane system of molding, tubs may be poured continuously or at the end of the shift. In the continuous system of pouring, the mold is taken by an overhead crane from the molding

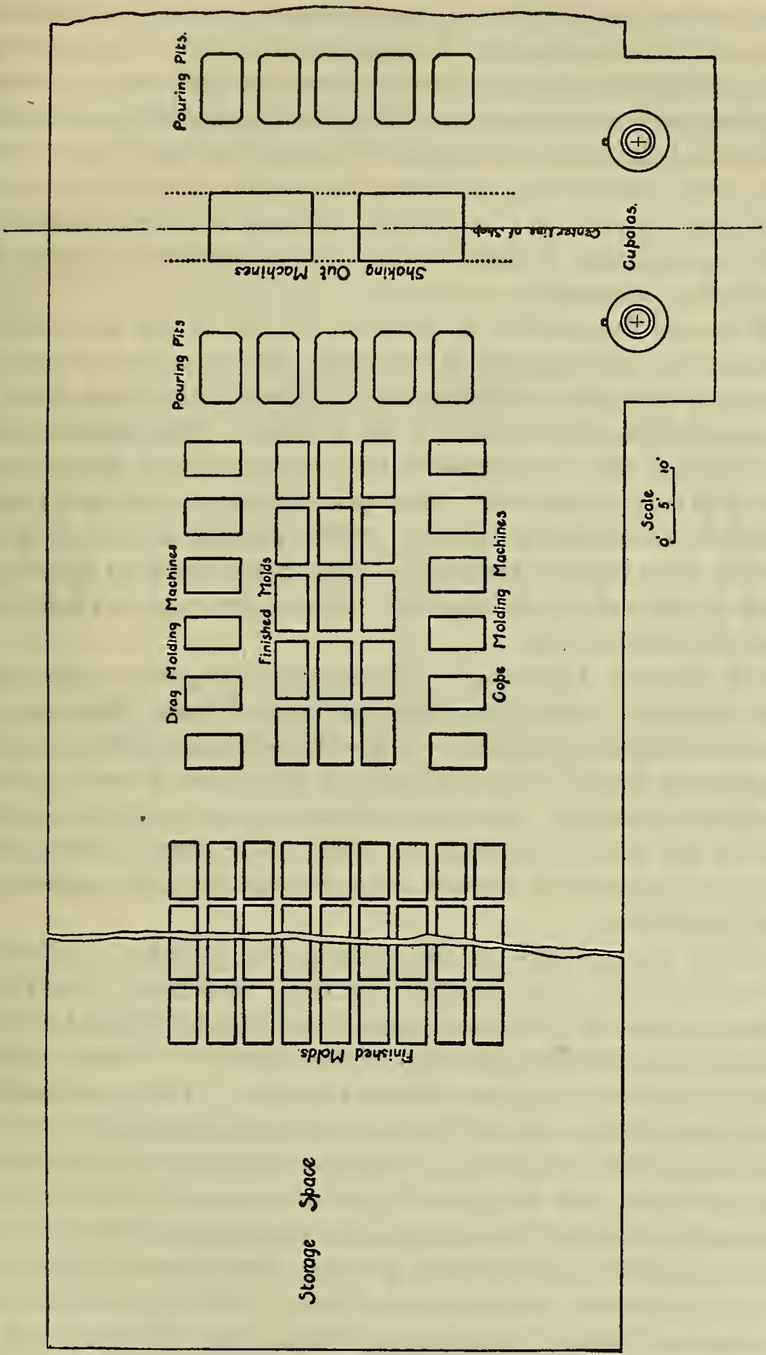

FIG. 2.—*Floor plan of a bathtub foundry operating on the crane system*

station to a pouring pit. From there it goes to the shake-out rack, which is agitated by a huge eccentric. The casting is carried away to the cleaning room by a truck or light trolley, the flask is taken back to the molding station, and the sand drops down on to a large belt conveyor leading to the sand elevator. As the sand falls on to the belt it is wet down by a spray of water, so that by the time it passes up the elevator, through the hoeing conveyors and into the sand hoppers of the various molding stations, it is thoroughly tempered.

When all the pouring is done at the end of the heat, the sequence of operations is about the same. As fast as they are needed, flasks are brought to the molding stations by the crane from the storage spaces at the ends of the foundry. The finished molds are stored in the space between the rows of molding stations until near the end of the shift. More pouring basins are used than in the case of continuous melting. When pouring is started, it progresses quite rapidly, the empty flasks being taken to the storage space at the end of the foundry. Often a few may be placed near each molding station.

This method of pouring requires more flasks, more room, larger sand bins, and somewhat more handling of flasks than the continuous method of pouring. It has the advantage that it is easier to produce good hot iron of uniform quality in periodic than in continuous melting. Since no pouring is done during the greater part of the time that molds are being made, there is more chance for systematized and prompt crane service with the periodic system of pouring.

In the track system of tub making, the foundry is oblong as before with the cupolas at one side near the center. (See Fig.3.) From in front of the cupolas large ovals of light weight industrial track extend toward each end of the foundry. The equipment and operation of these two ovals is the same. Two cope machines are situated in one end of the oval near the cupolas and two drag machines in the other end. A large hoeing conveyor, feeding from both ends to a belt conveyor, is placed at ground level inside the oval and paralleling the side opposite the cupolas. This conveyor is covered with a substantial grating, usually made from 2-inch gas pipe, and acts as a shake-out box. The belt conveyor leads to a bucket elevator in the center of the oval. This elevates the sand on to an overhead hoeing conveyor, which distributes it to sand bins feeding directly into the molding machines. Running across the oval above each machine is an I-beam trolley track on which a trolley with a power hoist, generally operated by compressed air, is suspended. Since, in this system of molding tubs, open flasks, the large air rammer, and bottom boards are usually employed, a short section of trolley track, from which the large rammer is suspended, is placed over the drag machines.

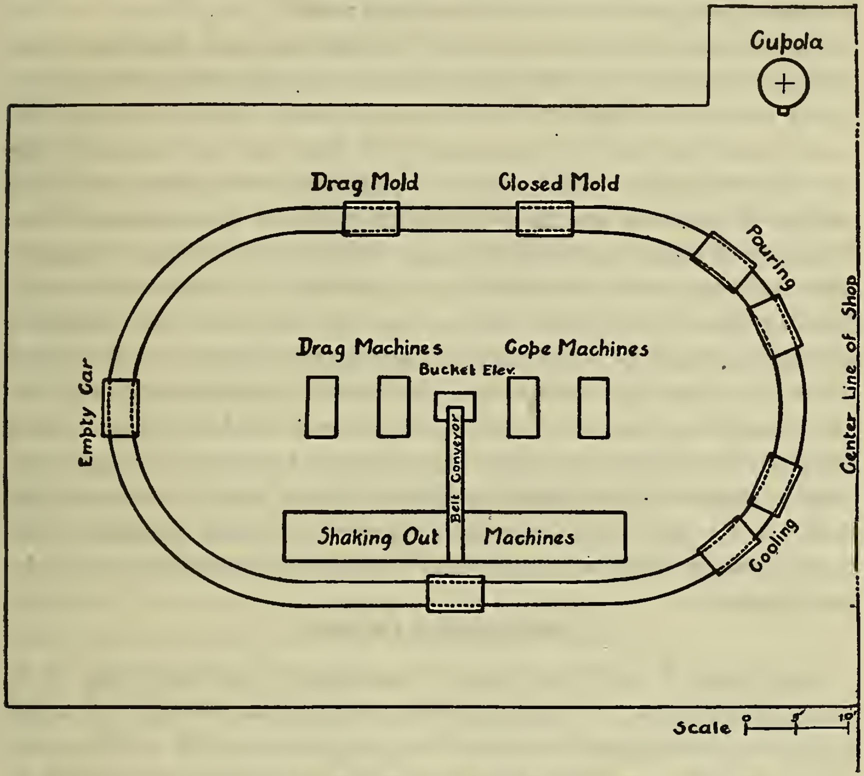

FIG. 3.—*Floor plan of a bathtub foundry operating on a track system*

When completed, the drag molds are carried by the trolley and hoist and placed on a four-wheeled car on the side of the oval track toward the cupolas. This car is run down opposite the corresponding cope mold machine, and as soon as a cope mold is completed it is closed over the drag. The completed mold is run down on to the end of the oval in front of the cupolas and, when three or four have accumulated, they are poured. After the iron has set, the molds are run around opposite the proper cope machine. The cope flask is picked off by a trolley and hoist and carried over to the machine, any adhering sand being knocked out while it is suspended over the shake-out pit. Next, the tub is picked off and carried to the cleaning room. The car is then pushed forward to a position opposite the proper drag machine; the flask, bottom board and overlying sand are lifted over the shake-out pit, and dumped. The flask and bottom board are then carried on to the drag machine. As sand accumulates in the shake-out pit, it is wet down and is well tempered by the time it reaches the sand bins. The empty car is pushed up a slight incline, around the end of the oval, to the receiving position for another drag mold.

In this system more men are worked on each machine than in the crane system, and the number of tubs produced from a given number of patterns and flasks is much larger. As high as 75 tubs can be made in a 10-hour shift from one pattern with the use of five flasks. The cost of equipment and power per unit output of ware is less in this system than in the crane system. The cost of labor is about the same, with a possible advantage in favor of the track system if it is operated at highest efficiency. The drawback with the track system is that it is very difficult indeed to coordinate the various operations of such a large group of men so that they all fit into the desired schedule properly. If one man slows down in his work, he delays the whole group. This difficulty is also present in the crane system but not to so great an extent, since only four men work in a group, and if one group is delayed it does not necessarily hold up other groups. The track system has been put into successful operation in only a few plants.

3. COMPOSITION OF IRON

Any kind of cast iron can be enameled, provided that it is mechanically clean. Therefore the composition of the iron used is generally dependent more on the requirements of the foundry than of the enameling room. A mixture is required which is fairly fluid when hot, so that it can be used to pour castings of large area and thin section, and one that produces castings free from blowholes and slag pits.

(*a*) SILICON.—Since high-silicon iron costs more than low-silicon iron, the foundryman desires to keep the silicon as low as possible. The lowering of the silicon content tends to produce close-grained, white iron, low in free carbon or graphitic carbon. From the standpoint of enameling this is an advantage, for, other things being equal, cast iron low in graphitic carbon gives less trouble in enameling than iron high in graphite. There is always a tendency for the graphite to reduce any metallic oxide with which it comes in contact, and to be converted into carbon dioxide gas, which causes blisters. In fact it was once believed that white iron was the only kind suitable for enameling.[101] On the other hand, low-silicon iron does not run large, thin castings well, unless poured very hot, and many of the castings contain minute slag pits. Quite commonly these pits are almost closed, being connected to the surface of the castings by a very minute hole, almost invisible to the naked eye. If not discovered and punched open, each of these pits will be the cause of a blister, due to the expansion of the air it holds, when the casting is being enameled. In practice, the silicon content of castings to be enameled varies from 1.5 to 2.5 per cent.

(*b*) PHOSPHORUS.—Phosphorus produces fluid iron that runs well in thin castings. The higher the phosphorus the lower the silicon content can be. On the other hand, when the phosphorus content rises much above 1 per cent in cast iron, it tends to produce weak castings. The phosphorus content of cast irons in this country is largely a matter of location. The pig irons produced in the northern part of the United States are low in phosphorus, about 0.5 per cent, and the castings produced there are correspondingly low in that ingredient, averaging from 0.5 to 0.65 per cent. The pig irons produced in the southern Apalachian States are high in phosphorus and the castings for enameling produced from these are consequently higher in that element. When northern and southern pig irons can be had at the same price, a mixture giving about 0.8 per cent phosphorus is very satisfactory.

(*c*) MANGANESE, SULPHUR, AND CARBON.—The manganese content of American pig irons is rather definitely fixed by the available ores at about 0.5 per cent. This is fairly satisfactory, although a little higher manganese will give stronger iron. Sulphur should, of course, be kept low, since high sulphur causes misruns in the foundry and produces castings that are full of slag holes and very brittle. It should never exceed 0.1 per cent. The carbon content is controlled by that of the other elements and so is not specified. The total carbon usually runs about 3.5 per cent.

J. Grunwald [102] gives the following limits for cast iron for enameling according to German practice:

	Per cent
Silicon	2
Phosphorus	1.4–1.8
Manganese	.5–.7

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[101] Only recently H. Vogel has advocated the use of a layer of white iron on gray for enameling purposes. Keramische Rundschau, 23, p. 109; 1915.

[102] Stahl und Eisen, 30, pp. 1201–1206.

The composition of castings used in enameling shops in this country is about as follows:

	Per cent
Silicon	1.50–[a]2.50
Phosphorus	.50–.60
Manganese	.40–.60
Sulphur	.04–.08

In plants using southern iron, the compositions will run about the same, except that the phosphorus will vary from 0.75 to 1.25 per cent.

While, as has been said, almost any kind of iron can be enameled, it is very important from the standpoint of the enameler that the grade of iron used in the foundry be kept uniform. The harder cast iron is—that is, the lower in silicon and the higher in sulphur—the greater is its coefficient of expansion. Since increase in coefficient of expansion of enamels is generally secured by increasing the percentage amount of fluxing oxides, it is a general rule among enamelers that the harder the iron the softer (or more fusible the enamel must be. If the hardness of the iron in the castings coming from the foundry varies, trouble is likely to arise from chipping or crazing in the enameling room.

XIII. CLEANING-ROOM PRACTICE

In the cleaning rooms the castings are freed from sand by brushing and sand blasting, and are ground and filed until they are clean and smooth, especially on the surfaces to be enameled. In many plants the annealing or "burning out" of at least part of the ware and the welding of cracked castings is done by the cleaning-room force.

1. BRUSHING

Small pieces that are not to be enameled, such as tub feet, brackets, hangers, etc., are cleaned in ordinary foundry tumbling barrels. The larger pieces are generally brushed with wire scratch brushes to remove loosely adhering molding sand. The removal of this sand does not materially facilitate sand blasting, except as it greatly reduces the amount of dust in the sand-blast room, and enables the men there to work with greater comfort and speed. It is a humane measure that pays for itself. However, brushing of castings is omitted in some plants, the ware being taken direct from the foundry to the sand-blast rooms.

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[a] Generally about 2 per cent.

2. SAND BLASTING

Owing to the large size of the pieces to be cleaned and the great variety of shapes, automatic sand blasts have not come into general use. Several attempts to employ these have been made, especially for tubs, but at present most tubs and other wares are cleaned by ordinary, hand-operated sand blasts.

A sand-blast room usually consists of a chamber about 10 feet square, lined with cast-iron or sheet-steel plates at least to a height of 5 or 6 feet. The sand-blast machine is placed in one corner. The ware to be blasted is generally piled on a grated floor but tubs are often placed on a small turntable while being blasted. Beneath the grating is a semiconical chute which feeds the used sand to a bucket elevator, which delivers it to coarse inclined screens from which in turn it runs to the sand hoppers over the blasting machines. An exhaust pipe, connected to a powerful fan, leads from the room at some point, usually from above the ware that is being blasted.

Of course there are many variations of this arrangement. The sand-blast machine may be placed underneath the blasting rooms, thus avoiding the use of an elevator. In another system the exhaust used is so strong that the bulk of the used sand is sucked up. The grains coarse enough to be used over again are separated in a dust collector located above the level of the sand-blast machine and returned to it by a chute. This is not an economical method of elevating sand, but the strong exhaust is a great aid to working conditions in the blasting room. Of course in the typical arrangement it is not necessary to have the machine in the room. In fact, for ease of repairs, filling, etc., it is better to locate it just outside the wall of the blasting room. If it is placed too far away, there is difficulty in returning the used sand to it.

Two men generally work at a sand-blast chamber. One does the actual blasting, while the other trucks the ware in and out and attends to the sand supply. Occasionally they exchange places in order to give the blaster some relief from dust. In addition to an exhaust for removing dust from the blasting chamber, the operator is usually protected by a helmet with a cloth curtain hanging down all around on to his shoulders. In front of the eyes, this curtain is supplied with a glass, celluloid or fine wire gauze window.

Glass and celluloid rapidly become frosted and nontransparent from the action of flying particles of sand. Moreover, glass is apt to break and to blind the workmen. Gauze lasts longer than either glass or celluloid and generally is preferred by the workmen. Over his mouth and nostrils the blaster usually wears a damp sponge, either in one of the rubber holders called respirators or tied on by a handkerchief. Most men find the respirators too heavy and clumsy for comfort and prefer the handkerchief. Quite often arrangements are made to run a hose into the top of the helmet to supply the blaster with fresh air. This hinders him in his work, and he usually discards it.

There is no question but that sand blasting, as usually conducted, is injurious to the health of the operator. The workmen are very subject to pulmonary diseases. The difficulty of affording them the proper protection is increased by the fact that they are generally ignorant men working on the piecework basis and will not take precautions that interfere materially with their earning power, or that cause them temporary inconvenience. Payment by the day improves the situation slightly as regards the health of the workmen but cuts down the output of work very greatly. The nature of the work and workrooms precludes careful supervision, and the class of laborers available will not give a good day's work unless under the eye of a foreman. The devices used for protecting the men must be simple and foolproof. In addition to those already described, mention may be made of the use of an air curtain and steel sand.

The air curtain is a European device. It consists of a sheetlike blast of air shot in from a slot in the floor in front of the operator and sucked out of a similar slot about the level of his head by an exhaust fan. This curtain overcomes the objections to all cloth curtains, that they interfere with rapid blasting and movement of the ware. It must be remembered that it is often necessary to turn a single piece into three or four positions during the blasting operation. The writer does not know of an air curtain ever being used in this country, but if it can be maintained properly it certainly should be an efficient protection to the workmen. It would seem that it would be easier to maintain an air curtain over a smaller area than the side of a sand-blast room. This could be arranged by having the ware run on cars through a cabinet, one side of which, above the level of the car floors, would be an air curtain. All turning of the pieces could be done outside the cabinet. Of course it would be possible to turn the pieces by reaching through the curtain.

A very successful means of reducing the dust in sand blasting which is now employed in several plants is the use of a mixture of crushed steel and round steel shot. It has been found in practice that the use of round steel shot alone tends to peen the iron, closing the pores, and that crushed steel alone does not clean off the sand effectively. Mixtures of the two do very effective cleaning without closing the pores of the iron. Various mixtures are used. One that is quite satisfactory is composed of two-thirds crushed steel that passes a 10-mesh and remains on a 20-mesh sieve and one-third of round shot that passes a 20-mesh and is retained on a 40-mesh sieve. When the castings are well brushed before going to the blasting room and a strong exhaust draft is kept up, the dust in the sand-blast room is very slight, indeed, compared with what it is with even the best sand. While the steel sand costs much more per ton than silica sand, it lasts so much longer that it is cheaper in the end. In addition, the expense and bother of handling and drying large quantities of sand are eliminated. The use of this material seems the most practical way of reducing the dust menace in sand blasting large castings.

Various types of sand-blasting machines are used. The most popular for this class of work use low-pressure air, 20 to 60 pounds, but a few machines employing air at 80 to 100 pounds are used. In general, it may be said that the less complicated the construction of the machine the more satisfactorily it works.

The collection of the dust drawn out of the blasting chambers is often quite a problem. This dust is always a nuisance and if carried into the enameling rooms is a serious cause of loss. Attempts have been made to collect it by blowing it through water or through spray chambers, but these have not been satisfactory. The fine particles of dust seem to be covered with an envelope of air that keeps them from being wetted readily. A stream of dust will rise through several inches of water and float away. One method that has been employed[103] is to blow the dust into the bottom of a tower about 20 feet high, 5 feet wide at the bottom, and 3 feet wide at the top. Near the top of the tower, which is open, a steam jet is directed downward. As the dust rises, the steam condenses on it and precipitates it.

A cleaner method and a more commonly used one is the collection of the coarse dust in ordinary dust collectors and the fine dust on a series of cloth screens. The dust is jarred loose from the

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[103] Underhill, Dillan, Foundry, 35, p. 266.

screens once a day and carted away. If this sort of installation is large enough, practically all the dust can be collected.

3. GRINDING AND FILING

After the ware is blasted, all fine and rough protuberances are ground off. For this work stationary, swinging-frame, flexible-belt, and portable grinders, operated by air or electricity, are employed. Carborundum stones are commonly used. In some shops machines working on the principle of a planer are used for grinding the rims of tubs. Machines of this type are sold by various grinding machinery makers and a homemade one is described by Underhill.[104]

Next the tub is filed and rubbed with carborundum stones until every part of the surface to be enameled is smooth and free from sand. Any small spot of grease that may have fallen on a piece is removed with a rag dipped in gasoline. If the spots are large or numerous, the piece is given a second light blasting. In hot weather it is advisable to reblast all ware after cleaning, for the soluble salts in the perspiration that gets on the ware from the hands of the workmen are liable to cause blistering of the ground coat during the enameling operations.

4. WELDING

When the amount of ware produced at a plant is large, it pays to have an oxy-acetelyne or an oxy-hydrogen welding outfit to mend small cracks, slag holes, and cold shots in castings.

5. ANNEALING OR BURNING OUT

It has long been known that if castings are heated to bright redness before they are enameled they are less likely to crack in the enameling furnace and the tendency for the foramtion of blisters is greatly reduced. This process is sometimes termed "annealing," but the shop phrase "burning out" is more expressive, since the chief object is to burn out sulphur, iron hydroxide, grease, and other impurities that cause blistering during the enameling. A few plants burn out all castings, but most of them compromise by burning out only rusty and greasy castings all the time and all pieces whenever excessive blistering due to "dirty" castings develops. In some cases the burning out is done before the tubs are blasted. This obviates a second blasting with most of the castings, but burnt-out tubs are harder to blast than green ones.

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[104] Foundry, 35, p. 268.

The better way is to clean and file the ware ready for enameling and then burn it out. It then goes to the sand blast for a second blasting and thence direct to the enameling room. Any pieces that have stood in a damp atmosphere for a few days after blasting should be burned out, even though they do not look rusty, for rust forms in the pores of the iron and causes blisters during the enameling. Likewise all pieces on which plumbago or other facings have been used must be burned out. In order to get rid of all blister-forming ingredients, the burning-out temperature should be approximately that of enameling.

As explained in the discussion of crazing, the burning out of castings has a decided effect on their contraction when cooling after being enameled and therefore on the tendency of the enamel to craze or chip. Burned-out castings require an enamel with a higher coefficient of expansion, in general a softer enamel, than green castings do.

XIV. THE ENAMELING PROCESS

1. APPLICATION OF THE GROUND COAT

After being cleaned, the castings should be kept in a dry, warm place until ground-coated, which should be done within a few hours. The ground coat can be applied by painting, pouring, or spraying. In painting, a ground-coat composition of about the consistency of thick gravy is spread over the surfaces to be enameled by means of flat painters' brushes. Four-inch brushes are used for tubs and 2-inch for small ware. The brush marks are likely to show through the enamel, especially if the piece is heated strongly during the firing of the ground coat of enamel. The heat causes incipient blistering and swelling of the heavier ridges left by the brush. For this reason painting of ground coats is not extensively practiced. Sometimes when certain parts of a piece are to have an especially thick coat, these are painted before the piece is poured or sprayed.

In pouring, enamel of about the consistency of cream is poured over the casting. If the piece is small, it is turned in various positions and rocked backward and forward on two rods extending over a drip tub until the ground coat is smooth on the surface of the whole piece. The thicker beads, that accumulate at the edges, are removed by running a finger along them.

In the case of tubs and other large pieces the ground coat is poured on as uniformly as possible, then the piece is stood in various positions and pounded with a rawhide mallet. The vibration tends to cause the coat to run smooth. When done by a skilled man, working with ground-coat enamel of proper consitstency, coatings of very fair uniformity can be produced by pouring. It is a more rapid method than painting but not as rapid as spraying.

It is by spraying that the most uniform coats are applied, and at the same time with the greatest speed. The spraying devices are operated by compressed air, various types being sold for the purpose. In addition, a number of kinds of home-made sprayers are used in different plants. In general, it has been found that sprayers which depend on suction for their supply of coating give finer-grained and more uniform sprays than those depending on pressure. The sprays should be as fine grained as is consistent with reasonable speed of operation. The ware usually is placed on a turntable while being sprayed. In some shops, small ware is sprayed on a regular small-ware enameling table.

In spraying only one-third to two-thirds of the material coming from the spray nozzle lights on the ware. Therefore, the spraying space should have a smooth wooden floor and smooth wooden walls on three sides. If the castings are clean all over before they go to the spraying cabinet and the workmen do not carry in dirt on their feet, the ground coat on the floor and sticking to the walls may be gathered up, sieved, and used over again. Dust from cement or brick walls and floors is liable to contaminate the ground coat.

If an exhaust fan is used to carry away the vapors from the spray chamber, a large box or collection bin should be placed in the pipe line. This will act like a dust collector and most of the material carried away will be deposited. It is best not to try to use this recovered ground coat alone but to mix it in small proportions with fresh coat.

The following simple device for conserving labor and material in the spraying of tubs is in use in several plants. The tub is run on a truck into a three-sided wooden stall having a runway around the top of the sides, which extend a few inches above the rim of the tub. The operator walks around the tub on this runway, spraying as he goes. The waste material is caught by the sides of the stall and can be reused.

After being ground coated the ware must be kept until enameled in a dry, warm place in order to avoid incipient rusting of the iron. This time should be brief, 24 hours at the most. Usually the pieces are stored near the enameling furnaces.

2. ENAMELING-ROOM EQUIPMENT

The enameling room is usually rectangular in shape with furnaces along one side. This room should be well lighted and ventilated and have a high roof, the lowest girders being at least 20 feet from the floor. A high roof not only makes a better ventilated room but reduces the amount of enamel powder and dust that lights on the girders and drops or is blown down from time to time. Latticed monitors and in fact any kind of ventilators that can retain dust are also objectionable. The overhead girders and underside of the roof should never be whitewashed, as the coating peels off and spoils any hot enameled surface on to which it drops. When furnaces are built on both sides of the room it is likely to be dark and is always very hot.

(*a*) FURNACES.—The furnaces used for enameling cast iron are large rectangular ovens with an arched roof and a wide door at one end. If coal is used for fuel, the sides and arch are built double, forming a tight muffle. If gas is used, the inner arch is sometimes omitted, thus making a semimuffle. For tubs the inside dimensions of the muffles are about 9 feet long, by 6 feet wide, by 5 high to the crown of the arch. Small-ware furnaces are made about 6 feet square by 4 high, inside dimensions.

Various types of furnace are used, most of the variations being made in the flue systems. Very elaborate flue systems have been embodied in furnace construction with the idea that the longer the length of travel of the flue gases in the furnaces the greater the amount of heat given up. This of course is not necessarily true. These elongated flues are generally placed in the roof and sides of the furnace, which receive large amounts of heat by radiation and conduction from the muffle and heating flues proper, and it happens often that the combustion gases leave the flues at a temperature fully as high as that at which they entered. In other words, heat can not be withdrawn from hot gases by leading them through heated flues. In other cases, these flues are placed farther away from the hot parts of the kiln and nearer the outside surfaces. The gases then leave the flues at temperatures somewhat lower than the entering temperatures. However, the heat given up simply goes to heat portions of the kiln exterior that are normally cool and to increase the radiation from these. The only way possible to extract heat in useful form from hot flue gases is to use the hot gases for heating the air used for combustion by means of some form of regenerator or recuperator.

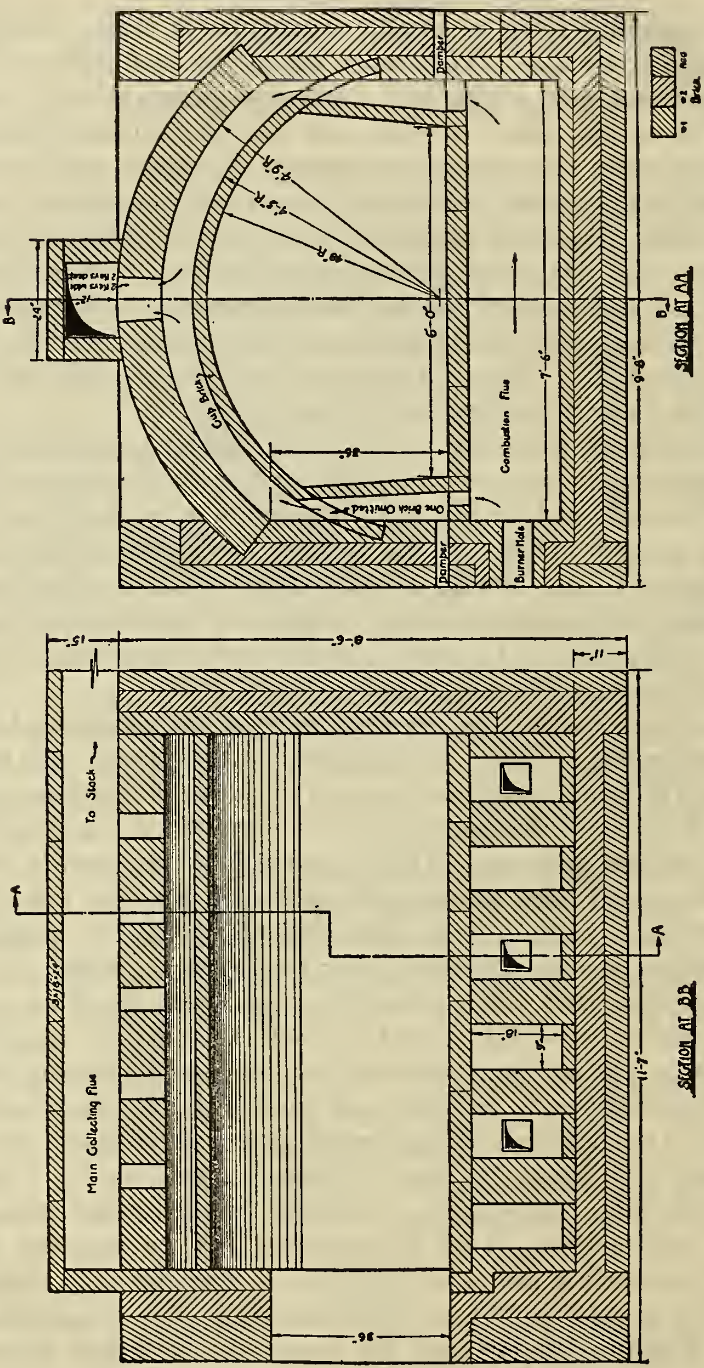

FIG. 4.—*Direct-fired muffle oven*

In general, it may be said that the simple types of furnace give the greatest satisfaction. Complicated flue systems are prone to result in poor draft and frequent stoppage of flues with soot. The more complicated the construction of a kiln, the greater is the probability of it going to pieces under the strains incident to expansion and contraction of the furnace on heating and cooling. Complicated furnaces are expensive to build, difficult to operate, and expensive to keep in repair.

In Fig. 4 is given the plan for a tub furnace that has been used with good results in several plants. Part of the flame from each burner goes directly up along the wall and over the top to the central collecting flue. The main portion passes under the floor, up the opposite side, and over the top to the same collecting flue. The distribution of the flame is controlled by the dampers. By using a short flame most of the heat is generated under the bottom and in the lower ends of the side flues, and the products of combustion enter the collection flue at a comparatively low temperature. The material for this furnace can be had at reasonable prices, since the construction calls for no special shapes, except the cup bricks for the muffle, and these are used in large quantities by the enameling and other industries. As shown, the furnace is intended for the use of natural gas, producer gas, or oil. The burners are placed alternately on the sides of the furnace. When used for coal, fire boxes are added at one side, each fire box serving two flues, and all the firing is done from the one side. By removing the top arch of the muffle, this furnace can be converted readily into an open arch, or, in other words, a semimuffle furnace.

In a few plants double-chamber furnaces of this type are used in which the firing is all done on one side. One part of the products of combustion passes under the floor of both chambers and up the far wall of the second. The other part passes entirely over the top of the first chamber, through the division wall near the floor level and up the inner side of the second chamber. The first chamber is always a tight muffle, but the second usually is operated as a semimuffle furnace. The final melting of the ground coat and all baking of enamels is conducted in the first chamber, which is kept at ordinary enameling furnace temperatures. The second chamber, which usually is at a dull red heat, is employed for preheating the tubs, covered with ground coat, to dull redness.

From a double furnace more pieces can be turned out in a given time with less expenditure of fuel per piece than from a single furnace. However, since the double furnaces save nothing in labor, this rapid rate of working is very severe on the workman and often causes dissatisfaction.

Another type of furnace which has come into use in a few plants burning gas or oil has no fire boxes. Flames are turned directly into the furnace chamber so as to heat it to a temperature suitable for enameling. The supply of fuel is then shut off and the tub is enameled simply by the radiant heat of hot furnace walls. As soon as the tub is removed from the furnace the flames are turned on again. This type of furnace is cheap to construct and very economical in the use of fuel.

In Europe, where fuel is very expensive, a number of types of enameling furnaces equipped with recuperators have been built. A few such furnaces have been constructed in this country after European designs. In Fig. 5[105] are shown the plans of a European furnace with a recuperator built integral with it. It will be noticed that the large firebox is, when covered with a very thick bed of fuel, really a gas producer. This feature is one of the chief advantages of such furnaces. The air for combustion of the gases produced travels around the tubes of the recuperator and is preheated by the outgoing combustion gases. According to Damour[106] recuperation of secondary air for furnaces with a working temperature of 1800° F will give a fuel economy of 30 per cent over direct firing. These furnaces give good satisfaction, but it is a question how much of this efficiency is due to the recuperative feature and how much to the gas producer and heavy, heat-retaining construction in general. The first cost of these furnaces is quite high, usually about double the cost of a simple direct-fired furnace.

The fuel consumption of any of the foregoing furnaces can be materially decreased by covering them with a layer of some of the heat-insulating materials now on the market. In regard to irons and braces, it can be said that the more substantial these are the less the cost for repairs to the furnace. In regard to the use of open arches versus tight muffles it is to be considered that while open arches call for much less fuel than closed arches, their use is more likely to give ware of poor finish and contaminated with dirt from the roof of the furnace.

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[105] Schott, E. A., Stahl und Eisen, 30, p. 1556.

[106] Damour, Emilio, Industrial Furnaces, p. 127.

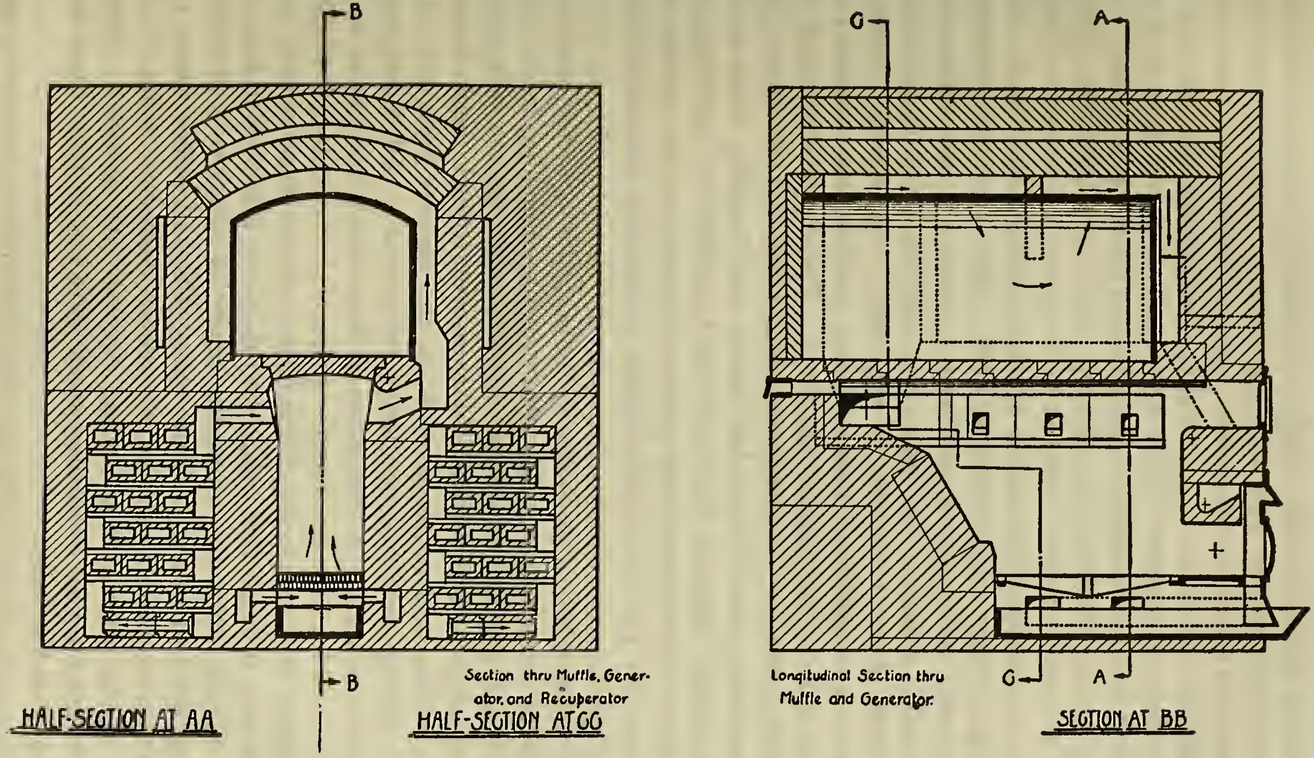

FIG. 5.—*Muffle oven with recuperator system*

The doors to the furnace may swing sidewise, rise, or drop down. Swinging doors, whether single or double, suck out hot air when opened and push in cold air when closed. Lift doors are liable to cause dirt to be dropped onto a piece of ware being taken out of or put into the furnace. Dropping doors are the cleanest and do not cause air currents. The only disadvantage is that it is not possible for the enameler to open them a little way in order to observe a piece of ware in the furnace. Of course, opening a door to look at ware is merely a matter of habit and convenience, for the piece can always be inspected through a peephole left in the door. Rising doors are most commonly used. In most plants compressed air is used for operating tub-furnace doors, a simple hoist with a wire cable running over sheaves being the common apparatus. In some plants electricity is employed. Occasionally power is used to open small-ware furnace doors, but the more common practice is to have them opened by hand. Power-operated rising and dropping doors are counterpoised so that they are self opening, the power being used simply for closing and keeping them closed. This greatly reduces the mechanical problem of operating the doors and at the same time gives assurance that the furnace will be open for the extraction of ware if anything goes wrong with the power.

(*b*) SUPPORTING THE WARE.—The ware, while being enameled, is placed on a rack or table known as an enameling table. This is fitted with gears and levers which permit the top being tilted at any angle to the perpendicular, or even turned upside down in some types, and revolved while in the various positions. Any good master mechanic can design such a table and consequently many varieties are in use, most of them being indigenous to the shops in which they are found. In general, the tables are tilted on the main horizontal axle of the frame and revolved around a pin extending through this axle. In tables not intended to have the top turned completely over, the center of rotation is placed between the two bearings of the main axle. In tables whose tops are to be completely reversed, the center of rotation is placed on an end of the main axle extending beyond both bearings. Similar tables are used for enameling small ware but in most cases these are operated by hand.

Formerly a hand crank was used for rotating enameling table tops, but in the more modern plants the tops are rotated by power. One type of table uses a reciprocating air motor, which produces a rotary movement by means of a series of cams articulating with gears. Such tables are jerky in their action. A much more satisfactory method is the gearing of a rotary air motor or small electric motor to the mechanism ordinarily used for rotating the table top by hand. The top should rotate at a speed of 10 to 20 revolutions per minute. With an air motor the speed can be largely regulated simply by the amount of opening of the foot valve used. The tilting is still commonly done by hand but in a few shops this is done by the use of a small air hoist and suitable sheaves and pulleys.

For supporting the ware in the furnaces while being heated, various sorts of racks, called "bucks," are used. These are generally made of heavy sections of cast iron. Sometimes old railroad rails are used for bucks for tubs and, less frequently, blocks of fire clay. The latter do not warp nor deteriorate by oxidation like metal, but are difficult to shift about into proper positions in hot furnaces. The best form of buck for tall cylindrical pieces, such as lavatory pedestals and drinking fountains, is a heavy base with an extension curved so that a long finger points horizontally toward the door of the furnace. The pieces are fired on this finger and, being in the horizontal position, are heated much more uniformly than when fired in an upright position.

The ware is put into and taken out of the furnaces by long, two-pronged forks, which are suspended either from a crane or from a trolley running on an I-beam. Sometimes dirt drops off the I-beam into ware, but the trolley system is steadier and easier to handle than the cranes. In a few plants the forks are pivoted on a truck running on tracks extending out from the front of the furnaces. This is a clean system, but does not permit of ready adjustment of the fulcrum point of the fork to ware of different heights.

(*c*) APPLICATION OF THE ENAMEL.—Enamel powder is kept more free from dust and is more readily obtained by the operators working at high speed while enameling, if it is kept in a covered receptacle from which it can be made to feed semiautomatically in fixed quantities into the enameling sieves or dredges. Such contrivances are generally known in the shops as "powder dummies." One form of dummy consists of a large funnel with a drum at the bottom divided into six wedge-shaped compartments. The drum rotates on its horizontal axis and, except at the bottom and top, is entirely incased by close-fitting walls. Whenever the contrivance is not being operated, one of these compartments forms the lower end of the large funnel. When he needs enamel powder, the operator pushes with his sieve on a rod reaching below the drum, the movement of this rod operates a pawl which causes the drum to rotate one-sixth of its circumference. In this way one of the compartments is emptied into the sieve.

A much more simple form of dummy consists of a large circular funnel with a tubular extension on the bottom. This extension is closed by a swinging slide with a weighted projection at the bottom. To operate this dummy, the enameler pushes with his dredge on the weighted projection. The slide is thus pushed back and the sieve brought into position under the tube, the enamel in the tube immediately dropping into the dredge. When the pressure is removed, the weight on the projection causes the slide to close. The enamel in the funnel proper slowly drops down to fill the tube again. This simple contrivance is much less likely to get out of order and costs less for repairs than any of the more complicated dummies.

For protecting tubs from drafts during cooling, covered stalls, called "dog houses," just large enough to hold one tub on a truck, are provided. The front of these stalls may be open or may be provided with loose-fitting doors. Tight doors do not allow a tub to cool fast enough and thus favor the growth of minute crystals on the surface of the ware, which cause dull finish. These stalls may be built of any solid material. Sheet iron is not suitable, especially for the roof. The light sections of metal buckle with heat from a hot tub and throw dirt on to the still soft enamel. It is not customary to use cooling chambers for small ware.

The dredges used for sifting the enamel on to the ware consist of circular sieves attached to handles about 5 feet long. In order to have the enamel pass through the screen in an even stream, the sieves must be vibrated. In a few shops this is still done by rapping the wooden handle of a dredge with a beater. The beater consists of a small oval hoop of about three-eighth-inch round iron having a wooden handle fastened to one end. The oval is placed around the handle of the dredge and worked rapidly up and down by the right hand of the enameler while the dredge is held by his left hand, and, in the case of large sieves, partially supported by a counterpoise.

The more common method of vibrating dredges is by means of a small air or electric vibrator attached to the end of a gas-pipe handle on the dredge. The common form of air vibrator is a small chipping hammer with a blunt point substituted for the chisel. This may be a long rod with its tapping end beating against a plate attached to the wall of the sieve, or it may be very short and beat against a hardened disk held in a case at the end of the dredge handle. Since the whole dredge, including the handle, must be vibrated in either case, the point of application of the blows is obviously immaterial. Electrically operated vibrators of several types have been used but they have not proved as satisfactory as the air hammers. The introduction of mechanical vibrators for enamel dredges has been a great boon to the enameling industry. They enable the workmen to produce more and better ware with much less effort. Formerly, paralysis of the hand used for beating was not uncommon among enamelers. For hand-vibrated dredges, 30 to 40 mesh wire gauze is used, while for power-vibrated 40 to 60 mesh is employed.

3. ENAMELING A BATHTUB

Having previously been coated with ground coat, which must be perfectly dry, the tub is caught up along the under side of the rim by one of the large forks, operated by the two enamelers, and placed in the furnace. In from 7 to 10 minutes, the iron is a bright, cherry red, and the ground coat has melted evenly. The piece is quickly withdrawn and placed on the revolving table. One man sifts enamel onto the rim through a small sieve while the other man coats in the same manner the sides and bottom. The heat of the iron fuses the enamel enough to make it stick to the surface. In about three minutes the piece is covered thoroughly, and immediately is put back into the furnace. In a few minutes the enamel has melted smooth, and the tub is drawn and given another coat. This runs smooth in a few minutes, and the piece is again drawn. Any blisters appearing are patched by being perforated by a steel point and covered with a little mound of enamel powder. The tub is given a third light coat and allowed to bake. It is then drawn, any enamel that has run over the edge of the casting is trimmed off with a large knife, and the piece is allowed to cool in a "dog house."

The proper enameling of a tub is a matter of considerable skill and judgment. Each dredge must be evenly distributed over the piece. If it is too thin in places, blue spots will show on the finished ware; if too thick, crazing or chipping of the enamel may occur. One fault especially difficult to avoid is the tendency of the enamel to run and collect in rolls or beads at certain points.

This spoils the appearance of the piece and very often results in crazing when the tub cools.

The temperature at which practically all tub enamels mature is very close to 1000°C (1800° F). It may not be much higher, for cast iron heated much above 1000° C (1800° F) in an oxidizing atmosphere becomes exceedingly weak and brittle. It can not be much lower, on account of the increased cost. An enamel that would mature in a commercially feasible time at a much lower temperature would have to be considerably higher in the more expensive fluxes. Another important consideration is that an enamel which would mature at a lower temperature would be a softer glass, more readily soluble and more liable to deteriorate under ordinary conditions of use.

Though the enamel matures at 1800° F, the furnace is fired to a considerably higher temperature. The temperature is kept down by the process of enameling. Every 30 minutes, or thereabouts, a cold tub weighing 200 to 300 pounds is put in, heated to 1800°, drawn out three times, allowed to cool considerably and heated up again after each cooling. This process keeps the furnace and the men busy, insuring a maximum output of ware, but it calls for skill and watchfulness on the part of the enameler. Each coat of enamel is baked very quickly; it is melted down in from two to five minutes in a rapidly rising heat. Exposure for a minute too long in the furnace during any one of the four heating periods may ruin the piece. The defect may be burning up of the slush coat, sulphur bubbles, running off of the enamel, etc. If the tub is not heated sufficiently, the result will be pinholes in the coldest parts, and a rough, uneven coat, of poor luster.

After the tub is cold, it is carefully inspected as to defects in application and fit of the enamel, color, luster, etc. Minute crazes are readily detected by rubbing the surface with a rag filled with black grease. The tub is then painted on the outside, supplied with feet and fittings, and taken to the ware room.

WASHINGTON, July 24, 1919.

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