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ENAMELS

The Preparation, Application, and Properties of Vitreous Enamels

BY

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are very satisfactory; compositions eight and thirteen having been checked by the author.

Summarizing these compositions for jewelry and copper enamels, the chemical composition shows them to be essentially lead silicate glasses with small additions of the alkalies. They are, in general, opacified with about five and one-half per cent of arsenic oxide.

In some experiments, the author has had considerable success in the enameling of copper with regular sheet iron cover enamels. The opacity of these enamels is not as strong as that of the regular copper enamels, but they have the advantage of cheapness and freedom from lead and arsenic. No ground coat was used, but two coats of the cover enamels were necessary to develop a good white. The compositions in the center of the field illustrated in Figure 62, specifically, numbers five, six, nine, ten, and eleven, were very satisfactory.

CHAPTER 8

Frit Making

Although antiquated methods for making frit are still used in many plants, the more modern concerns have developed highly efficient equipment and methods. The enamel frit manufacturing companies have been foremost in this development and the benefits to the enameling industry have been far reaching.

The mechanical methods of handling the raw materials and protecting them from contamination have been highly developed. The weighing, mixing, smelting, and quenching have been put on a systematic, economical basis. Control has been installed wherever possible and the variation of the product brought to a minimum. Frits of uniform chemical and physical properties are now made for practically every type of enameling, and the plants which are unable to produce their own frits economically can buy them from the larger concerns.

Frit making may be divided into three divisions: raw material preparation, smelting, and frit handling. A flow sheet of the principal operations is shown in Figure 64. Control methods are not shown, but they are essential and will be discussed as each operation is considered. Magnetic separation of iron particles may follow either weighing or drying or both.

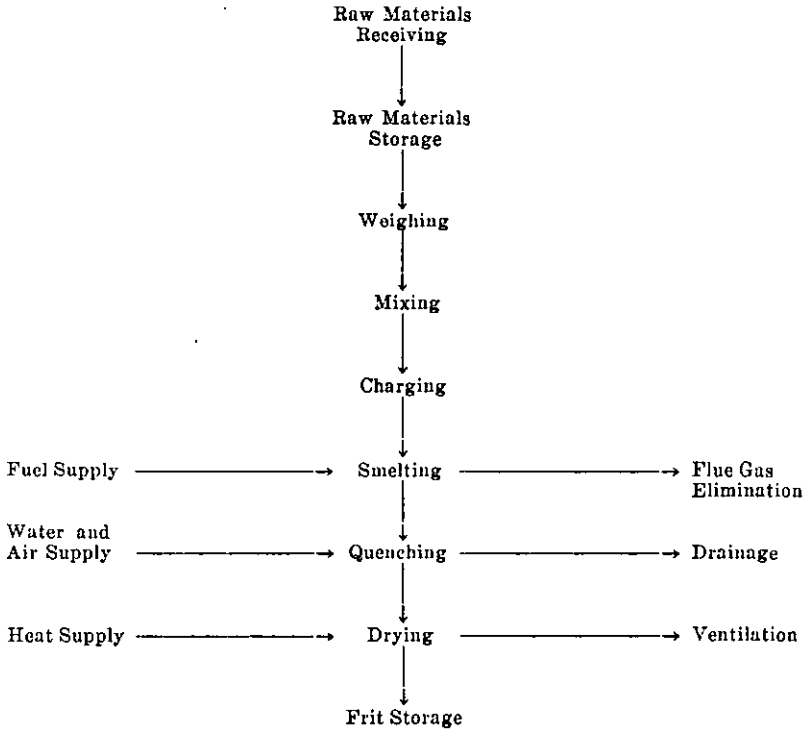
Receiving and Storage. The chemical manufacturers have co-operated with the enameler in shipping the raw materials in a manner that will aid his handling. Most of the materials are received in bags or barrels which permit ready mechanical or manual handling and storage. Where the production is large, bins holding one to two carloads are used. These are made in the shape of hoppers, which can be discharged from the bottom where the batch is weighed. Mechanical elevators are used to raise the materials to the charging floor over the bins, and manholes in the floor serve to charge the bins. Such materials as quartz, borax, feldspar, fluorspar, and cryolite can be handled in bulk, provision being made to keep them from "hanging up" in the bins. Most chemicals can be bought to advantage in carload lots, which gives the large consumer quite an advantage. The chemical control of these raw materials, which involves chemical analyses, is also considerably simplified where large shipments are received.

Where the use of bins is not feasible, the bags and barrels are stacked in the storage room where they are convenient for batch-

making. Monorail conveyors are often used to aid the stacking and weighing of these packages. The batch scale itself is often mounted on wheels so that it can be moved from place to place as the different materials are weighed. Where the storage and batch-making equipment are well arranged, it should be possible to make up batches of eight to ten chemicals in about ten minutes.

FIGURE 64

FLOW SHEET FOR FRIT MAKING



In a modern handling and storage department the bins are arranged in a straight line with space below for the batch-making equipment. Such an arrangement aids in keeping the enamel formula secret as it permits the weighing to be done by bin number rather than by material.

The discharge doors of bins used for the raw materials are located at the bottom and must be so constructed as to give perfect control of the flow. If the material "hangs up" in the bin, it may fall with a rush and, if not controlled, will force itself out through the discharge.

Weighing. The making of the enamel batch requires a careful, dependable, intelligent workman. It is often necessary to intrust this man with the formulæ and few concerns care to have their enamel compositions known to their competitors. To avoid this, numerous methods are resorted to. The use of numbers rather than the names of the raw materials has already been mentioned, but such a method is subject to criticism. A man familiar with the appearances of the different materials can identify them, or they can be identified by simple chemical tests or comparison. The system of making two batches by different men and mixing them together is cumbersome and expensive. If the two men compare notes they can figure the formulæ. The method of weighing the bulk of the batch in the weighing room and a small addition of such constituents as fluorspar, cryolite, and small amounts of the bulk materials in the laboratory is fairly satisfactory. This method is often used and, if modified from time to time, will confuse attempts at solution.

The use of the blind scale or the dial scale without numbers is quite satisfactory, especially if the order of the additions is modified from time to time. This method in conjunction with the method of weighing a part of the batch in the laboratory is probably the most secret method, if the man doing the weighing cannot be trusted with the formulæ.

In some modern installations of weighing equipment the actual weighings are recorded by an automatic recording machine, so that any mistakes or carelessness will be exposed. The recording machine is usually locked to prevent tampering and a violation of the weighing procedure is not permitted. On such records even small variations are readily detected, which, if checked, eliminate the human element from influencing the accuracy of weighing.

The scale is usually built on wheels and is preferably moved along a track, which permits the weighing at each storage bin. If a stationary scale is used, the scale should be set in the floor so that the hopper used for weighing is at a convenient height for the addition of the different materials. Either monorails or trucks are used for bringing the materials to the scale.

The weighing hoppers are usually square or round sheet iron boxes with the bottom tapering to an opening about one foot square, which is closed by a sheet iron sliding door. The hoppers are handled by means of an overhead monorail.

Mixing. The mixing of the raw batch is usually preceded by a coarse screening to break up any lumps of material and to eliminate such refuse as wood, string, cloth, or nails, which may get into the materials from packages. Sometimes an electro-magnet is also used. The simplest method of mixing is that of using a hoe and a box similar to the old method of mixing mortar. The more modern methods are: the use of large cylinders similar to concrete mixers, hexagonal cylinders, or horizontal mixers. The horizontal mixers are generally trough shaped, containing a revolving shaft on which are mounted paddles or spirals to mix the materials. The batch is usually fed into these mixers at one end and discharged at the other. The barrel or concrete mixer types are charged with the batch and rotated for five or ten minutes and then discharged.

The complete mixing of the materials in the batch is very important. Since the batch is made up of refractories and fluxes, the speed of reaction during smelting is dependent on a uniform mixture. If good mixing is not obtained, a longer time is required to smelt the batch, since the rate of reaction is directly proportional to the surface contact, and the more intimate the mixing, the more surfaces of contact exist between the particles of the flux and refractories. Good mixing also aids in the development of uniform color and opacity. Enamel glasses are quite viscous, therefore the distribution of different materials after melting is slow and often incomplete. The fact that all of the materials entering the enamel batch are not of the same size, shape of particles, or specific gravity, makes mixing difficult, but good mixing is a great aid to good smelting and should be attained.

The batch, on discharge from the mixer, is received in a hopper and is then ready for charging to the smelter.

Smelting. Although the literature contains very little on the smelting of enamels, it is a very important operation and one which must be carefully controlled.

Smelting involves the melting together of the raw materials entering the enamel composition until a fairly uniform glass is formed. The successful accomplishment of this result is dependent on the thorough mixing of the raw materials, the proper heating, and the distribution of the heat through the batch. Some of the materials entering the batch are volatile, some fuse readily, some decompose readily, and others are highly refractory. The more fusible materials melt first, giving the batch the characteristic of being wet like slush in a spring thaw, thereby hindering the rapid evolution of gases and the loss of the more volatile constituents. These volatiles become occluded

and absorbed by the melt which takes them and the more refractory materials into solution.

The physical and chemical changes taking place in the smelting of enamels are quite complicated and are not entirely understood. The fundamental changes are, however, the interaction of acids and bases, decomposition, fusion, and solution. The exact nature, the degree, and the order of these changes, however, depend upon many conditions, such as temperature, the combinations of raw materials present, and the agitation.

Even in the early stages of smelting pronounced changes take place in the batch. Sodium nitrate melts first (586° F) forming a mobile liquid dissolving and reacting with the other constituents. Borax ($Na_2B_4O_7 \cdot 10H_2O$) begins to give up some of its water of crystallization as steam, and melts at about a red heat. This evolution of steam and melting causes a considerable agitation in the batch, which can be observed in the early stages of smelting. The molten borate readily dissolves metal oxides and initiates chemical action among the other constituents. It is quite probable that the presence of the steam itself greatly accelerates the rate of chemical reaction in the batch. If magnesium carbonate is present, it decomposes into carbon dioxide gas and magnesium oxide, which is a strong base. White lead gives up its water and carbon dioxide at about 752° F and red lead a part of its oxygen at 932° F. At temperatures of from 1500 to 1700° F the soda ash and lead oxide melt, and whiting is decomposed into carbon dioxide gas and lime.

The gases being evolved at temperatures up to 1700° F therefore include steam, carbon dioxide, oxygen, and possibly some of the nitrogen oxides from the sodium nitrate which has reacted with the other constituents. The molten soda ash is an active flux at these temperatures, attacking the more acid constituents with the elimination of additional carbon dioxide. The fluorides are soon taken into solution with an evolution of some fluorine and volatile fluorides. The melt becomes more mobile and active with these fluoride additions and increases in its attack on the feldspar and quartz grains. Antimony compounds are either oxidized to antimony pentoxide by the sodium nitrate or they are dissolved in the melt. Other opacifiers, such as tin, and zirconium oxides, are partially dissolved and, if excessively heated, they may be taken entirely into solution. Antimony oxide, unless it is kept oxidized to the pentoxide, melts at 1213° F, a much lower temperature which may account for its ready solution in some melts. The opacity of enamels is very sensitive to the smelting procedure and the

composition of the melt. Tin oxide must be present in the melt as a suspension. Arsenic oxide and the fluorides appear to dissolve in the melt and crystallize out on cooling. Zirconium oxide appears to form an immiscible glass dispersed in the melt, but its nature is not definitely known. Antimony pentoxide must be present as a suspension in the glass. The exact natures of these high temperature phenomena are, however, not known. The use of the X-ray will probably contribute much to our knowledge of them.

In a consideration of the physical and chemical changes of the batch, it is also necessary to study the effect of the furnace refractories and the furnace gases. The refractories used for smelter linings are high alumina clay brick or blocks with a low iron content. The iron content must be low, because the melt rapidly absorbs the iron, causing a green discoloration. If light colored or white enamels are being smelted, the refractories containing appreciable iron contents may cause dark specks in the frit. A highly aluminous refractory (flint fire clay type) is more slowly attacked by the fluxes in the enamel than are those high in silica.

When considering the furnace gases in the smelter, it is again important to return to the frit batch. The enamel batch itself provides a sort of gaseous blanket over its surface, which prevents the furnace gases from affecting it during the early stages of smelting. An enamel, for example, containing 35 per cent of borax and 10 per cent of soda ash loses about 165 pounds of water and 42 pounds of carbon dioxide for every 1000 pounds of frit. This is equivalent to 3290 cubic feet of water vapor at 32° F and a pressure of 29.9 inches of mercury. At a furnace temperature of 1700° F this would be equal to 14,500 cubic feet, or over a period of thirty minutes, about 483 cubic feet per minute or 8 cubic feet per second. With 42 pounds of CO_2 eliminated over the same period, which would be at a rate of one cubic foot per second, there would be a total gas evolution from the enamel of about nine cubic feet per second, disregarding that evolved from the nitrate. This protects the enamel from contact with the fuel gases during the early stage of smelting.

Figure 65 shows the content of carbon dioxide and oxygen in the atmospheres over an enamel batch plotted against time of melting. It is evident from the curves that the carbon dioxide is given off gradually, and also that the sodium nitrate keeps up the oxygen content of the atmosphere.

Rate of Evolution of Carbon Dioxide and Oxygen. It has been shown that atmospheres of carbon dioxide and atmospheres of nitrogen up tc one hundred per cent are not detrimental to the smelting of enamels.[1] Reducing gases are not detrimental to the smelting of most enamels, although those high in lead may be affected after the completion of the first evolution of gases from the enamel. Under extreme reducing conditions, lead, antimony, and tin compounds may be

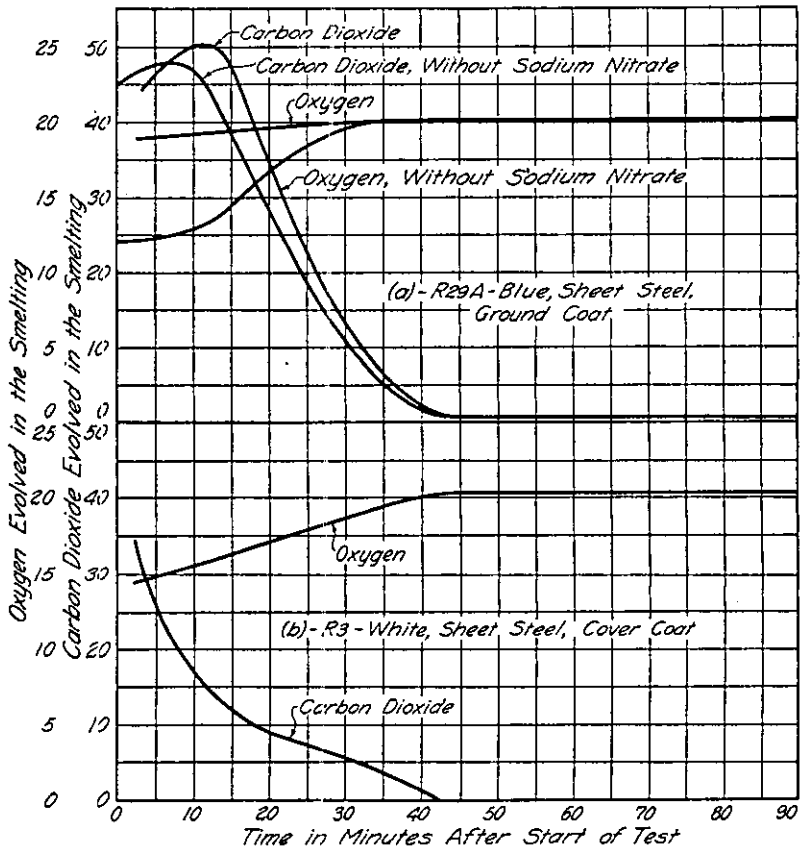


FIGURE 65. Rate of Evolution of Carbon Dioxide and Oxygen with the Furnace Preheated.*

changed to the metallic form, in which case they settle as metallic beads in the bottom of the smelter.

Sulphur oxides in the smelter gases are absorbed by the enamel during smelting, forming an immiscible sulphate melt on the surface, which is soluble in water and is eliminated in the quenching operation.

[1] University of Illinois, Engineering Experiment Station, Bul. 224.
* *Ibid.*

Dust, dirt, and soot must be avoided in the smelter atmosphere, since solid particles may be caught in the batch and cause specks and blisters in the enamel.

It is evident on considering the nature of these changes that time is an important factor in smelting enamels. Heat applied too slowly will not give ideal conditions, because the first melt formed will then react only very slowly with the most refractory constituents, consuming excessive time and causing a loss of efficiency. A temperature sufficient to vaporize these more fusible materials might not be high enough to volatilize them, if they were in chemical combination with the more refractory constituents. By holding the low temperature for a long period of time, these original fluxes would be gradually vaporized. The loss of efficiency, however, because of the low production of the equipment when smelting at excessively low temperatures, makes this practice very uncommon.

Since a rapid application of heat results in increased production, it is a common fault in smelting. If the enamel batch is heated too rapidly, the more fusible constituents are melted and volatilized before they have a chance to react with the more refractory materials. This results in a final batch, which is harder (less fusible) than it would have been if less of the fluxes had been driven off. Excessive smelting, after the melt is ready to pour, results in a similar condition and, if carried on long enough, necessitates a further increase of temperature to permit pouring.

Enamel batches vary considerably in their smelting characteristics, so that a careful study of each composition is necessary to determine the best temperature and time for proper smelting. There is considerable latitude in these conditions, but for each type of enamel and equipment there is a combination producing the best frit with the greatest economy.

Enamel ground coats are usually smelted much harder than cover enamels. The sheet iron ground coats are generally smelted until they are free from bubbles and particles of unfused material. They are smelted to a fairly uniform glass, but must not be heated too long and at too high a temperature or they become brittle. Dry process cast iron ground coats are viscous and refractory and are seldom melted to a good glass. They contain bubbles, but the less fusible constituents are generally entirely taken into solution. They are poured in a viscous condition, no attempt being made to heat them to a mobile melt. If over-smelted they, like the sheet iron ground coats, become brittle and refractory.

Most copper enamels contain opacifiers, which must not be taken into solution during the melting operation. These opacifiers serve their purpose only when they appear in the frit as inclusions uniformly

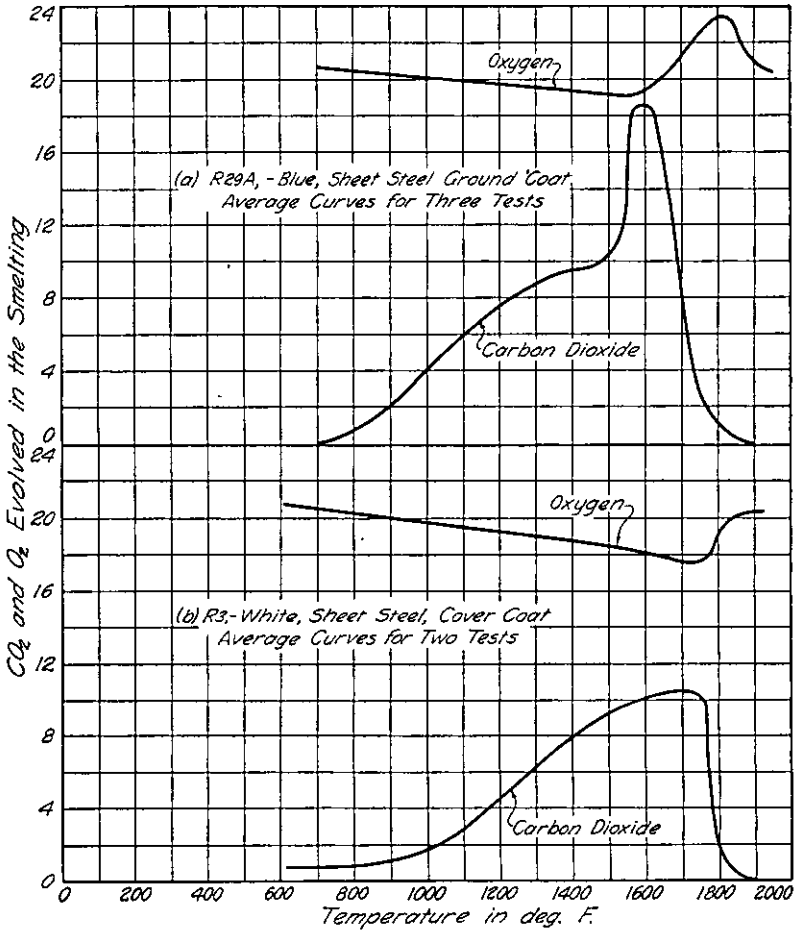


FIGURE 66. Rate of Evolution of Carbon Dioxide and Oxygen Heating from Room Temperature.*

dispersed in the matrix of glass. In some cases they dissolve in the melt and recrystallize on cooling, while in others they are present in the molten glass as immiscible melts or solids. Cover enamels must in general be smelted much more carefully than ground coats to avoid the

* *Ibid.*

loss of opacity. Enamels containing antimony compounds as the opacifiers are not smelted until they form a smooth thread; they are only smelted until the bubbling ceases. Since dry process cast iron enamels depend entirely upon the frit for their opacity, they are even more sensitive than the wet process types.

Many defects of enamels have their origin in the smelting operation. Insufficient smelting may cause blistering, loss of weather or acid resistance, poor gloss, and poor texture in the finished enamel. Over-smelting may cause loss of opacity, fishscale, poor gloss, refractoriness, and discoloration. The color and opacity of many cover enamel frits are sensitive to the degree of smelting. In some white enamels a distinct blue develops and in others, shades from yellow white to blue white.

In some enamel compositions, especially those containing lead, antimony, or tin compounds, reducing conditions in the smelting atmospheres may cause serious defects. These defects are usually present as brown or black specks in the enamel frit, but in extreme cases they consist of metallic beads in the bottom of the smelter. These specks, however, must not be confused with those arising from contamination by dirt in the raw materials, or those getting into the enamel from careless practice. It is possible for dirt specks to get into the enamel from the fuel and the air used in smelting.

Quenching. The principal object of quenching the molten enamel is to facilitate grinding. If the glass is slowly cooled it forms hard lumps, which are difficult to crush or grind. It is, therefore, important to obtain as complete and uniform quenching as possible. The milling of poorly quenched frit requires much more time than that properly quenched. A non-uniform quenching procedure results in a non-uniform product and considerable variation in the milling times and efficiency.

Molten enamel poured into water is chilled only on the surface, a layer of steam forming over it, which prevents rapid cooling. Chunks of frit will, therefore, remain hot for considerable periods of time and will not be shattered. If the fluid molten enamel passes through a blast of air and water, it is broken up into small droplets and threads, which, as they strike the water, are quickly cooled, causing them to shatter because of the strains set up in the glass. A good frit is not only broken into small pieces, but each piece is intersected with cracks, which make further reduction of size quite easy. In the interest of reduced cost of milling (an expensive operation), the frit should be thoroughly shattered.

Attempts have been made to quench the molten enamel by blowing it with air alone into a large chamber. Reports of this method claim a

better product than that of the air-water quench, but the trade has not adopted the method. It involves considerable space for quenching, careful control, and greatly increased storage space. The frit formed by air quenching is fluffy and for a given weight occupies much more space than the air-water quenched frit. It is claimed, however, that it is much more easily ground and that the product has better opacity and better acid resistance.[2]

Drying. After quenching, frits may or may not be dried, depending upon the operations to follow. If the frit is to be milled wet, it is sometimes charged to the mill without drying, but in such cases the water content should be determined. Frit which has been drained and allowed to stand in the air may contain from five to fifteen per cent water. This amount of variation will affect the milling and the properties of the slip to a great extent; therefore, if the frit is added to the mill in the wet condition, a correction for the water content should be made.

Three different types of equipment are used for drying frit: the drying table, the stationary dryer, and the rotary dryer.

The drying table is a flat hearth on which the wet frit is dumped. Heat is applied from beneath the hearth and the frit is raked by hand to accelerate the drying. This method is crude and wasteful of fuel, unless waste heat is used. The frit is subjected to contamination by settling dust and considerable labor is required for handling.

The stationary type of frit dryer is usually a sheet iron chamber into which the basket of frit is placed. The air used for drying the frit is heated by passing it through an interchanger on the flue of the smelters. This air is passed down through the basket of frit and is then exhausted into the flue. The method is desirable, because it utilizes waste heat and clean air can be used, thus avoiding the danger of contamination.

The rotary method consists of dumping the frit into a rotating cylinder. The cylinder is usually lined with porcelain and tilted slightly to one end, causing the frit to move through it continuously. A convenient size is about two feet in diameter and twenty feet long. Air warmed from the waste heat of the smelters moves slowly from the lower end of the cylinder over the frit to the upper end, where it enters a stack. The frit is charged at the upper end of the cylinder and is continually agitated as the cylinder rotates. The dry frit is discharged at the lower end. This method of drying frit is economical and effici-

[2] A. Malinovsky, Method of Cooling Enamel by Compressed Air, J. Amer. Ceram. Soc., 6, 972-3 (1923), and Stefan Wiester, Air Cooled vs. Water Quenched Enamels, J. Amer. Ceram. Soc., 6, 973-4 (1923).

ent. The frit is protected from contamination and in addition is broken up slightly by the motion. If the frit is to be screened to give it a more uniform size for milling, it has the advantage of a preliminary preparation for the screens.

In some plants, particularly those supplying frit to the market, magnetic separation of iron-bearing impurities in the frit is becoming quite popular. Regardless of the care exercised in manufacture, particles of iron or iron-bearing slag may get into the frit and, if not removed, they produce black specks in the enamel.

TABLE 30

Decomposition and Fusion Properties

Material	Formula	Decomposition		Melting Temp.	
		Product	°F.	°C.	°F.
Feldspar	$K_2O \cdot Al_2O_3 \cdot 6SiO_2$	.....	.....	1170	2138
Borax	$Na_2B_4O_7 \cdot 10H_2O$	$Na_2B_4O_7$ & H_2O	167	741	1366
Quartz	SiO_2	.....	.....	1710	3110
Fluorspar	CaF_2	.....	.....	1360	2480
Cryolite	Na_3AlF_6	.....	.....	1000	1832
Soda ash	Na_2CO_3	gradual	.....	851	1564
Soda nitre	$NaNO_3$	gradual	.....	308	586
Red lead	Pb_3O_4	PbO & O_2	932	888	1630
White lead	$2PbCO_3 \cdot Pb(OH)_2$	PbO, CO_2 & H_2O	752	888	1630
Litharge	PbO	.....	.....	888	1630
Barium carbonate	$BaCO_3$	BaO	2642	1923	3493
Whiting	$CaCO_3$	CaO & CO_2	1517	2570	4658
Magnesium carbonate	$MgCO_3$	MgO & CO_2	662	2800	5072
Zinc oxide	ZnO	.....	.....	>1800	>3272
Antimony oxide	Sb_2O_4	Sb_2O_3 & O	1654	1550	2822
Sodium antimonate	$NaSbO_3$	.....	.....	.....	.....
Zirconium oxide	ZrO_2	.....	.....	2700	4892
Titanium oxide	TiO_2	.....	.....	1640	2984
Sodium silicate	Na_2SiO_3	.....	.....	782–1080	.....
Cobalt oxide	Co_3O_4	Co_2O_3, CoO, Co & O	.....	.....	.....
Manganese oxide	MnO_2	MnO & O	995	1650	3002

The magnetic separator usually consists of a belt on which the frit travels and auxiliary belts, behind which electro-magnets are located. As the frit on the conveyor belt passes these magnets, the iron particles or even particles of frit containing small amounts of iron are drawn to the magnetic belts. These belts convey the magnetic material away from the batch and drop it in a container at one side. The frit passes to the frit storage or the hoppers for use.

SMELTERS

Three different types of furnaces are used for the smelting of vitreous enamels: crucible or pot furnaces, hearth (box) type furnaces, and rotary furnaces.

Crucible furnaces are used only where the batches are small, as in

the making of jewelry enamels, in laboratory tests, and in making special colors. Although this type of furnace is not economical of fuel, it has advantages for special work. The enamel batch smelted in a crucible can be kept out of contact with furnace gases and, where desirable, can be covered. In the making of jewelry enamels containing arsenic oxide, the covered crucible prevents excessive loss of this volatile oxide and the accompanying danger from the poisonous fumes.

The Crucible Type. The crucible type furnaces are usually fired with gas or oil, but can be heated by electricity. The combustion chamber in the gas and oil furnaces surrounds the crucible. The electric furnace is of the resistance type, the elements being placed vertically around the crucible. The refractory and fuel costs are high, since the heat must pass through the crucible to the batch.

In the operation of the crucible furnace the well mixed batch is charged into the hot crucible, and, toward the end of the smelting, it is stirred with a clean iron rod. Samples are taken and threads drawn from time to time to determine the progress of smelting. When thoroughly smelted the melt is poured in a fine stream into cold water, shattering the frit. With some enamels containing arsenic oxide the melt is poured on a flat plate, because better opacity is sometimes obtained with slow cooling. Figures 67 and 68 show diagrams of an electric and a gas-fired crucible smelter.

The Hearth Type Smelter. The hearth type smelter has for many years been the most common type of furnace used for making enamels. This type of smelter has the advantage of simple construction, fairly efficient operation, and long life. It can be easily insulated, and the refractory lining can be readily replaced when badly worn. The design of this type of smelter varies considerably from one plant to another. It consists essentially of a refractory box or tank (Figure 69) with the bottom sloping to a point near one side, where the tap hole is located. The side walls support a crown, which extends over the furnace. Brick and insulation are built around this with steel rods and clamps holding it in shape. The modern furnaces are fired with fuel oil or gas, the flame being so adjusted that it passes over the surface of the enamel batch. The burner or burners are placed at one end with the flue at the opposite end. In the smaller furnaces of this type one burner is sufficient, but in the larger type two or more are used. The batch is charged through a hole in the crown of the furnace and is leveled out with a rod or rake through a port hole in the side. The discharge is through the tap hole at one side in the floor. These furnaces vary in size from the fifty-pound laboratory smelter to the large commercial

types smelting several thousand pounds. An 800-1000 pound smelter is a common size in most plants. The smelters are often built in pairs having one side common to the two.

The ordinary hearth sizes of these smelters are 22 x 30 inches for 100 pound batches, 5 x 7 foot for 1000 to 1200 pound batches of raw material, and the 6 x 8 or 7 x 9 foot sizes used for dry process enamels.

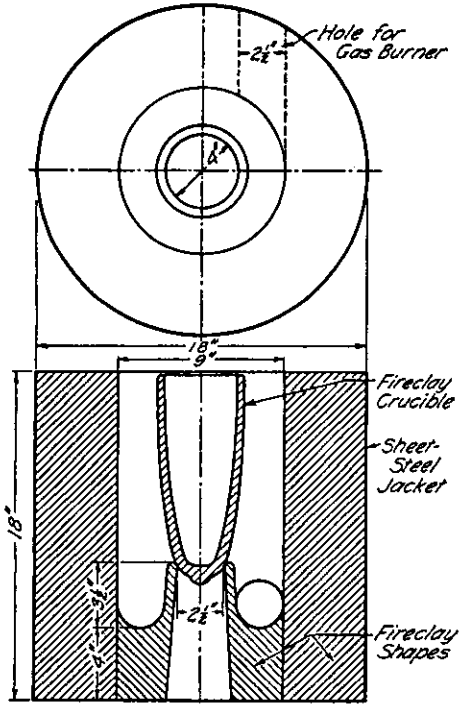


FIGURE 67. Crucible Smelter.*

These larger smelters will take batches of 2500 or 3500 pounds. The general rule, as given by F. M. Burt,[3] for the capacity of smelters is that for sheet iron frit 25 to 35 pounds of batch can be smelted for each square foot of hearth area. Also 30 to 40 pounds of wet process cast iron enamels or 45 to 50 pounds of dry process cast iron frit can be produced for each square foot of hearth area.

* A. I. Andrews, Uni. of Ill., Eng. Exp. Sta., Bul. 201 (1930).
[3] Ceram. Ind., 16, 381 (1931).

The hearth of these box type smelters usually has a slope toward the tap hole of one inch in two or three feet. The curb wall is built around this hearth, the blocks extending three or four inches below the surface of the hearth. An upper course of curb wall brick is built on this and around the outside; a wall of nine-inch straights runs two feet above the hearth to support the crown, which is also made of stan-

FIGURE 68. Commercial Smelting Room.*

dard fire clay bricks. The selection of the refractories to be used in smelters is an important consideration, a good grade of high aluminous fire clay usually being considered preferable.

When gas is used as the fuel, several burners are usually employed at one end of the smelter. The proportional type mixer burner is generally used, and the burner fits closely into the wall of the smelter, no auxiliary air being used. These burners may be of either the type using fifteen to twenty pounds of gas and the appropriate amount of air to give good combustion, or of the inspiration type. In the latter type the gas is under a low pressure and is inspirated into the burner by the flow of compressed air or gas through a venturi.

* Courtesy of the Titanium Alloy Manufacturing Co.

If oil is used as fuel, one burner is usually sufficient. The oil flame is very long, which in some cases necessitates the installation of the oil burner at the same end of the smelter as the flue. The flame then travels the length of the smelter and returns to the flue. By proper operation very little short-circuiting is encountered and the temperature distribution is good.

Most smelters are equipped with pyrometers of the thermocouple type. The location of these is an important consideration and, once the most desirable smelting temperature conditions are obtained, they should be strictly adhered to. The furnace temperature for sheet iron ground coats is usually 2050 to 2200° F, for white cover or color enamels 1900 to 2100° F, for special hard enamels and one coat grays

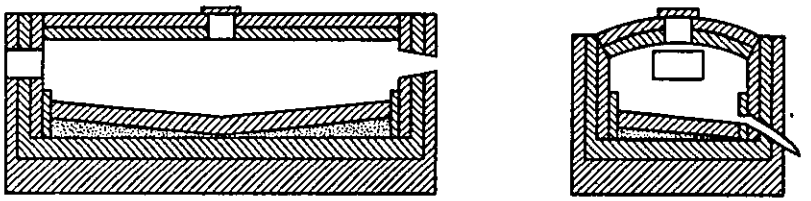


FIGURE 69. Hearth Smelter.

2500° F, and for dry process cast iron enamels 1900 to 2100° F. It is doubtful, however, if the enamel itself ever exceeds a temperature of 2100° F, although the furnace temperature is much higher. The temperature and time of smelting must, however, be determined for each enamel composition. Some enamels require rapid smelting at high temperatures, while others require a low temperature over a longer period of time. The conditions for each enamel composition should be determined and standardized, otherwise the properties of the frit will vary considerably.

The heat in the flue gases can be used to preheat the incoming air, to dry the enamel frit, or to heat the smelter room. An interchanger is often used for this purpose, thus eliminating the objectionable flue gases.

A pit is generally built on the side of the furnace under the tap hole. This pit contains a tank filled with water and a monel metal basket just fitting the inside of the tank and large enough to receive one charge of frit. As the molten enamel flows off the end of the trough under the tap hole, it is usually blown into the tank by means of a spray of water and air which aids greatly in breaking up the frit. The basket

is then raised out of the tank of water and drained, after which it is transferred to the dryer and finally to the frit storage bin.

Operation. The box type of smelter is brought up to temperature before the batch is charged into it. This requires many hours, therefore the smelter is usually run continuously, one batch following another until a considerable quantity of frit has been accumulated.

Before charging the batch into a smelter, the burners are turned off and the flue closed to prevent the dust from being carried up the flue. The batch is charged from a hopper through the door in the crown and leveled off by means of an iron rod or hoe. The flue is then re-opened and the burners are lighted.

The batch melts from the surface down, although considerable heat is obtained from the hot hearth. As the heat penetrates the batch, the borax gives up its water as steam, causing an agitation, which aids the mixing of the batch. Later the decomposition of the carbonates contributes to this and the batch passes through the stages of a solid powder to a mush and, finally, a mobile melt. As it approaches the melt stage, it bubbles violently and then subsides to a quiet liquid. It is usually stirred with an iron rod at some time during these last stages of the operation to make it more homogeneous and to aid the temperature distribution.

Several methods are used to determine when the enamel is completely smelted. The *thread test* is most common. A thread of glass is drawn from the melt and examined. Sheet iron ground coats are smelted to a condition where the thread is free of air inclusions or unfused material. Cover enamels may not be fired beyond the disappearance of the entrapped bubbles. The operator becomes very proficient in judging the degree of smelting by the appearance of this thread.

Sometimes a sample is analyzed for silica as a check on the operator's estimate. High silica content, other things being equal, indicates over-smelting, and low silica, under-smelting. The use of phenolphthalein indicator on the crushed and screened frit is quite common in some cases. If the enamel is under-smelted, the phenolphthalein turns red quite promptly, while, if the enamel is over-smelted, the reaction is much slower. This change is dependent on the solubility of the alkalies of the frit and is suitable only for certain compositions, such as those used for gray ware kitchen utensils.

It is customary to gather a portion of the melt in a shovel as it runs out of the tap hole. The sample is allowed to cool and is then broken

and examined and often kept as a record. The fracture should be smooth and free from both air bubbles and unfused material.

When the smelting is completed, the tap hole is opened and the melt allowed to flow down the spout into the path of the air-water spray and into the basket in the water tank. The frit in the basket is usually stirred to prevent its collecting in lumps and to insure thorough quenching. The operator uses a steel rod to loosen any enamel which tends to cool and adhere to the spout. When removing the wad of clay in the tap hole, the dirt and first enamel passing over the spout are caught in a shovel and discarded. When the enamel ceases to flow, a new wad of clay is put in the tap hole and another batch of raw materials is charged into the smelter. The basket of frit is then raised out of the water tank, allowed to drain, and transferred to the dryer.

The operation of the smelter requires control of the temperature, the products of combustion, and the frit batch.

The temperature is usually controlled by means of the thermocouple installed in the smelter and the hand adjustment of the burners. It is possible, however, to use automatic control for this. Either the thermocouple or radiation pyrometer can be used to actuate the equipment for operating the burner adjustment. The hand adjustment is, however, necessary in some cases (particularly with the rotary type smelter) and in such cases a definite schedule should be followed.

It is possible to adjust the air and gas pressures of the smelter so that, not only will the combustion be most efficient, but a definite temperature can be produced. The upper curve in Figure 70 is derived by plotting the gas pressure against the air pressure for conditions of most efficient combustion. The other curves represent the corresponding data for different percentages of excess oxygen, as indicated. When the temperatures produced in a given furnace have been experimentally determined, they can be noted along these curves and, if a given temperature and given excess oxygen are required, the pressure of the gas and air can be set to reproduce them.

By making Orsat gas analyses of the products of combustion in the stack with different adjustments at the burner, data can be obtained which are valuable in the control of the burners.

The Rotary Type. The rotary smelter is cylindrical in shape and is mounted so that it can be rotated and also tilted. The ends are made conical to retain the batch while rotating. An opening in one end serves for the burner and an opening in the opposite end serves as a flue. A diagram of the American type of rotary smelter is shown in Figure 71. The rotary smelter is built with a sheet steel jacket and

lined with special refractory shapes. It rotates in either direction and can be tilted to a vertical position for pouring the molten enamel. It can be fired with either oil or gas (city, natural, or butane) and is built in various sizes to take from 60 to 1100 pounds of enamel batch. Table 31 shows the dimensions, capacities, and approximate fuel consumptions of these furnaces.

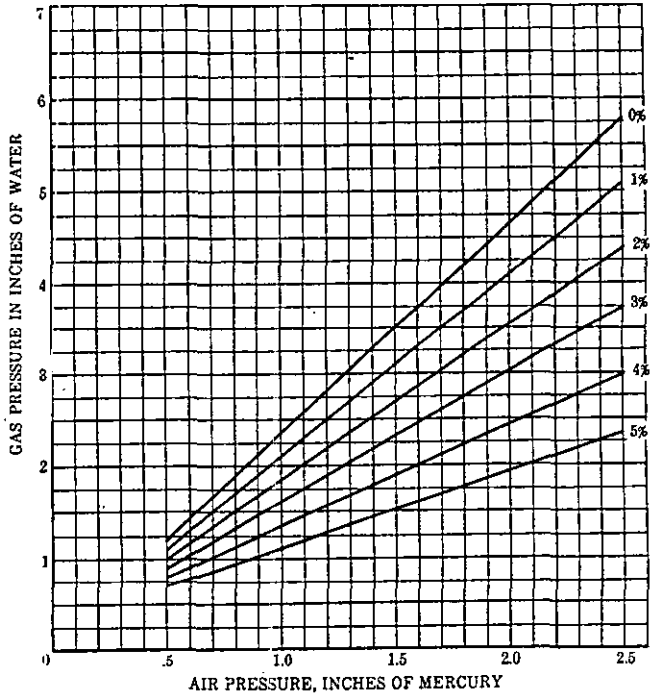


FIGURE 70. Air-Gas Pressure Relation in a Smelter.*

Operation. The rotary smelter is best charged by means of a screw type charger which can reach through the door to the back end of the furnace and deposit the batch as it is withdrawn. It is possible, however, to shovel the batch into the furnace, but in any case it must be distributed to avoid blocking the path of the flame. The charging is always made through the burner opening into the hot furnace. The burner is then swung into place and lighted. The smelter is rotated only far enough to bring the batch up on one side so that the material, as it melts, can roll down to the bottom of the smelter. This subjects new batch constantly to the flame and gives maximum speed in

* W. C. Martin, A. O. Smith Corp.

smelting. The unmelted material is raised up the side by rotating the furnace slightly at frequent intervals. When the batch has practically all rolled down, the furnace is rotated half around, bringing the enamel melt into contact with the hot crown which is then under it. This causes violent boiling and the enamel fines rapidly, after which it quiets down. The furnace is then rotated constantly, which mixes the molten enamel. It is generally necessary, however, to stir the enamel from front to back of the furnace with a steel rod. As the melt ceases

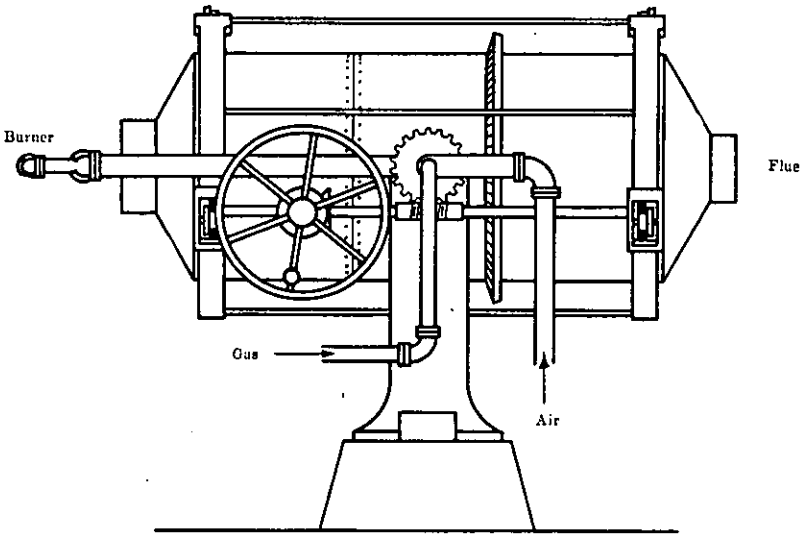


FIGURE 71. Rotary Smelter.

to bubble, samples are taken, and when completely smelted, it is poured.

Pouring is accomplished by tilting the furnace with or without the burner in operation. It is tilted by means of a crank on one side and can be controlled perfectly by one man. The melt is best poured slowly to permit good quenching as the stream passes through the air-water spray and into the Monel metal basket resting in the water tank under the smelter. A very convenient quenching arrangement consists in forcing the enamel frit down an incline, around a curve, and into the frit basket. This agitation makes the shattering of the glass more complete and produces a uniformly fine product.

The rotary type of smelter has an advantage over the box type in that it gives a better mixing of the batch and can, therefore, smelt the

enamel more rapidly. It is economical of floor space and labor, one man being able to operate several smelters. The charge can be readily observed through the door, although this advantage is lost when an auxiliary door is used to increase the economy of the furnace. The charging and pouring can be rapidly done and easily controlled. The rotary smelter has a large fuel consumption and there is no convenient method of automatic temperature recording or control. An optical pyrometer sighted on the batch is generally used to measure the temperature.

TABLE 31

SPECIFICATIONS OF U. S. ROTARY ENAMEL SMELTING FURNACES

	No. 1 Furnace	*No. 2 Furnace*	*No. 3 Furnace*	*No. 4 Furnace*	*No. 5 Furnace*
Enamel Capacity	60 lbs.	150 lbs.	350 lbs.	750 lbs.	1100 lbs.
Melting Time	30 min.	45 min.	1 hr.	1¼ hr.	1½ hr.
Size Charging Hole	8″	8″	10″	16″	16″
Size Pouring Hole	4″	5″	8″	10″	10″
Shipping Weight	2100 lbs.	3380 lbs.	6725 lbs.	10,930 lbs.	13,400 lbs.
Floor Space	7′ x 7′	8′ x 8′	10′ x 10′	12′ x 11′	12′ x 13′
Head Room	9′	10′	13′	15′	20′
Approximate Oil per Hour	6 gal.	9 gal.	17 gal.	25 gal.	30 gal.
Approximate Gas per Hour	900	1500	2500	5,000	6,000
Connersville Blower	No. 35-B	No. 40-B	No. 50-B	No. 60-B	No. 60-B
Motor for Rotating	¼ H.P.	½ H.P.	¾ H.P.	1 H.P.	2 H.P.
Inside Diameter Chamber	13¾″	17¾″	25″	33″	33″
Thickness, Fire Brick	3″	4½″	5″	5½″	5½″
Capacity Cubic Inches	585	1785	5138	9500	14,750

Figures are approximate.

While the box type furnace requires many hours to bring it up to a smelting temperature, the rotary type can be heated in a very short time. This is very convenient where intermittent smelting is done. The original cost of the box type smelter is less than that of the rotary, the preference for one or the other type depending upon local conditions.

The relining of either type of smelter requires first-class refractories which fit closely in the furnace. Joints should be made as thin as possible, fire clay being used as the bond. The fire clay is preferably the same as that used in making the bricks. The early smelters were built with large blocks (6″ x 14″ x 30″ or 6″ x 12″ x 24″) to avoid joints, but the more modern types use either small blocks (2½″ x 6″ x 13½″, 4″ x 6″ x 13½″, or 5″ x 9″ x 9″) or standard bricks. The

large blocks are made by hand and are objectionable because of their expense and their low density. The machine-made dry pressed standard shapes are much denser and will withstand the fluxing of the enamel melt much better than the hand-made product. A good flint fire clay refractory (high in alumina) is generally considered to be most satisfactory. Clays with a high silica content do not withstand the fluxing action of the enamel. The refractory used should have a fusion point (P. C. E.) of cone 32 to cone 33, or 3092° to 3173° F. The porosity should not greatly exceed eight per cent and the brick should be burned uniformly to cone ten or eleven. Brick for smelter purposes should not contain iron slag inclusions or specks, since these are readily absorbed by the enamel batch. Light colored refractories are much less objectionable than dark from the standpoint of contamination.

The lining of a rotary type smelter has an average life of about 350 melts, but in some cases it lasts much longer, possibly 600 and rarely 700 melts. The lining of a batch type smelter will last from 1000 to 2400 melts, the curb walls being repaired or replaced as necessity requires. Enamels of the sheet iron type are least destructive to the smelter hearth, while those of the high-lead type attack the refractory quite rapidly.

Most frit manufacturing plants are equipped with a number of smelters, since colored and white compositions cannot be made in the same smelters. The ground coats, blue, and black colors are usually made in the same smelters, while the white opaque enamels and the glazes are made in others.

Ventilation. The smelting furnace room should be well ventilated, because some of the fumes from the enamel practically always escape even with good flue systems. The fluorine gases, lead vapors, and dust are detrimental to health and should be reduced to a minimum. With rotary smelters hoods are often built over the top of the entire smelter to draw off any escaping gases. The frit-making rooms should always be kept clean, for dust accumulating on the floor or equipment leads to contamination of the frit and causes defects in the finished enamel difficult to trace to their source.

CHAPTER 9

Milling and Mill Additions

The milling of enamels is an operation requiring careful control, since it affects the working properties of the enamel and the quality of the finished ware. It involves not only the reduction of the size of the particles, but the accomplishment of this without injurious contamination, and in a manner which can be duplicated from one batch to another. Vitreous enamels are practically always ground in ball mills and usually in those of the batch type.

Although practically all enamels are required to pass a No. 60 to No. 100 sieve, the percentage of fines varies over a considerable range. The specifications for the milled enamels, therefore, generally call for a certain per cent of residue on a somewhat finer sieve. The milling operation must be so controlled as to produce a usable product, because it is not practicable to screen out the excessive fines or any great amount of the over-sized material.

In the milling of white or light-colored enamels, special care is necessary to avoid contamination by dark-colored materials. All enamels must be kept free from refractory materials, which will show as lumps or specks in the enamel coating, and foreign materials, which tend to react with the enamel glass or form bubbles and blisters. This problem of avoiding contamination is very serious, since there are many places where dirt may get into the batch. The raw materials, the water, the air, and even the equipment used for handling and milling must be constantly checked.

The operation of the milling equipment is of primary importance in the control of the product, but good equipment and satisfactory accessories for control are essential to good operation. Poor or inadequate equipment greatly handicaps the operation and is not usually an economy. The greatest efficiency is obtained when the mill room is properly equipped. If the mills used for white enamels are also used for colors, a considerable amount of labor, time, and materials is necessary in cleaning the mills after each change and the hazard of contamination is greatly increased. Frequently it is desirable to have separate mills for different colors. The capacity of the mills used should be adapted to the scale of operations, for an over- or under-sized batch in a mill is ground very inefficiently. Usually several sizes of