THE CONTROL OF THE LUSTER OF ENAMELS.¹

By HOMER F. STALEY, Washington, D. C.

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 salt 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 to 1100° C, 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 metals, 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 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.

Effect of Viscosity.

The most simple method of overcoming the tendency to crystal-

¹ By permission of the Director, Bureau of Standards.

lize 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 iron ware is cooled so rapidly, sufficient time is not given in the cooling process for an 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, the addition of silica to any melt increases the 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 of 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,¹ the viscosity decreases rapidly as the temperature rises. The glass was found to be three times as viscous at 750° C as it was at 1000° C. The first temperature approximates that at which crystallization 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—boric oxide glasses:

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

It is noteworthy that the presence of compounds and eutectic compositions produced no noticeable effect on the viscosity curves.²

¹ "The Viscosity of Molten Glasses," Original Communications, *Eighth International Congress of Applied Chemistry*, 5, p. 127.

² Cf. *Trans. Am. Ceram. Soc.*, 13, 675 (1911).

The viscosity of borate glasses decreases with rise of temperature in the same general way as that of fused boric oxide, but not as rapidly. The effect of increasing the boric oxide in cast iron enamels is to increase the viscosity at the 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 but, in the case of many enamels, is actually lowered.

Kaolin (china clay) has a very decided tendency to raise the viscosity of enamels but is not much used in American 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.

Effect of Concentrations.

With the exception of boric oxide, all of the materials in enamel compositions known as fluxes, *i. e.*, 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 or lower are reached,¹ 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 and yet not producing a 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 crystall-forming fluxes increases a greater variety must be used.

¹ Cooper, Shaw and Loomis, *Am. Chem. Jour.*, 1909, p. 461.

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

	Raw.	Melted Percentages.
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	5.0 sodium oxide
Cryolite.....	12.0	4.8 aluminium 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 the accompanying table:

TABLE SHOWING EFFECT OF COMPOSITION ON LUSTER.

Num- ber.	Na ₂ O from soda ash.	BaO from barium carbon- ate.	CaO from calcium carbon- ate.	ZnO from zinc oxide.	PbO from red lead.	B ₂ O ₃ from boric acid.	Luster.
1	25						mat
2		25					semi-mat
3			25				not melted
4				25			mat
5					25		bright
6						25	bright
7	12.5	12.5					semi-mat
8	12.5			12.5			mat
9	12.5					12.5	semi-mat
10		12.5		12.5			semi-mat
11		12.5				12.5	bright
12				12.5		12.5	bright
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		bright
16	5.00	8.33		8.33		3.33	bright

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 the metal in the best possible shape for enameling before the operation commences, and by employing the most skilful workmen to apply the enamel.

Sulphur Compounds.

It is well known that sulphur compounds in an enamel tend to separate on the surface in feather-like 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.¹ 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, 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. Mellor² 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. An experienced enamel mixer informs me 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 satura-

¹ "Collected Writings of Herman A. Seger," p. 646. Published by Am. Ceram. Soc.

² J. W. Mellor, "Clay and Pottery Industries," Vol. 1, p. 63, published by Chas. Griffith and Co., London.

tion 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-ventilated muffles are used than when the air currents in these are sluggish. Cracks in the floor of the muffle which allow the products of combustion to leak in are a common cause of sulphured ware. Open-arch or semi-muffle 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, it 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. It sometimes pays to pile quicklime over a temporary patch in the floor of a muffle, but even then the lime should be changed daily.

Index of Refraction.

Aside from the question of glasses being dulled by the presence of crystals or sulphur compounds on their surfaces, the brilliance of the glasses themselves will vary. The brilliance of a glass is measured by its refraction for light, the higher the index of refraction, the more brilliant the glass. In any one class of glasses, the index of refraction is higher the greater the density of the glass.¹ Since lead oxide, barium oxide and zinc oxide tend to

¹ H. Hovestadt, "Jena Glass," pp. 388-393, published by The Macmillan Co., New York.

produce very heavy glasses, they also produce glasses of great brilliance. Potassium oxide makes more brilliant glasses than sodium oxide, and the 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.

COMMUNICATED DISCUSSION.

E. P. POSTER: We were very much interested in the remarks under the heading "Sulphur Compounds," in which Mr. Staley has referred to the presence of sodium sulphate on the surface of enamels, introduced by sulphur in the raw materials entering into the enamel mixture or by sulphur gases in contact with the enamel during burning.

We have carefully studied this particular type of trouble under two different sets of circumstances in connection with steel enamels applied by the wet process.

The first instance came to our attention while endeavoring to work, on a semi-commercial scale, an enamel which, through the experimental stages, had been very difficult to bring to a proper condition for spraying. The clays which were in use in "setting up" commercial formulas at that time did not properly suspend the enamel in question—without the addition of an amount which caused a definite dullness of the surface. Using less clay, it was necessary to add such an excessive amount of magnesium sulphate solution as a vehicle that a very definite sulphur scum was produced.

The other instance in mind came to our notice while we were endeavoring to burn commercial formulas on an experimental scale in a small furnace which was being fired by producer gas under conditions such that the products of combustion came in contact with the enamel. This took place at a time when it became necessary to find a substitute for natural gas in firing a direct-fired enamel furnace. The natural gas had never given trouble from sulphur scum. The first producer gas used was made from a coal which contained 2.79 per cent sulphur and the second test was made with a gas made from a coal containing 0.77 per cent sulphur. In both cases there was a very definite sulphur

scum which did not appear immediately on cooling but which was very evident after 24 hours.

It is particularly interesting to note that in the several cases of scumming—due to magnesium sulphate and the producer-gas fuel—the sulphur scum was carefully tested and identified as sodium sulphate, a fact which confirms very definitely the statements of Mr. Staley and of the other authors to whom he refers.

THE ELYRIA ENAMELED PRODUCTS CO.
ELYRIA, OHIO.