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OPALESCEENCE AND THE FUNCTION OF
BORIC ACID IN THE GLAZE

BY

R. T. STULL AND B. S. RADCLIFFE

URBANA, ILL.

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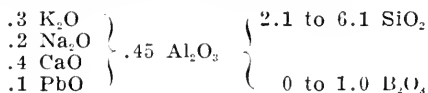
OPALESCENCE AND THE FUNCTION OF B_2O_3 IN THE GLAZE.

BY

R. T. STULL AND B. S. RADCLIFFE, Urbana, Ill.

In the study of whiteware glazes, at the University of Illinois, the class in glaze making constructed a group of glazes which showed all stages from clear colorless through opalescence to opaque white.

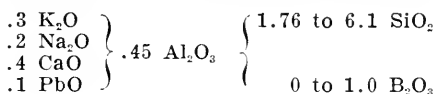
The group consisted of six series having nine members, each covering the following field:



The glazes were applied to biscuit wall tile, set on edge in flat tile saggars and burned to cone 3. Examination of the trials seemed to indicate that opalescence was not a function of the quantity of boric oxide, since glazes having small molecular quantities appeared as opalescent or opaque as those having larger quantities.

There also seemed to be a dividing line between the clear and the opalescent glazes. Although the glazes had run and beaded along the edge of the tile, the thickness of the glazes against the white background of the tile was not sufficient to determine accurately the dividing line between the clear and the opalescent fields.

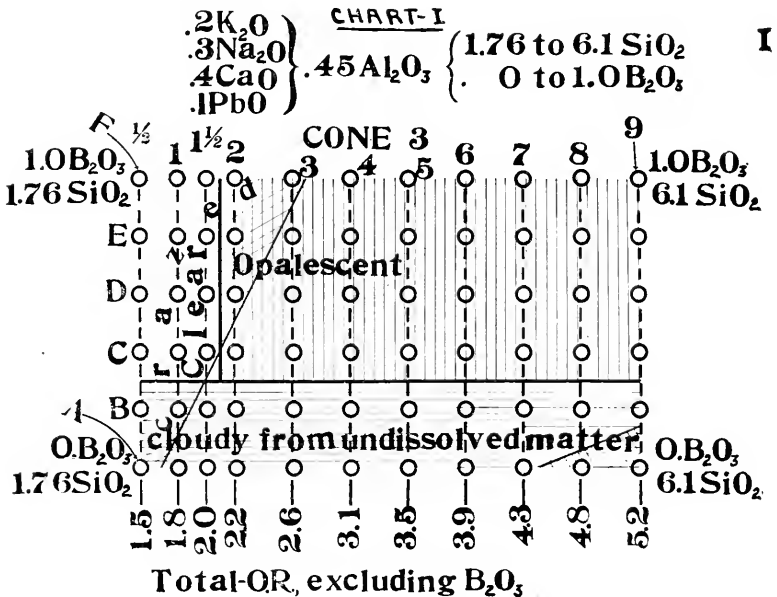
In order to determine more accurately this line, a series of glazes was inserted between what appeared to be the clear and opalescent fields, and another series added to the left of the group, thus covering the following limits:



Each circle on the diagram (Chart I) represents a glaze. In the lower left hand corner is low boric oxide and low silica. In the lower right hand corner is low boric oxide and high silica. At the upper left corner is high boric oxide and low silica. In the upper right corner is high boric oxide and high silica.

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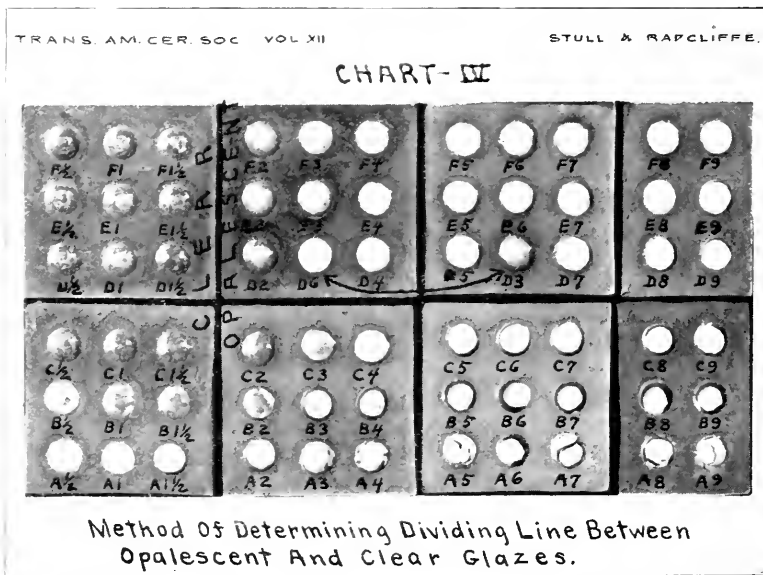
STULL & RAYCLIFFE



In the series running horizontally from left to right, boric oxide is constant and silica increases, while in the series running vertically from bottom to top silica is constant and boric oxide increases.

In order to detect faint opalescence it is necessary to examine thick layers of the glazes. For this purpose tiles from stoneware clay were made having conical depressions one-half inch in diameter and one-fourth inch deep (Chart IV). These depressions were filled with the glazes, the wall tiles were dipped and the trials burned to cone 3.

Examination of the trials showed opalescence strongly in Series 2 running vertically. Glazes having low boric oxide seem to show as strong opalescence as those having higher quantities. The members in vertical Series 1½ do not show the slightest trace of opalescence. To the right of the dividing line, opalescence increases, while glazes in the field to the left are perfectly clear.



Some very interesting points with respect to crazing are observed. In the A series, A-1½ is a basic matt and crazed. A-9, which is high in silica, is badly devitrified and crazed. A-8 is slightly devitrified and slightly crazed.

In the case of these two extremes of crazing the addition of boric oxide has had diametrically opposite effects. Boric oxide added to A-1½ has increased crazing, the crazing increasing with increase in boric oxide. In A-8 and 9 the addition of boric oxide has overcome crazing and also devitrification.

In his article¹ on "The Function of Boron in the Glaze Formula," Professor Binns says: "It was noticed that from its position in the periodic curve and from its valence, boron might be presumed to act like alumina, functioning as a base with strong acids and as an acid with strong bases."

He also points out, that in a glaze having the formula $RO, .2 Al_2O_3, 1.6 SiO_2$, whose oxygen ratio is one to two, if $.3 B_2O_3$ be added it is necessary to raise the silica to two and one-half according to practice, and that if B_2O_3 be considered as base the oxygen ratio then becomes one to two.

Professor Binns further states: " * * *, the opinion is further expressed that B_2O_3 undoubtedly is basic when melted with silica or silicates, and that it may be used to replace alumina partially or entirely, with the exception of its exercise of the property of fusibility."

Dr. Zimmer says:² "While I admit that all the facts brought out seem to indicate that boron will act as a base, there are surely conditions under which it will act as an acid."

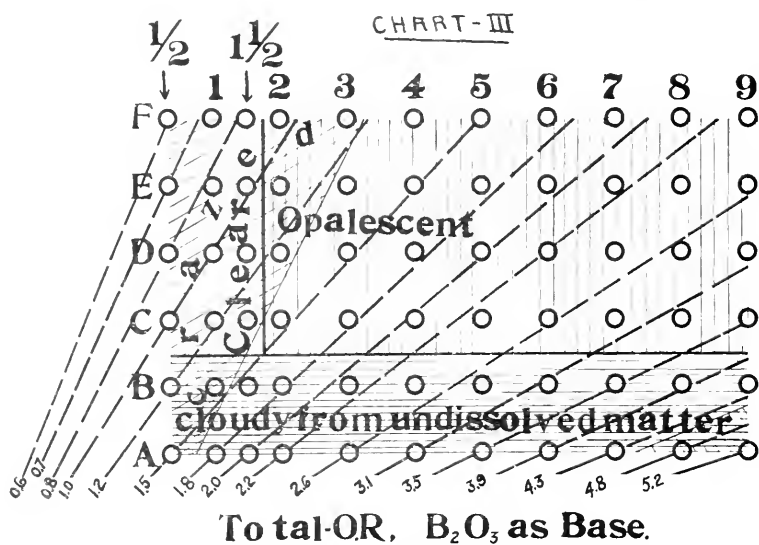
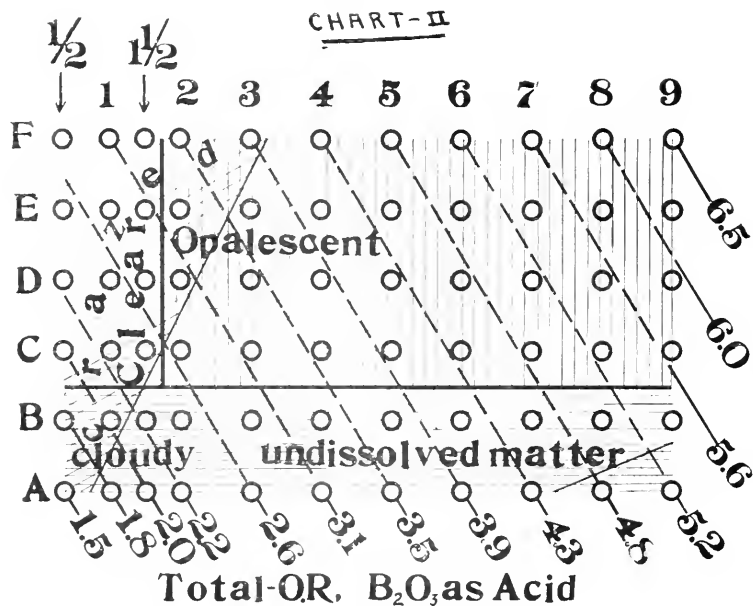
If we arrange the oxides of the elements in groups according to the periodic system, we find, as a rule, that the bases of low molecular weight produce best opacity and bases of high molecular weight least opacity. With respect to acids, we find the opposite, i. e., acids of high molecular weight produce best opacity and acids of low molecular weight least opacity.

According to Seger's rules for crazing, bases of low molecular weight produce least crazing and bases of high molecular weight produce most crazing. Whether the opposite is true of acids has not been definitely shown.

By calculating the oxygen ratios of the glazes including boric oxide, lines of equal oxygen ratios are obtained running vertically across the diagram, as shown in Chart I.

¹ Vol. X, Trans. A. C. S., p. 159.

² *Ibid.*, p. 168.



Considering boric oxide as an acid, lines of equal oxygen ratios run diagonally downward from left to right (Chart II). Calculating oxygen ratios in which boric oxide is assumed to be a base, gives diagonal lines running upward from left to right which appear to radiate from a common center, (Chart III).

In Chart I it is observed that the dividing line between the clear and opalescent glazes runs parallel to and between the oxygen ratio lines of 1 to 2 and 1 to 2.2. Since opalescence is shown so strongly on the total oxygen ratio line of 1 to 2.2, it is reasonable to suppose that the true dividing line between clear and opalescent glazes lies on or very near to the total oxygen ratio line of 1 to 2.

In consulting Charts II and III, it is evident that the lines of equal oxygen ratios in which boric oxide is calculated either as an acid or a base, do not bear any definite relation to the dividing line between the clear and opalescent glazes.

Boric oxide fuses at a low temperature, forming a thin water-like fluid. In this condition it is one of the strongest igneous solvents at our command, and there are few inorganic oxides that it is not capable of dissolving. Silica added to it is dissolved and evidently combined, since silica is strongly acid in character in igneous fusion, the combination is probably some silicate of boron which produces a milky precipitate.

Opalescence in glasses containing boric oxide is not caused by crystallization, nor by that peculiar form of segregation which sometimes precedes it. If it were, then sudden cooling would leave the mass in an amorphous condition, thus giving a clear glass. A fusion of silica and boric oxide when suddenly cooled will show strong milkiness. Fritts containing boric oxide frequently show opalescence though cooled suddenly by quenching in water.

It is true that a glaze cooled slowly will show stronger opalescence than the same glaze cooled quickly, but it must be remembered that precipitates require time to form. As

an example, the complete precipitation of magnesia by sodium ammonium phosphate requires several hours.

CONSIDERATIONS ON CRAZING.

Boric oxide when added to A- $\frac{1}{2}$ (which is basic in character), undoubtedly plays the part of an acid. Increasing boric acid has increased crazing. The more boric acid present, the greater is the degree of crazing.

In the case of A-8 and 9, which are highly acid in character, it is more than probable that the addition of boric oxide has combined as a base, and in so doing has overcome both devitrification and crazing.

In comparing the dividing line between crazing and non-crazing glazes, with lines of total oxygen ratios on the three different charts, we find that this line does not conform to any oxygen ratio lines, whether boric oxide be excluded from the calculations, or included either as acid or as base.

It has been noted that crazing has increased with increase in boric oxide in glazes whose previous total oxygen ratios are low. It has also been stated that this crazing is due to the presence of boric oxide as an acid, and as such, whether free or combined, its tendency is to reduce crazing. If boric oxide combines as a base, its influence should be that of overcoming crazing, since it is a base of low molecular weight (in accordance with Seger's rule).

If boric oxide when combined as a base acts like alumina and can replace alumina, then, any increase in boric oxide would decrease crazing the same as alumina, in accordance with the statement of Purdy and Fox.¹

Boric oxide present as acid and boric oxide present as base influence crazing in opposite directions, which might be expected since the properties of bases and acids are opposite in character. In glazes which craze from excess boric acid, an addition of silica has a double influence in

¹ Fritted Glazes - Trans. A. C. S., Vol. IX, p. 178.

preventing crazing. By converting boric acid to boric base it decreases crazing acid and increases non-crazing base.

The reason that the line between crazing and non-crazing glazes does not conform to any oxygen ratio lines is because both free crazing boric acid and combined non-crazing boric base may both be present, and it takes a definite amount of the one to overcome the influence of the other. With reference to the dividing line between devitrified and crazed glazes and non-devitrified and non-crazed glazes, Chart III shows that the line coincides in direction with the oxygen ratio lines when boric oxide is considered as a base. But when referred to Charts I and II, it is shown that the line does not conform to the oxygen ratio lines in either of these two cases.

Although there are no absolute chemical proofs at hand, the following theories are advanced from the foregoing evidence:

First, boric oxide when added to a glaze whose previous oxygen ratio is less than 1 to 2 is present as an acid, combined, tending to produce a chemical equilibrium. Any excess is present in acid, uncombined, in solid solution. When present in the acid form its influence is that of producing clear glazes and crazing.

Second, boric oxide when introduced into a glaze whose previous oxygen ratio is 1 to 2, is present as an uncombined acid in solid solution, imparting clear and crazing tendencies to glazes.

Third, boric oxide when introduced into a glaze with a previous total oxygen ratio greater than 1 to 2 tends to produce chemical equilibrium by combining as a base, thus producing opalescence and non-crazing tendencies. Any excess boric oxide is present as an uncombined acid in solid solution.

Fourth, opalescence is caused by the precipitation of a silicate in which boric oxide is evidently basic. The intensity of opalescence does not depend upon the quantity of boric oxide present but upon the quantity combined as a silicate.

It is interesting to note that, although the line dividing crazing and non-crazing glazes does not conform to any oxygen ratio lines, it conforms nearest to the lines of equal oxygen ratio when boric oxide is assumed to be base. The oxygen ratio line of 1 to 2, when boric oxide is considered a base, passes through the middle of the field of best glazes found in this group.

DISCUSSION.

Mr. Parmelee: I have this suggestion that I wish some of those interested in the matter of opalescence would determine whether that is opalescence or fluorescence. Opalescence, as I understand it, is due or at least commonly attributed to internal fractures, while fluorescence is a different thing. It would be a comparatively simple thing to take a sample of glaze showing this description of opalescence and determine which it is. I think it would be a matter of some interest.

Mr. Stull: The trials just came out of the kiln a little while before the convention. The intention was to have thin sections made of them and examine them microscopically. We used the term opalescence because that is the term most generally understood, and because it appears like opalescence,—it has the color. We know that some precipitates are opalescent in appearance. The precipitates of aluminum hydroxide and silicic acid are suggestively opalescent. Richards, in his work on the determination of the atomic weight of silver, produced strong opalescence in the silver chloride which passed through the filter. The presence of minute solid particles in suspension may give the reflection of light nearly as well as cracks or flaws will do.

Mr. Shaw: I have had some experience with borax but I do not believe I can add anything. I have been wondering what is the relation between opalescence and opacity. Substances that produce opacity if fused hard enough will produce opalescence. I have produced white enamel

and very often had it "burned." The opacity is all burned out of it, and the glaze after that time very often shows a great amount of opalescence.

Mr. Binns: Would you define opalescence as a partial opacity?

Mr. Shaw: That is exactly what I think.

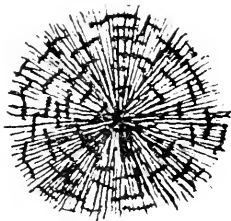
Mr. Stull: I agree with that, that opalescence is a "dilute" state of opacity. Here is F9, (exhibits trial), the one highest in B_2O_3 , and highest in silica. It shows opaque white.

Mr. Binns: I would like to ask Mr. Stull whether he has any explanation of the connection between devitrification and crazing. We have generally considered the two things were influenced by opposite conditions. I would be interested to know what suggestions he has to make on that point.

Mr. Stull: Most generally crazing is conceded to be a function of the co-efficient of expansion and contraction, but personally I think there is another factor which we do not consider, and that is crystalline tension. We know that crystals form from gases, from fluids and from solids. As a time-worn illustration, the iron beams of railroad bridges frequently become so crystalline from the jar of the trains that they become weak and break. We have plenty of evidence of crystallization going on in solids. A substance in crystallizing usually does one of two things, it either increases in volume or decreases in volume. In either case if crystallization should continue down into the solid glaze it would produce a tension strong enough to cause crazing. In experimenting with crystalline glazes of the type which crystallize in assicular groupings, I have failed to make one crystalline glaze yet which did not craze. In these crystals which radiate from centers, it is interesting to note that the craze marks did not run in irregular zigzag lines, but ran approximately in broken concentric rings around the crystalline center in this manner. (Indicating on the board as shown herewith.) If it

is not due to crystalline tensions, then what is it due to? Crystalline glazes with oxygen ratios all the way from one to one up to one to five will craze if they are crystallized. In practice I tried to overcome it by slow cooling from vanishing red heat down. The slower the cooling the worse the crazing appeared.

*Assicular Grouping
Showing Craze Marks
Running Concentrically.*



Mr. Binns: I would like in that connection to make another suggestion. We commonly theorize or philosophize this way: Silica in a body, being crystalline, has a high co-efficient. In the case of excess of silica in the glaze and consequent devitrification, it seems to me quite possible that the silica has returned to its crystalline form, and thus regained its high co-efficient. I have no doubt that *Mr. Stull's* theory of crystalline tension strains has something to do with it. At the same time I think the fact that the silica has returned to its crystalline form is also an important factor. I have frequently noted in that connection that a short fired glaze almost invariably crazes simply because the silica has not been thoroughly taken into the solution, and has thus not reached the amorphous form with the low co-efficient.

And now the question of boron, in which I am naturally very much interested. I would like to say just a word on that. This is the first time it has been alluded to since I brought it up two years ago. It is quite gratifying to find that at least a portion of my contention is substantiated. *Dr. Singer* showed, in his paper, that it was possible to produce compounds in which boron sesquioxide, or boric oxide, functions as a base.

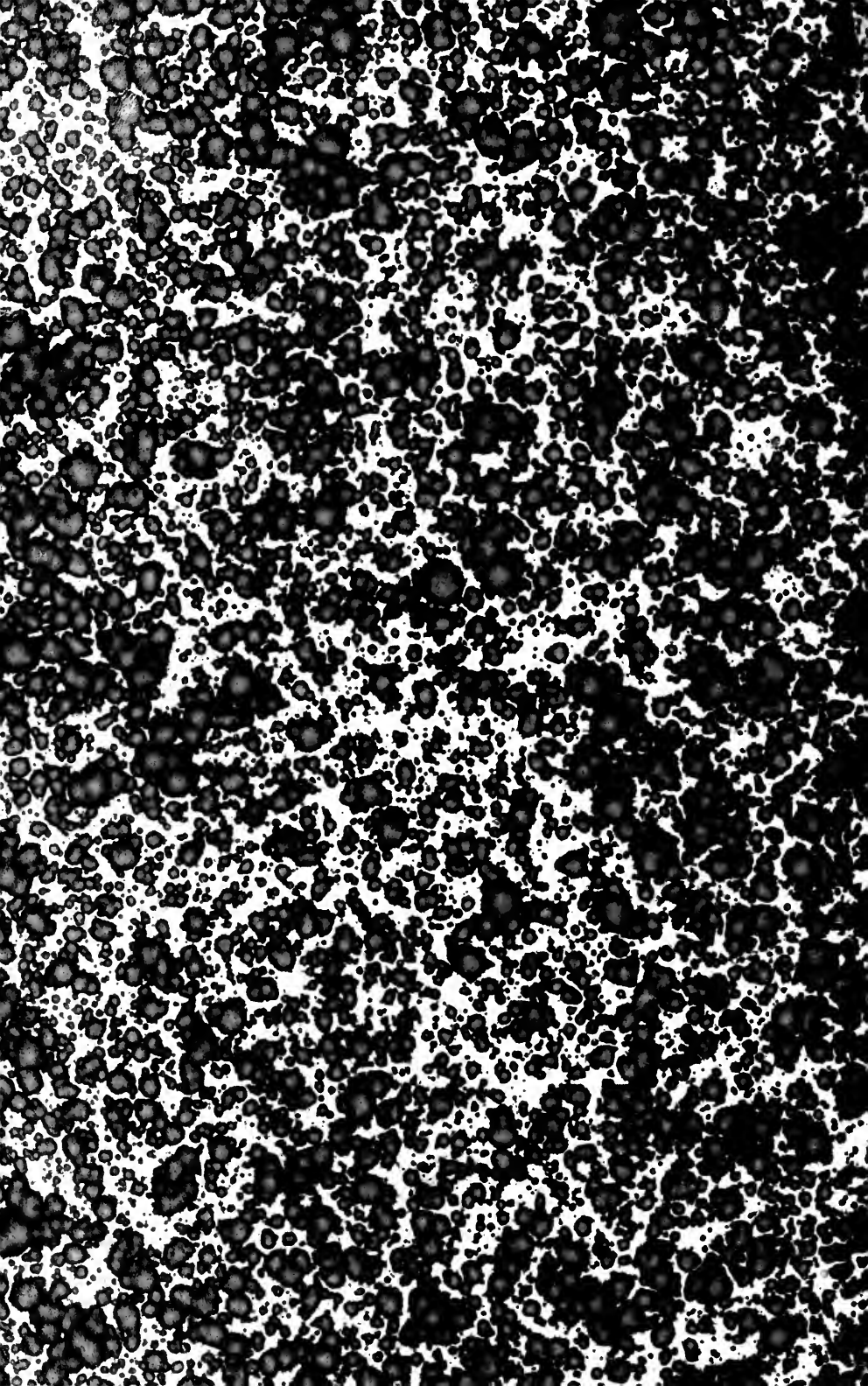
Ever since the paper was presented two years ago I have worked upon the theory, which I then enunciated, that in a normal glaze under normal conditions boric oxide functions as alumina. And my students in the blackboard work have said to me, why do you put boric oxide under the alumina when all the books do the other thing and put it under the silica? I tell them if they live long enough they will find that all the books will have it under alumina.

Mr. Stull has brought up certain exceptional conditions, as for instance, in a highly basic glaze, where it is quite probable that a portion of the boric acid or all of it may function acidically. And by the way, I wish we had some better term than acid and base to express this action.

For many years I groped in the dark with regard to fritted glazes, and I believe a good many are doing so still. But when we once established that the bi-silicate ratio was the best thing for a clear glaze under proper conditions, there did not seem to be any philosophy or working reason why fritted glazes should not come under the same rule, in other words, why boric oxide should introduce an entirely new set of laws. But by the simple arrangement of placing boric oxide with the sesquioxides the whole thing is solved: Fritted glazes now obey the same law. They are normally bi-silicate, or closely approximating it. I have no more difficulty now in laying down fritted glazes than I used to have in raw glazes. But until this point was reached there was no law which could be used as a guide.

We are very glad to have this word from Mr. Stull not only on the boric question, but on that rather obscure and interesting phenomenon of opalescence which has occupied us today. He has also demonstrated his work in a very interesting manner. His enclosing the panel of glaze in the cell is quite a new idea and one well worthy of consideration, when we come to deal with the consistency of the glaze matter.







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