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A study of opacity produced by insoluble refractory opacifiers

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A STUDY OF OPACITY PRODUCED BY INSOLUBLE
REFRACTORY OPACIFIERS

By

THEODORE JOHN MARION PLANJE

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
BACHELOR OF SCIENCE IN CERAMIC ENGINEERING

Rolla, Missouri

1940

Approved by Paul G. Herold
Head of Ceramic Engineering Dept.

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OBJECT

To investigate opacification produced by insoluble, refractory opacifiers in an effort to obtain some knowledge and reliable data concerning the electrical charge on the particles- its quality and quantity, and the effect of heavy metallic ions upon the flocculation and deflocculation of the opacifying particles.

JUSTIFICATION FOR THE INVESTIGATION

The opacity of ceramic glazes, enamels, and glasses has been investigated extensively for many years, mostly in an effort to determine the extent of the opacity produced by various opacifiers and auxiliary opacifiers, their effect upon the physical property of the resultant fusion, and the compounds formed in the final glass due to their presence. Little or no work has been done in an effort to improve the opacity produced by investigating the physical characteristics of the opacifier while it is suspended in the fused glassy matrix. Heretofore, the only control over the extent of the opacification has been manifested in the fact that the extent of the resultant opacity is proportional to the fineness and dispersion of the dispersed phase. In the following study the intent is to obtain

some knowledge concerning the flocculation and the deflocculation of the opacifying particles in a few simple glasses. This fundamental study will then be applied to more complexed systems for further study.

With such knowledge well formulated it is more than possible that opacification costs may be greatly reduced, or, at least, a greater control may be had by simple variations in the glaze composition.

THEORY

Enamels and glazes are either simple or complexed glasses which are adjusted to "fit" a surface of metal or clay to which they are to be applied and adhere to that surface by fusion. This results in the penetration of the glass into the pores of the surface and the formation of compounds at the interface between the surface and the glassy phase. Being glasses these glazes are primarily colorless or highly transparent, and in order to obscure the character of the surface of the body to which they are applied, it is necessary to add to the glass some opaque metallic oxide or salt with a higher or lower index of refraction which will remain suspended in the final glass as minute particles. This highly dispersed phase in the glass may in most

cases be considered as being in the colloidal state, and the whole system may be referred to as a solid sol. The resulting opacity is dependent upon the differences in the refractive indices of the suspended and the suspending phase.

In this investigation only opacification produced by insoluble, refractory materials will be considered - such as that produced by materials which are added either to the batch or to the frit, and remain suspended in the final glassy matrix in their original forms.

Colloids are divided into two major classes: (1) lyophilic colloids, (2) lyophobic colloids. In the case of the lyophobic the density, viscosity, and surface tension of the final solution are practically the same as those of the dispersion medium, however, in the lyophilic colloids the density, surface tension, and the viscosity are likely to be quite different for the colloidal solution than for the dispersing medium. General observations denote that the colloidal state existing between the glass and the opacifier must be one rather lyophilic in nature. This is evidenced by

(1) Weiser, H.B., "Colloidal Chemistry", P. 338

(2) Andrews, A.I., "Enamels" P. 46

(3)

the increase in the incipient fusion temperature; thus, indicating increased viscosity which in turn is accompanied by increased surface tension. Since the opacifiers of this class - as stannic oxide - are for the most part very dense, two or three times greater than the other materials composing the glass batch, and since it is not attacked by the glass but remains as originally added, the density of the final glass must be increased proportionally to the amount of the oxide added. Since many commercial glazes and enamels contain as much as ten or fifteen per cent of stannic oxide, the density increase must be considerable. Thus, one is inclined to conclude that the system is a lyophilic one. Yet, a primary requirement for the lyophilic system is that the suspended phase have a great mutual affinity for the dispersing medium. In view of earlier considerations this classification cannot be made - that is; refractory, insoluble particles. This classification will be considered during the investigation.

If a colloid state does exist, there must be in the fused glass and about the opacifying particles some force or forces which keep the denser particles dispersed through the glass; thus, keeping the concentra-

tion of the opacifier at the lower portion of the glass equal to that at the top.

Glasses in most cases are considered to be solid solutions; this feature and the fluidity of the glass at fusion are to be the factors which permit the following discussion to be used as an analogy. The forces which keep colloidal particles in suspension are two-fold. The first is the kinetic behavior which considers the constant movement of the particles - the Brownian movement. The suspended particles are moving ceaselessly and irrationally, and are not affected by light or convection currents within the solution. This factor is dependent upon the viscosity of the dispersing medium. The second is an electrical property possessed by the particles during suspension which assumes that, due to the large surface area offered by the vast number of minute particles, they must respond in one of two ways: firstly, the particles may have ions attached to them which maintain their adherence by inducing dipole attraction or rather by inducing a charge of the opposite sign on the nearest atom in the particle; thus, producing the ion-induced dipole attraction; secondly, the particles behave much the same as

individual ions of high molecular weight- "Gegenionen". Due to the charges on the particles it is possible to move them through the solution by means of an external potential drop. Colloids which are positively charged will migrate to the cathode, while those negatively charged will move to the anode. This is one of the purposes of the investigation - to determine the electrical charge on the particles.³

The ability of the dispersed particles to remain in the colloidal state is dependent upon the concentration of the ions. Yet if an addition of oppositely charged ions is made the particles will lose their dispersing power and will be coagulated. Thus the particles may be either flocculated or deflocculated by the addition of the properly charged ions.

To determine the electrical charge on the particles it is necessary to determine the absolute electrical charge, because the surface film completely envelopes the particle and endows it with its own properties; thus, the force of repulsion is determined in terms of the potential difference. This charge may be determined by means of the

(3) Weiser, H.B. , "Colloidal Chemistry "
PP. 162-242.

Lamb-Helmholtz equation which follows:

$$Z.P. = \frac{4 n v \pi}{K x}$$

Where Z.P. is the zeta potential or the potential drop between the surface of the particles and the surrounding film of the molten glass.

η is the viscosity of the glass at its maturing temperature.

v is the velocity of the migration in centimeters per second.

x is the potential gradient between the electrodes

K is the dielectric constant of the surface layer of glass which surrounds the particle.

For example, having found the charge on the particles its quality and quantity, it is possible to add to the system the proper ions which will give the maximum stability which means the maximum deflocculation of the particles will be acquired. The ion to be added must have a charge of the same sign as that of the opacifying particle, and its effectiveness will increase in ratio to its valence. This increase in ion concentration may be made directly and simply in the event that the particles are positively charged, since metallic ions may be readily introduced.

The addition of the stabilizing ions will increase the charge on the inner layer of the double layer. This increase will increase the zeta potential. With the zeta potential increased the mobility will be proportionally greater under the same potential gradient. Theoretically, this proportion will be a straight line function between the zeta potential and the mobility, but the additions of metallic ions will have a marked effect upon the character of the resultant glass. The most important effect will be the changing of the fluidity or viscosity of the fusion. This factor will no longer be constant, and will approach an indeterminate, since it is not the viscosity of the bulk of the glass that is to be considered, but it is the viscosity of the glass between the surface of the particle and the extreme portion of the outer layer. In practice it will be sufficient to use the bulk viscosity, since variations in the viscosity due to temperature changes will well exceed the difference before mentioned.

A further possibility of investigation is the study of systems to note any similarity to isoelectric points in liquid systems. Such should result as the ion concentration is increased. At first the ion con-

centration on the particles will become established, and the zeta potential will undoubtedly increase proportionally. Further additions will increase this feature, but there will be a concentration at which the surface will become concentrated and further additions will not create marked changes in the zeta potential.

PROCEDURE OF INVESTIGATION

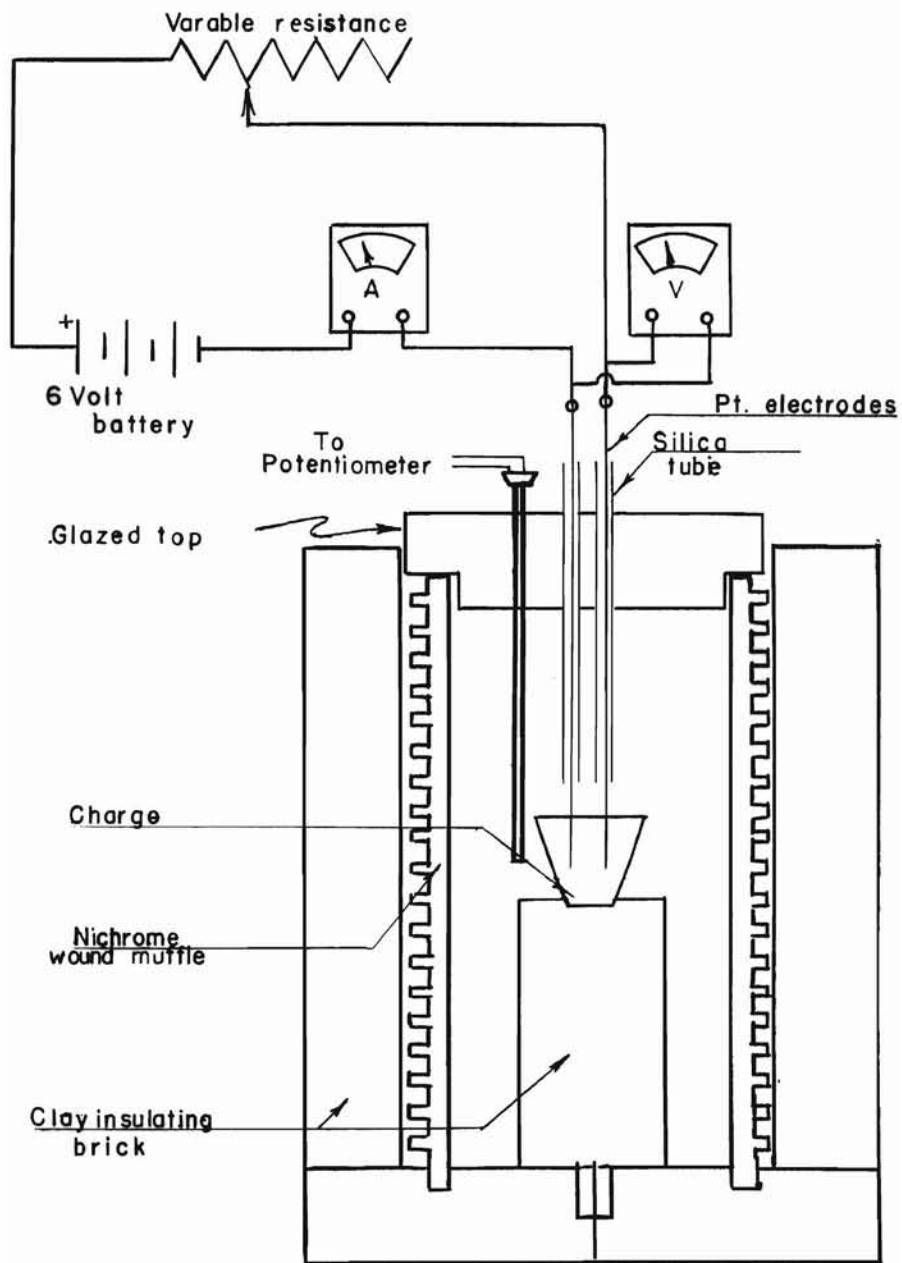
The factors of melting temperature, simplicity of composition, and compound forming ability of boric oxide (boric anhydride) made it the most desirable for the use as a simple glass, or suspension medium. Since boric anhydride is not produced commercially, it was necessary to produce it for this use by dehydrating boric acid. This dehydration takes place at a low temperature, but the volume of the water to be removed is large and the difficulties are many. The most satisfactory method was to fill a liter beaker about half full of boric acid and place in a drier capable of temperatures up to five hundred degrees fahrenheit along with a piece of plate glass about a foot and one half square. The maximum temperature must be maintained for four or five hours, after which time the mass will reduce to a very

thick, glassy, tan colored melt which may then be poured on the plate glass where it may cool. After cooling the glass was broken and ground in an agate mortar until fine enough to aid accurate weighing.

Standards were first prepared by adding two percent stannic oxide to about ten grams of the glass in a fifty cubic centimeter, unglazed, porcelain crucible. This charge was given a preliminary heating with a Fisher burner to remove the remaining water and gasses and to start the fusion. The charge received a final heat treatment in a nichrome wound muffle.

Having developed the standards it was then necessary to develop the apparatus for the determination of the charge on the particles. A nichrome wound muffle was used for a source of heat, being placed vertically on a platform of cellular clay insulating brick and surrounded with the same material. A top was made from an insulating brick impregnated with a higher temperature clear glaze which was pre-fired. This prevented the loose material from falling into the crucible. Silica glass tubes were mounted in the top to act as separators for the electrodes. The electrodes were

Figure 1
Apparatus for charge determination



seventy-five one-hundredths millimeter diameter platinum ten percent rhodium wires about eighteen inches long. The potential for the electrodes was supplied by a six volt storage battery with an ammeter, voltmeter and variable resistance in series in the circuit.

Several runs were made under these conditions - the results of which will be found in the " Results and Conclusions ". Due to the lack of time and equipment it was necessary to change the plan of investigation, since to determine the quantity of the zeta potential it is necessary to ascertain certain quantities which ^{are not} readily acquired with the equipment available.

The next plan was to add the necessary ions to further deflocculation in steps and note the effect. Two phase systems between boric anhydride and a compound (as sodium metaborate) were used as the basis of the approach. Again the glass was charged in a crucible with the determined amount of the metallic oxide in the form of a carbonate and two percent stannic oxide. These, too, were given a final dehydration with a Fisher burner before placing in the muffle for final heat treatment. Two such systems were

studied - $K_2B_4O_7$, B_2O_3 and $Na_2B_4O_7 \cdot B_2O_3$.

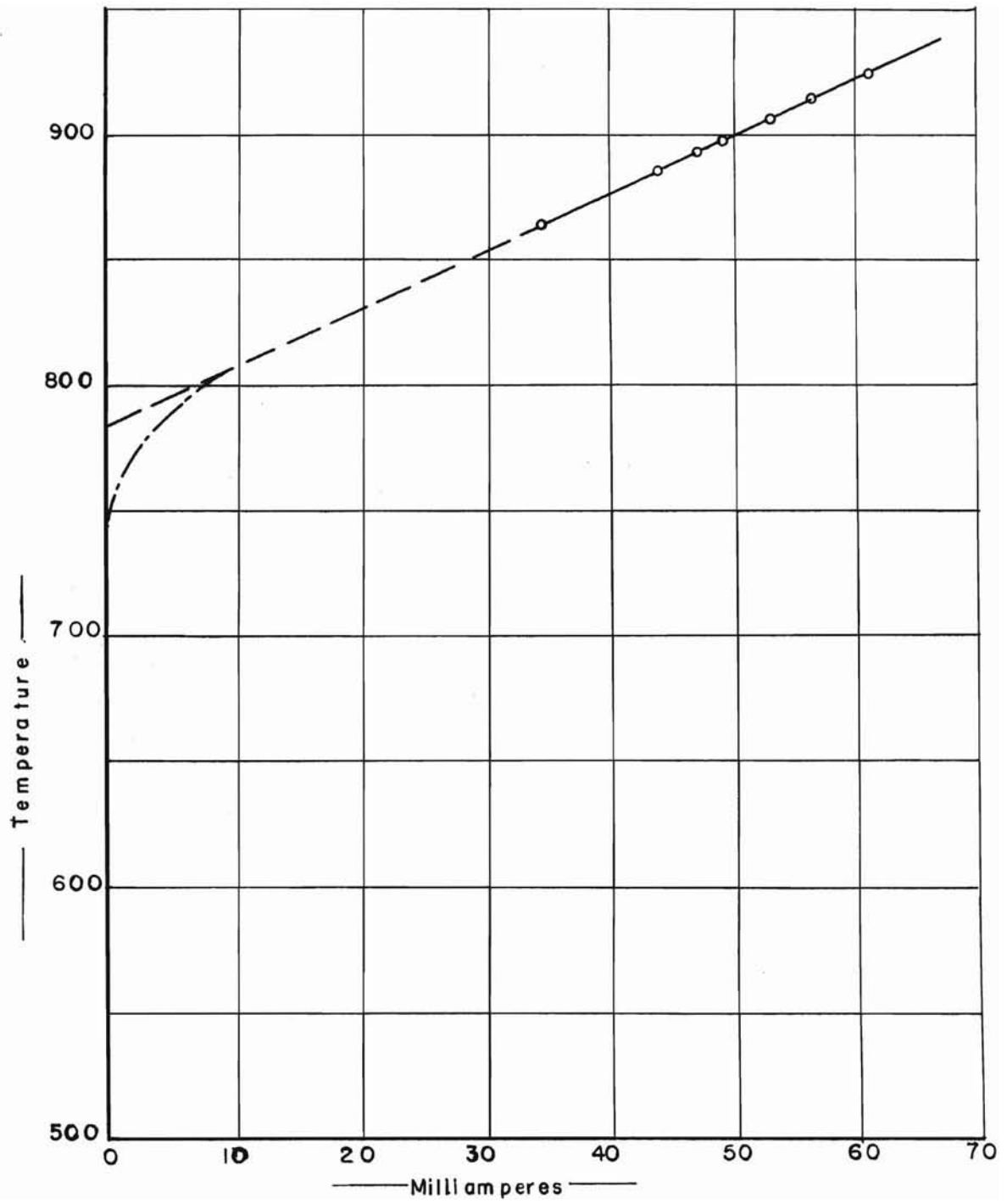
In all cases before the potential was applied the heating was carried to a temperature well above that of fusion and maintained for a short period of time until the emissivity of the fusion became uniform. this insured uniform fusion and constant fluidity through the whole mass between the electrodes. The current in the heating element for the cell was reduced, and the milliamperage and temperature values for the cell were recorded at regular intervals until the potential was removed.

DATA

A Typical Sample of Electrophoresis Data

| Time (min.) | Temperature (°C.) | Amperage (milli-) | Voltage |
|----------------|----------------------|----------------------|------------------|
| 00 | 924 | 61 | constant 6 V. |
| .5 | 914 | 55 | |
| 1.0 | 906 | 53 | |
| 1.5 | 899 | 49 | |
| 2.0 | 892 | 47 | |
| 2.5 | 888 | 44 | |
| 3.0 | 865 | 35 | |
| 3.5 | 855 | 30 | |

The charge on the tin oxide particle was one of positive quality.



DISCUSSION OF DATA AND RESULTS

The stannic oxide particles, under the force of the potential applied to the electrodes immersed in the molten glass, moved to and collected around the negative electrode; therefore, the particles while suspended in the fused glassy media were endowed with a positive charge. This is true when the glass was either sodium tetraborate or boric anhydride.

The plotting of the electrophoresis data - milli-ampere against the temperature - gave in all cases a straight line over the working range of the cell. This direct proportionality may be explained, and the final results justified by the following:

From Ohm's law

$$I = \frac{E}{R}$$

where in this application

I is the current through the cell

E is the applied cell potential

R is the electrical resistance of the cell

Since the resistance of the cell is equal to the length of the path between the electrodes divided by the product of the cross-sectional area and the conductivity - $R = l/KA$

Ohm's law equation may then be written :

$$I = \frac{E A K}{l}$$

The H in Lamb-Helmholtz equation for the calculation of the electrophoretic velocity is equal to the applied potential divided by the length of the path between the electrodes $H = E/l$; therefore:

$$I = H A K$$

The area being constant for a single cell charge, and the potential gradient maintained constant

I is proportional to K

The conductance of a cell increases with increases in the temperature of the system, since the viscosity of the medium decreases rapidly with increasing temperature after the glassy phase has been produced, or one might say the fluidity (the reciprocal of the viscosity) increases. It follows, then, that fluidity increases as the conductance of the cell increases. Then, since the conductance is the reciprocal of the resistance, it follows that a decrease in electrical resistance is produced by decreased fluidity. Such being the case, the decrease in electrical resistance parallels the decrease in the resistance offered to the flow of the particles by the

glassy media by increases in the fluidity of the glass. Hence, it follows that the increase in conductance is largely due to the decrease in the resistance offered by the glassy phase to the movement of the particles. conducting the flow of current through the cell.⁴

Since current is the rate of transfer of electricity, we may formulate the following:

$$I = N q v \quad (1)$$

where:

N is the number of charges or particles per cubic cm.

q is the quantity of electricity carried by each particle

v is the velocity of the particles under the applied potential.

From Stoke's law the velocity of a particle in the direction of an electrode can be expressed in terms of the force acting upon the particle. The force on the particles is given by the product of the potential gradient between the electrodes (H) and the quantity of electricity carried by the particles (q); therefore,

$$v = \frac{H q}{f} \quad (2)$$

⁴ Millard, E.B., "Phy. Chem. for Colleges" P. 198

⁵ Webb, T.J., "Elementary Prin. in Phy. Chem." P112

where:

v is the velocity of the particles

H and q are the same values in equation

1.

f is a frictional factor dependent upon the

shape of the particles and the resistance

offered by the suspending media

simplifying equations 1 and 2

$$I = \frac{N q^2 H}{f}$$

Since the quantity of electricity held by each particle is so very small and this value is then squared, it is reasonable to conclude that this factor may be considered a constant (physically the current will not be affected to a measurable degree by the slight variation in the charge per particle). The potential gradient may be maintained constant: therefore,

$$I = \frac{C}{f}$$

Where

C is a constant since also the number of particles in any one charge must be constant.

The value of f in stoke's law is the frictional force, or that force resisting the electrical forces.

For spherical particles: $f = 6\pi n r$. The particles cannot be considered spherical, and, therefore, the value of f may be generalized as:

$$f = C_1 n d$$

Where

C_1 is a constant

n is the viscosity of the fusion

d is one half the average cross-sectional dimension.

form of equation becomes:

$$I = \frac{1}{n d}$$

Earlier in the discussion the following proportionalities were expressed:

$$T \propto K, \quad T \propto \frac{1}{n}, \quad T \propto F, \quad K \propto \frac{1}{n}$$

Where T is the cell temperature.

Therefore:

$$I \propto K T$$

$$I \propto \frac{1}{n} T$$

$$I \propto F T$$

$$I \propto T$$

This verifies the experimental results as well as the applicability of the equations for the calculation of the values for hydrosols to the similar calculation of values for solid sols. The most outstanding is the

conformity to the Lamb-Helmholtz equation for the calculation of the zeta potential.

By extending the curve in fig. 2 until it intersects the temperature axis a temperature value of 780 °C. is found at which the current becomes zero. This temperature is about forty degrees higher than the "freezing" or Melting point of the glass at which temperature the viscosity would approach infinity, and the current should be zero. Therefore, it is reasonable to conclude that a straight line relationship does not fully describe the conditions between amperage and the temperature of the full range, but as the melting point is approached the curve will turn downward- current decreasing slower than the temperature. This hysteresis effect or tendency for the current to lag the temperature may be due to the fact that through a section cut vertical to a mass of cooling glass the "freezing" will not be homogeneous; that is, the surfaces exposed will be more viscos than the central portions, and the viscosity will vary with the distance from the outer surfaces. It is evident that due to this resistance to the particle movement as the outer surfaces are approached the effective velocity of the particles will become an average of the total velocities which will be a value

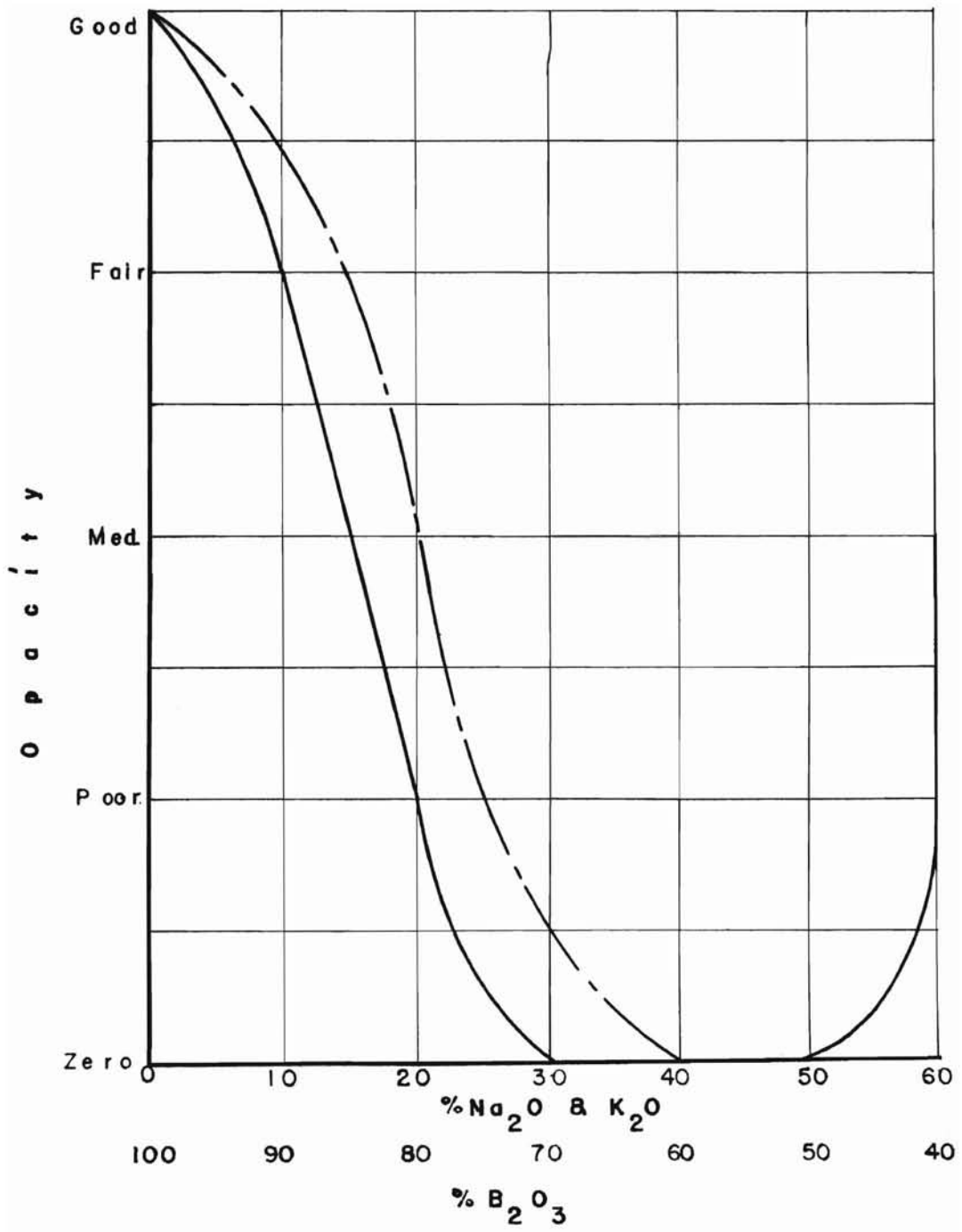
less than the true value at that temperature. For this portion of the curve the earlier conclusions will not hold, yet, since this portion is so small it may at present be ignored until remainder has been thoroughly studied.

Systems of $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ with constant additions of two percent stannic oxide gave very unusual results.

The system of $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ had glasses of fair opacity up to about ten percent K_2O . A glass containing twenty percent had its opacity concentrated in the surface of the glass, and some portions of the surface were rather clear. The opacity was zero in the glasses containing thirty, forty and fifty percent K_2O . The stannic oxide was found to be at the bottom of the fusion in small aggregate. The composition giving potassium metaborate (57.5 % K_2O) on fusion gave a glass of good opacity - as good as that containing ten percent K_2O , while the glass of the composition of potassium tetraborate was in that group of zero opacity. It is reasonable to conclude that the formation of compounds does not have any effect upon the resultant glass, or, at least, the formation does not have a constant affect on the

resultant condition. The glasses shattered on cooling and in some cases cracked the portion of the crucible under it. In all cases the walls of the crucible was cracked free at the edge of the glass. Yet, as the K_2O content increased the shattering and cracking of the porcelain increased.

The system $Na_2O-B_2O_3$ gave better opacity than the $K_2O-B_2O_3$ system. The opacity of the glass containing ten percent Na_2O had almost as good opacity as that containing pure boric anhydride and equal amount of the oxide. The opacity of that containing twenty percent Na_2O was equally as good as that containing ten percent K_2O . This twenty percent Na_2O glass had a scattered white precipitation of the stannic oxide on the surface. The thirty percent Na_2O gave a glass with better opacity than that containing twenty percent K_2O . Here again the stannic oxide was found to be concentrated in an even more concentrated condition than in the earlier case. In both cases some of the oxide was found to be deposited in the bottom of the fusion as an aggregate. In the case of Na_2O glasses the adjustment and reduced cracking of the crucible was accompanied with the higher Na_2O content.



Classes of lead tetraborate gave characteristic green glasses, and the opacity was almost zero. The stannic oxide was concentrated into large aggregates which formed at the upper edge of the fusion.

The curves in fig. 3 are characteristic to the deflocculation and flocculation curves for hydrosols-as clay. This indicates that there is probably some deflocculative and flocculative qualities attainable by the additions of heavy metallic ions. This phase of the investigation demands further study and work to obtain the true significance of the phenomena.

SUMMARY OF RESULTS AND CONCLUSIONS

1. The particles of stannic oxide in a glassy fusion are charged and will migrate under an applied potential. In the systems of Boric anhydride - two percent stannic oxide and sodium tetraborate - two percent stannic oxide the particles had a positive charge.
2. The equations for transference, electrophoresis, etc. which has been developed for hydrosols hold true in the case of solid sols over a considerable range.
3. The addition of metallic ions to the glass does not function completely as first proposed, but the deflocculation or flocculation of the particles is dependent upon such additions.
4. Compounds formed in the glassy phase do not effect the resultant opacity.

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