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AVENTURINE GLAZES

BY

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A

THESIS

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Approved by ....

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AVENTURINE GLAZES.

INTRODUCTION.

The production of an aventurine efface consists in the addition of an excess of a metallic oxide to an alkaline glaze. The glazes are mostly fritted and in the glost fire the glaze liquifies and dissolves more or less of the metallic oxide or oxides present.

It is the concensus of most writers that at the maturing temperature it is a supersaturated solution. In cooling the capacity of the glazzy liquid to hold the dissolved oxide in solution is lessened, and the excess is precipated as thin plate like crystals or spangles.

Crystalline segregations are not new in colored glazes. Aventurine effects are found on Japanese vases made centuries ago.[1]

Dr. Maeckler, by request of Director Dr. Heinecke, of the Royal factory at Berlin made the first scientific investigation of the phenomenon, which was published in 1896.[1]

In a publication by G. Vogt, technical manager of the National factory at Sevres, says that the first crystallized glazes were made at Sevres in 1884.[1]

J Koerner[2] noticed that Uranium Oxide combined with lead had a great inclination to form an aventurine like glass. He found this also to be true with Bismuth.

Riddle[3] made a good aventurine by supersaturating the following frit with some coloring oxide, ferric oxide working especially well, giving a rich red color.

Following is the empirical formula and batch weight for Riddle's glaze.

$0.25\ K_2O$
$0.25\ Na_2O \quad 0.75\ B_2O_3 \quad 2.25\ SiO_2$
$0.50\ CaO$

Batch weight.

Potassium Nitrate -- 13.95 parts.
Calcium Carbonate -- 13.81 parts.
Flint ---------- 37.29 parts.
Borax ------------- 26.38 parts
Flaky boric acid -- 8.53 parts

Petrik[4] found that by melting dehydrated iron vitriol and common salt together, flakes of iron oxide are produced which dissolve only with great difficulty in a molten mass and give accordingly an aventurine effect.

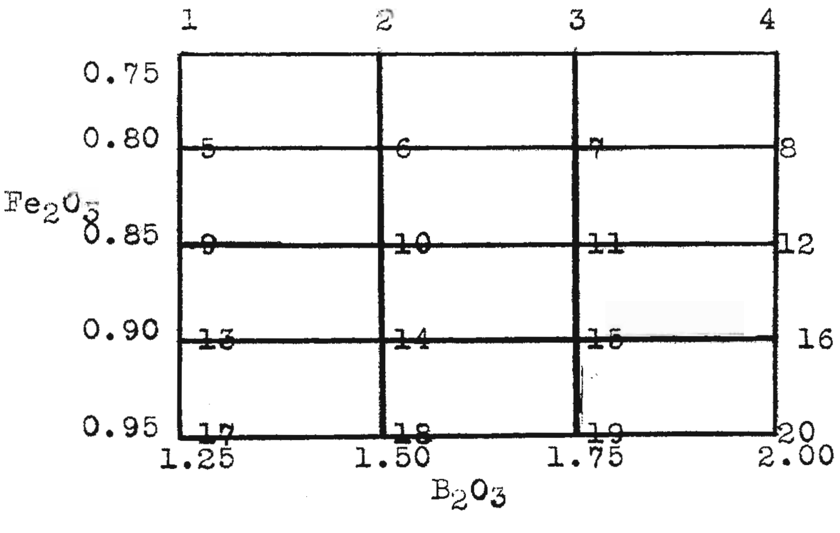
SCOPE OF INVESTIGATION

The object of this study was to notice the effect produced upon the crystalline growth in the glaze by the variation of B_2O_3, Fe_2O_3, and SiO_2, and to notice the effect of cooling upon the crystalline growth in the glaze.

METHOD OF INVESTIGATION

The following glazes were selected for the end members of a 20 member rectangular system.

The graph shows the position of each of the 20 members in each series.



The composition in terms of equivalents of the corner members for both series; "A"(5.0 equivalents SiO_2) and series "B"(6.0 equivalents SiO_2) is presented in table I

Table I

Series A.

	Corner No. 1	4	17	20
Na_2O	1.0	1.0	1.0	1.0
Fe_2O_3	0.75	0.75	0.95	0.95
Al_2O_3	0.10	0.10	0.10	0.10
B_2O_3	1.25	2.00	1.25	2.00
SiO_2	5.00	5.00	5.00	5.00

Series B

	Corner No. 1	4	17	20
Na_2O	1.0	1.0	1.0	1.0
Fe_2O_3	0.75	0.75	0.95	0.95
Al_2O_3	0.10	0.10	0.10	0.10
B_2O_3	1.25	2.00	1.25	2.00
SiO_2	6.00	6.00	6.00	6.00

MATERIALS USED

The materials used were flint, No. 4 Kentucky ball clay, borax, iron oxide (red), and soda ash (Na_2CO_3).

METHOD OF PREPARING GLAZE.

Frits were prepared for corners number 1, 4, 17, and 20. For each of these members, all the ingredients were fritted except 0.10 equivalents Al_2O_3 and .20 equivalents SiO_2, which were later added as ball clay to help suspend the frit.

The composition of the raw frit batches are given in table II

Table II

Batch weights of the corner members.

Series A.

Member	Borax	Na_2CO_3	Ferric Oxide	Flint
1	238.5	39.75	119.6	288.0
4	381.4		119.6	288.0
17	238.5	39.75	151.71	288.0
20	381.4		151.71	288.0

Series B

Member	Borax	Na_2CO_3	Ferric Oxide	Flint
1	238.5	39.75	119.6	348.0
4	381.4		119.6	348.0
17	238.5	39.75	151.7	348.0
20	381.4		151.7	348.0

25.8 parts of ball clay was added to each frit for the 0.10 equivalents of Al_2O_3 and .20 equivalents SiO_2.

The four corners were fritted, the drip method of fritting being used. The frit was dried and then ground in a porcelain lined pebble mill until the frit passed through a 150 mesh screen.

0.10 equivalents of Al_2O_3, in the form of ball clay, was added to the frit, and the frit again ground, with water, in a porcelain lined pebble mill until the glaze passed through a 150 mesh screen.

The specific gravity of the glaze was adjusted to 1.48, and the intermediate members of the rectangular system were made by volume blending of the corners.

Table III (on next page) presents the percentages used for blending of the intermediate members.

Table III.

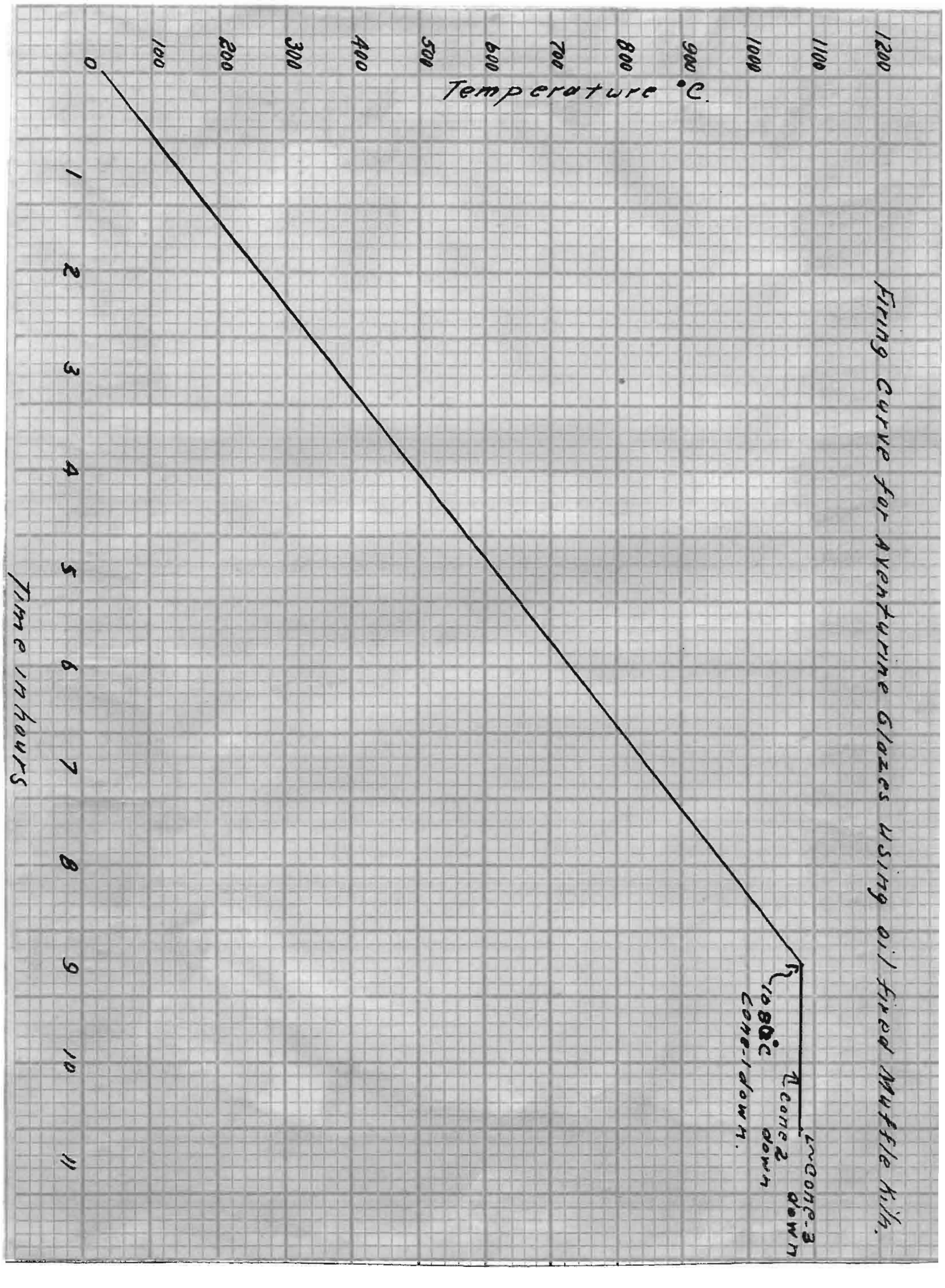
Member	Corner No. 1	4	17	20
1.	100.0%			
2.	66.67	33.33%		
3.	33.33	66.67		
4.		100.00		
5.	75.00		25.00%	
6.	50.00	25.00	16.67	8.33%
7.	25.00	50.00	8.33	16.67
8.		75.00		25.00
9.	50.00		50.00	
10.	33.33	16.67	33.33	16.67
11.	16.67	33.33	16.67	33.33
12.		50.00		50.00
13.	25.00		75.00	
14.	16.67	8.33	50.00	25.00
15.	8.33	16.67	25.00	50.00
16.		25.00		75.00
17.			100.00	
18.			66.67	33.33
19.			33.33	66.67
20.				100.00

APPLICATION OF GLAZE

The frit settled out so fast that it was impossible to dip or spray the glaze on the trials; therefore the glaze was applied with a small camel hair brush.

Firing

The trials were fired in two saggers in a muffle kiln to cone 3. The kiln was fired at the rate of 110° Centigrade per hour to cone 1, which was reached at 1080° Centigrade, and cone 2 and 3 were soaked down as this temperature was maintained for 1½ hours.



Firing Curve for Aventurine Glazes using oil fired Muffle kiln.

DISCUSSION OF RESULTS.

The glost fire of the bottom sagger reached cone 3, and along with this glost fire, the top sagger containing duplicate trials of both series resulted in a cone 2 fire.

Series A.

The members No. 1,2,3, and 4 of series A in the bottom sagger (cone 3) had very little crystalline formation. The glaze had a brown color and some crystalline growth was noted around the edges of the trials. These trials had the lowest amount of Fe_2O_3 (0.75 equivalents),and the B_2O_3 content varied from 1.25 equivalents for No. 1 member to 2.00 equivalents for No. 4 member.

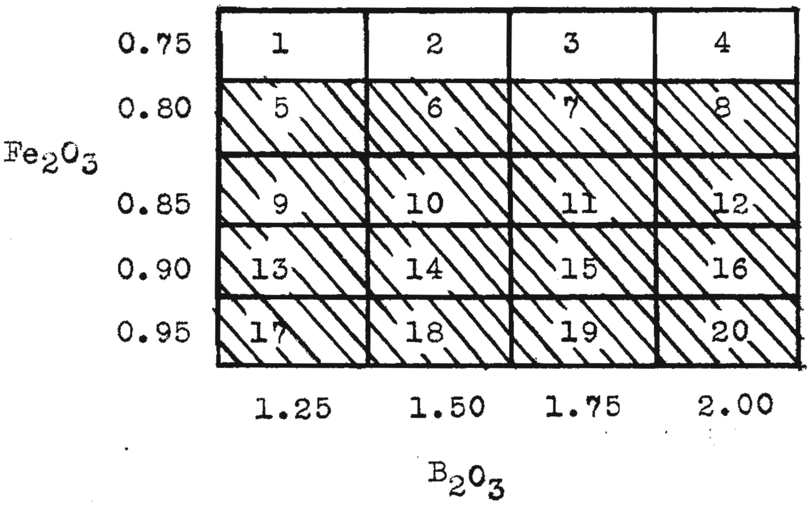
The other members of the series showed a great amount of crystalline growth, with No. 9, 10, 11, and 12 members showing the largest crystals. These members had a medium amount of ferric oxide (0.85 equivalents), and the B_2O_3 content varied from 1.25 equivalents for No. 9 member, to 2.00 equivalents for No. 12 member.

When viewed under a microscope, the sturcture of the glaze resembled a mass of colored broken glass, but when examining a trial with a little crystalline growth, very definite crystals were seen . They were identified by Professor Muilenburg[5] as hexagonal basal pinacoidal crystals of hematite. The crystals were of various colors.

The members of series A in the top sagger (cone 2) showed the same characteristic as the members in the bottom sagger (cone 3), with the exception that the crystalline growth was not as great. The crystals in members 13,14,17,18,19, and 20 were small, resembling small brassy particles.

The following graph shows the members of series A having the greatest crystalline growth. The cross hatching indicates the areas of greatest crystalline growth.

Graph No. 1



Fe_2O_3 \ B_2O_3	1.25	1.50	1.75	2.00
0.75	1	2	3	4
0.80	▨ 5	▨ 6	▨ 7	▨ 8
0.85	▨ 9	▨ 10	▨ 11	▨ 12
0.90	▨ 13	▨ 14	▨ 15	▨ 16
0.95	▨ 17	▨ 18	▨ 19	▨ 20

Series B.

The members of series B, in the bottom sagger (cone 3) that showed the best crystalline growth were No. 1,2,15,16,19, and 20.

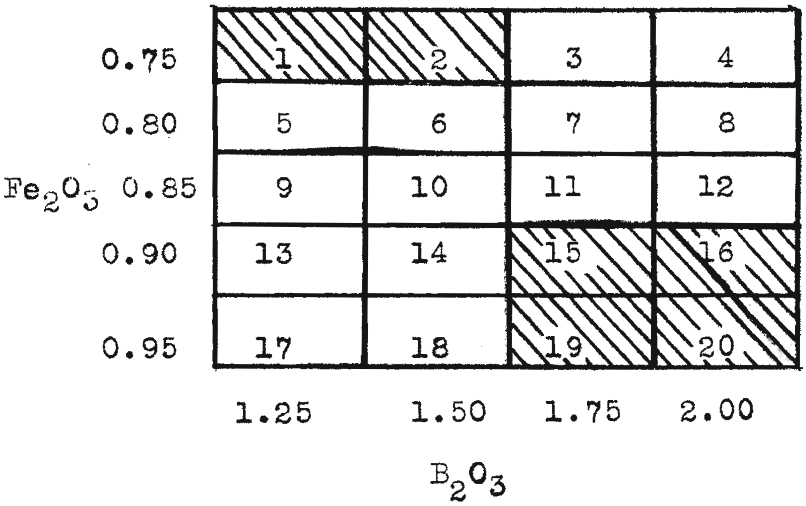
The crystalline growth decreased in the members containing low ferric oxide content with the increasing content of borax. The crystalline growth increased in the members of high ferric oxide content and with the increasing content of borax. The members that contained high ferric oxide and low borax content had very little aventurine affect. The had the same brown color that was encountered in a few members of series A.

Members No. 5,6,7,10,11, and 12, had a peculiar appearance. It seemed as if the glaze had crazed and then annealed. The surface was perfectly smooth.

The cracking of the crystals, in trials which had a very great crystalline growth, was caused by the unequal expansion and contraction of the hematite crystals and the glass.

Graph No. II (on next page) shows the members of series B having the greatest crystalline growth. The cross hatching indicates the areas of greatest crystalline growth.

Graph II


0.75
0.80
Fe_2O_3 0.85
0.90
0.95
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
1.25
1.50
1.75
2.00
B_2O_3

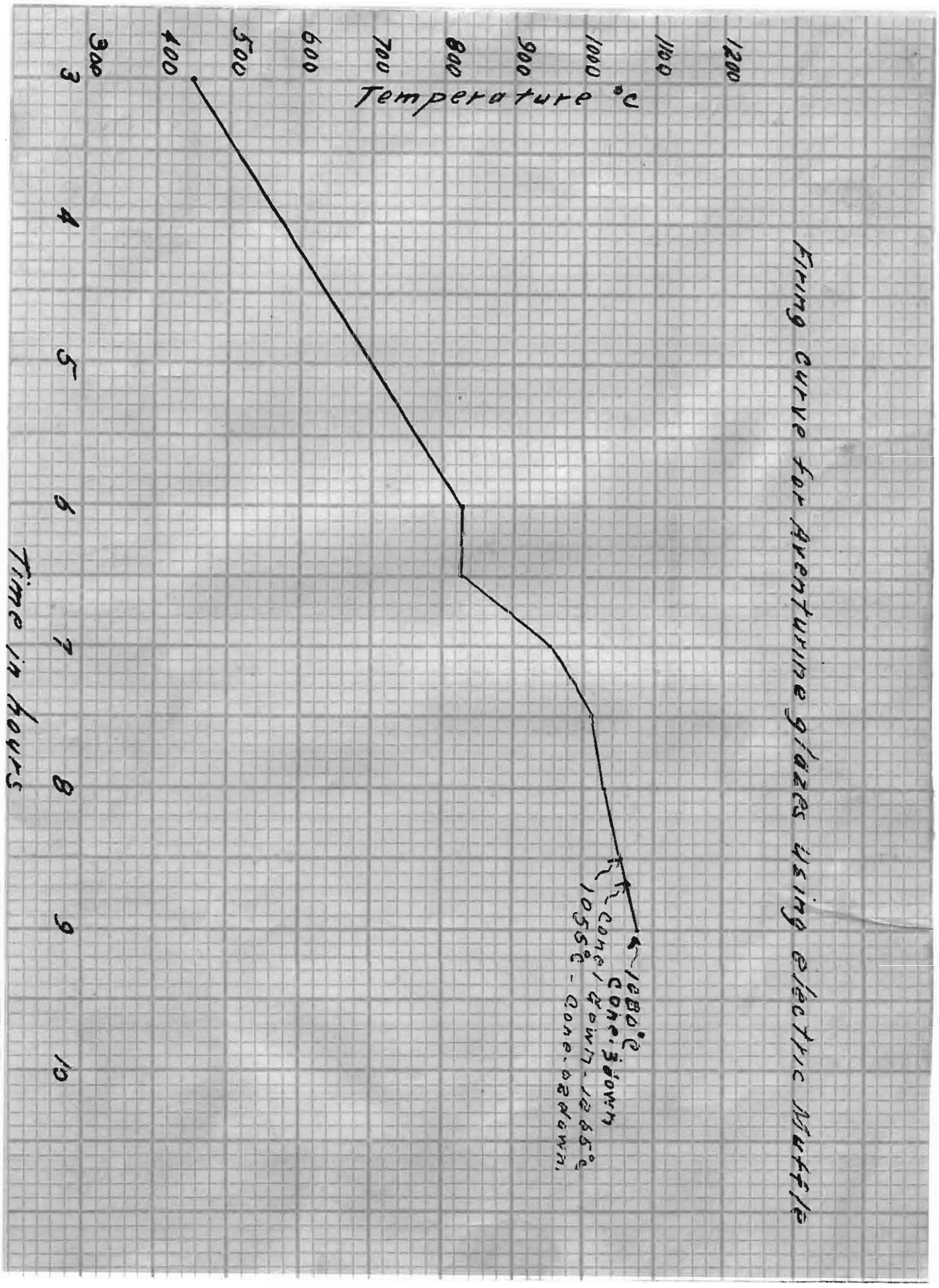
EFFECT OF CONTROLLED COOLING RATES.

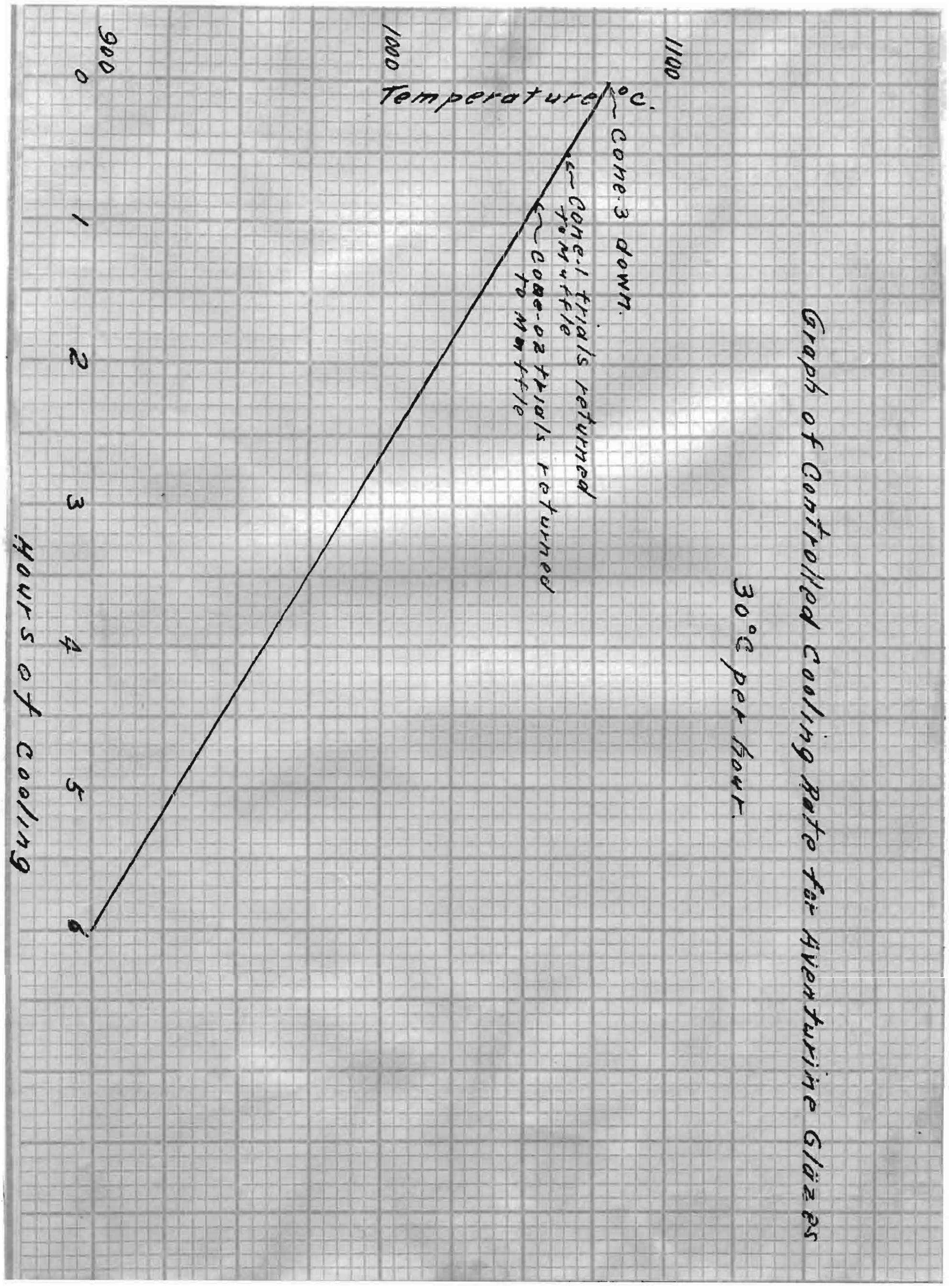
It was readily seen from the results of the investigation to date, that the control of the cooling enhances the growth of the aventurine crystals.

The effect of controlled cooling rates on the crystalline growth was tried on member No. 5 of series A.

Fifteen trials were fired in an electric muffle. Five trials were fired to cone 02, five to cone 1, and five to cone 3. The trials were drawn out at their respective temperatures.

When cone 3 was reached, the cooling process was begun. The furnace was cooled at the rate of 30° Centigrade per hour. When the temperature, at which the trials of cone 1 were drawn out, was reached, the trials were returned in the furnace. The same was done with the trials of cone 02. Trials were drawn at every hour, until the furnace had cooled to 900° Centigrade.


Firing curve for Aventurine glazes using electric Muffle
Temperature °C
300
400
500
600
700
800
900
1000
1100
1200
Time in hours
3
4
5
6
7
8
9
10
1080°C
Cone 3 down
Cone 1 down - 1065°c
1055°C - Cone 02 down.



Graph of Controlled Cooling Rate for Aventurine Glazes

30°C per hour.

DISCUSSION OF RESULTS

Trials that were fired to cone 3.

The first trial, drawn after one hour of cooling, showed little crystalline growth. A few crystals were noticed around the edges of the trial.

The trial drawn after two hours of cooling showed a greater amount of crystals, and also larger crystals.

The trial drawn after four hours of cooling showed the crystals growing in size and having a multitude of colors.

The trial having five hours of cooling contained a large amount of multi-colored crystals still growing in size.

One trial was allowed to cool in the furnace, and it contained the greatest amount and also the largest crystals.

Trials fired to cone 1.

The first trial that was drawn out had a brassy color, and did not have any crystalline growth.

The second and third trials had a little crystalline growth, but the crystals were very small.

The trial that had five hours of cooling had fairly large multi-colored crystals, while the trial that was allowed to cool in the furnace showed an increase in the size of crystals, but the trial was not yet completely covered with crystals. The edges of the trial did not have a crystalline formation.

Trials fired to cone 02.

The first trial drawn did not have a crystalline growth,, but the trial drawn after two hours of cooling showed a large number of very small multi-colored crystals.

The trial drawn after four hours of cooling contained a large number of small brassy looking particles or crystals, while the trial allowed to cool with the furnace showed the crystals increasing in size, but the maximum crystalline growth not yet having been reached.

CONCLUSIONS

It is concluded that:

1. Glazes having a low content of Fe_2O_3 (0.75 equivalents), and a low content of B_2O_3 (1.25 equivalents), will give a small crystalline growth.

2. Glazes having a low content of Fe_2O_3 (0.75 equivalents), and a high content of B_2O_3 (2.00 equivalents), will give a small crystalline growth.

3. Glazes having a low amount of B_2O_3 (1.25 equivalents), and a high content of Fe_2O_3 (0.95 equivalents), with a high silica content (6.0 equivalents), will not give a good aventurine effect.

4. Glazes giving the best aventurine effect contain a moderate amount of Fe_2O_3 (0.85 equivalents), low or high content of borax or B_2O_3 (1.25 or 2.00 equivalents), and a low content of SiO_2 (5.0 equivalents).

5. The crystals have a definite crystalline shape.

6. The cracking of the crystals is due to the unequal expansion and contraction between the crystals and glass.

7. A slow rate of cooling will give the greatest crystalline growth and also results in larger crystals.

RECOMMENDATIONS.

For further work on this subject, it would be advisable to study more thoroughly the effect of various controlled cooling rates on the crystalline growth of the glaze, and a further study could be made on the temperature at which the maximum amount of crystals, or when the crystals have stopped growing, is reached, so that the kiln may be cooled rapidly when the temperature reaches this point.

An extensive study could be made on agents that would suspend the glaze, so as to make spraying suitable for this type of glaze.

The organic agents that could be tried as aids to the suspension of the glaze are:

1. Gum Arabic.
2. Gum Tragacanth.
3. Gum Karaya.
4. Dextrine.
5. Gelatine.

Another method that could be tried is to add a strong ammonia solution to the glaze.

APPLICATION TO THE INDUSTRY.

Due to the cost of materials, the cost of fritting, and the trouble encountered in applying the glaze to the ware, makes this a glaze too expensive to apply to ordinary ware. This glaze could just be used for decorative art ware.

ACKNOWLEDGMENT.

I wish to acknowledge the kind assistance and practical advice rendered by Mr. A.J. Paul and Professor C.M. Dodd of the Ceramic Department, and Professor G.A. Muilenburg of the Geology Department.

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T.A.C.S. Vol. 10, P. 61, 1908

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T.A.C.S. Vol. 8, P. 336, 1906.

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J.A.C.S. 7 (11) P. 824, 1924.

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ABSTRACTS.

Notes on the Production of Crystalline Glazes.

Ray T. Stull. T.A.C.S. Vol 16, P. 186, 1904.

Crystalline glazes may be divided into two classes, (1) those in which the crystals are produced by the so-called supersaturation method, and (2), glazes in which the entire mass has a crystalline structure.

The first class comprises the aventurine glazes as the "Goldstone" or "Tiger-Eye". Such a glaze is produced by a mixture in which there is an excess of one or more metallic oxides, or by applying these oxides to the body or bisque before dipping in the glaze. Upon firing, the glaze proper or glassy matrix liquifies. This liquid is capable of dissolving more or less of the metallic oxide or oxides present. In cooling, the capacity of the glassy liquid to hold its dissolved material in solution is lessened, hence the excess is deposited as crystals within a glassy matrix, or produces an opaque result due to incipient crystallization.

An experiment was carried on to determine what ceramic materials gave to glazes the best tendencies to crystalize. The results of these experiments seemed to permit the following general deductions.

1. The strongest crystalline tendencies are given to glazes by those chemical elements of low atomic weight whose oxides go to make up the RO, such as sodium, potassium, magnesium, calcium, manganese, iron, zinc, etc.
2. Those metals of high atomic weight, such as barium, lead, etc., seem to impart a glassy nature to silicates when used in sufficient quantities, which is unfavorable to crystallization.
3. Those chemical elements of higher atomic weight whose oxides make the acid portion of a glaze, such as silicon, titanium, phosphoreous, etc., produce the best crystallizing agents, while those of lower atomic weight, as for example, boron, having an atomic weight of 11, impart a fluidity and brilliancy to a glaze which is detrimental to crystallization.
4. The introduction of an R_2O_3 materially assists crystallization in some cases, while in others it is detrimental to it.

Crystalline Glazes.

Ross C. Purdy and Junius F. Krehbiel.

T.A.C.S. Vol 9, P. 401 1907.

The authors discuss various types of crystalline glazes, and they state that of the two alkalies, potash and soda, the latter was found to be the most conducive to the development of crystals.