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The use of fluorspar as a flux ingredient in ceramic bodies

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THE USE OF FLUORSPAR AS A FLUX INGREDIENT IN CERAMIC BODIES

BY

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A

THESIS

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INTRODUCTION

The term "flux" is a relative one and does not refer to any particular class of substances. A flux is any material which will lower the softening, fusion, or liquifying temperature of another material. Bases act as fluxes to siliceous substances while in basic compositions like Portland cement, silica is a flux. Feldspar is a flux for white ware mixtures, and is regarded as a refractory in the low temperature enamels.

Although fluorspar is used in considerable quantities in many divisions of the ceramic industry, namely: the glassware division, the enamels division, and in the manufacture of cement, its use in the white wares division has been very limited. Because it is a powerful flux, fluorspar should make an excellent auxiliary flux to Potash feldspar, Soda feldspar, or a mixture of Potash and Soda feldspars. An eutectic composition of these three materials should make an ideal flux for the white wares industry. If successfully brought about, this flux would be another step towards successful competition with European manufacturers.

JUSTIFICATION FOR RESEARCH

For the last three decades, manufacturers of ceramic wares have been experimenting with fluorspar as a substitute for feldspar. In 1900, Mr.C.H.Binns[1] experimented along this line, using fluorspar as a substitute for feldspar, but his results were of a very unsatisfactory nature. Since then many experiments have been run of the same nature, but all results have only confirmed those of Mr.Binns'. Nowhere in the literature of the industry is there found any data concerning a mixture of feldspar and fluorspar to be used as a fluxing ingredient for ceramic bodies.

Fluorspar is subject to the fault of all lime salts; that of shortening the vitrification range and lowering the viscosity to such an extent that when used as a basic flux, it is more harmful than helpful to the product. The vitrification range of fluorspar is so short that it is impractical to use more than 2% by weight, in a body which must be vitrified to develop a density of less than 3% absorption. Also, at times, there is evidence that

[1] Trans.Amer.Cer.Soc.,vol.2, p.194

a gas is evolved after vitrification has set in. All of these facts make fluorspar a very unreliable flux; that is when it is used in an uncombined state in the body.

Potash feldspar is a safe and reliable flux, because of its high viscosity when melted. It is a slow acting flux which provides a long vitrification range. It matures about cone 9 but its fluxing action generally requires a temperature from cone 11 to cone 12 for good results.

Soda feldspar has a shorter vitrification range than potash feldspar, yet the range is longer than that of fluorspar.

With these facts in mind an eutectic formed by these three materials was sought; so as to bring about a lower vitrification temperature, and yet keep the vitrification range as long as possible.

MATERIALS

The materials used in the investigation were commercial products, which are used in everyday practice. These products were:

1. Buckingham Potash Feldspar
2. Goudy Soda Feldspar
3. Kentucky Fluorspar Co.,Fluorspar

OUTLINE OF PROCEDURE

To develop the desired flux, an eutectic of the three materials was sought. This was done in the following manner:

A twenty-one member ternary system, Table I, was made up, having as end members 100% potash feldspar, 100% soda feldspar, and 100% fluorspar. The ingredients for each member were mixed dry and then a solution of dextrin was added to form a bond and to add plasticity to the body. From these mixtures cones were formed in a standard pyrometric cone mould; each cone was then stamped with its member number and allowed to dry. The cones were then set in a cone plaque as shown in Fig.1.

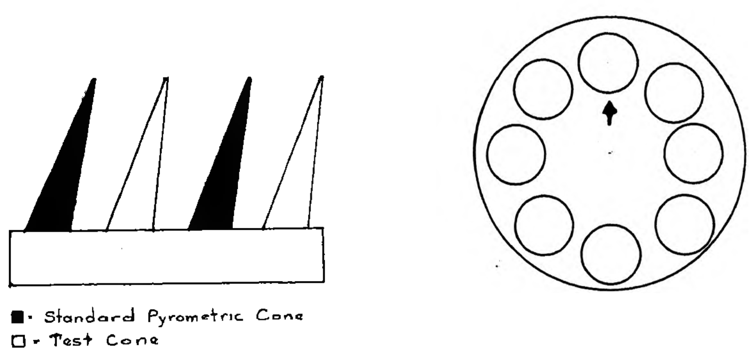

Fig.1.

The cones in the manner shown, alternating with standard pyrometric cones, gave a range of four standard cones; hence their P.C.E. value was easily obtained. The cones were tested in a Fulton-Coursen[1] electric furnace, and as the deformation temperature was reached, it was checked with a Leeds and Northrup optical pyrometer.

The three members of the twenty-one member triaxial shown in Fig.2 having the lowest deformation temperatures were noted and the intermediate members within that area were made up and tested in the same manner.

TABLE I

Member	%KSpar	%NaSpar	%FSpar	Member	%KSpar	%NaSpar	%FSpar
1	100	0	0	12	20	60	20
2	80	20	0	13	20	40	40
3	80	0	20	14	20	20	60
4	60	40	0	15	20	0	80
5	60	20	20	16	0	100	0
6	60	0	40	17	0	80	20
7	40	60	0	18	0	60	40
8	40	40	20	19	0	40	60
9	40	20	40	20	0	20	80
10	40	0	60	21	0	0	100
11	20	80	0				

1. Chem. & Met.Eng.XII,p.154 (1914)

Note: See Table I
for Composition

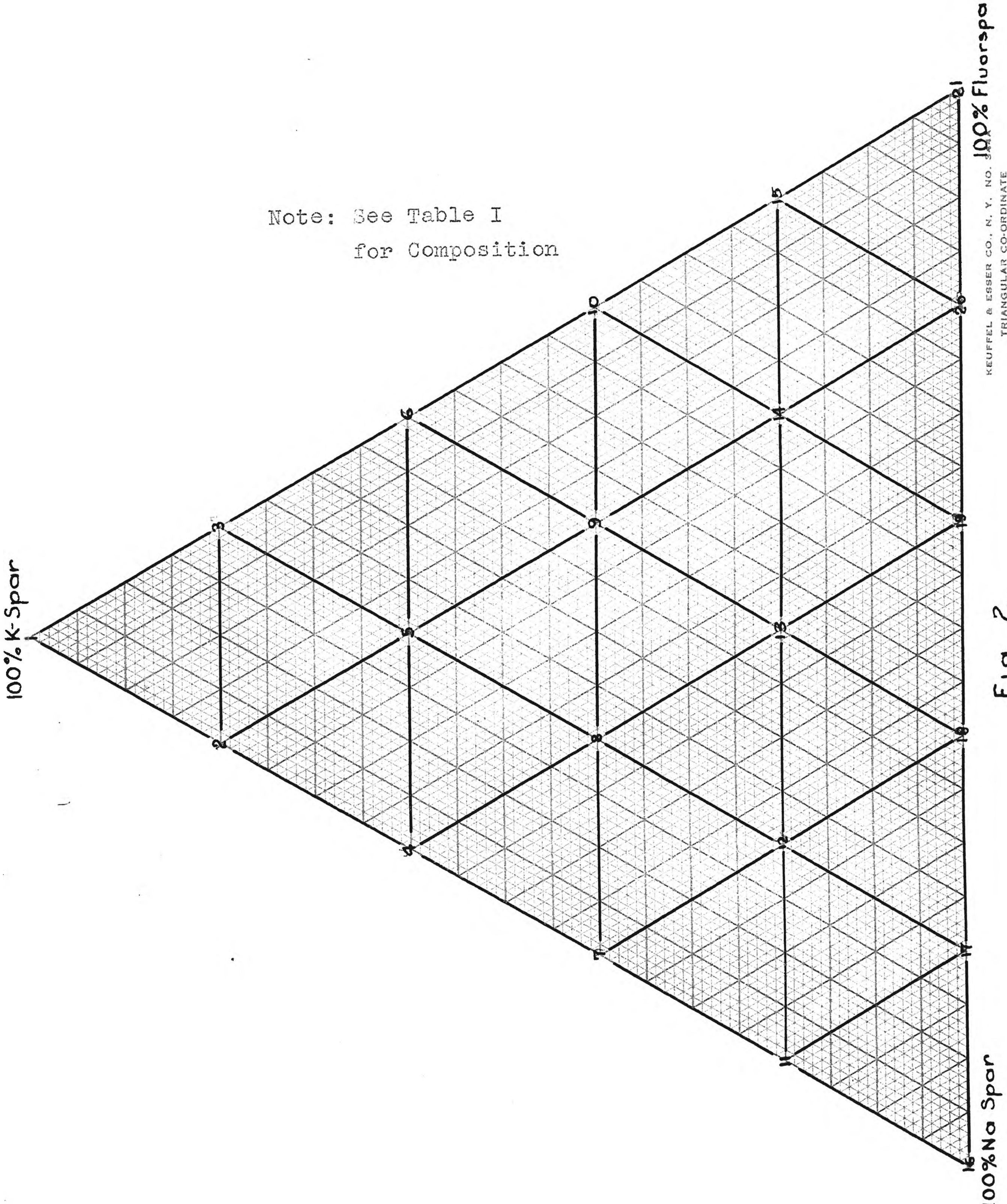

Fig. 2

TABLE II

Deformation test on 21-member system

K Spar - - Na Spar - - Fluorspar.

Member	P.C.E.	Degrees Centigrade	Member	P.C.E.	Degrees Centigrade
1	9-10	1290°	12	1-2	1160°
2	9	1275	13	1-2	1165
3	6	1230	14	1-2	1160
4	6-7	1245	15	1	1160
5	4	1190	16	7-8	1255
6	04-03	1080	17	2-3	1165
7	6	1230	18	2-3	1165
8	01-1	1155	19	3-4	1180
9	01	1145	20	4-5	1200
10	1	1160	21	8	1260
11	5-6	1220			

DISCUSSION - RESULTS

From the results obtained, (see Table II) the area bounded by members 3, 8, and 10 was taken as the "low" area. The bending intervals of the members within this area (3, 5, 6, 8, 9 and 10) were very short; however, they did not turn into a fluid slag as did many of the other members.

Members 14, 15, 19, 20, and 21 came down at the P.C.E. and temperatures recorded, but before they were able to be withdrawn from the furnace they had changed to a fluid slag.

Members 1, 2, 4, 7, 11, and 16 came down at the temperatures and P.C.E. as recorded in Table II; member 11 is the lowest of the binary system and gives evidence that an eutectic is formed in the neighborhood of a proportion of 20% K-Spar, and 80% Na-Spar.

Members 17 and 18 give rise to a formation of an eutectic in the neighborhood of 75% Na-Spar and 25% Fluorspar.

Member 6 came down between standard cones 04 and 03, and the temperature as read with the optical pyrometer was 1080°C. This was by far the lowest temperature of any of the members of the system,hence the area previously described was decided upon. These intermediate members were sought to define more definitely the location of the eutectic of the series. These members were made up and marked as shown in Table III and Fig.3; They were tested in a manner identical to the first series.

TABLE III

Composition of Members of

Intermediate Series

Member	%KSpar	%NaSpar	%FSpar	Member	%KSpar	%NaSpar	%FSpar
3	80		20	v	50	15	35
a	75	5	20	w	50	10	40
b	75		25	x	50	5	45
c	70	10	20	y	50		50
d	70	5	25	z	45	35	20
e	70		30	aa	45	30	25
f	65	15	20	bb	45	25	30
g	65	10	25	cc	45	20	35
h	65	5	30	dd	45	15	40
i	65		35	ee	45	10	45
5	60	20	20	ff	45	5	50
j	60	15	25	gg	45		55
k	60	10	30	8	40	40	20
l	60	5	35	hh	40	35	25
6	60		40	mm	40	30	30
m	55	25	20	nn	40	25	35
n	55	20	25	9	40	20	40
o	55	15	30	oo	40	15	45
p	55	10	35	pp	40	10	50
q	55	5	40	ss	40	5	55
r	55		45	10	40		60
s	50	30	20				
t	50	25	25				
u	50	20	30				

Note: See Table III for

Composition.

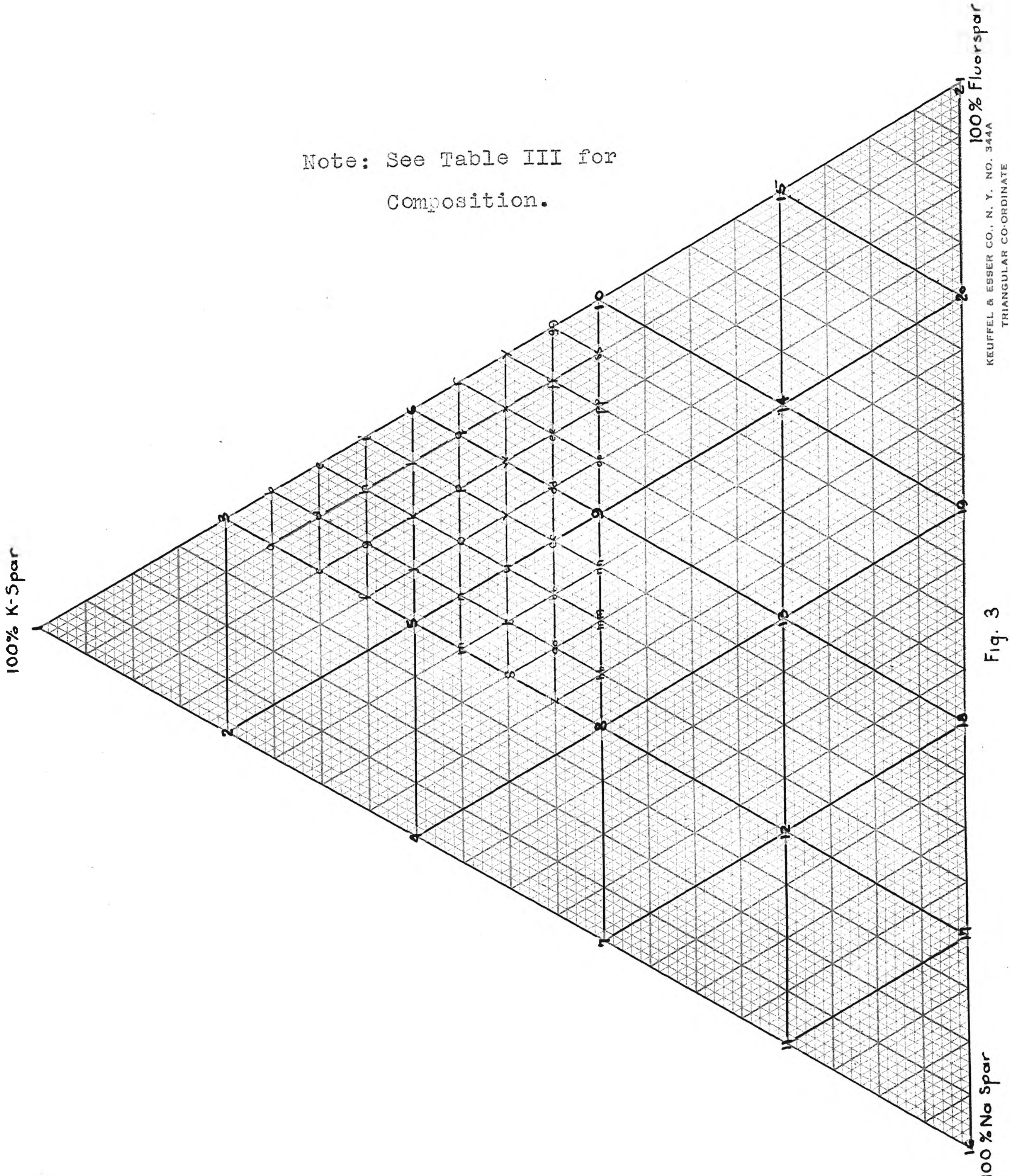

Fig. 3

TABLE IV

Results of Test Run of Members of Intermediate Series of "Low" Area.

Member	P.C.E.	Temp.°C.	Member	P.C.E.	Temp.°C.
3	6	1230	u	1-2	1163
a	3-4	1175	v	3-4	1167
b	5	1200	w	3	1165
c	01-1	1150	x	3-4	1180
d	3-4	1180	y	3-4	1180
e	4	1190	z	3-4	1168
f	3-4	1175	aa	3-4	1168
g	01-1	1150	bb	02-01	1140
h	3	1175	cc	3-4	1168
i	02-01	1135	dd	03-02	1120
5	4	1190	ee	03-02	1120
j	2-3	1165	ff	3-4	1172
k	01-1	1150	gg	3-4	1175
l	04-03	1100	8	01-1	1155
6	04-03	1080	hh	1-2	1150
m	2	1165	mm	02	1125
n	3	1172	nn	03-02	1120
o	3	1175	9	01	1145
p	02-01	1130	oo	01-1	1155
q	02-01	1130	pp	1-2	1163
r	02-01	1130	ss	1	1160
s	01-1	1155	10	1	1160
t	1-2	1163			

The results as indicated by the data in Table IV confirm those results of the first test run, that member 6 is the approximate eutectic of the binary system of K-Spar and Fluorspar. It cannot be called the true eutectic of the mixture, because not enough points have been run on the system to definitely locate the true eutectic. However, this percentage composition was close enough to the true eutectic to be used commercially as such.

There were no outstanding peculiarities among the various intermediate members tested; all of the members came down as solids, none of them transformed into a fluid slag.

The area surrounding members "dd" and "ee", seemed to be a low area, and would probably bear a more thorough investigation; however, because it was not as low as the area surrounding member 6, this investigation was not gone into.

CONCLUSIONS

The evidence brought out by this thesis promises to throw a new light upon the use of fluorspar as flux ingredient in ceramic bodies; not to be used uncombined, but as an integral part of the major flux of feldspar. True, the action of fluorspar alone as a flux may cause a vesicular structure in the body; but the stabilizing effect of the slow maturing feldspar should more than offset this undesirable quality. The temperature of member 6 was materially lower than that of member 1, yet the bending interval of member 6 and the bending interval of member 1 were the same; this then, is conclusive evidence that fluorspar will lower the vitrification temperature yet should not materially shorten the vitrification range.

The use of fluorspar as a flux ingredient should lower the maturing temperature of a white-ware body about four cones; hende a body maturing at cone 10 would mature at cone 6. This would prove a boon to the manufacturers of white ware, as it would enable them to cut the cost of manufacture thru the saving effected in the total fuel consumption, to say nothing of the increased output due to shorter firing schedules and a reduction in total time of firing and cooling.

RECOMMENDATIONS FOR FURTHER RESEARCH

That a further investigation be made of the study is recommended, also that the area within members 3, 8, and 10 be made up again and then fritted before being tested for their deformation temperatures.

The members of both the fritted flux and the raw flux should then be incorporated in a white ware body which, without the aid of an auxiliary flux would mature at cone 10; upon these bodies then, should be run a complete firing behavior test, which will include all of the tests of the physical properties. A comparison of the value of member 6 as an auxiliary flux could then be made.

A test should be run to determine the water solubility of member 6, both in the fritted state and in the raw state.

Tests should be run in the same manner as described in this thesis with the other Potash feldspars other than Buckingham.

The above investigation coupled with this thesis would then give a very comprehensive study of the effect of fluorspar as a flux ingredient.

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Part I

ABSTRACTS

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Progress of Vitrification and Solution in Some Porcelain Mixtures, Jour.Amer.Cer.Soc.,vol.21, p.400, 1919. The substitution of Soda feldspar for Potash feldspar has a marked effect both in the degree of quartz solution and in the Sillimanite development. The quartz grains go into solution to a degree in excess of that allowed in any of the other bodies studied. It was noticeable that the sillimanite crystals were at least five times as large as those in any of the other bodies studied. The introduction of calcium flux did not apparently add to the sillimanite development; although it undoubtedly increased the solution of the quartz grains at any given temperature.

The Action of the Different Forms of Calcium as a Flux in Porcelain Manufacture, A.S.Watts, Trans.

Amer.Cer.Soc.,vol.10,p.265, 1910. More variation as to the physical properties is to be expected where any quantity of calcium flux is added than where a plain feldspar body is manufactured. A small addition of calcium flux, if properly handled will improve the color. Fluorspar is to be condemned for use since it appears faulty under any other than ideal conditions, which is due to the fact that its action begins so early in the burn that the clays and spars of the body have not shrunk sufficiently to form a close body and thus it invites an excessive absorption of gas. Upon gradual heating and cooling, a fine white body was obtained when fluorspar was used.

The Use of Mixed Potash-Soda Feldspars in Porcelains, A.S.Watts, Trans.Amer.Cer.Soc.,vol.16, p.212, 1929. In the trials run, warpage was the worst when the amounts of soda feldspar and potash feldspar were about equal. Shrinkage increases with the soda content, but only slightly so after the ratio equals one potash to one soda feldspar. Translucency increases with soda feldspar content, but when fired above cone 8 the translucency decreases with increased heat treatment in all of the members studied.

Auxiliary Fluxes in Ceramic Bodies, Paul F.Collins, Jour.Amer.Cer.Soc., vol.15, p.17, 1932. The purpose of the research was to develop a new type of body flux which, though added in small quantities would be capable of exerting powerful solvent action during the normal process of body vitrification. Twenty-five synthetic fluxes composed of ceramic materials, compounded in their eutectic proportions, and fused to clear glasses were added to a body of semi-vitreous type in varying amounts; their effect on vitrification was studied. It was found possible to reduce the feldspar content of such a body to 8%, and by an addition of 2% auxiliary glass, to develop almost any desired degree of body vitrification between 0.5 and 7.0% at a temperature as low as cone 6. The auxiliary fluxes dealt with in the research were chosen from among the more simple low temperatures fusing mixtures of alkaline or alkaline earths, and SiO_2 and B_2O_3; and between alkalis or alkaline earths, and SiO_2 and B_2O_3 or Al_2O_3.

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PART II

ADDITIONAL REFERENCES

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