



THE WETTING OF ALUMINA BY VITREOUS ABRASIVE WHEEL BONDS

by

Almitra Pheroze Sidhwa

B. Sc., University of Bombay
S. B., Massachusetts Institute of Technology

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Signature of Author

 Signature redacted

Department of Metallurgy
August 1959

Thesis Supervisor

 Signature redacted

Professor F. H. Norton

Chairman
Department Committee on
Graduate Students

 Signature redacted

Professor J. T. Norton



Metall

Thesis

1959

THE WRITING OF ALUMINA AND ALUMINA ABRASIVE BODIES

by

Almita Pierce Adams

S. B., Massachusetts Institute of Technology
E. Sc., University of Toronto

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Almita P. Adams

Department of Metallurgy
August 1959

Signature of Author

J. F. Norton

Professor J. F. Norton

Thesis Supervisor

J. F. Norton

Professor J. F. Norton

Chairman
Department Committee on
Graduate Studies

TABLE OF CONTENTS
THE WETTING OF ALUMINA BY VITREOUS ABRASIVE WHEEL BONDS

by

Almitra Pheroze Sidhwa

SUBMITTED TO THE DEPARTMENT OF METALLURGY ON
AUGUST 27, 1959, IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

ABSTRACT

This paper deals with the effect of various additives upon the wetting of alumina by a calcium aluminosilicate glass commercially used as a vitreous abrasive wheel bond. The sessile drop method was used, and contact angles at various temperatures were measured directly as a measure of wettability.

It was found that lead and boron improved wettability. Molybdenum was particularly effective, lowering the contact angle in proportion to the amount added; 1.5 and 3.0 percent of the sesquioxide resulted in almost complete wetting of the surface. Vanadium lowered the contact angle when 1.5 or 3.0 percent of the pentoxide was added, but 0.3 percent increased it. Manganese had negligible effect. Lithium did not affect the contact angle, but lowered the softening temperature of the glass in proportion to the amount added.

The use of molybdenum and lithium in commercial grinding wheel bonds was found to be commercially feasible.

It was proposed that a relation of the form $\theta = \theta_0 t^n$ holds between contact angle and time at a given temperature for the range one minute to sixteen minutes.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	ii
TABLE OF CONTENTS	iv
TABLE OF ILLUSTRATIONS	vii
LIST OF PLATES	viii
LIST OF TABLES	ix
ACKNOWLEDGEMENT	x
I. INTRODUCTION	1
II. MANUFACTURE OF GRINDING WHEELS	2
III. LITERATURE SURVEY	5
A. Concept of Surface Tension	5
B. Interfacial Energy and Contact Angle	6
C. Factors Affecting Contact Angle	8
D. Measurement of Contact Angle in Sessile Drops	12
E. Previous Work on Effect of Additives	14
IV. PLAN OF WORK AND MATERIALS USED	16
A. Plan of Work	16
B. Choice of Materials Used	16
V. EXPERIMENTAL PROCEDURE	19
A. Apparatus and Materials Used	19
1. Furnace	19
2. Camera	19
3. Preparation of Specimens	22

B.	Experimental Procedure	24
1.	Firing Cycle	24
2.	Measurement of Contact Angle	26
VI.	RESULTS	27
VII.	DISCUSSION OF RESULTS	41
A.	Effect of Additives	41
B.	Change of Contact Angle with Time	44
VIII.	ECONOMICS OF USING ADDITIVES	46
IX.	SUMMARY AND CONCLUSIONS	48
X.	SUGGESTIONS FOR FURTHER RESEARCH	49
XI.	BIBLIOGRAPHY	51
	APPENDIX	53
1.	1.5% Additive	31
2.	3.0% Additive	32
3.	0.1% Additive	33
4.	V_2O_5 as Additive	34
5.	MgO as Additive	35
6.	CaO as Additive	36
7-16	Contact Angle vs. Time	37-46
17.	V_2O_5 as Additive	57
18.	MgO as Additive	58
19.	CaO as Additive	59
20.	1.5% Additive	60

TABLE OF ILLUSTRATIONS

<u>Figure Number</u>	<u>Title</u>	<u>Page</u>
1	Contact Angle and Liquid-Solid-Gas Interfacial Forces	7
2	Schematic Diagram of Equipment Used in Obtaining Photographs of Glass Drops .	20
3	Schematic Diagram of Camera Optics . . .	21
4	Firing Cycle	28
5-12	Temperature vs. Contact Angle ,Frits.A .	29-36
5	0.0% Additive	29
6	0.3% Additive	30
7	1.5% Additive	31
8	3.0% Additive	32
9	0.3% Additive	33
10	V_2O_5 as Additive	34
11	Mo_2O_3 as Additive	35
12	Li_2O as Additive	36
13-16	Contact Angle vs. Time	37-40
13	V_2O_5 as Additive	37
14	Mo_2O_3 as Additive	38
15	Li_2O as Additive	39
16	1.5% Additive	40

LIST OF PLATES

<u>Plate Number</u>	<u>Title</u>	<u>Page</u>
1	Polished Sections of Grinding Wheels	3
2-15	Effect of Temperature on Contact Angle	68-86
2	Frit AL ₁ (0.3% Li ₂ O).	68
3	Frit AM ₁ (0.3% Mo ₂ O ₃).	69
4	Frit AV ₁ (0.3% V ₂ O ₅).	70
5	Frit ALM ₁ (0.15% Li ₂ O + 0.15% Mo ₂ O ₃)	71
6	Frit AL ₂ (1.5% Li ₂ O).	72
7	Frit AM ₂ (1.5% Mo ₂ O ₃).	73
8	Frit AV ₂ (1.5% V ₂ O ₅).	74
9	Frit AL ₃ (3.0% Li ₂ O).	75
10	Frit AM ₃ (3.0% Mo ₂ O ₃).	76
111	Frit AV ₃ (3.0% V ₂ O ₅).	77
12	Frit AN ₁ (0.3% MnO ₂).	78
13	Frit AP ₁ (0.3% PbO).	79
14	Frit AB ₁ (0.24% B ₂ O ₃).	80
15	Frit A (no additive)	81

LIST OF TABLES

<u>Table Number</u>	<u>Title</u>	<u>Page</u>
1-14	Change of Contact Angle with Time and Temperature . . .	53-66
1	Frit AL ₁ (0.3% Li ₂ O)	53
2	Frit AM ₁ (0.3% Mo ₂ O ₃)	54
3	Frit AV ₁ (0.3% V ₂ O ₅)	55
4	Frit ALM ₁ (0.15% Li ₂ O + 0.15% Mo ₂ O ₃)	56
5	Frit AL ₂ (1.5% Li ₂ O)	57
6	Frit AM ₂ (1.5% Mo ₂ O ₃)	58
7	Frit AV ₂ (1.5% V ₂ O ₅)	59
8	Frit AL ₃ (3.0% Li ₂ O)	60
9	FritAM ₃ (3.0% Mo ₂ O ₃)	61
10	Frit AV ₃ (3.0% V ₂ O ₅)	62
11	Frit AB ₁ (0.3% B ₂ O ₃)	63
12	Frit AP ₁ (0.3% PbO)	64
13	Frit AN ₁ (0.3% MnO ₂)	65
14	Frit A (no additive)	66
15	Chemical Analysis of Frits A and AM ₃	67

I. INTRODUCTION

In vitreous bonded grinding wheels, particles of abrasive material are held together into a loose network by bonds of vitreous material. The properties of this glassy or porcelainous bond are of great importance in determining the strength, hardness and wear resistance of the grinding wheel. Perhaps the most important property of the glass is its ability to attach itself to the grains firmly and over a large area.

ACKNOWLEDGEMENT

The author wishes to express her deep gratitude and thanks to Professor F. H. Norton for his guidance and encouragement during this investigation.

The cooperation of the Mid-West Abrasive Company and A. P. de Sanno and Son, Incorporated, in supplying bond formulae for trials is also appreciated.

I am thankful to Mr. Donald Guernsey for performing crucial chemical analyses at a time when every minute counted.

A further object of the study was an estimate of the probable cost of using these additives on a commercial scale.

The effectiveness of the additives was determined by a study of their effect on the contact angle between glass and alumina. Pellets of the ground frit with and without additives were placed on sintered alumina plaques and photographed during the wetting process. The contact angle of the sessile drops was measured directly from the photographs, and plots of contact angle against temperature and against time were used to evaluate the effect of the additives.

I. INTRODUCTION

In vitreous bonded grinding wheels, particles of abrasive material are linked together into a loose network by bonds of vitreous material. The properties of this glassy or porcelanic bond are of great importance in determining the strength, hardness and wear resistance of the grinding wheel. Perhaps the most important property of the glass is its ability to attach itself to the grains firmly and over a large area. This again depends on the extent to which the glass "wets" the aluminum oxide or silicon carbide grain. In practice, certain metal oxides believed to promote wetting are added to the glass to improve its adherence to the grain .

The following study was undertaken to determine whether these additives did in fact have any influence on the wetting properties of the glass, and if so, to what extent. It was also desired to find out which of these additives was most efficient, and in what amounts. A further object of the study was an estimate of the probable cost of using these additives on a commercial scale.

The effectiveness of the additives was determined by a study of their effect on the contact angle between glass and alumina. Pellets of the ground frit with and without additives were placed on sintered alumina placques and photographed during the melting process. The contact angle of the sessile drops was measured directly from the photographs, and plots of contact angle against temperature and against time were used to evaluate the effect of the additives.

II. MANUFACTURE OF GRINDING WHEELS

A grinding wheel is composed of grains of abrasive material held together in the form of an open network by connecting posts of bonding material, as shown in Plate I. The abrasive is almost always either synthetic silicon carbide or fused alumina, and the bond may be glassy (for alumina) or porcelaneous (for the carbide) or a thermo-setting plastic.

In the case of vitreous wheels, the bond, in the form of raw materials or frit or both, is mixed with the grain and a temporary binder, and damp pressed to shape. The wheels are slowly dried in hot air or steam chambers and fired to either Cone 1 (1125°C) for low temperature bonds or to Cone 12 (1310°C) for high temperature bonds. The fired wheels are finished to size, tested for hardness, soundness and structure (open or dense network) and are then ready for dispatch.

The important measurable properties of a grinding wheel are its hardness (tested by resistance to impact or to penetration of a loaded knife-edge), its toughness (determined by modulus of rupture tests), and its resistance to wear in service. This last is measured by the Grinding Ratio, or the ratio of the volume of wheel worn away during grinding to the volume of metal removed over the same period. The wear resistance of the wheel is a measure of the ease with which a blunted grain can be torn from the wheel, and depends on both hardness and toughness of the wheel, and also on whether rupture occurs between the grain and the bond, or across the grain. The latter is preferable, since it exposes new cutting faces and makes the best use of each grain.



(a)



(b)



(c)

PLATE 1. Polished Sections of Grinding Wheels.

(a) silicon carbide, 100X (b) aluminum oxide, 50X (c) same, 100X

Light area = grain, grey area = bond, and dark area = pores.

In order to ensure good adherence between grain and bond, it is necessary for the bond to wet the grain sufficiently and spread over a large area of it. Any additives that promote wetting thus improve the properties of the wheel, and also allow the use of a smaller amount of bond for a wheel of given hardness and structure.

Plate 1 (b and c) shows a polished section of an aluminum oxide wheel; the bond used has a contact angle of 52.65° on the grain.²⁰ Plate 1 (a) shows a silicon carbide wheel with a bond of considerably better wetting properties (the contact angle is 27.5°).²⁰ It illustrates how well the bond flows over and covers each grain.

III. LITERATURE SURVEY

2. Interfacial Energy and Contact Angle

A. Concept of Surface Tension

A fundamental property of liquids is their tendency to assume a shape having minimum free surface area. This phenomenon may be explained in molecular terms. Within the body of a liquid, a molecule is subject to attractive forces arising from all of its neighboring molecules. Averaged over time, their resultant is zero, and the molecule is free to move about unrestricted. At the surface of the liquid, however, there are no molecules to one side of it, and the molecule is subjected to unbalanced forces with a resultant force acting inward from the surface. A molecule that moves to, or remains in, the surface against the action of this force will thus have a certain amount of energy associated with it, known as free surface energy or surface tension. It is in an effort to minimise this free energy that the liquid as a whole assumes a shape of minimum area. This is accomplished by the movement of molecules from the surface to the interior of the volume of liquid, until the concentration gradient (of molecules per unit volume) from the interior to the surface becomes large enough to oppose further migration.

The above holds true for a volume of liquid that is not restrained in any way. When, on the other hand, a liquid is in contact with a solid (or an immiscible liquid) there are adhesion forces between liquid and solid that compete with cohesion forces within the liquid to determine the shape of the drop; in other words, they determine whether or not the liquid will spread over and "wet" the solid or contract to expose close to its minimum surface area.

B. Interfacial Energy and Contact Angle

The wetting of a solid by a liquid is most commonly described in terms of the contact angle. This is illustrated in Fig.1 and is the angle (θ), measured through the liquid phase, between the solid-liquid interface and the tangent to the liquid surface at the point where solid, liquid and gas phase are in contact. Terminology differs, but in the following discussion wetting will be said to occur when θ lies between 0° and 90° ; an angle between 90° and 180° will indicate a condition of non-wetting.

The contact angle is determined by the surface energies at the interface between liquid and gas (γ_{lg} , or the surface tension of the liquid), between solid and liquid (γ_{sl}) and between solid and gas (γ_{sg}). The surface energy of a solid in air may be thought to arise, like that of a liquid, from the presence of unsatisfied chemical bonds at the surface of the phase --- regardless of whether these bonds are ionic, covalent, metallic or Van der Waals'.

Consider again the sessile drop shown in Fig. 1, showing the vectors γ_{sl} , γ_{lg} and γ_{sg} acting at the point of contact, A.

Balancing the horizontal components of these forces, we find that

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta$$

or,
$$\cos \theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \dots \dots (1)$$

Thus θ may be decreased (i.e., $\cos \theta$ increased) by decreasing γ_{lg} or by increasing the difference $\gamma_{sg} - \gamma_{sl}$. In practice, the former is accomplished by the use of additives in the liquid phase, and the latter by a change in the gas phase ^{8,9,11}.

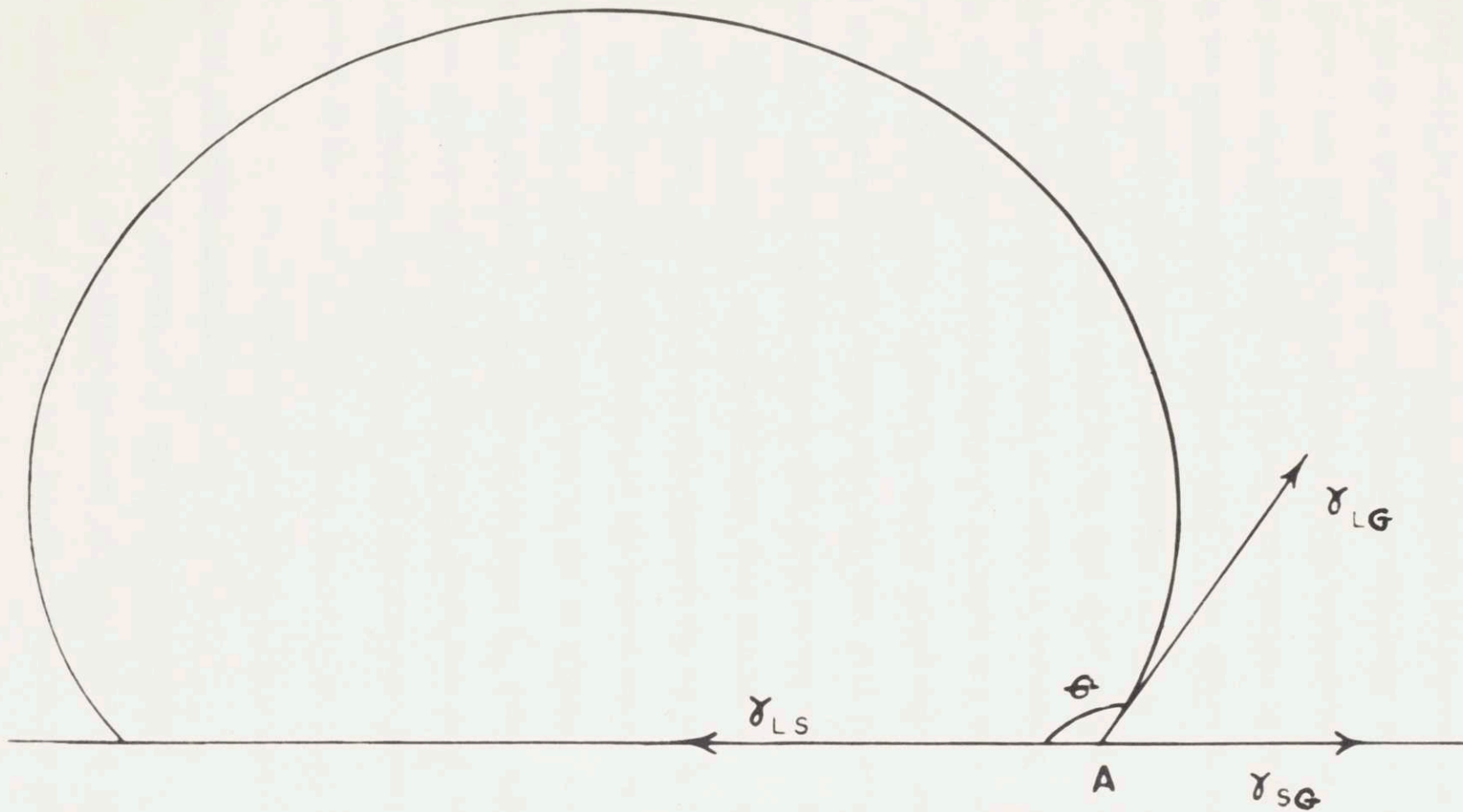


FIG. 1. Contact Angle and Liquid-Solid-Gas Interfacial Forces

In cases where a liquid contains more than one component, the surface will be composed of those molecules which make the free surface energy a minimum, i.e., of molecules with lower ionic potential. Hence if an added component has a lower ionic potential than the bulk phase and tends to lower the surface tension, it will concentrate in the surface and be "surface active". This effect is expressed mathematically by Gibbs' adsorption isotherm.¹

Some general rules² apply to the choice of surface-tension-reducing agents. The ionic potential of atoms is reduced with increasing atomic size, proceeding from left to right across the periodic table or from top to bottom. Secondly, highly polarizable ions are aligned at the surface of the liquid in a way that will minimize the ionic potential acting upon them, and will thus reduce the surface tension. Thirdly, it is a qualitative rule that solutes of smaller surface tension than the bulk phase will concentrate at the surface.

Since the determining factor is the excess concentration of the additive at the surface over that in the bulk phase, a very small amount of additive is often enough to lower γ_{lg} substantially. This in turn results in a marked decrease in θ and increased wetting of the surface, unless the presence of the additive also lowers γ_{sl} (see Equation (1)).

C. Factors Affecting Contact Angle

The angle of contact of a sessile drop is defined by two planes, one lying in the interfacial plane between solid and liquid, and the other the tangent plane to the liquid surface at the point of contact of solid, liquid and gas phases.

Under ideal conditions, there is a specific "contact angle" which is characteristic of the fluids and the solid at a given temperature and pressure. This contact angle is determined, as described above, by the interfacial energies of the three interfaces. This "contact angle", however, may often be very different from the angle of contact actually obtained under the given conditions.

One of the reasons for this discrepancy is a constraint similar to the frictional resistance characteristic of the sliding of solids over solids. This constraint prevents free movement of the liquid drop over the solid surface, giving larger values for advancing angles and smaller values for receding ones.³ In the latter case the forces of adhesion are also significant; movement of the line of contact implies replacing an intimate contact of the solid and one fluid by intimate contact between the solid and the other fluid. Where adhesion is present (it always is), this involves irreversible effects, and energy must be expended to overcome the constraints and accomplish the changes.⁴ The only case where this friction-like resistance is absent is that in which the solid surface is covered by a very strongly adherent fluid film, which cannot be displaced. Under these conditions, the second fluid will flow over the film of the first; since only one interface will exist, namely that between fluid and fluid, spreading will be unhindered and a zero angle of contact will result.⁴

Several additional factors may operate to prevent attainment of the true contact angle. One of them is the viscosity of the

liquid. This may slow down very considerably the rate of flow of the liquid drop; it does not prevent ultimate attainment of the true contact angle, assuming that there will be no change in surface conditions or in the composition of the three phases, but it may delay it for a very considerable period of time. In practice, it is seldom possible to allow for attainment of true equilibrium in the case of very viscous fluids, not only from the point of view of time and economy, but also because of the dangers of contamination or chemical reaction.

The formation of a chemical interface is a common source of error in determining the true contact angle. Slow oxidation of even a noble metal surface, for instance, or adsorption of a particular element or compound, will result in measurement of a liquid - metal-oxide or other contact angle rather than a liquid - metal contact angle. In most cases, contamination of the surface leads to a lowering of the angle of contact.

The roughness of the solid surface has a very considerable effect upon the angle of contact. For angles of θ less than 90° , a liquid spreading out over a rough surface will appear to have a contact angle smaller than the true value; for cases where θ is large, the angle of contact will be larger than on a smooth surface.³

This may be easily explained by simple mathematics. Consider unit area of a geometrical plane which has been roughened so that its real surface area is σ times that of the unit "smooth" surface.⁴ Then the energy gained in forming the solid-liquid interface will be

given by $\sigma(\gamma_{sg} - \gamma_{sl})$

and the new contact angle θ' will be given by

$$\cos \theta' = \frac{\sigma(\gamma_{sg} - \gamma_{sl})}{\gamma_{lg}} \dots \dots (2)$$

Now σ will always be greater than unity for a completely wet rough surface. Thus for positive values of $\cos \theta$ ($\theta < 90^\circ$), $\cos \theta' > \cos \theta$, or, θ is decreased ($\theta' < \theta$). When non-wetting occurs, $\gamma_{sl} > \gamma_{sg}$, and $\cos \theta'$ is negative. Hence, algebraically, $\cos \theta' < \cos \theta$, and $\theta' > \theta$, i/e. the contact angle has increased. The equation (2) does not hold for rough surfaces where the liquid does not wet the entire surface. Here the treatment may be similar to that for porous surfaces, if an estimate can be made of the area σ_1 of unit "smooth" surface in actual contact with the liquid, and of σ_2 , the area of unit surface where liquid and air are in contact ($\theta = 180^\circ$). Then it can be shown⁴ that the apparent contact angle θ'' for the composite surface is given by

$$\cos \theta'' = \sigma_1 \cos \theta_1 - \sigma_2 \dots \dots (3)$$

where θ_1 is the real contact angle between the liquid and the solid with which it is in contact.

A phenomenon universally associated with contact angles is a hysteresis effect: the equilibrium contact angle for a liquid advancing over a surface is different from the equilibrium angle of a liquid receding from a surface which it has wet. This can be observed in the sliding of a raindrop down a windowpane --- the trailing edge leaves the glass reluctantly and the angle of contact here is much

smaller than the advancing angle. The difference may often be as much as fifty degrees³, and the angle of contact may have any value between these two, though after repeated cycling it tends toward one particular value. The decreased contact angle of a receding liquid boundary is thought to be partly due to the penetration of the surface by the liquid; probably a liquid film remains on the surface.³ In addition, the receding liquid may tend to sweep the solid surface clean of impurities. The liquid may also fill up irregularities in the surface and eliminate roughness effects.

In the case of a coarse surface, such as that of a refractory brick, the effect of roughness is quite pronounced. Large pores hinder the flow of the glass; this has been explained very lucidly by Comeforo and Hursh.⁶ A spreading (advancing) drop will tend to hang over the edge of the pores in the same manner that a tumbler of water may be overfilled without spilling; this increases the observed value of an advancing angle of contact. Once the liquid has filled the pore, it has a contact angle against a surface of itself, which lowers the value of the observed contact angle.

D. Measurement of Contact Angle in Sessile Drops

Contact angles of liquids on solid surfaces are commonly determined by immersing a plate of the solid at an arbitrary and convenient angle into the liquid, moving the plate in and out, and measuring the advancing and receding angles directly by means of a protractor immersed in the liquid.³ A similar method has been adapted for wires and fibers.⁷ The contact angle of liquids on powders is determined by measuring the pressure required to stop the advance of

the liquid through a block of the compressed powder.⁷

None of these methods is as easily applicable to molten glass as the sessile drop method, largely because of the corrosive nature of the glass and the high temperatures involved. The contact angle of sessile drops can be measured either directly from photographs or from a projected image of the drop on a ground glass plate or a screen.^{2,6,8,9} Direct measurements of the angle are accurate to within 3° for the same observer, and to within 5° for two observers.¹² Others report slightly better results.

The angle of contact may also be derived from various mathematical formulae. All of these require a knowledge of the height h of the drop (from apex to liquid-solid interface), and of its radius x at the base of the drop (along the liquid-solid interface). One formula¹³ gives the contact angle as

$$\cos \theta = 1 - \frac{h^2}{h^2 + x^2}$$

assuming the drop to be a spherical segment. Ellefson and Taylor⁹ used

$$\theta = 2 \tan^{-1} \left(\frac{h}{x} \right) \text{ for } \theta < 90^\circ$$

and perfect spherical segments. They obtained values for $\theta > 90^\circ$ from tables by Bashforth and Adams, by determining two parameters: b , the radius of curvature of the apex of the drop, and β , which involves a knowledge of the density of the liquid at the appropriate temperature. Both parameters involve the measurement of meridional sections of the drop. The formulae for spherical segments are accurate only for small drops, where deformation due to gravity is negligible; however, with small drops accuracy of measurement of height and base width is difficult. Comeforo and Hursh⁶ and Halden² found good agreement between

calculated values of the contact angle and values measured directly from photographs.

Another method of measuring the contact angle involves reflecting a narrow beam of light off the surface of the drop. The angle of incidence at which the reflection disappears gives the value of the contact angle.

E. Previous Work on Effect of Additives

Only one paper, by Amberg,¹⁶ is known to deal with possible oxide additions to bond glasses from the point of view of improving the properties of grinding wheels. He found that molybdenum trioxide, tungsten trioxide, and arsenous oxide in amounts of one percent and three percent lowered the surface tension of a soda-lime-silica glass, as did three percent vanadium pentoxide, although one percent vanadium pentoxide raised it.

Badger et al.¹⁸ found the surface tension of another soda-lime-silica glass lowered ten percent by lead and twenty-three percent by vanadium. Amberg also found that antimony, nickel, cobalt, manganese, and vanadium were effective in lowering the surface tension of a glaze and/or an enamel, but all were found to raise the surface tension of glass.

A theoretical discussion by Dietzel¹⁷ of the surface conditions of a glass concludes that the surface tension is lowered by lead and vanadate ions; they are readily deformed (polarizable) and accumulate at the surface to fit into spaces from which attached atoms are missing. Boron, like zinc, silicon, aluminum, and titanium, is a cation which forms complex anions of large diameter. It therefore

affects the surface tension only slightly, but its behavior is never anomalous; it always lowers surface tension in proportion to the amount added to the mix.

Lithium carbonate has a lower surface tension than the corresponding sodium or potassium salt, and is commonly used in porcelains and sanitary ware.¹⁹

Other work has been done on the effect of a dissolved component like calcium oxide on simple two-compound systems like soda-silica melts,²¹ but does not include an investigation of the additives selected for study here.

B. Choice of Materials

Almost all previous wetting studies have been made on soda-lime-silica glasses. A calcium aluminosilicate glass was chosen for this study, as such glasses are also used in the manufacture of grinding wheels. An analysis of the frit is given in the Appendix.

Lithium, sodium, potassium, vanadium and manganese salts were fairly widely used in industry; they were chosen in order to determine whether their use was economically justified, and to determine their wetting characteristics, if any. Lead was tried because it is known to wet well with silicates. The relative efficacy of different surface-tension-lowering mechanisms was also considered worth investigating in a preliminary manner. Boron, lithium and vanadium all lower surface

IV. PLAN OF WORK AND MATERIALS USED

A. Plan of Work

The effect of different potential wetting agents was tested by incorporating them in a commercially used glassy bond. The raw materials together with the additive were fritted, and a pellet of the milled frit was melted on a sintered alumina placque. Photographs of the molten sessile drop were taken at a series of temperatures during the melting process. A series of photographs was also taken at different time intervals while the frit was at its softening temperature. Angles of contact were measured directly from the photographs, and the values were plotted against temperature and against time.

B. Choice of Materials

Almost all previous wetting studies have been made on soda-lime-silica glasses. A calcium alumino-silicate glass was chosen for this study, as such bonds are also used in the manufacture of grinding wheels. An analysis of the frit is given in the Appendix.

Lithium, molybdenum, vanadium and manganese salts are fairly widely used in industry; they were chosen in order to determine whether their use was economically justified, and to determine their optimum percentages, if any. Lead was tried because it is known to react with alumina. The relative efficacy of different surface-tension-reducing mechanisms was also considered worth investigating in a qualitative manner. Boron, lithium and vanadium all lower surface

tension, but for different reasons; boron forms complex anions, the vanadate ion is easily deformed (polarized), and lithium carbonate has a lower surface tension than corresponding alkali salts.

In the case of lithium, molybdenum, and vanadium, three different percentages were tried. Amberg added one percent and three percent of the oxides to his base glasses; 1.5 percent and three percent were used here. Since such large amounts would not be economically feasible in practice, 0.3 percent was also tried; this was also the percentage used when only one trial of an additive was made.

Borax was used instead of boric oxide, in spite of the fact that it introduced soda as well. The tetraborate is commercially available so much more cheaply than the oxide or other compounds of boron that in practice it would be by far the most suitable source of the boron ion.

In most aluminum oxide grinding wheels of medium grain size, the grains are simple crystals. However, for reasons of convenience, sintered alumina discs were used as the solid phase rather than sapphire. The discs were sliced from slip cast rods prepared as follows:

Norton alumina of 220 mesh size was ball milled for twenty-four hours, added to distilled water and passed several times through a Ferro filter to free it of iron. It was leached with hydrochloric acid, washed, and cast into rods which were sintered at 1800°C. The porosity varied from ten to twelve percent. Data by Comeforo and Hursh indicates that this corresponds to a pore size of less than 7.5 microns. The rods were 1.7 centimeters in diameter and were

sliced into discs seven millimeters thick. They were polished on a sixty micron diamond lap, washed, dried, and stored under the cleanest possible conditions.

1. Furnace. The construction of the furnace used is illustrated in Figure 2. The furnace tube was of alumina, two inches in diameter and 17.5 feet long. It was surrounded by high-purity carbide heating elements in series, the whole contained within a refractory brick and transit structure. The assembly was mounted on four leveling screws.

A platinum - platinum-ten-percent-rhodium thermocouple inserted into the furnace tube as shown was used to measure temperature. The temperature could be controlled to within one degree Centigrade by means of a Collect-ray relay. The highest temperature attainable was 1375°C.

Hot air escaping from the tube at higher temperatures gave rise to considerable distortion of the camera lens. This was reduced somewhat by extending the ends of the alumina tube well beyond the ends of the heating elements. In addition, an optically flat sycor disc one quarter inch thick was clamped over the end of the tube nearest the camera; this completely eliminated lens profiles. The camera assembly was protected from radiation by a large transit screen that fitted over the end of the tube assembly. In addition the camera lens was protected by a rubber lens cover and a sheet of heavy aluminum foil.

2. Camera Assembly. On account of the high temperatures involved, a lens of very long focal length was used. The construction of the camera is illustrated by the ray diagram, Figure 3.

V. EXPERIMENTAL PROCEDURE

A. Apparatus and Materials Used

1. Furnace. The construction of the furnace used is illustrated in Figure 2. The furnace tube was of alumina, two inches in diameter and two feet long. It was surrounded by six silicon carbide heating elements in series, the whole contained within a refractory brick and transite enclosure. The assembly was mounted on four levelling screws.

A platinum - platinum-ten-percent-rhodium thermocouple inserted into the furnace tube as shown was used to measure temperature. The temperature could be controlled to within one degree Centigrade by means of a Celect-ray relay. The highest temperature attainable was 1375°C.

Hot air escaping from the tube at higher temperatures gave rise to considerable distortion of the camera image. This was reduced somewhat by extending the ends of the alumina tube well beyond the ends of the heating elements. In addition, an optically flat Vycor disc one quarter inch thick was clamped over the end of the tube nearest the camera; this completely eliminated the problem. The camera assembly was protected from radiation by a large transite screen that fitted over the end of the tube as shown. In addition the camera lens was protected by a rubber lens cover and a sheet of heavy aluminum foil.

2. Camera assembly. On account of the high temperatures involved, a lens of very long focallength was used. The construction of the camera is illustrated by the ray diagram, Figure 3.

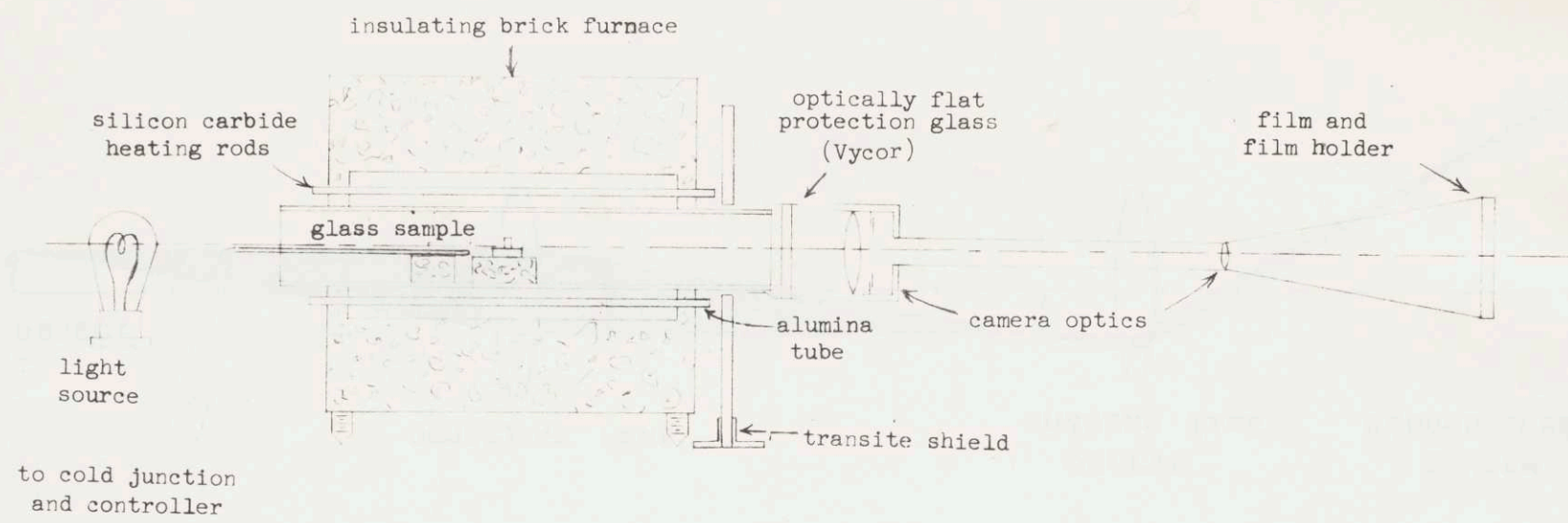


FIG. 2. Schematic diagram of the equipment used in obtaining photographs of the glass drops.

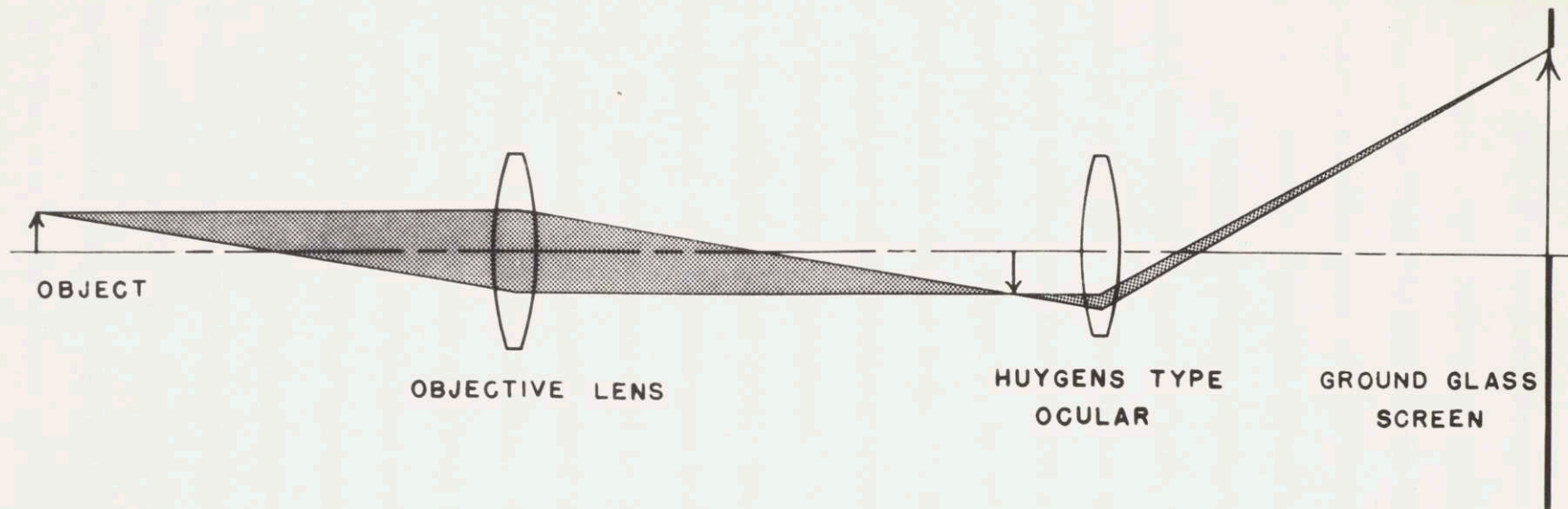


FIG. 3. Schematic Diagram of Camera Optics

The image of the drop appeared right side up and unreversed on a $3\frac{1}{4} \times 4\frac{1}{4}$ inch glass screen, which could be replaced by the film holder. Since both focal length and screen size were fixed, it was not possible to photograph the full width of the drop at higher temperatures, as can be seen from the series of photographs in Plate 15. The light source was a one-hundred-watt tungsten-filament bulb ninety-five centimeters from the camera lens. Kodak Contrast Process Orthofilm was used, with an exposure time of two-thirds of a second. It was of the greatest importance to line up the light source, the base of the specimen, and the axis of the camera, as shown in Figure 2, in order to get a clearly focussed profile of the sessile drop. To facilitate this, the camera was mounted on three levelling screws.

3. Preparation of specimens.

a. Preparation of frit. The raw materials for the glaze were weighed in two-hundred-gram batches on a balance accurate to 0.1 gram. The additives, being used in small quantities, were weighed on a laboratory balance and mixed into the weighed amount of one of the ingredients with a spatula. The weighed ingredients were screened four times through a 28 mesh sieve to ensure thorough mixing, and then loosely packed in clay crucibles (Morgan, England) which were remarkably resistant to corrosion by the glass. The batches were gas fired open in a small pot-kiln. The temperature was raised until fusion occurred (about 1340°C), then raised about 20° and held there until the glasses were well fired (four to six hours). In almost all cases, however, a very large smooth round

cavity was found in the center of the mass of glass, probably as a result of a large bubble that could not escape and hence grew in size. The glasses were too viscous to be poured into cold water, and raising the fluid temperature did not render them substantially fluid; in addition it was thought desirable to minimize chances of contamination by corrosion. The glasses were therefore quenched by dropping the whole crucibles into cold water and then breaking each of them into two or three pieces under cold running water.

The glass was then broken up and large clear pieces, free of adhering pieces of the crucible wall, were selected. These were ground in a porcelain mortar to pass an 8 mesh sieve, and the ground glass was further pulverized by ball-milling for seventy-five minutes in a porcelain mortar with one-half- to one-inch alumina balls. This was the minimum time required to reduce all of the glass to powder. This pulverized glass was then used in the preparation of samples.

b. Preparation of specimen. The powdered glass sample was hand-pressed in a steel die to a pellet $3/16$ inch in diameter and between $1/8$ and $5/32$ inch high. A weighed amount was not used since it was preferable to avoid excessive handling. No binder was used—the pellets were held together by the addition of one or two drops of water before pressing. The amount of water varied somewhat, but a run on two pellets of the same frit having very different amounts of water showed that their behavior was unaffected except in the first stages of melting (constant contact angle). Here the pellet with excess water showed greater shrinkage

and a larger contact angle than the other.

The glass pellet, after pressing, was lifted by hand onto an alumina disc, this having been found to be the gentlest method of handling. The pellet and disc were immediately placed in the center of the furnace tube, supported by a refractory plug in the shape of a solid half-cylinder. Considerable difficulty was experienced in inserting and aligning the specimens, particularly when two specimens were tested simultaneously to save time (this was the usual procedure). The problem was solved by making two round depressions in the surface of the plug just large enough to hold the two discs. To bring the surfaces of both discs into the same plane, finely powdered flint was sprinkled into the depressions as needed, and packed into the m by rotating the discs. The two discs to be used were placed on the plug and a very clean glass slide laid on their surface to determine which disc needed to be raised or levelled.

B. Experimental Procedure

1. Firing cycle. The specimens were inserted into the furnace, and the temperature raised according to the typical firing schedule plotted in Figure 4. The temperature was taken up gradually at first, and was held for thirty-five to forty minutes at 80°C to dry out the specimens. It was again held constant for about twenty minutes at 165°C , and then taken up rapidly at a rate of about six hundred degrees per hour until the edges of the pellet first rounded off (about 980°C). At one thousand degrees, and every seventy-five degrees thereafter until softening occurred, the temperature was held constant for fifteen minutes, and for five minutes at the twenty-five-degree intervals between. After softening occurred, it was held

constant for sixteen minutes for every twenty-five-degree rise. It was found that before softening, the contact angle did not change with time. This justified the slight shortening of the firing cycle (i. e., holding for five minutes instead of fifteen minutes at 1025° and 1050° , etc.).

In order to determine the length of time required for the glasses to reach equilibrium, frit A was held at its softening temperature for ninety minutes and the contact angle at different times was plotted as shown in Figure 16. It can be seen that the curve may be approximated by two lines of different slope. The first, from zero to seventeen minutes, is the change in contact angle as it approaches equilibrium. The second part of the curve, beyond seventeen minutes, was taken to represent the reaction of the glass with the alumina. On this basis, seventeen minutes was chosen as the length of time required for the contact angle to reach equilibrium. This was confirmed by holding frit AM₂ (which was the second frit tested) at its softening temperature for sixty-four minutes. For this frit, the two parts of the curve intersected to give an "equilibrium" time of thirteen minutes (Figure 16). Unfortunately, the contact angle versus time curves for the other glasses were not plotted until almost all of the runs had been completed. It then appeared that seventeen minutes was insufficient for equilibrium to be attained. Hence the values of contact angle at the softening temperatures are not at equilibrium. However, earlier studies on frit A had shown that above the softening temperature, the contact angle decreased very slowly with time, falling generally two to at most five degrees between zero time and thirty minutes when held at these higher temperatures. Since these latter points lie on

a smooth curve, the error in equilibrium angle of contact at the softening point was not as serious as might at first appear. Time considerations did not permit repeating all the runs, allowing longer times for reaching equilibrium, but this is recommended for future tests.

2. Measurement of contact angle. The angles of contact were determined directly from positive prints of the photographs. These were attached to a clean sheet of paper, a straightedge laid along the solid-liquid interface and along the tangents to the drop, the lines extended backward on the paper and the angle measured with a protractor, to the nearest quarter of a degree. Successive measurements of one angle gave a maximum difference of three degrees. The difference between the measurements of two observations was four degrees. This is in keeping with the findings of Halden² and of Fulrath et al.,¹² who found direct measurement accurate to within three degrees for the same observer and within five degrees for two observers.

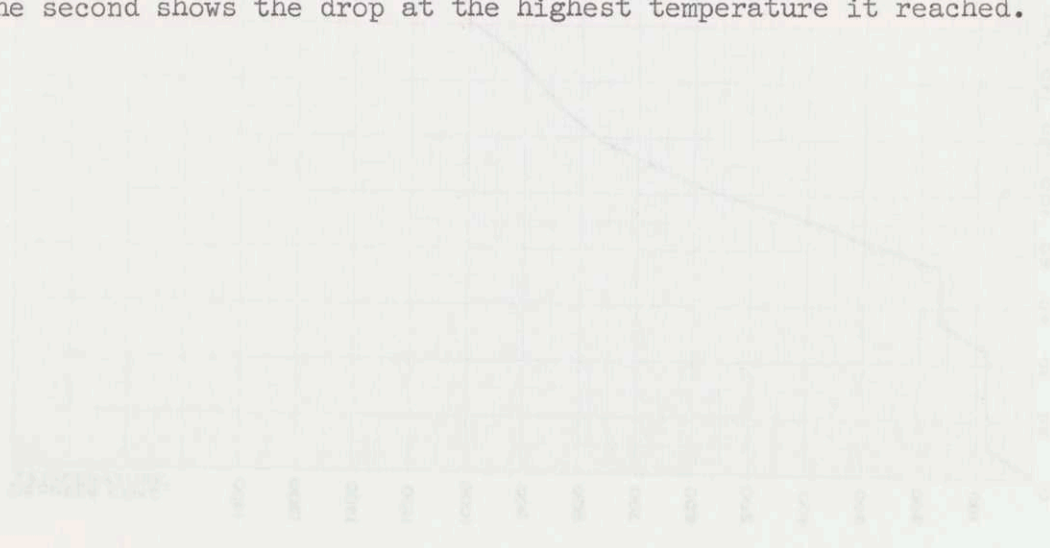
The point where solid, liquid, and gas come together is poorly defined, especially in the case of large angles where optical effects introduce large errors due to apparent rounding of corners. For this reason, in order to be consistent, all tangents were drawn at a point one-eighth inch up from the solid-liquid interface, measured along the circumference of the drop.

VI. RESULTS

The results of the experiments are presented graphically in Figures 5 through 9, in the form of graphs of temperature versus angle. The values of the angle of contact plotted for a given temperature are those corresponding to the last of a series of photographs taken at that temperature, when more than one picture was taken at a given temperature.

In Figures 10, 11, and 12, the curves for three percentages of one additive are shown together. Figures 13, 14, and 15 are log-log plots of the contact angle versus time at a given temperature. Figure 16 exhibits the same parameters on rectangular coordinates.

Tables listing the individual and average values of the angles of contact for each photograph are listed for each frit. In addition, a complete series of photographs for frit A is presented. In the case of the other frits, only two photographs of each are presented. One shows the frit in the first stages of melting, while the second shows the drop at the highest temperature it reached.



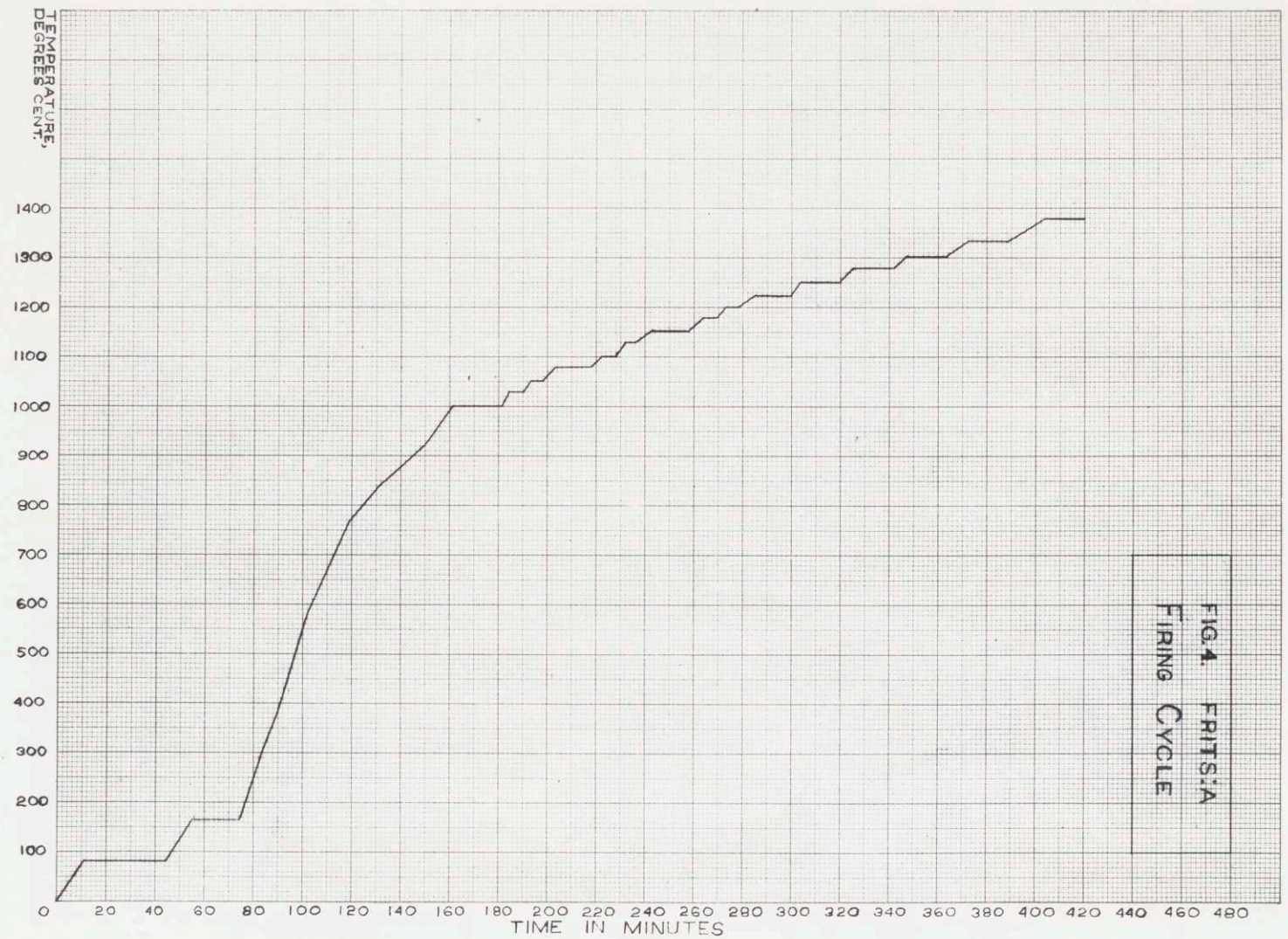
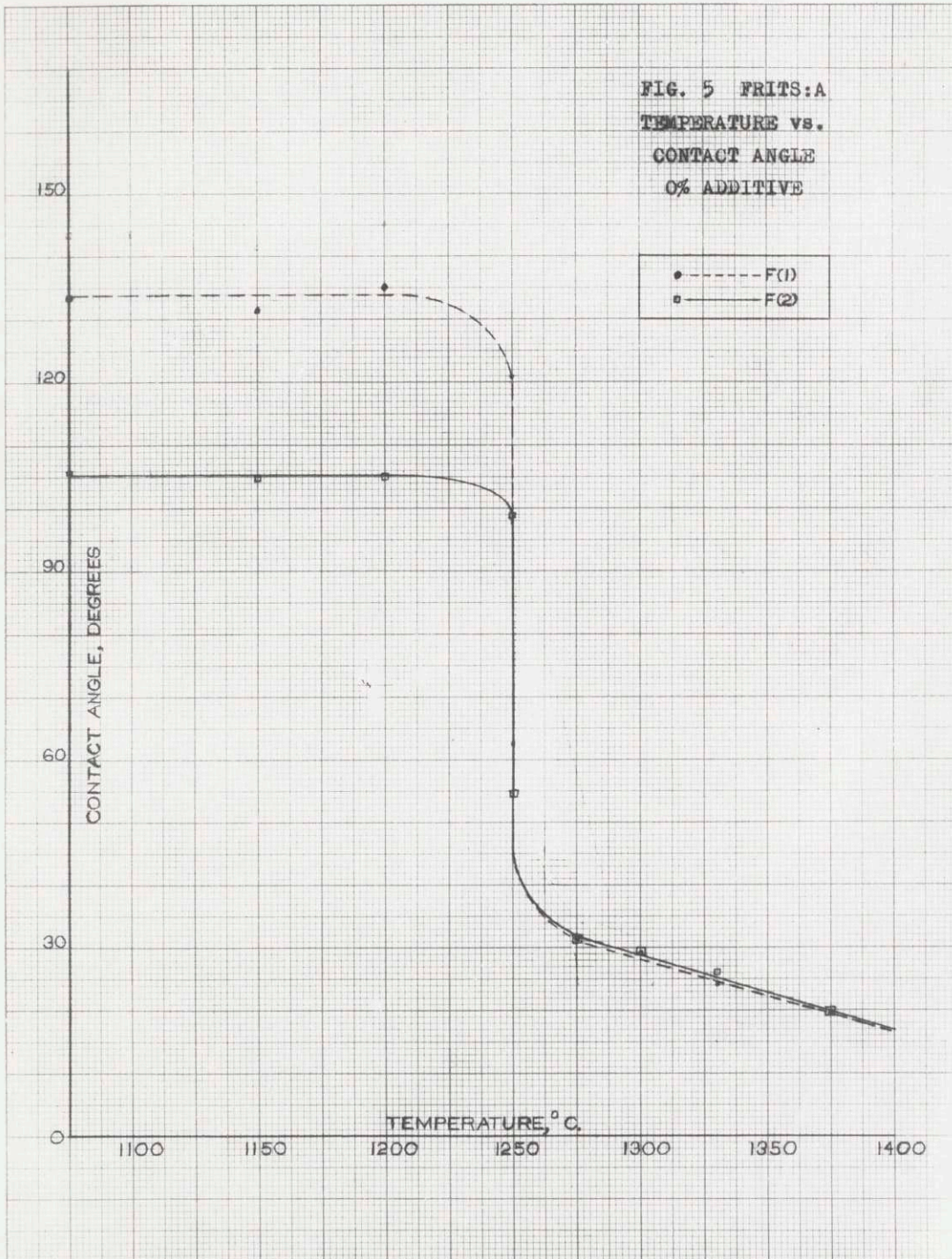
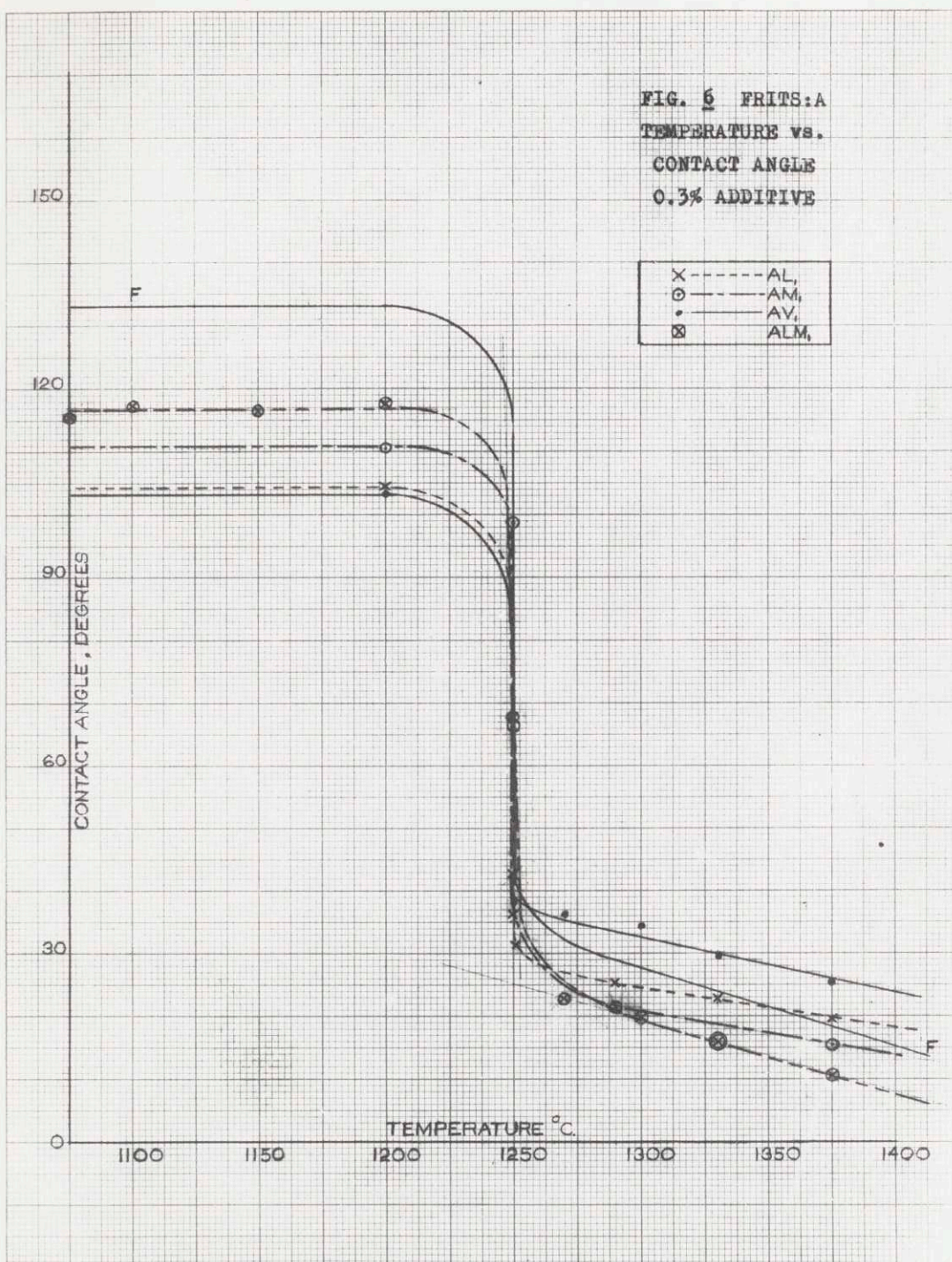
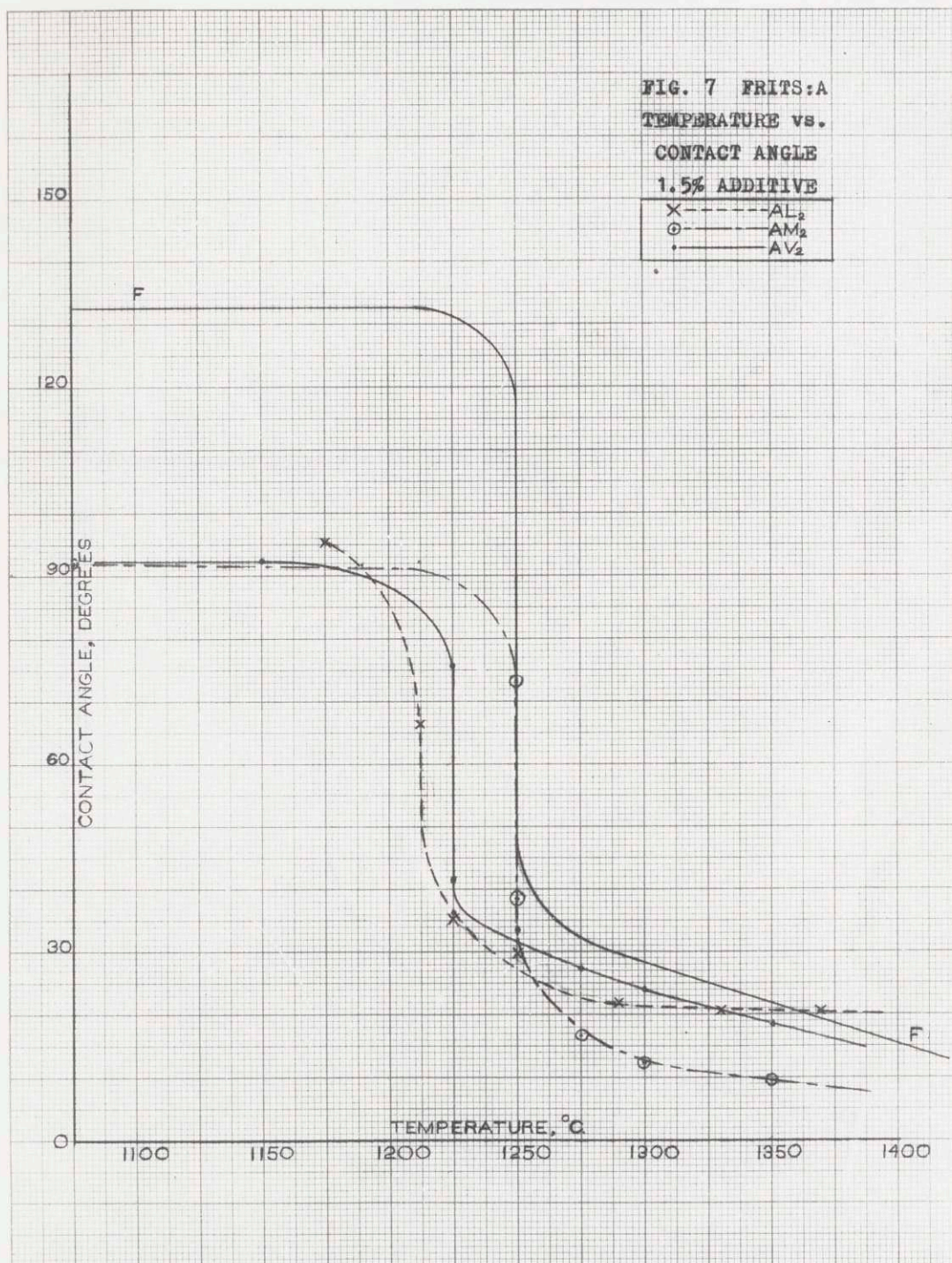


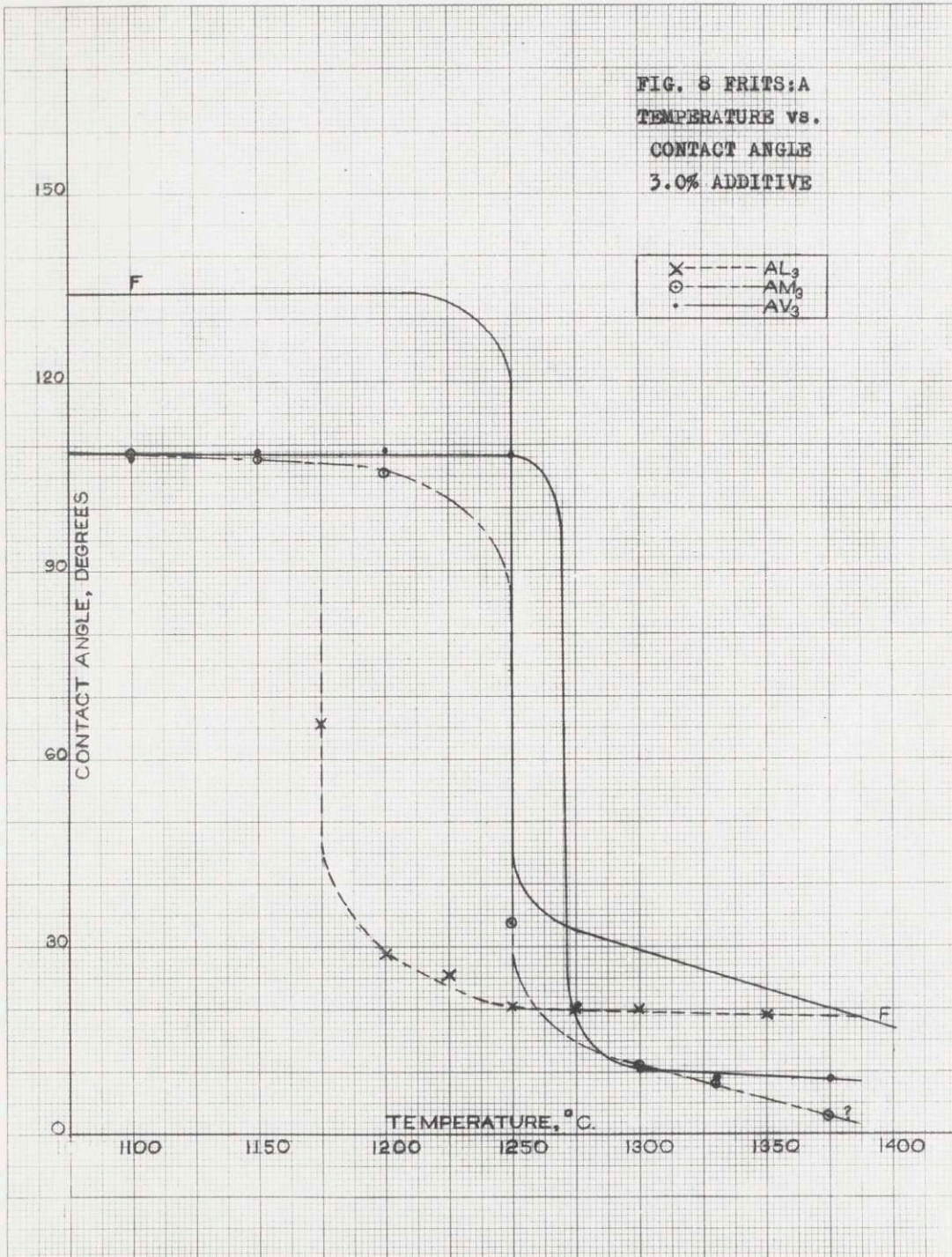
FIG. 4 FRITS:A
FIRING CYCLE

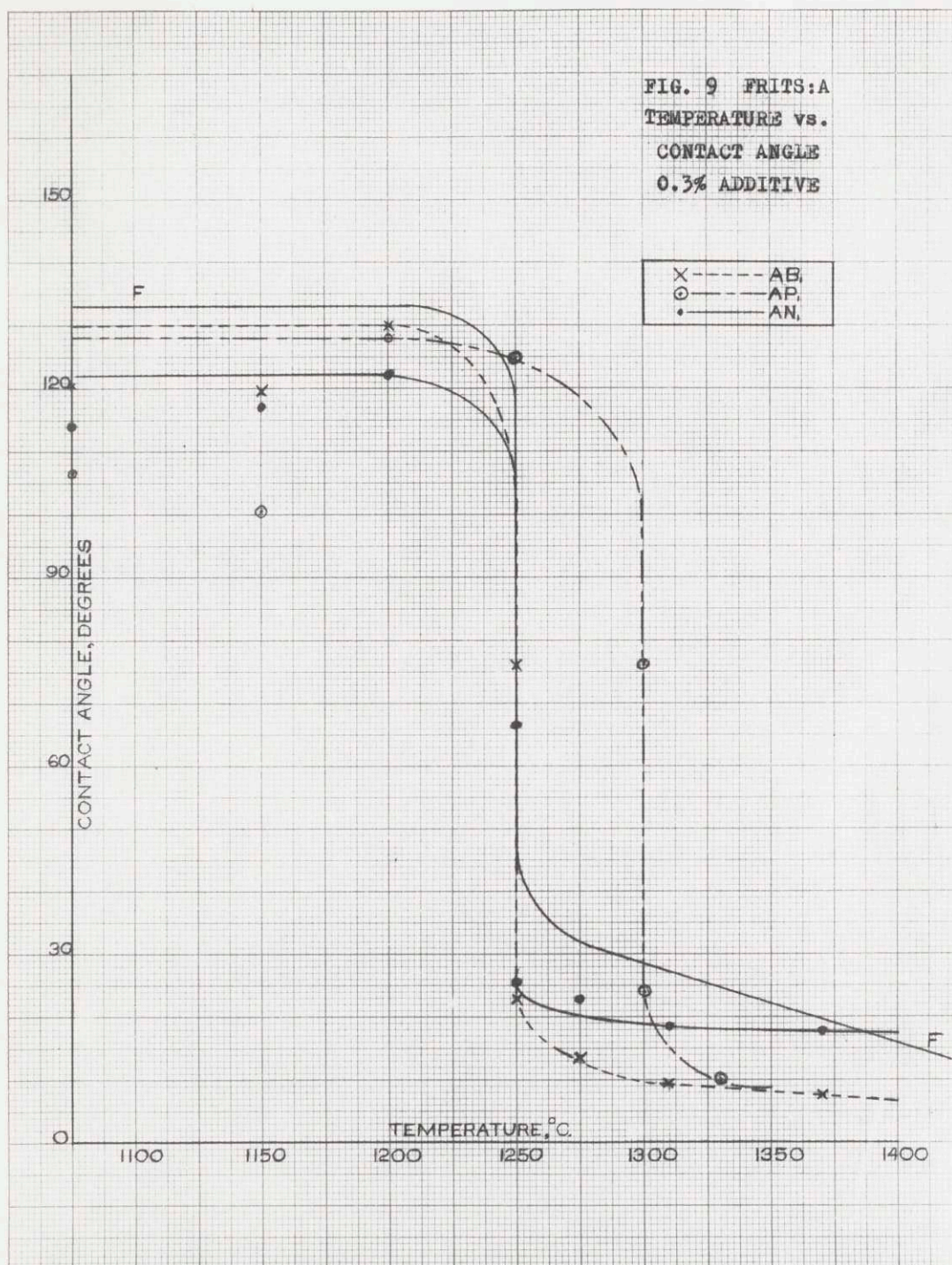


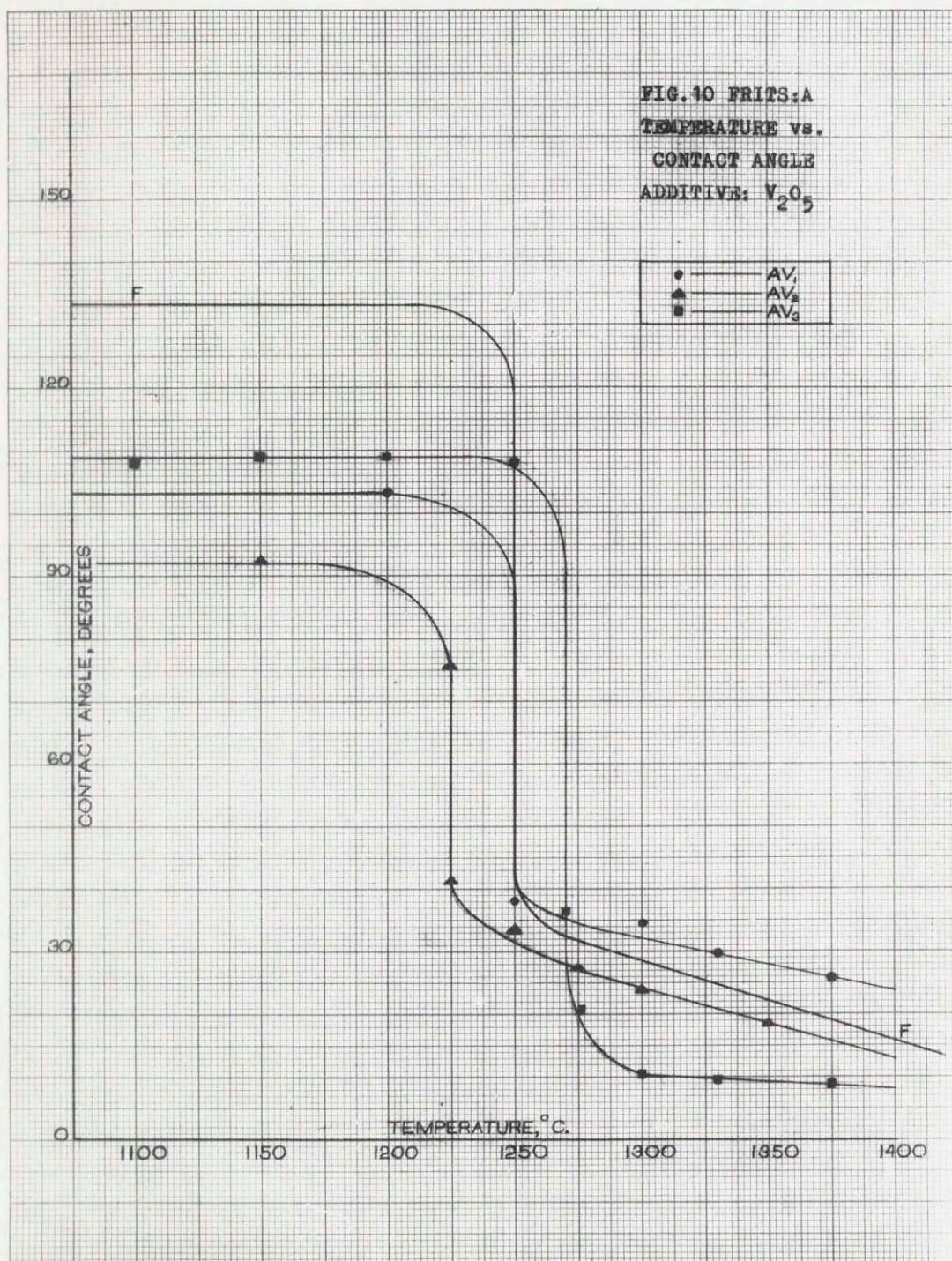


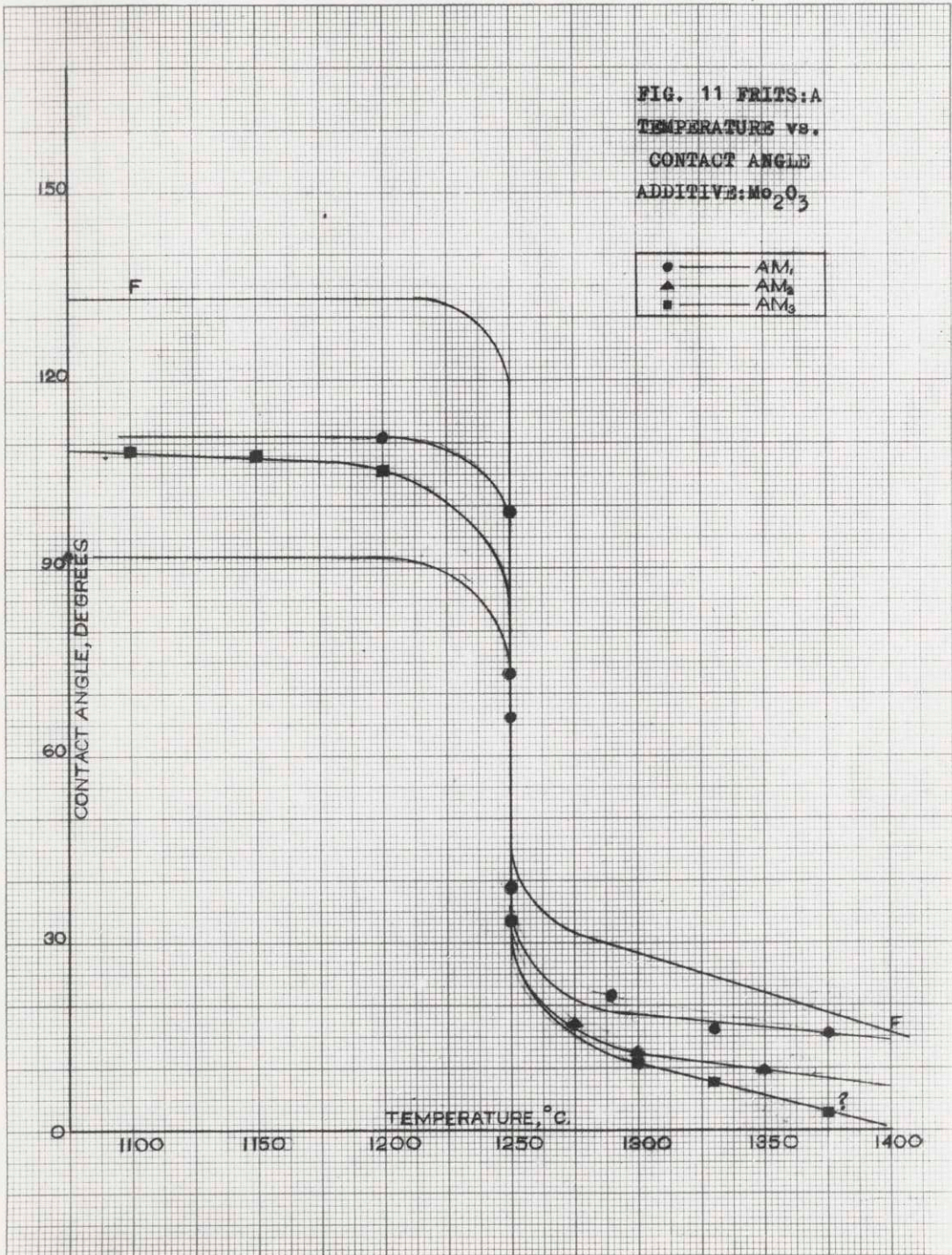
2

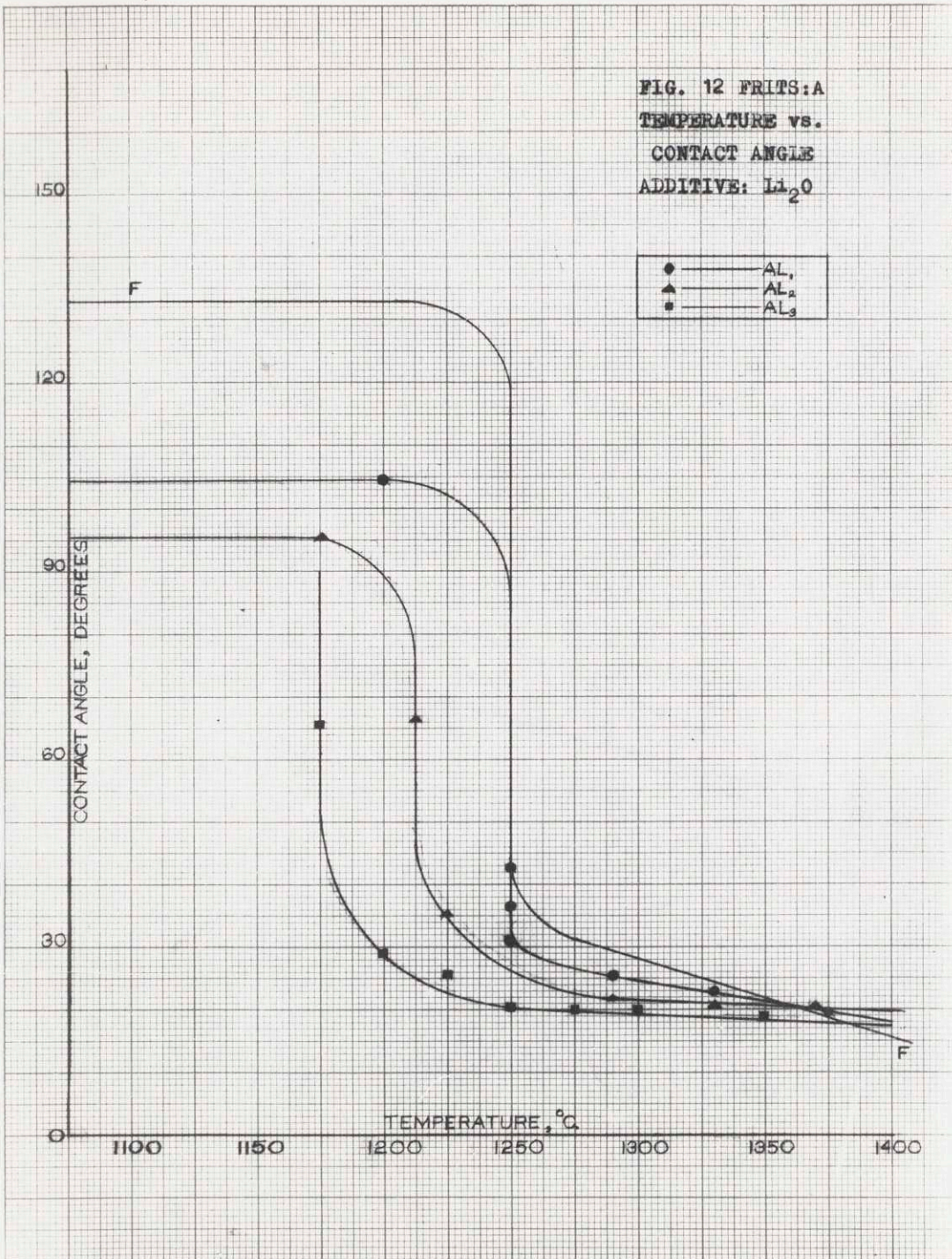


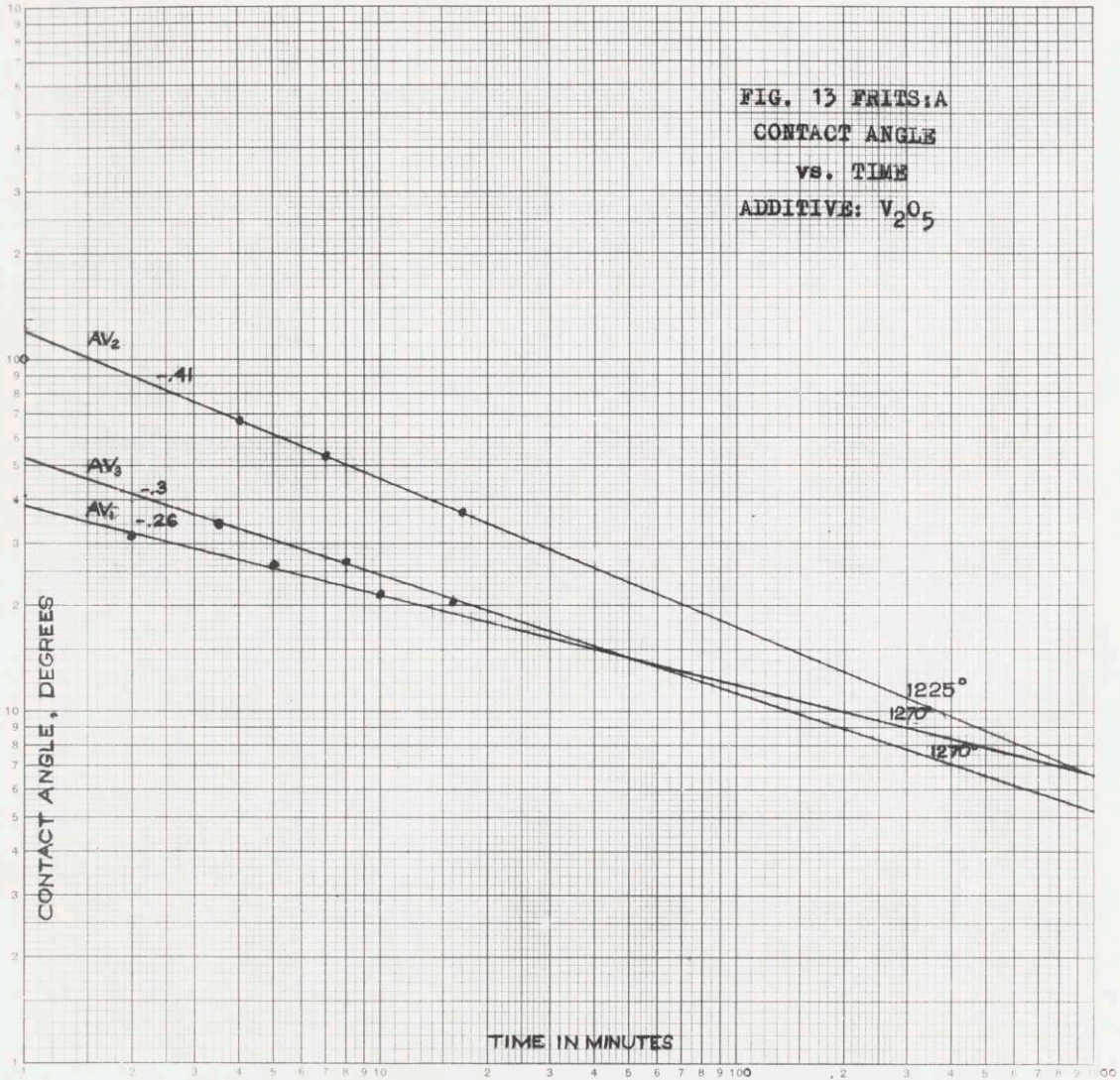












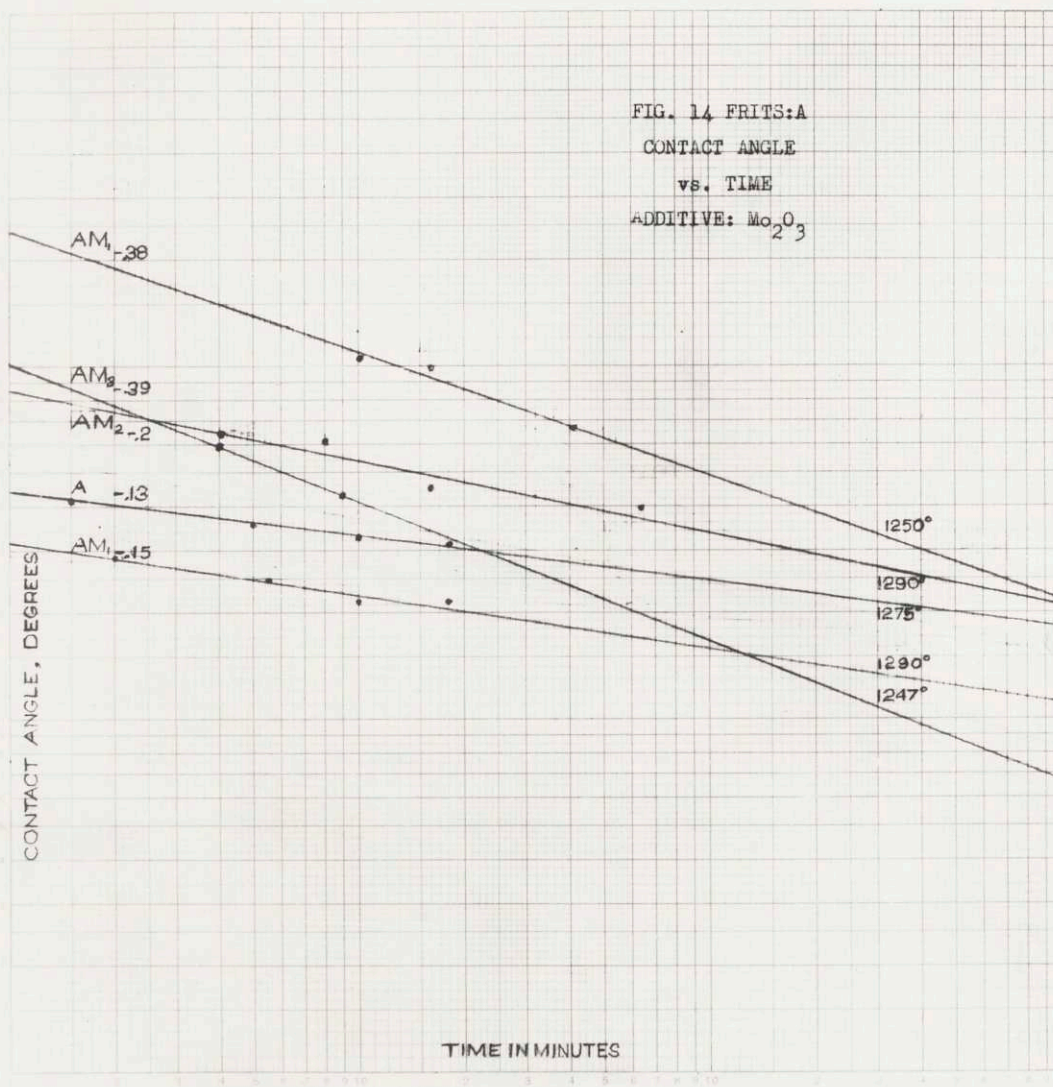
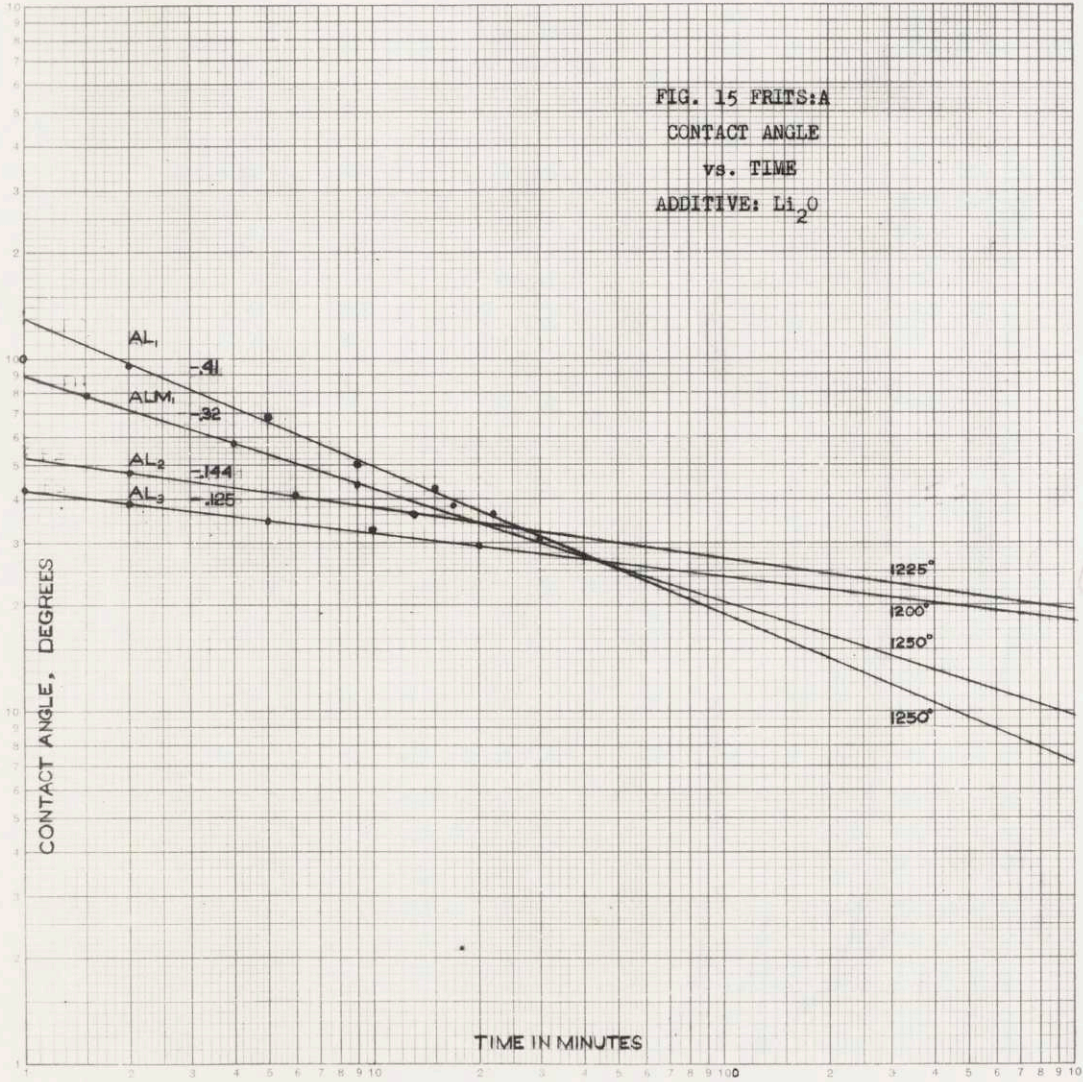
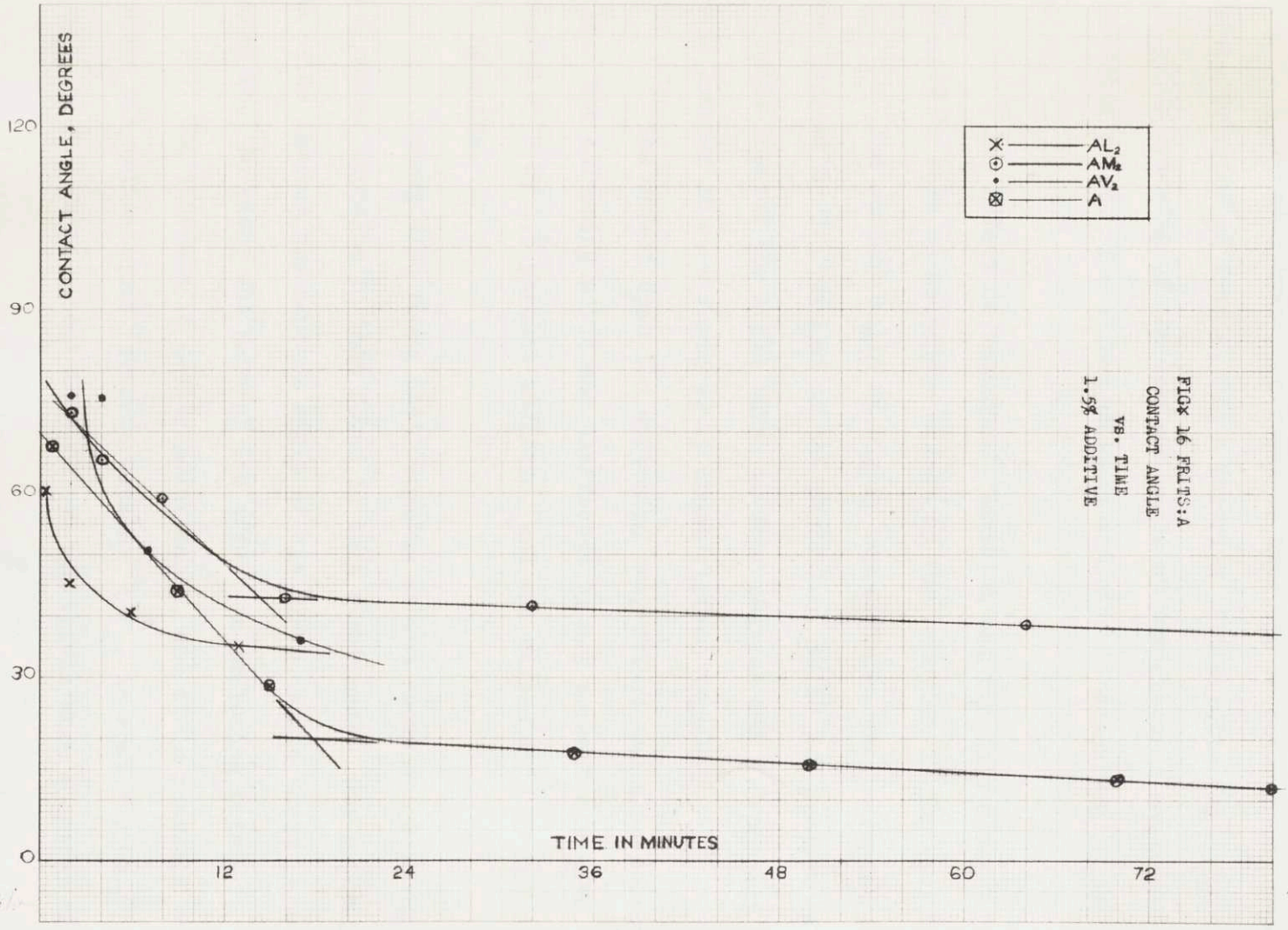


FIG. 15 FRITS:A
 CONTACT ANGLE
 vs. TIME
 ADDITIVE: Li_2O





VII. DISCUSSION OF RESULTS

A. Effect of Additives

The additives were found to have one or both of two effects on the behavior of frit A, (1) a lowering of the softening temperature and (2) a lowering of the contact angle at temperatures above the softening point. The effect of each additive is described separately below.

1. Effect of vanadium. Vanadium was the only element that appeared to have an anomalous effect on the behavior of the base frit.

The contact angle at higher temperatures was increased about five degrees by 0.3 percent of the pentoxide, while 1.5 percent of the oxide lowered the angle three to four degrees and 3.0 percent of oxide lowered it even further, by about fifteen degrees.

The effect upon the softening temperature was also anomalous. The softening point was unaffected by 0.3 percent additive, was lowered 25°C by 1.5 percent additive, and was raised 25°C by 3.0 percent of the oxide.

Amberg also found that vanadium showed anomalous behavior, but in a manner opposite to that found in this experiment. One percent of the oxide lowered the contact angle of his glass, while three percent raised it. No study was made of its effect on softening point.

The vanadate is easily polarizable, and it is possible that it affects the solid-liquid "surface tension" (γ_{sl} in equilibrium $\left[\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \right]$) to an extent that is not negligible when compared to its effect upon liquid-gas surface tension (γ_{lg}). Under conditions where γ_{sl}

and γ_{lg} are lowered by addition of oxide, but respond differently with respect to the amount added, anomalous effects may be expected. In certain cases, even this is not a necessary condition. For instance, $(\gamma_{sg} - \gamma_{sl})$ may be lowered proportionately more than γ_{lg} , and as a result cosine θ will decrease—i. e., the contact angle will be increased—even though γ_{sl} alone may have decreased proportionally to the same or even a lesser extent than γ_{lg} .

Without knowing the absolute values of the interfacial tensions involved, it is difficult to explain the behavior of vanadium in the glass, but the results seem to indicate that a process like the above is at work.

The author was unable to find an explanation for the anomalous effect on softening points of increasing amounts of additive.

2. Effect of molybdenum. The effect of molybdenum was in accord with the findings of Comeforo and Hursh, Amberg, and others. The contact angle was lowered by six degrees at 1350°C by 0.3 percent of the sesquioxide. Both 1.5 percent and 3.0 percent of oxide lowered the contact angle to very near zero. Although the curve for three percent oxide appears to be lower, the specimen pellets for both percentages looked very similar after the firing. In both cases, the glass had completely covered the surface of the disc, and had then run down the sides of the disc at what appeared to be a contact angle of one or two degrees. The glass had spread over the disc in so thin a film that it had the appearance of a glaze.

Molybdenum did not alter the softening point of the glass in any of the trials. It appeared to be the only additive tried that caused a true lowering in contact angle and improvement in wetting. It is possible, however, that it lowered the viscosity of the glass markedly,

and thus enabled it to reach its equilibrium contact angle in a very short time. This is borne out by the figures in Table 8 (1.5 percent additive), where equilibrium was reached in a very short time (at 1250°).

3. Effect of lithium. The addition of lithium did not alter the final contact angle by more than two or three degrees, which is within the range of experimental error of this experiment.

It did, however, lower the softening point of the glass quite markedly—37°C in the case of 1.5 percent oxide and 75°C in the case of 3.0 percent oxide. This was to be expected, since the glass contained no alkali. From a practical standpoint, this can mean a substantial saving in firing time and delivery time of a wheel using such a bond.

From the fact that the softening point was lowered and the surface tension unaltered, it appears that the lithium oxide was so firmly taken up into the body of the glass that none of it was free to migrate to the surface and increase the surface concentration of oxide, whereby the liquid-air surface tension would have been lowered.

It would be well worth while to investigate the effect of adding three to five percent of sodium and potassium oxide to the glass, along with one-half to one percent of lithia. The sodium and potassium oxides may be bound into the glass network, leaving the lithia free to concentrate at the surface and lower surface tension. In this manner it might be possible to produce a low temperature glassy bond with wetting properties at least as good as, and probably better than, the standard high temperature bond.

4. Effects of manganese, boron, and lead. None of these additives altered the softening point of frit A. Lead appears to have raised it by fifty degrees. This was not really the case, since a sample of frit A was tested in the same run, and also softened at the same temperature. This may have been due to a defect in the temperature control mechanism, or possibly a result of unusual atmospheric conditions, since the run was made on an unusually hot and humid day.

Boron had the greatest effect in lowering the ultimate contact angle, as was expected. It lowered the contact angle almost as much as molybdenum was found to do.

Lead is known to be quite reactive with alumina. However, 0.3 percent of the oxide was found to have the same effect as an equal amount of molybdenum oxide. This seems to indicate that in regard to the percentages used, chemical action does not play too large a part, at least over the time intervals considered in this study.

B. Change of Contact Angle with Time

When values of the contact angle at the softening temperature were plotted against time using Cartesian coordinates, no pattern could be found in the curves. The points were next plotted on semi-logarithmic paper. The result was downward-curving lines. This indicated that the angle decreased more rapidly than it would have if the curve were exponential, since the log of time was plotted against the contact angle. Finally, they were plotted on log-log paper. They gave straight lines of varying slope. These are shown in Figures 14, 15, and 16. The points available are too few to justify extending the

plot beyond thirty minutes, but at least within the range of values measured such an approximation is valid.

This seems to indicate that the curves are of the form

$$\log \theta = \log \theta_0 + N \log t \quad \text{or}$$

$$\theta = \theta_0 t^N,$$

where θ is the contact angle in degrees,
 t is the time in minutes,
 N is the slope of the line, and
 θ_0 is a constant, which is the value of the contact angle at time zero.

Lehmann and Singh¹⁰ made studies of the change of contact angle with time for several systems, for values of time up to ninety minutes. According to the abstract of their article, no simple quantitative relation was found to hold for the curves they obtained. It thus appears that the above relation would very probably break down when applied over a longer time interval.

VIII. ECONOMICS

Unless the use of surface-tension-reducing agents is economically feasible, they are of little practical value except for certain specialized applications. An approximate analysis of the cost of using these oxides was therefore undertaken.

A medium-sized grinding-wheel plant might produce about a thousand tons of wheels a year. With an average value of fifteen percent for the amount of bond used in the wheels, this would give an annual consumption of three hundred thousand pounds of bond. Only about half of the wheels, those for relatively specialized applications, would really benefit substantially from the use of additives. If 0.3 percent additive were used, this would mean a consumption of $.0003 \times 150,000$, or four hundred fifty pounds a year.

The average price of fabricated abrasives is about a dollar per pound. On this basis, the addition of lithium carbonate (at \$0.67 per pound)²² to half of the bond used would cost 0.0373 percent of the selling price of the wheels. In the case of molybdenum trioxide (at \$1.46 per pound)²², the increase in annual cost would be .0546 percent of annual sales. In the case of vanadium, which is not yet available on a commercial scale (the present price is \$6.17 per pound)²², the cost would be 0.139 percent of annual sales.

From this it may be seen that the use of lithium and molybdenum oxides are not only economically feasible but quite advantageous in grinding wheel bonds. The small cost of the additives is more than balanced by the improved performance of the wheels. It would probably be possible to lower the amount of bond needed for a given wheel when molybdenum is used, resulting in a small saving. Lithium, if used in larger amounts, would be able to lower the firing temperature of the wheels; the saving in fuel would be negligible, but the saving in time would be larger.

IX. SUMMARY AND CONCLUSIONS

1. The measurement of the contact angles of a sessile drop of glass on alumina is a convenient and useful method of studying the effect of additives on the wetting of alumina by glasses.
2. Molybdenum is very effective in promoting wetting, and generally improves the fluidity of the glass. It is effective in amounts of 0.3 percent oxide by weight of the fritted glass; 1.5 percent and 3.0 percent of the oxide result in almost perfect wetting.
3. Lithium does not lower the contact angle, but lowers the softening point in proportion to the amount added. Three percent of it lowered the softening point 75°C. It appears that the lithium did not migrate to the surface because it was too firmly held in the glass itself.
4. Vanadium had an anomalous effect; 0.3 percent of the oxide raised the contact angle, while 1.5 percent and 3.0 percent reduced it.
5. Lead and boron were also effective in lowering the contact angle; 0.3 percent of each lowered the final angle from twenty to ten degrees. Manganese had no effect.
6. A combination of 0.15 percent lithium and 0.15 percent molybdenum reduced the contact angle more than did 0.3 percent of molybdenum alone.
7. The change of contact angle θ with time t at a constant temperature followed, between one minute and sixteen minutes, the relation $\theta = \theta_0 t^n$, where n was the slope of the line when contact angle and time

were plotted on log-log coordinate paper.

8. The use of lithium and molybdenum for improving the properties of glassy abrasive wheel bonds is most advantageous. The added cost is insignificant in terms of the price of the finished product.

9. The effect of these additives on different types of glassy bonds could be determined by the following tests:
 1. These results would not be applicable to the use of silicon carbide or corundum bonds, but the effect of lithium on the viscosity-reducing and viscosity-increasing ability of these glasses in a manner similar to that described here.

2. It is also likely that the effect of the above additives used simultaneously will be more than cumulative. Studies of combinations of two or three additives, particularly of those that lead to glassy, amorphous, or partially crystalline structures, would be very fruitful.

3. With the help of fluxing agents and wetting additives, it should be possible to develop a low-temperature bond that replicates the wetting characteristics of a standard high-temperature bond.

4. The change of contact angle with time would be further studied, observing the drop over a period of three hours at the same temperature. This would indicate whether the behavior of the drop could be approximated by log-log plots of the type shown in Figures 10, 11, and 12, for periods of time longer than thirty minutes.

5. In the case of Frits A1, and A2, it was found that a drop held at a temperature just above its softening point for ten to fifteen minutes began to show signs of spreading. It would be interesting to hold each glass at a temperature 25°C or 50°C below its softening temperature for prolonged periods of time to find

IX. SUGGESTIONS FOR FURTHER RESEARCH

1. In addition to the additives studied here, the effect of tungsten, arsenic, and other known surface-tension-reducing elements¹⁶ on the glass could be studied.

2. The effect of these additives on different types of glassy bonds could be determined.

3. These results would not be applicable to the wetting of silicon carbide by porcelaneous bonds, but the effect of surface-tension-reducing and viscosity-reducing additives could be studied in a manner similar to that described here.

4. It is more than likely that the effect of two or more additives used simultaneously will be more than cumulative. Studies of combinations of two to three additives, particularly of those that lower surface tension as a result of different mechanisms, could be very fruitful.

5. With the help of fluxing agents and wetting additives, it should be possible to develop a low-temperature bond that duplicates the wetting characteristics of a standard high-temperature bond.

6. The change of contact angle with time could be further studied, observing the drop over a period of three hours at the same temperature. This would indicate whether the behavior of the drop could be approximated by log-log plots of the type shown in Figures 13, 14, and 15, for periods of time longer than thirty minutes.

7. In the case of frits AM₁ and AV₁, it was found that a drop held at a temperature not much below its softening point for ten to fifteen minutes began to show signs of softening. It would be interesting to hold each glass at a temperature 25°C or 50°C below its softening temperature for prolonged periods of time to find

whether it can be "forced" to soften at such a temperature. The contact angle is determined to so large an extent by the two intimately linked variables of time and temperature that further study of their relative influence on the angle would be of value.

8. It would be worth while to determine the effect of the firing cycle on the melting history of the glasses. One run could be made holding the temperature constant for periods of three minutes for every 25°C rise, and another run made holding the temperature constant for thirty to sixty minutes for every 25°C rise. It is more than likely that the contact angle at the final temperature would take the same amount of time to reach equilibrium in both cases. This would imply that in the firing of grinding wheels, and also of glazes and enamels, the temperature could be raised at a rate just slow enough to avoid harmful temperature gradients within the body resulting from its low thermal conductivity.

88th. (U.S.) Cong. Papers, 21, 563 (1926).

6. Comfort, J. A. and R. A. Borch, "Melting of Alloys by Refractories by Molten Glass", Part I, J. Am. Cer. Soc., 1928, 15, 110 (1928); Part II, ibid., 142.
7. Clayton, W., ASTERS AND REFRACTORY, Chemical Publishing Co., N. Y., Inc. (1937).
8. Anker, V. F., D. W. Newhall, M. P. Matoff and J. K. Fink, "Fundamentals of Glass-to-Metal Sealing, I", J. Am. Cer. Soc., 1955, 38, 86 (1955).

BIBLIOGRAPHY

1. Weiser, H. B., A TEXTBOOK OF COLLOID CHEMISTRY, John Wiley & Sons, Inc., N. Y. Second edition (1949).
2. Halden, F. A., EFFECT OF MINOR CONSTITUENTS ON LIQUID IRON SURFACE TENSION, M. I. T. Sc.D. Thesis, Department of Metallurgy, 1954.
3. Adam, N. K., THE PHYSICS AND CHEMISTRY OF SURFACES, Oxford University Press, London, Third edition (1949).
4. Cassie, A. B. D., "Contact Angles and the Absorption of Liquids", in SURFACE PHENOMENA IN CHEMISTRY AND BIOLOGY, editors J. F. Danielli, Pankhurst and Riddiford, Pergamon Press, N. Y. (1958).
5. Dorsey, N. E., "Measurement of Surface Tension", Nat'l. Bur. Stds. (U.S.) Sci. Papers, 21, 563 (1926).
6. Comeforo, J. E. and R. K. Hursh, "Wetting of $Al_2O_3-SiO_2$ Refractories by Molten Glass", Part I, J. Am. Cer. Soc., 35, 130 (1952); Part II, ibid., 142.
7. Clayton, W., WETTING AND DETERGENCY, Chemical Publishing Co., of N. Y., Inc. (1937).
8. Zackay, V. F., D. W. Mitchell, S. P. Mitoff and J. A. Pask, "Fundamentals of Glass-to-Metal Bonding, I", J. Am. Cer. Soc., 36, 84 (1953).

9. Ellefson, B. S. and N. W. Taylor, "Surface Properties of Fused Salts and Glasses", Part I, J. Am. Cer. Soc., 21, 193 (1938); Part II, ibid., 205.
10. Lehmann, H. and U. S. Singh, Am. Cer. Soc. Abstracts, 41, 118 (1958).
11. Parikh, N. M., EFFECT OF ATMOSPHERE ON SURFACE TENSION OF GLASS AT LOW TEMPERATURES, M. I. T. Sc. D. Thesis, Department of Metallurgy, 1954.
12. Fulrath, R. M., S. P. Mitoff and J. A. Pask, "Fundamentals of Glass-to-Metal Bonding, III", J. Am. Cer. Soc., 40, 269 (1957).
13. Goodway, M. E., "The Wettability of Metals by Glass", M. I. T. Term Paper, Department of Ceramics, 1958.
14. Langmuir, I. and Schaeffer, V. J., "The Effect of Dissolved Salts on Insoluble Monolayers", J. Am. Chem. Soc., 59, 2400 (1937).
15. Burdon, R. S., SURFACE TENSION AND THE SPREADING OF LIQUIDS, Cambridge University Press, Second edition (1949).
16. Amberg, C. R., "Effect of Molybdenum and Other Oxides on Surface Tension of Silicate Melts", J. Am. Cer. Soc., 29, 87 (1946).
17. Dietzel, A., Am. Cer. Soc. Abstracts, 20, 191 (1943).
18. Badger, A. E., C. W. Parmelee and A. E. Williams, "Surface Tension of Various Molten Glasses", J. Am. Cer. Soc., 20, 325 (1937).

19. Betz, G. C., "Lithium Minerals and Compounds in Ceramics", J. Am. Cer. Soc., 21, 189 (1938).
20. Sidhwa, A. P., A STUDY OF THE MICROSTRUCTURE OF VITRIFIED BONDED ABRASIVE WHEELS, ~~an~~ M. I. T. S.B. Thesis, Department of General Engineering, 1958.
21. Parmelee, C. W. and C. G. Harman, "Effect of Alumina on the Surface Tension of Molten Glass", J. Am. Cer. Soc., 20, 224 (1937).
22. Quarterly Report on Current Prices, Chem. & Eng. News, 37, n.13, 61 (March 1959).

TABLE I

Change of Contact Angle with Time and TemperatureFRIT: AL₁ (0.3% Lithium)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
975	16	114.5°	111.5°	113°
1000	15	116	114	115
1200	16	114.5	115	114.75
1250	2	94.5	96.5	95.5
1250	5	68.5	68	68.25
1250	9	50	50	50
1250	15	43	42.5	42.75
1250	22	36	36.5	36.25
1250	30	31	31	31
1290	1	28.5	27.5	28
1290	4	28	27.5	27.75
1290	17	25	25.5	25.25
1330	16	-	22.5	22.5
1375	19	-	19.5	19.5

TABLE 2

Change of Contact Angle with Time and TemperatureFRIT: AM₁ (0.3% Molybdenum)

975°C	17 min.	105°	106°	105.5°
1000	16	111	110.5	110.75
1200	16	110	110.5	110.25
1250	10	106.5	104.5	105.5
1250	16	99.5	98	98.75
1250	31	68	65	66.5
1250	41	67	66	66.5
1290	2	28	29.2	28.6
1290	5.5	24.75	-	24.75
1290	10	22.5	-	22.5
1290	18	21.25	-	21.25
1330	17	16	-	16
1375	18	15.75	-	15.75

TABLE 3

Change of Contact Angle with Time and TemperatureFRIT: AV₁ (0.3% Vanadium)

1000°C	18 min.	115°	115.75°	115.4°
1075	15	117.75	119	117.4
1150	15	116	117	116.5
1200	15	116	119	117.6
1250	18	64.5	70	67.25
1270	1	40.5	41.5	41
1270	2	30	33.5	31.75
1270	5	25	27	26
1270	10	22.5	24	23.25
1270	16	22.5	-	22.5
1300	16	19.25	-	19.25
1330	16	16	-	16
1375	16	10.75	-	10.75

TABLE 4

Change of Contact Angle with Time and TemperatureFRIT: ALM₁ (0.15% Lithium + 0.15% Molybdenum)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1075	16	96.5°	118°	107.25°
1150	16	99.25	117.75	108.5
1200	15	99.25	118.5	108.85
1250	1.5	75.5	81.5	78.5
1250	4	55	59	57
1250	9	43	44.75	43.85
1250	17	38	38.25	38.1
1270	17	36.25	-	36.25
1300	17	34.25	-	34.25
1330	17	29.25	-	29.25
1375	17	25	-	25

TABLE 5

Change of Contact Angle with Time and TemperatureFRIT: Al_2 (1.5% Lithium)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1175	5	95°	96°	95.5°
1210	0.5	90.5	93.25	91.9
1210	3	76.8	82	79.4
1210	9	63.5	69.25	66.4
1225	0.5	58.25	63.3	60.6
1225	2	44	46.5	45.25
1225	6	39.75	41	40.4
1225	13	35	-	35
1250	8	29.5	-	29.5
1290	8	21.8	-	21.8
1330	8	20.5	-	20.5
1370	8	20.5	-	20.5

TABLE 6

Change of Contact Angle with Time TemperatureFRIT: AM₂ (1.5% Molybdenum)

Temperature °C	Time held at Temperature, min	Left Angle	Right Angle	Average Contact Angle
1000	7	91°	92°	91.5°
1150	7	93.5	91.25	92.4
1250	2	74	72.25	73.1
1250	4	64.5	66.25	65.4
1250	8	58.3	60	59.1
1250	16	42.4	43	42.7
1250	32	41.5	41.5	41.5
1250	64	38	39	38.5
1275	7	16.75	-	16.75
1300	8	12.4	-	12.4
1350	7	9.4	-	9.4

TABLE 7

Change of Contact Angle with Time and TemperatureFRIT: AV_2 (1.5% Vanadium)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	5	90°	93.75°	91.9°
1050	7	90	92	91
1150	7	90.5	94	92.25
1225	2	77	74.25	75.6
1225	4	75	76.4	75.7
1225	7	50.5	50.25	50.4
1225	17	33.5	38.75	36.1
1250	8	-	33.4	33.4
1275	8	27.25	-	27.25
1300	8	24	-	24
1350	15	18.5	-	18.5

TABLE 8

Change of Contact Angle with Time and TemperatureFRIT: AL_3 (3% Lithium)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
925	15	90°	90°	90°
1175	15	65	66.5	65.75
1200	1	43	41	42
1200	2	40	38	39
1200	5	34.6	33.75	34.2
1200	10	33	-	33
1200	20	29.25	-	29.25
1225	14	25.5	-	25.5
1250	14	20.5	-	20.5
1275	14	20	-	20
1300	14	20	-	20
1350	14	19	-	19

TABLE 9

Change of Contact Angle with Time and TemperatureFRIT: AM_3 (3% Molybdenum)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	16	117.5°	114°	115.75°
1050	6	117.75	113.75	115.75
1100	6	118.5	118	118.25
1150	16	120	115.5	117.75
1200	16	119	112	115.5
1250	2	76.5	79	77.75
1250	4	59.5	57.5	58.5
1250	9	42.5	42.5	42.5
1250	16	34.25	33.5	34
1300	15	11	-	11
1330	17	8.5	-	8.5
1375	16	-	-	-

TABLE 10

Change of Contact Angle with Time and TemperatureFRIT: AV₃ (3% Vanadium)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	15	115°	113.5°	114.25°
1050	5	116.25	116.5	116.4
1100	5	118.5	117.5	118
1150	15	119.5	118.5	119
1200	15	118	120.5	119.25
1250	17	119.75	117.25	118.5
1275	1.5	47.5	51	49.25
1275	3.5	32.3	35.5	34
1275	8	-	26.75	26.75
1275	16	-	20.25	20.25
1300	16	-	10.5	10.5
1330	16	-	9	9
1375	17	-	9	9

TABLE II

Change of Contact Angle with Time and TemperatureFRIT: AB₁ (0.3% Boron)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	15	120°	126.5°	123.25°
1075	16	119	122.5	120.75
1150	16	120	118.75	119.6
1200	15	128	132	130
1250	2	75	77	76
1250	3	75	78	75.5
1250	6	58.5	58.5	58.5
1250	13	29.5	31	30.25
1250	25	22.75	-	22.75
1275	17	13.75	-	13.75
1310	17	9.5	-	9.5
1370	17	7.5	-	7.5

TABLE 12

Change of Contact Angle with Time and TemperatureFRIT: AP₁ (0.3% Lead)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	15	94°	97°	95.5°
1075	13	113.5	99.5	106.5
1150	15	102.75	98	100.4
1200	15	113	143	128
1250	16	108	142	125
1300	2	79	73.5	76.25
1300	4	51	56.5	53.75
1300	9	35	35.75	35.4
1300	15	-	24	24
1330	15	-	10	10

TABLE 13

Change of Contact Angle with Time and TemperatureFRIT: AN₁ (0.3% Manganese)

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	16	107.5°	118.5°	113°
1075	15	108.25	119.75	114
1150	15	110	124	117
1200	14	118	126	122
1250	1	66	67	66.5
1250	2.5	51	52	51.5
1250	5	35.5	40	37.75
1250	10	29	30	29.5
1250	25	-	25.5	25.5
1275	16	-	22.75	22.75
1310	16	-	18.75	18.75
1370	16	-	17.75	17.75

TABLE 14A

Change of Contact Angle with Time and Temperature

FRIT: A (no additive) Sample No. 1

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	18	136°	111°	123.5°
1025	7	133.25	123.75	128.5
1075	17	143.75	124.5	133.5
1150	17	140.5	123.5	131.5
1200	17	143.4	126.8	135.1
1250	5	126.25	115.25	120.75
1250	10	96	92.8	94.4
1250	16.5	62.5	62.5	62.5
1275	1.5	41.2	41.2	41.2
1275	5	37.3	34	35.65
1275	10	34.2	31	32.6
1275	18	32.7	30	31.3
1300	16	31	27.4	29.2
1330	17	25.4	23	24.2
1375	20	-	19.75	19.75

TABLE 14 B

Change of Contact Angle with Time and Temperature

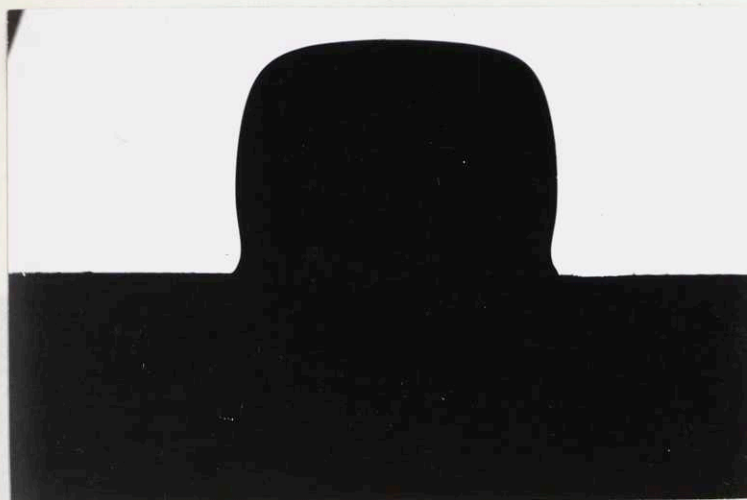
FRIT: A (no additive) Sample No. 2

Temperature °C	Time held at Temperature, min.	Left Angle	Right Angle	Average Contact Angle
1000	17	105°	105°	105°
1025	6	102.5	105	103.25
1075	16	105.5	106	105.75
1150	17	104.5	104.75	104.63
1200	16	104	106	105
1250	4	93.75	104	98.8
1250	9	67.5	69.5	68.5
1250	17	53.5	55	54.75
1275	1	42	38.75	40.3
1275	4	33.3	35.3	34.3
1275	9	33.2	34	33.6
1275	17	31.25	31.5	31.3
1300	15	29.3	29.5	29.4
1330	16	-	26	26
1375	20	-	19.75	19.75

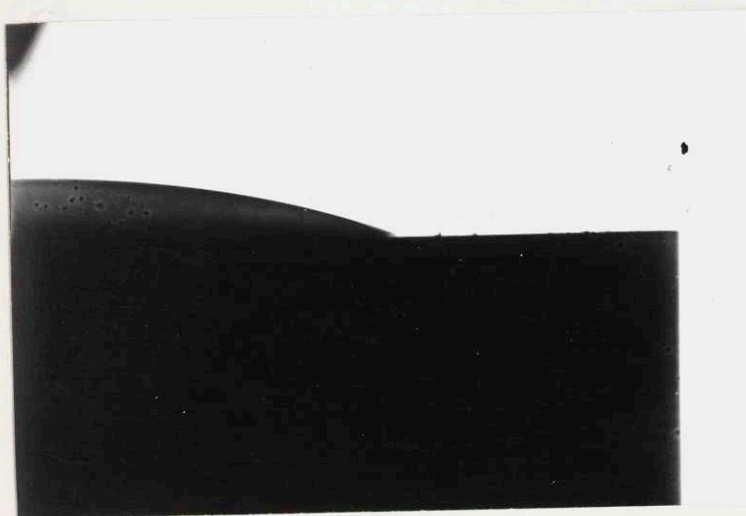
TABLE 15

Chemical Analysis of Frits A and AM₃

Constituent	Percent in Frit A	Percent in Frit AM ₃
SiO ₂	56.6	53.3
Al ₂ O ₃	17.6	16.0
CaO	25.5	27.8
Mo ₂ O ₃	-	2.66



2 minutes
at 1250°C

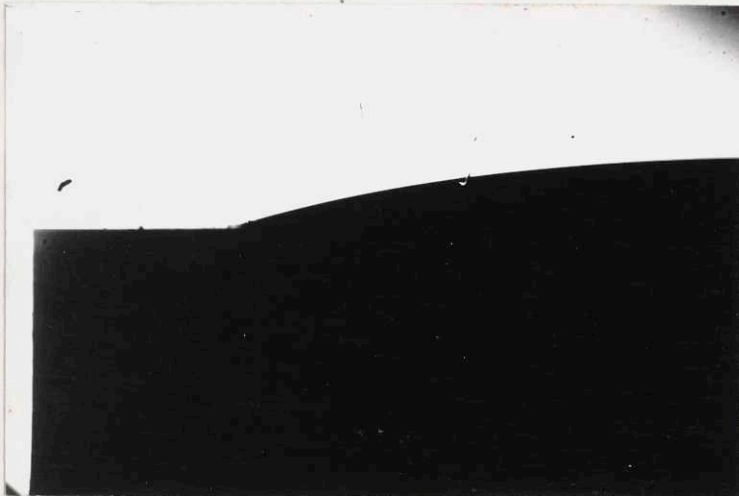


19 minutes
at 1375°C

PLATE 2. Effect of Temperature on Contact Angle
Frit AL_1 (0.3% Li_2O).

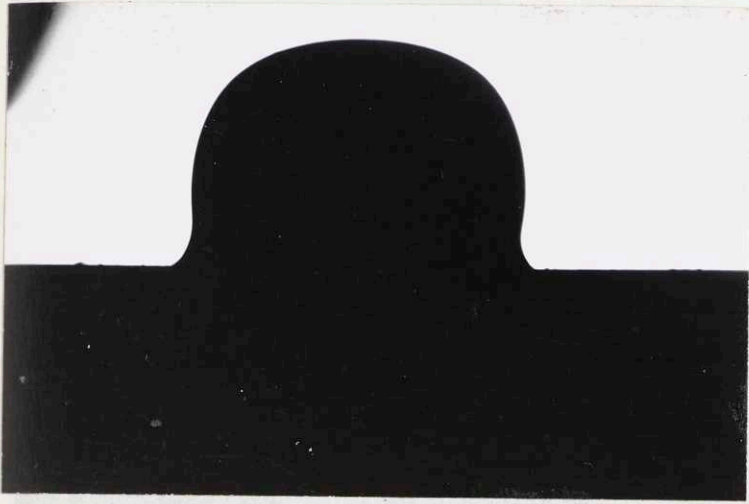


10 minutes ✓
at 1250°C



17 minutes ✓
at 1330°C

PLATE 3. Effect of Temperature on Contact Angle
Frit AM₁ (0.3% Mo₂O₃).



18 minutes
at 1250°C

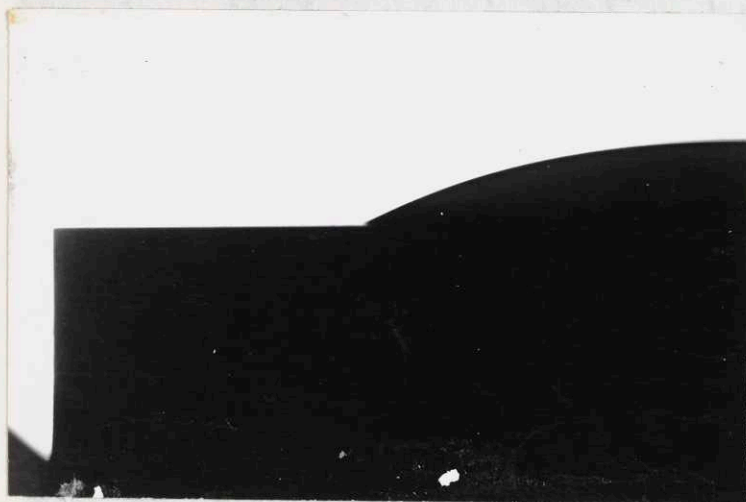


16 minutes
at 1375°C

PLATE 4. Effect of Temperature on Contact Angle
Frit AV₁ (0.3% V₂O₅).

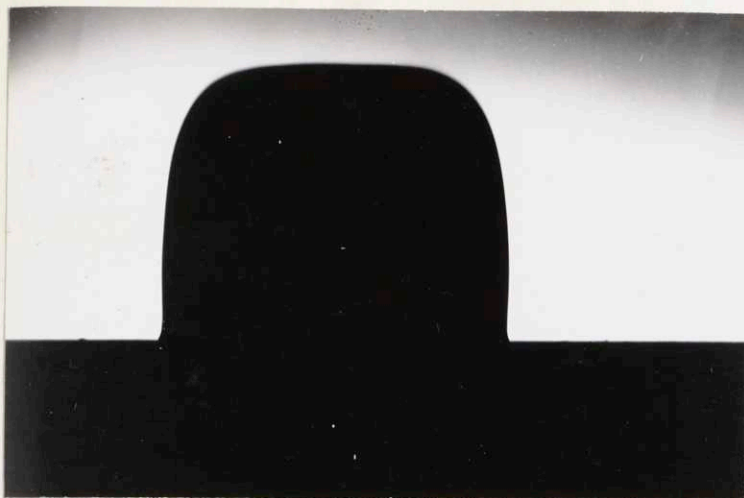


1½ minutes
at 1250°C

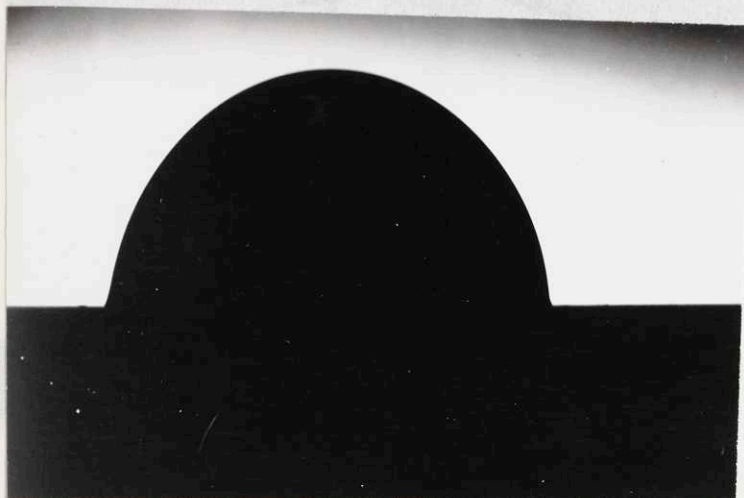


17 minutes ✓
at 1375°C

PLATE 5. Effect of Temperature on Contact Angle
Frit ALM₁ (0.15% Li₂O + 0.15% Mo₂O₃).



$\frac{1}{2}$ minute
at 1210°C

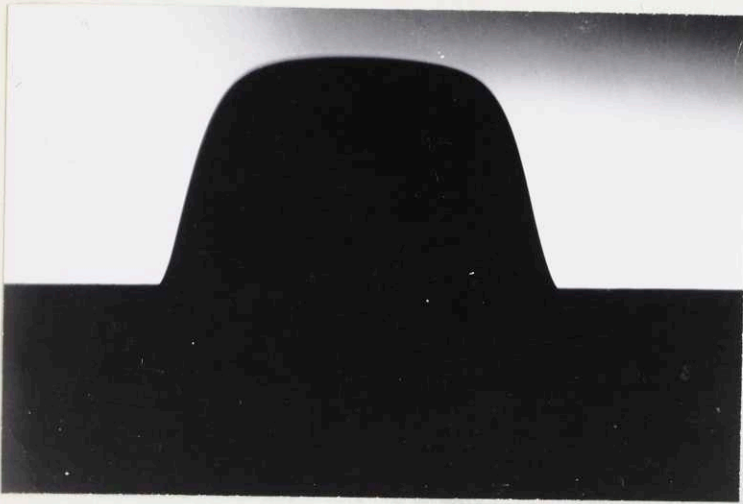


3 minutes
at 1210°C

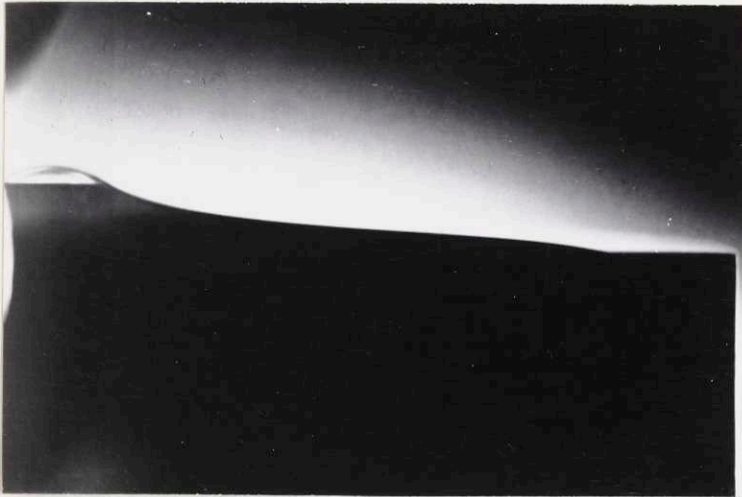


8 minutes
at 1370°C

PLATE 6. Effect of Temperature on Contact Angle
Frit Al_2 (1.5% Li_2O).

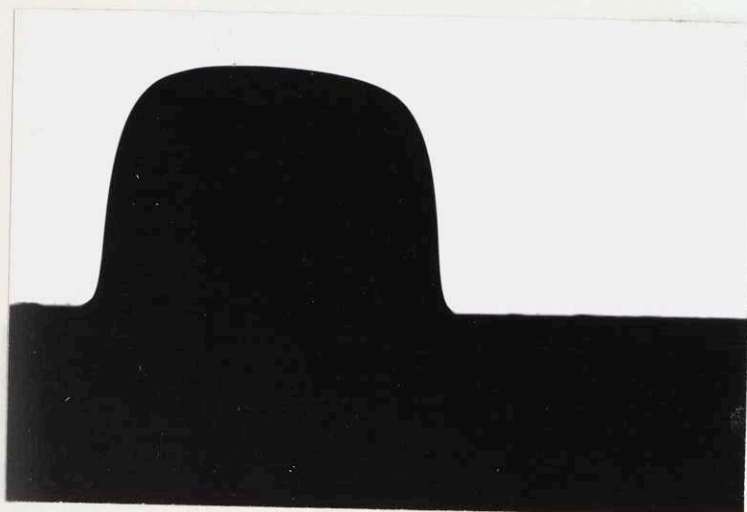


2 minutes
at 1250°C

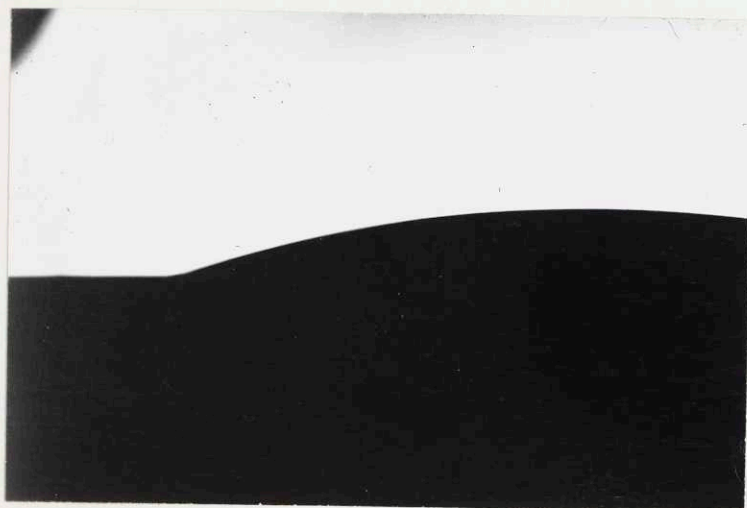


7 minutes
at 1350°C

PLATE 7. Effect of Temperature on Contact Angle
Frit AM₂ (1.5% Mo₂O₃).

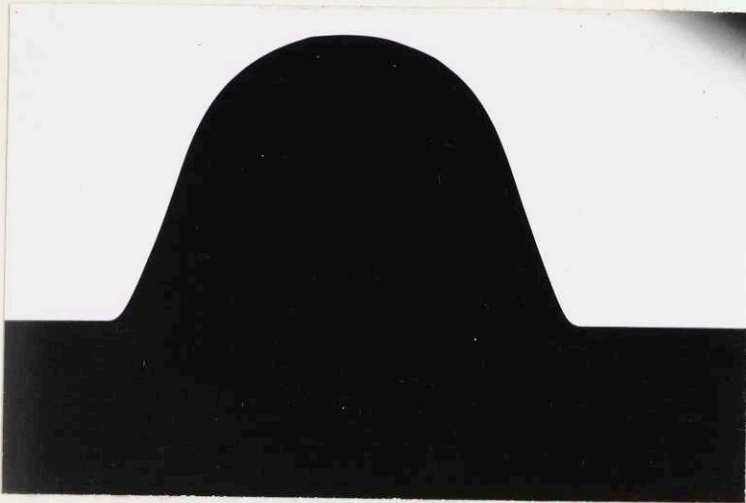


5 minutes
at 1150°C

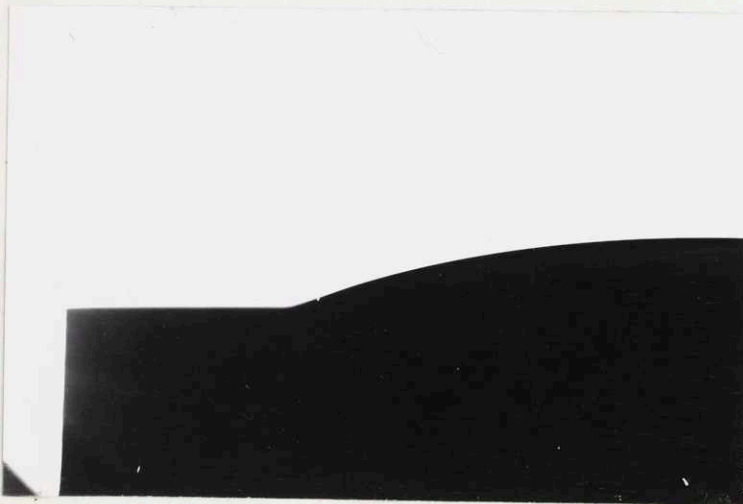


15 minutes
at 1350°C

PLATE 8. Effect of Temperature on Contact Angle
Frit AV₂ (1.5% V₂O₅).

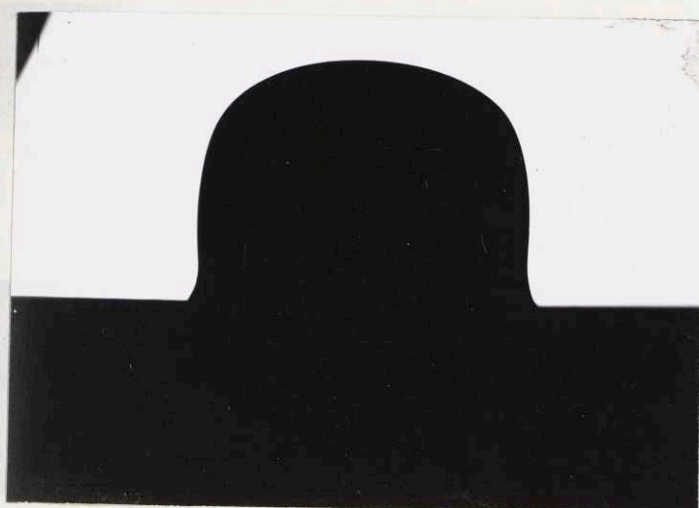


15 minutes
at 1175°C ✓

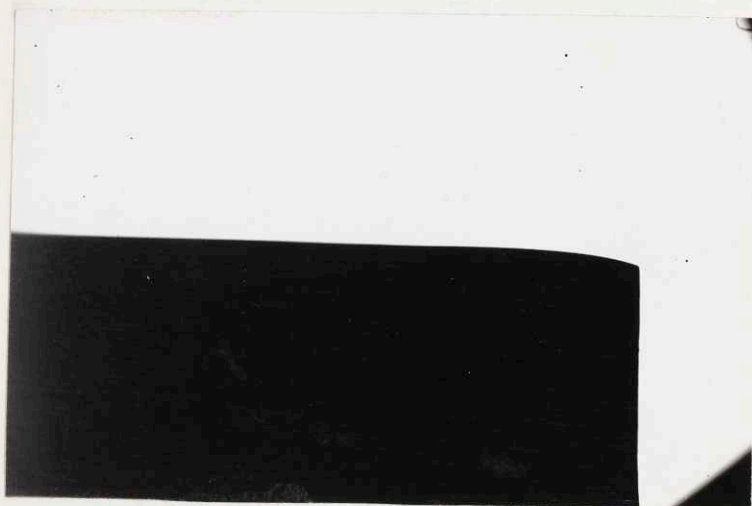


14 minutes
at 1350°C ✓

PLATE 9. Effect of Temperature on Contact Angle
Frit AL_3 (3.0% Li_2O).

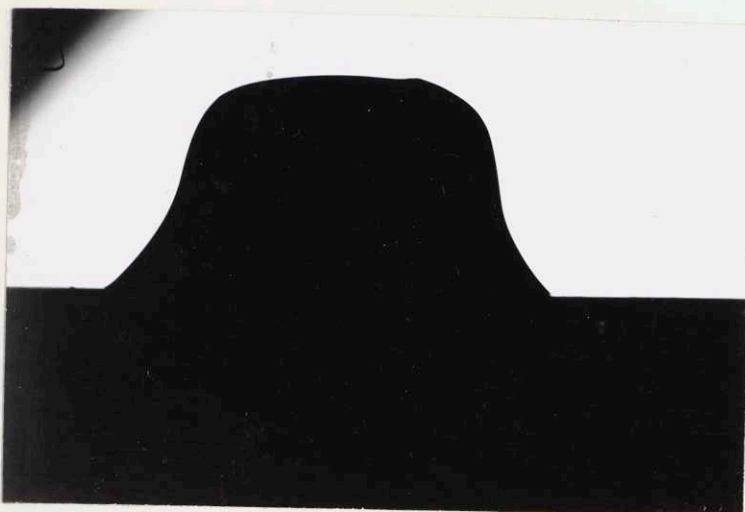


2 minutes
at 1250°C

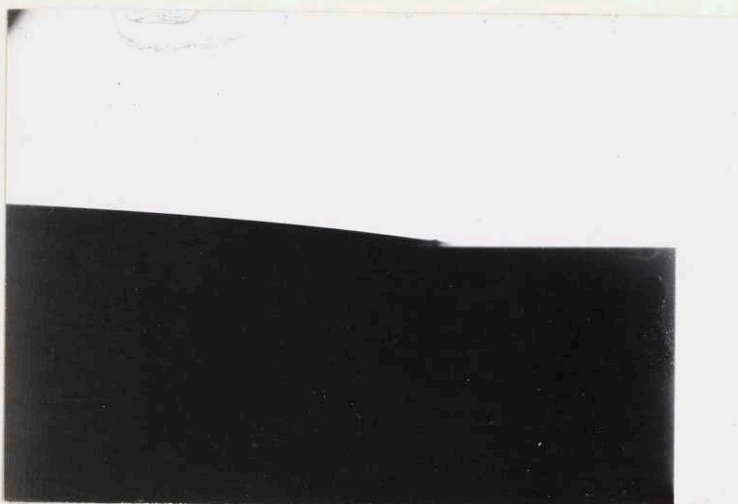


16 minutes
at 1375°C

PLATE 10. Effect of Temperature on Contact Angle
Frit AM₃ (3.0% Mo₂O₃).

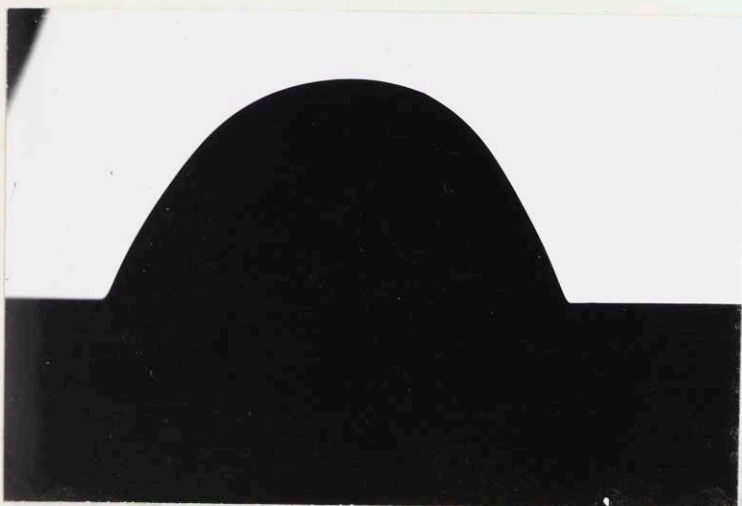


1½ minutes
at 1275°C

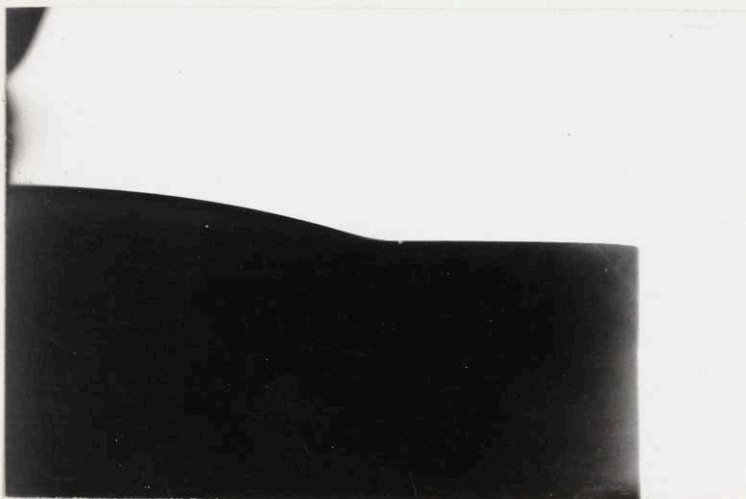


17 minutes
at 1375°C

PLATE 11. Effect of Temperature on Contact Angle
Frit AV₃ (3.0% V₂O₅).

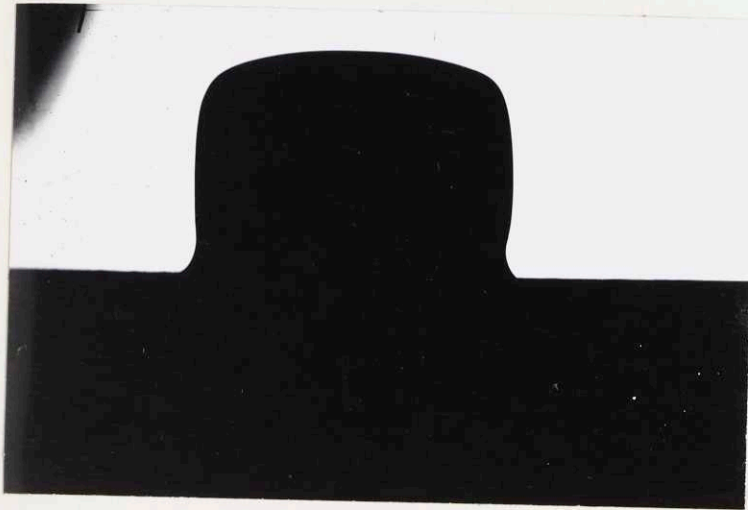


1 minute
at 1250°C



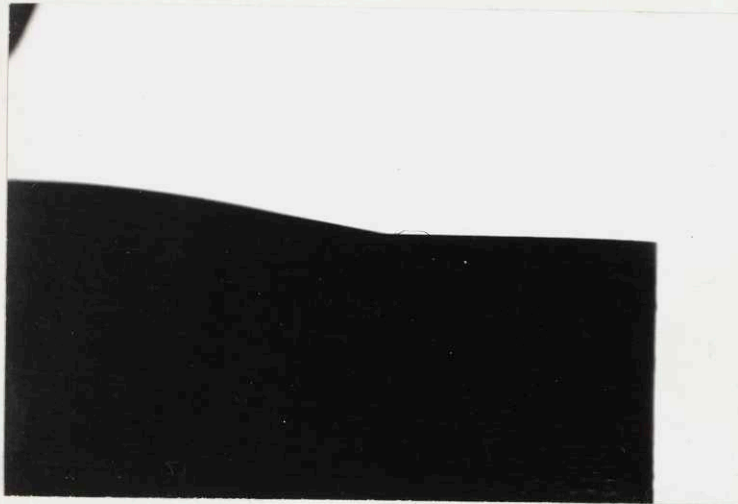
16 minutes
at 1370°C

PLATE 12. Effect of Temperature on Contact Angle
Frit AN₁ (0.3% MnO₂).



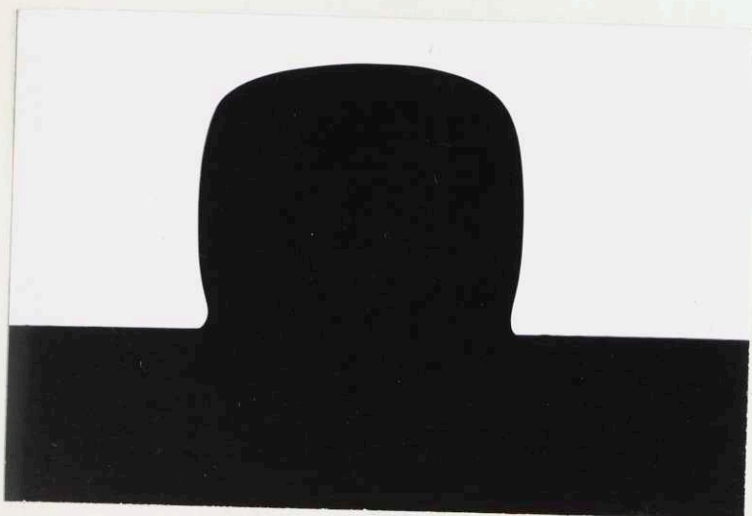
2

2 minutes
at 1300°C

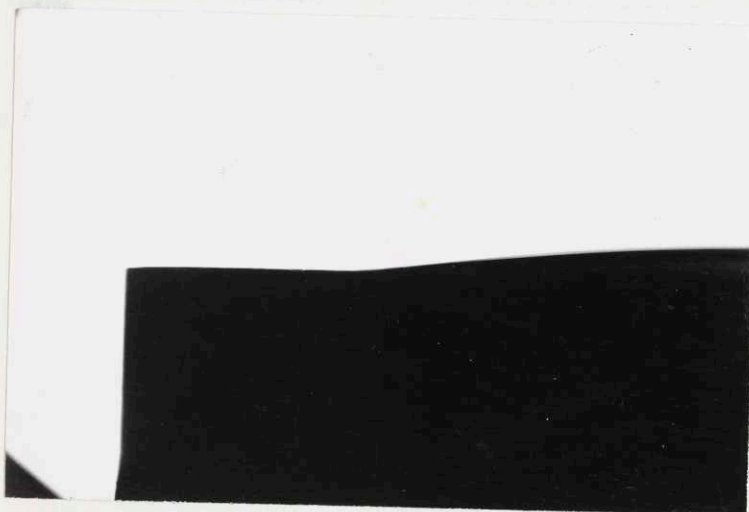


15 minutes
at 1330°C

PLATE 13. Effect of Temperature on Contact Angle
Frit AP₁ (0.3% PbO).

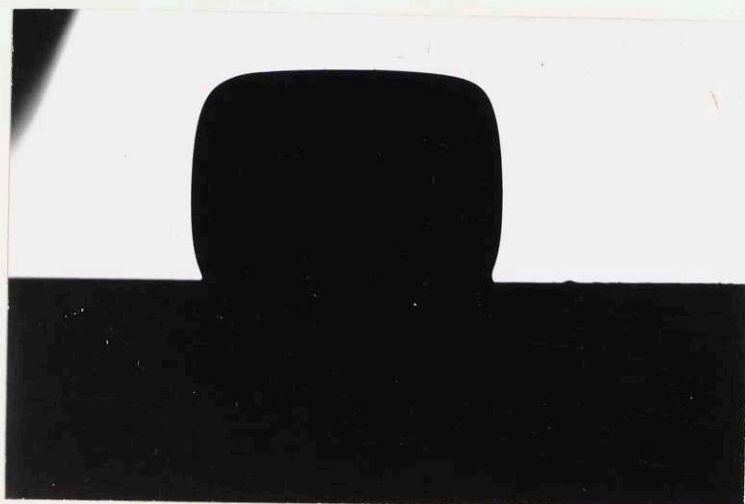


2 minutes
at 1250°C

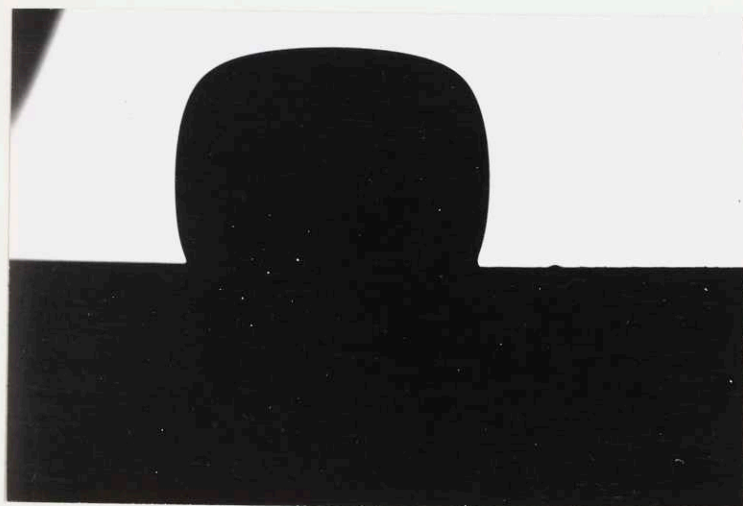


17 minutes
at 1370°C

PLATE 14. Effect of Temperature on Contact Angle
Frit AB₁ (0.24% B₂O₃ + 0.11% Na₂O).

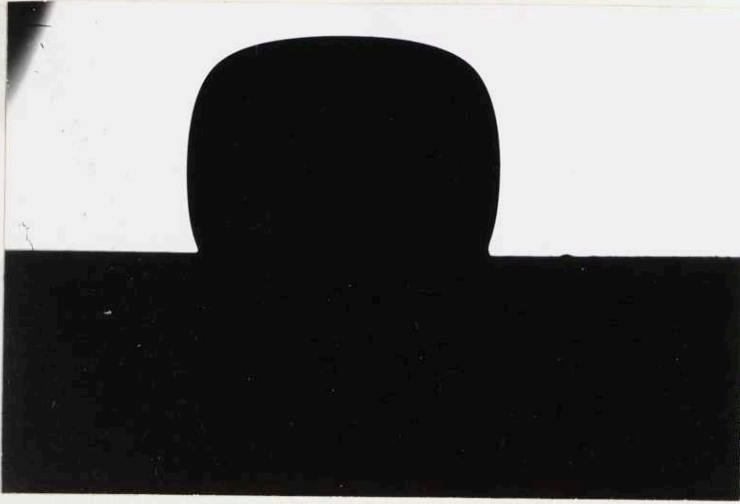


17 minutes
at 1000°C

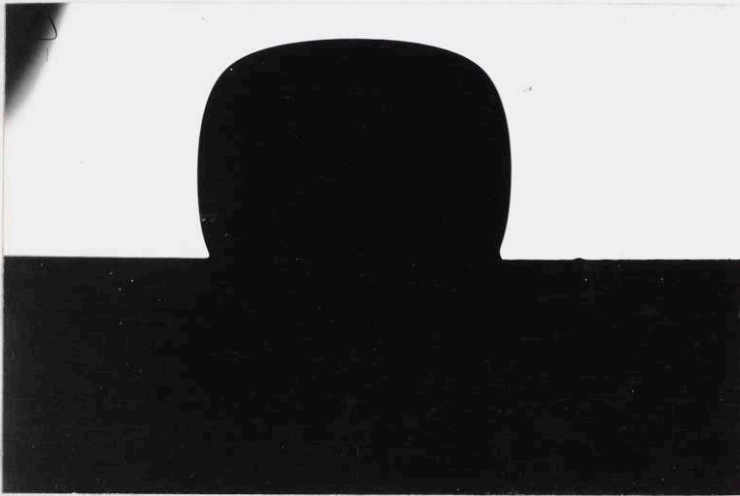


6 minutes
at 1025°C

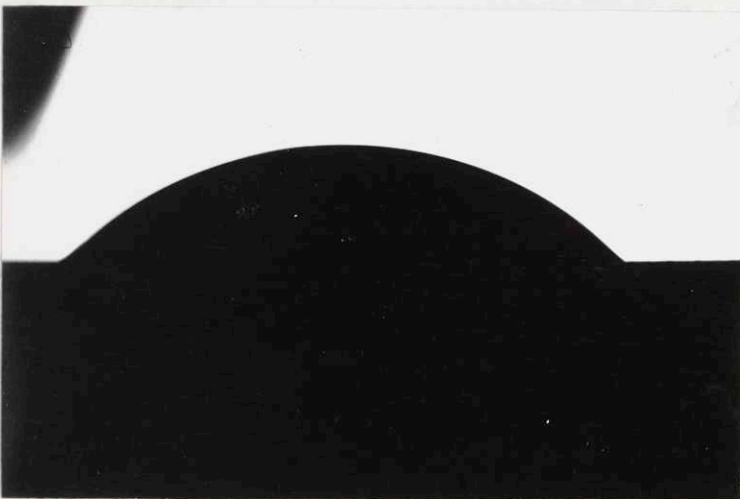
PLATE 15. Effect of Temperature on Contact Angle
Frit A (no additive), Sample No. 2.



16 minutes
at 1075°C

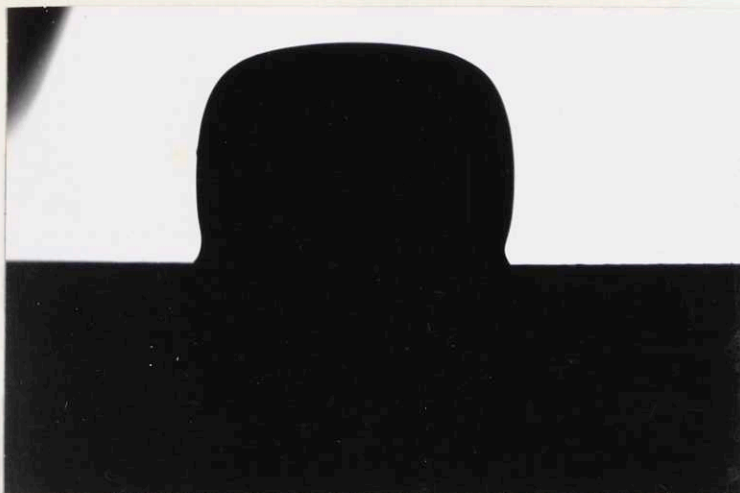


17 minutes
at 1150°C

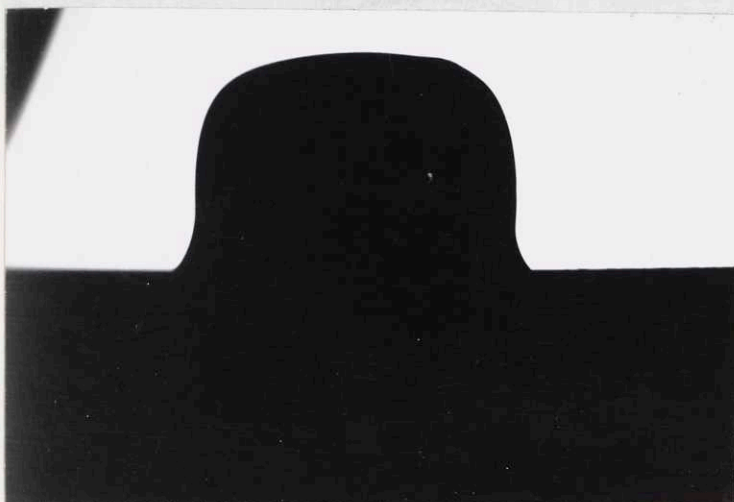


16 minutes
at 1200°C

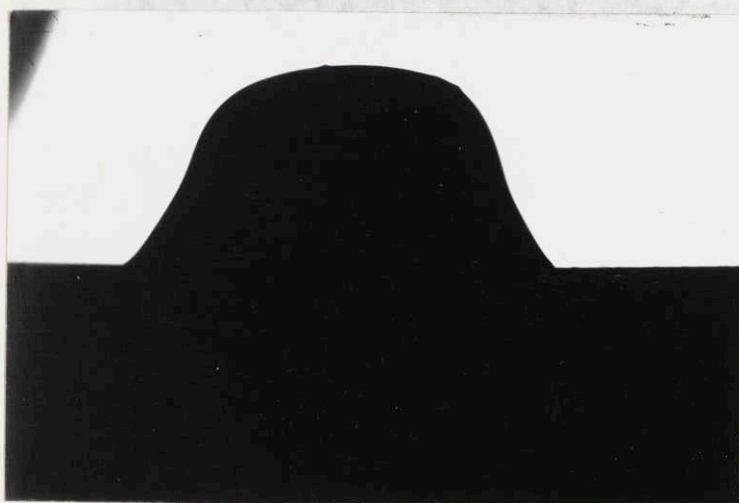
PLATE 15. Frit A.



4 minutes
at 1250°C

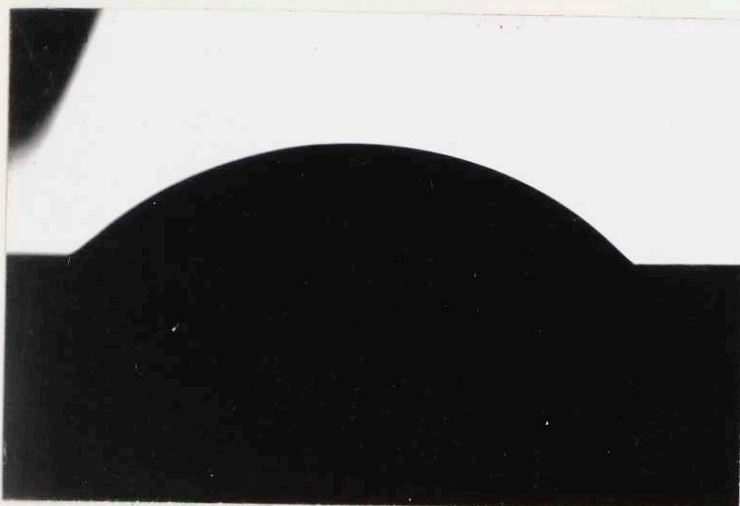


9 minutes
at 1250°C

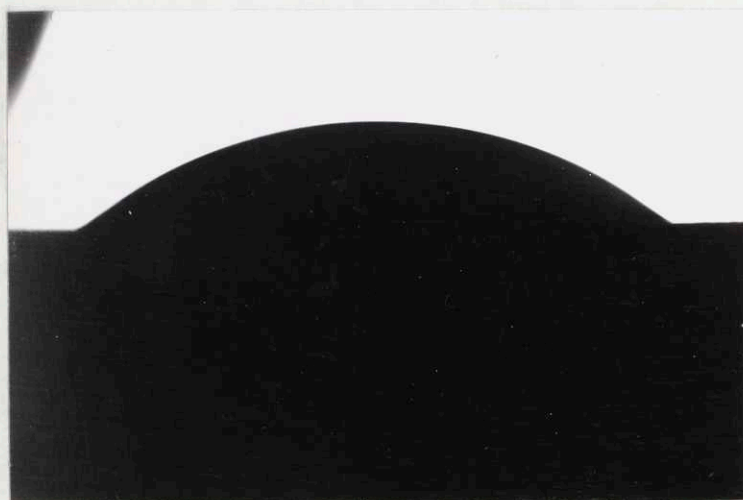


17 minutes
at 1250°C

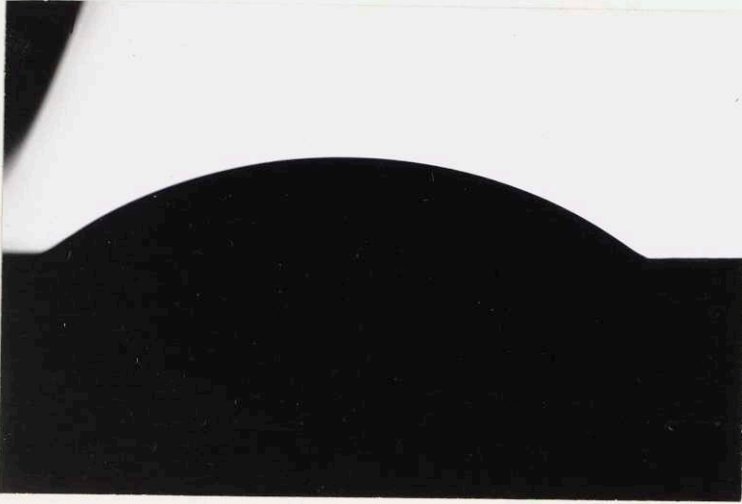
PLATE 15. Frit A.



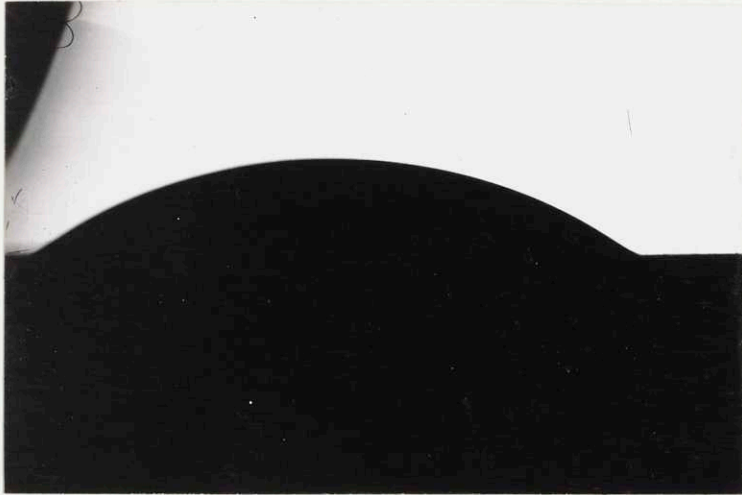
1 minute
at 1275°C



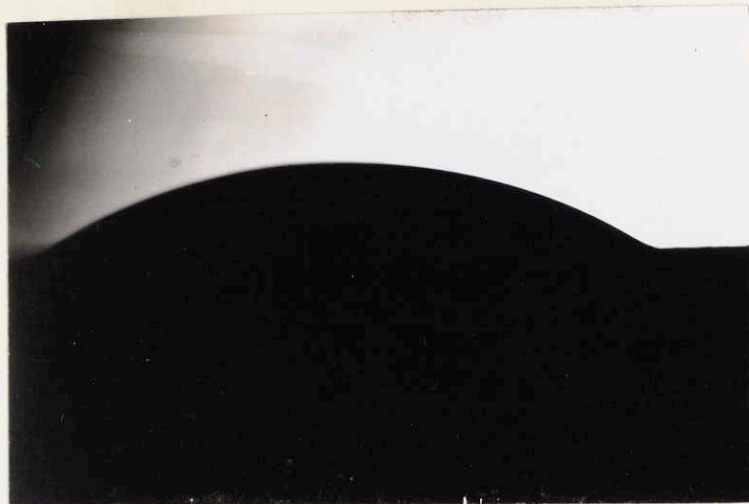
4 minutes
at 1275°C



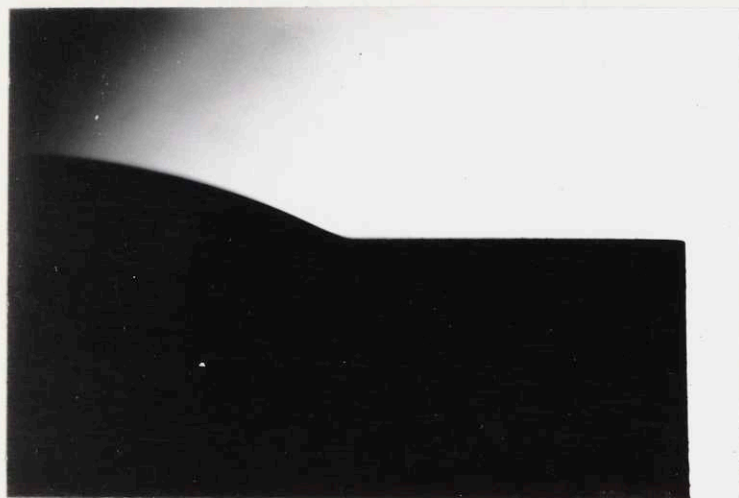
9 minutes
at 1275°C



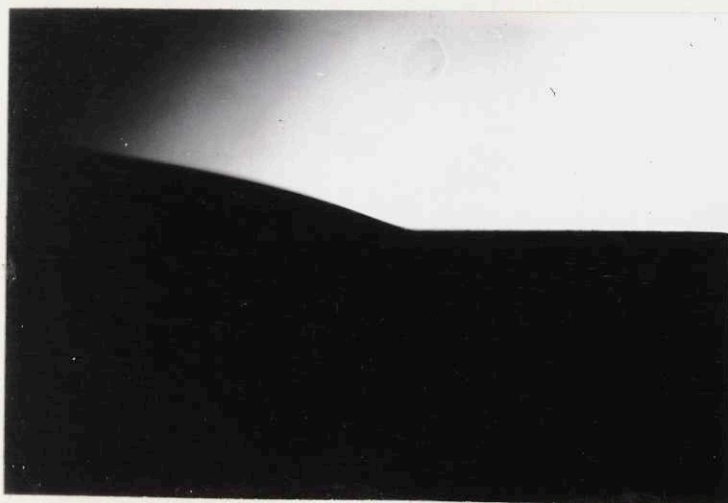
17 minutes
at 1275°C



15 minutes
at 1300°C



16 minutes
at 1330°C



20 minutes
at 1375°C