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Wetting properties of enamel glasses and relation to adherence

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WETTING PROPERTIES OF ENAMEL GLASSES AND RELATION TO ADHERENCE.

BY

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A

THESIS

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INTRODUCTION

Various investigators have tried to find the cause of adherence of enamel glasses to iron metal and they have put forward different theories to explain this phenomena of adherence. In spite of much work done on adherence, no theory has generally been accepted to explain the function of adhering oxides like cobalt, nickel or manganese, etc., in sheet iron ground coats.

In this investigation it was thought to find out whether adherence promoting oxides have any effect on the wetting abilities of enamel glasses at elevated temperatures or not, and further, whether this different wettability caused by the different adherence promoting oxides have any relation with adherence of enamel glasses to steel or not.

It is a fact that the addition of some compounds to some liquids chage wettability of a liquid to the solid in quite great proportion. Natural cryolite, when fused in a platinum crucible yields a wetting melt, but extremely minute amounts of (1 part in 5000) lead, bismuth or thallium compounds change this wetting melt into a monwetting melt.[1] Thus it seems that the addition of a very small amount of certain compounds may effect

1. Scott T.R., "Anomalous Behaviour of Fused Cryolite"., Nature, 157, (3989), 480-81, (1946).

the wetting of liquid to the solid in a great amount.

Stuckert[2] believes that the adhering oxides added in enamel glass reduce the surface tension of the enamel in contrast with that of the iron surface. He believes that this reduced surface tension causes better network formation between enamel and the iron and hence better adherence is produced.

In colloid chemistry, it has been shown that the liquids which wet the solids have better adherence than those liquids which do not wet.[3,4.] In this investigation it has been tried to find the wetting of enamel glasses to solid at higher temperatures.

Definitions of the Certain Terms:

Before we discuss further, certain terms such as wetting, degree of wetting, adhestion, and surface tension need to be defined properly to avoid any misconception of the terms used in this investigation.

Wetting:

"A phenomena which occurs when a solid phase and

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2. Keyser W., "Adhering Oxides", Keram. Rundschan, 41, (18), 228, (1933).

3. Weiser H.B., Colloid Chemistry, John Wiley & Sons, New York, pp. 59-65, 1939.

4. Alexander, Colloid Chemistry. Vol. 5., Reinhold Publishing Corp., New York, pp. 41-60, (1933).

a liquid phase come into contact in any manner, so as to form a solid-liquid interface."[3,5]

Degree of Wetting:

"Degree of wetting means the amount of change in free surface energy which occurs (or the work done by the system) when a solid and liquid are brought together.

Surface Tension or Interfacial Tension:

It is a force which acts parallel to the boundary surface of liquid enamel at elevated temperature.

Adhesion:

It is defined as the tendence to 'stick' or adhere. It is a force by means of which molecules dissimilar in character adhere together. Cohesion is very similar to adhesion but in cohesion the molecules of the same kind or of the same body are held together.

THEORY:

In order to measure the wetting power of liquids various methods have been suggested. Among all the different methods, the determination of surface tension is one of them.[6] Vermorel and Dantony at first believed that surface tension values, as determined by the capillary tube method, gave a satisfactory indication of the wetting

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5. Ellefson and Taylor, "Surface Properties of Fused Salts Glasses: 1 Sessile-Drop Method for Determining Surface Tension and Density of Viscous Liquids at High Temperatures", J.Am. Ceram. Soc., Vol. 21, pp. 193-213. (1938)

6. Brunnich and Smith, Quennsland Agri., J.2, 81, (1914).

power of liquid, but they later,[7] decided that the surface tension alone was not sufficient to determine the wetting power.

It is now quite generally appreciated that 'wetting power' is a function not only of the surface tension of a liquid, but also of the specific attractions operative between the solid and liquid. An indication of the magnitude of this attraction or force of adhesion between solid and liquid can be obtained in case the contact angle between solid and liquid is known.[8] Thus evaluation of wetting power needs the knowledge of two main things: (1). surface tension of a liquid, and (2) the angle of contact between the solid and a liquid.

When a liquid drop lies on a horizontal solid plate, the area of contact between liquid and solid depends on the contact angle, θ, between air, liquid, and solid, and on the density and surface tension of the liquid.

The surface tension of a liquid tends to give the drop the shape of a part of a sphere (since the sphere has the smallest relative surface). Gravitation on the other hand tends to flatten the drop. Thus the actual shape of the drop is determined by the simultaneous action of both

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7. Vermorel and Dantony, Compt. rend., 151, 1144 (1911), also, 154, 1300 (1912).

8. Bartell F.E. and H.J. Osterhof, "The Measurement of Adhesion Tension Solid Against Liquid", Colloid Symposium Monograph, Vol. 5, Chemical Catalog Co., New York, pp. 113-134. (1928.

these factors.

From the above discussion it seems that if a contact angle and density are measured and the calculation of inter-facial tension between solid and a liquid is done by some suitable formula, wetting ability of enamel glasses may be easily known, and the relation of wetting to adherence may be computed. In this research both wetting and adherence were found out independently and their correlation was sought.

PREVIEW OF LITERATURE

The adherence of enamel to steel is one of the most widely talked subjects in enamel field. A brief review of the different theories has been given here. Andrews[9], King[10], and Bahnsen[11] have done a good survey of the various theories published to explain the phenomena of adherence.

1. Grunwald advanced the theory that the coefficient of the enamel was brought close to that of the iron by the addition of metallic oxidesto to enamel.[12]

2. Cobalt silicate is reduced by metallic iron and silicate. In this low state, oxidation cases the adherence.[13]

3. The oxygen released by the above chemical change cleans the surface of the iron, and to this clean surface of the iron enamel sticks.[14]

4. Cobalt present in enamel is reduced to the metallic state and alloys with the iron forming a cobalt-iron alloy to which the enamel adheres.

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9. Andrews A.I., Enamels, The Twin City Printing Co., Illinois, pp. 166-68, 1935.

10. King R.M., "Nature of Enamel Adherence", Finish, 4, (9), 37-39 & 56, 1947.

11. Bahnsen M.J. "A Review of the Theories of Adherence of Sheet Steel Enamels.", Enamelist, pp. 16-17 & 64, Sept., 25 (1935).

12. Grunwald J., Theory and Practice of Enameling on Iron and Steel.

13. Mayer M. and B. Havas, Sprechssal, 43, 737, (1910), and Schaarschuh; Glashutte, 63, 811, (1933).

14. Vondracek R. "Function of Ground Enamels", Sprechssal, 44, 15(1911).

All the above theories in which reduction of cobalt is involved were replaced by the second group of theories. In this second group, necessity of oxygen was brought out.

5. Berndt claimed that the oxygen liberated by the iron oxide is fixed by the cobalt oxide, preventing the excessive bubble formation in the enamel, thereby resulting in a stronger structure and better adherence.[15]

6. Vielhaber[16] added to his theory of Berndt, stating that the cobalt oxide saturated the enamel to such an extent that the iron oxide did not dissolve in it. He believed that the enamel adhered to the iron oxide layer.

7. Cooke's theory was somewhat similar to the above theory, in which he believed the inter-facial layer was partially enamel and iron. This layer was assumed to be rich in iron on the enamel side and rich in enamel on the iron side, thus improving the adherence of the enamel to steel.[17]

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15. Berndt M., "Role of Cobalt in a Ground Coats for Sheet Steel Enamels", Keram. Rund., 22, 262 (1924).

16. VielHaber L., "Behavior of Metal Oxides in Ground Coats on Sheet Steel", Keram. Rund., 33, 53 (1925).

17. Cooke R.D., "The Effect of Furnace Atmosphere on the Firing of Enamel", J. Am. Ceram. Soc., 7, 277 (1924), and "Making and Firing of Sheet Steel Ground Coats"., J. Am. Ceram. Soc., 10, 454, (1927).

8. Cobalt and Nickel oxides act as oxygen carriers in the enamel and supply additional oxygen to the iron, foeming a heavier coat of iron oxide than would be formed if the carriers were absent.[18]

Thus far the theories have all been based on the 'Chemical bond' between the enamel and iron, but the third type of adherence depends on a 'mechanical bond'. This is caused by the penetration of the enamel into the pores of the metal.

9. Clauson concluded from a series of experiments that the adherence of the cobalt ground coat was caused by the ability of the cobalt glass to penetrate the pores of the steel and actually etch its way to a good contact.[19]

10. King R.M.,[20] disagrees with several of the foregoing theories and believes that the adherence is obtained through the formation of dendrites of alpha iron on the surface of the iron and these 'hooks hold the enamel in close contact with the iron. He also pointed out the necessity of oxygen for this phenomena to occur.

11. Staley[21] tried to show that the metals between iron and copper in the electromotive series of metals,

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18. Konetschnigg A., also Anon, Glashutte, 61, 304 (1931).

19. Clauson C.D., "A Study of Adherence of Ground Coats to Sheet Steel", Cer. Ind., 13, 164, (1929).

20. King R.M. and Associates; J. Am. Ceram. Soc., (14) 777, 782, 788, (1931); (5), 476, 480, 483, 486, 488, (1932); (17), 208, 215, (1934); (5), 232-238 (1933).

21. Staley H. F., J. Am. Ceram. Soc., 17, 163 (1934).

when present in glasses, are plated out on the iron base during the firing of the glasses. These metals, of which cobalt is one, plate out in the form of dendrites. These dendrites promote adhesion.[22,23].

12. Dietzel[24] tried to combine certain points of some of the previous theories. His theory includes the reduction of cobalt oxide to metal cobalt, corrosion of iron at the surface, and penetration of enamel into this corroded surface causing adherence, and lastly, change in coefficient of expansion of the enamel due to adhering oxides.

13. Stuckert's theory which has been explained before[25] was based on the reduction of surface tension due to the presence of adhering oxides in enamel glasses.

14. Kautz presented a theory[25] taking into consideration all the dataon equilibrium between iron and its oxides. Kautz showed the inadequacy of Staley's electrolytic potential theory. He also dismissed the idea of a gripping theory where dendrites or unevenness of the metal-enamel interface prevents the enamel from tearing away.

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22. Kautz K., Paper presented at the Am. Ceram. Soc. Conv., Buffalo, N.Y., 1935.

23. Heimes F., Sprechsaal, 67, 231 (1934).

24. Dietzel A., Sprechsaal, 68, 3, 20, 34, 53, 67, 84, (1935)

also - Dietzel A. and K. Meures., J. Am. Ceram. Soc., 18, 37(1935.

25. Kautz K., "Random Experiments on Enamel Adherence", J. Am. Cera. Soc. 21, 303-307. (1938).

He devised the theory of Lord[26] and his coworkers, but he substituted two kinds of iron particles, viz, residual iron and secondary iron formed by the decomposition of ferrous oxide. Kautz tried to show that the adherence of enamel to iron is by solutions at the surfaces.

It seems from the above various theories that the actual theory behind the phenomena of adherence is still yet not well understood despite of several efforts done by many investigators

Methods of Measuring Surface Tension:

The methods used for measuring surface tension can be divided into two groups. Under first group comes all the static methods and under the second all dynamic.

Static Includes:

1. Sessile drop method in which Quincke's approximation formula is used for calculation.[27]

2. Sagging-fibre method.[28]

3. Hanging Cylinder method, in reality a static modification of the anchor-ring method.[29]

4. Soap bubble method. It involves difficulty of maintaining bubble.[30]

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26. Lord J.O., "A Critical Analysis of Some Statements and Experiments on the Adherence of Sheet-Steel Ground Coats." J. Am. Ceram. Soc., 1937. pp. 111-114. Also, Lord and Rueckel, "Mechanics of Enamel Adherence." J. Am. Ceram. Soc., 14(10), pp. 777-781, 1931.

27. Quincke G., Ann. Phys. Chemie, 135, 621 (1868).

28. Griffith A.A., "Phenomena of Flow and Rupture in Solids" Phil. Trans. Roy. Soc. (London) A221, 163 (1920).

30. Pietenpol W.B., "Surface Tension of Molten Glasses", Physics, 7(1) 1936, pp. 26-31; Ceram. Abs., 15(18), pp. 235, 1936.

Dynamic Includes:

5. The ripple method.[31]

6. Vibrating jets of fluid method.[32]

7. Drop weight method.[33]

8. Maximum bubble pressure method (Jaeger).[34]

9. Maximum bubble pressure method (Parmelee)[35]

Ellefson has discussed the practical applicability and the preciseness of all these methods in his original thesis, [36] so the discussion on that is not included here.

Barrett and Taylor [37] in their study of the flow characteristics of glasses and slays at elevated temp-

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31. Dorsey N.E., Sci. Papers Bur. Stand., 21, 563 (Sci. Paper 540). This paper contains an excellent discussion of the methods of measuring surface tension. (1926).

32. Ibid.

33. Tillotson E.W., "Surface Tension of Molten Glasses", Jour. Ind. Eng. Chem., 3, (1911), pp. 631-37; 4, pp. 651-52, (1912).

34. Jaeger F.M., "Temperature coefficient of Free Molecular Surface Energy of Liquids between 80°C and 1650°C.," Z. Anorg. Allgem. Chem., 101, pp. 1-214, (1917)

35. Parmelee G.W., and C.G. Harman, "Effect of Alumina on the Surface Tension of Molten Glass", J.Am. Cer. Socl, 20(7), pp. 224-30, 1937.

36. Ellefson B.S., An Original Thesis on the Surface Tension of Some Glasses by Sessile Drop Weight Method, (Submitted for the partial fulfilment of the requirements for the degree of Doctor of Philosophy, Pennsylvania State College, Penn., 1937.

37. Barrett and Taylor, "New Method for Studying Flow Characteristics of Glasses and Slagg at Elevated Temperatures," J. Am. Ceram. Soc., 19(2), pp. 39-44, 1936.

eratures measured the contact angle of a glass drop by means of a protractor attached to telescope. This method is rather inaccurate but it was stated that "the measurement of contact angle need not be made with high precision in order to determine quite accurately the temperature at which wetting begins because a large change in angle corresponds to a relatively small change in temperature.

Lampman[38] studied the flow of glazes on flat and inclined surfaces by means of four methods among which contact angle was one of them. The contact angle method used was similar to that employed by Barrett and Taylor.[37] In his investigation he assumed that the angle of contact should be at least 90° for wetting phenomena to take place. The contact angle was plotted versus temperature, showing that a glaze (2H) had a better wetting ability than the rest of the glazes.

Amberg[39] studied the effect of different adhering oxides on the surface tension of enamel glasses at elevated temperatures and he showed that some adherence promoting

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37. Barrett and Taylor, "New Method for Studying Flow Characteristics of Glasses and Slags at Elevated Temperatures", J. Am. Ceram. Soc., 19(2), pp. 39-44, (1936).

38. Lampman C.M., "Flow of Glazes on Flat and Inclined Surfaces;" Bull. Amer. Ceram. Soc., 17, (1), 1938, pp. 12- also, "The Effect of Different Bodies on Some Wetting and Flow Characteristics of Glazes". J.A. Ceram. Soc., 252-58., 1938.

39. Amberg C.R., "Effect of Mo. & Other Oxides on S.T. of Silicate Melts". J.Am. Ceram. Soc., Vol. 29, (4), pp. 87-93, 1946.

oxides decreased the surface tension while some increased it. He found the surface tension of all the different enamel glasses at some one fixed temperature. Amberg's work suggests the possibility of some relation between the surface tension and the adherence.

EXPERIMENTAL PROCEDURE

A standard enamel batch was taken for all frit preparation. Table 1. shows the batch composition used in making of all the frits. Three thousand grams of frit was prepared for each batch. Different adhering oxides taken to prepare frits were: Co_3O_4, NiO, CuO, MnO_2, As_2O_3, V_2O_5, TiO_2, MoO_3, and WO_3. One frit was made without any addition of adhering oxide, named the base.

Table 1.

Batch Composition.

Raw Materials.	Amount. % Bases.	Amount. Wt. Bases.
Buckingham Feldspar	24.90	747.0
Borax	34.82	1044.6
Potter's Flint	19.92	597.6
Soda Ash	6.48	194.4
Soda Nitre	3.91	117.3
Fluorspar	6.97	209.1
Adhering Oxide	3.00	90.0
Total	100.00	3000.00

In table two, the percent oxides present in the batch are given. Table three is for empirical formula.

Frit Preparation:

In preparation of the frit, first all the raw materials were weighed according to the batch composition and then thoroughly mixed in a ball mill for ten or fifteen minutes.

Fire clay refractory crucibles were used for smelting the batch in a gas fired pot furnace. In smelting all the precautions were taken to avoid over or under firings. All the batches were smelted between the 1100 and 1150 °C. temperature. Smelted frit was quenched in water and then placed in a dryer.

Table 2.

Melted Composition.

Constituents.	Amount. %.
Na_2O	13.4
K_2O	6.16
CaO	6.14
Al_2O_3	6.70
SiO_2	48.16
B_2O_3	11.63
F_2	4.15
Adhering Oxide	3.66
Total	100.00

Table 3.

Emprical Formula.

0.555 Na_2O		
0.1683 K_2O	0.159 Al_2O_3	1.97 SiO_2
0.2777 CaO	0.425 B_2O_3	0.2575 F_2

<u>Composition (Nature) of Metal Used:</u>

Good or bad adherence of enamel to steel depends on the quality of steel. Carbon content in steel higher than certain limit (usually between 0.2 and 0.5%) cause blistering.[40] A photomicrograph of the steel used in this investigation showed that it is a very low carbon steel, figure 1.

The sheet metal used in the tests was a commercially pure enameling iron.

The manganese, phosphorous, and sulphur and silicon content also should be very low for good enamel steel.

<u>Furnace:</u>

A special type of electric furnace was constructed for all the contact angle and surface tension measurements tests. Figure 2 shows a photograph of furnace and the other necessary set up for the measurements. Figure 3 on page 19 is a schematic diagram of the apparatus.

An Al_2O_3 refractory hollow cylinder with a diameter of three inches and length of six inches was wound with kanthal resistance wire. This cylinder was then placed into the four previously carved insulating bricks. Cracks were sealed with refractory cement. The one end of a furnace was sealed permanently. It was provided with a glass window and a glass tube to pass light and nitrogen gas in the furnace respectively. The other end B of the furnace

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40. Andrews A.I., Enamels; The Twin City Printing Co., Illinois., Chapter iv, pp. 56-72, ;935.

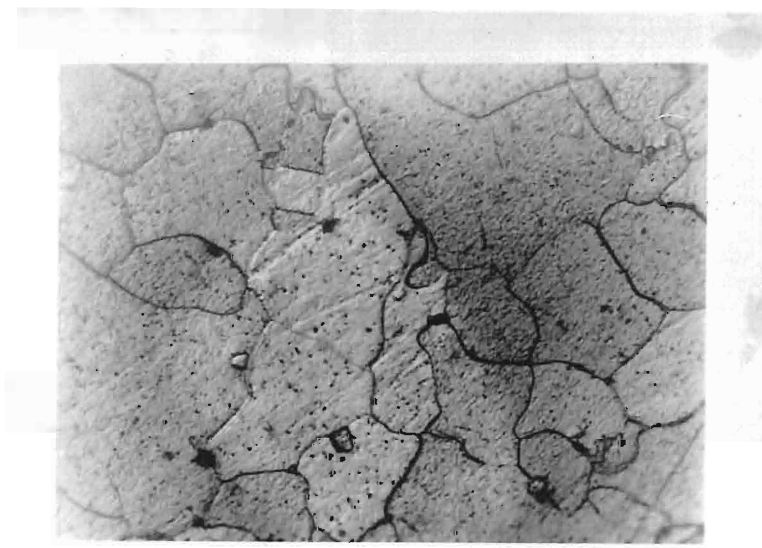

Figure 1.

The Microstructure of Enameling Steel.

(250 x , etched in 2% Nital.)

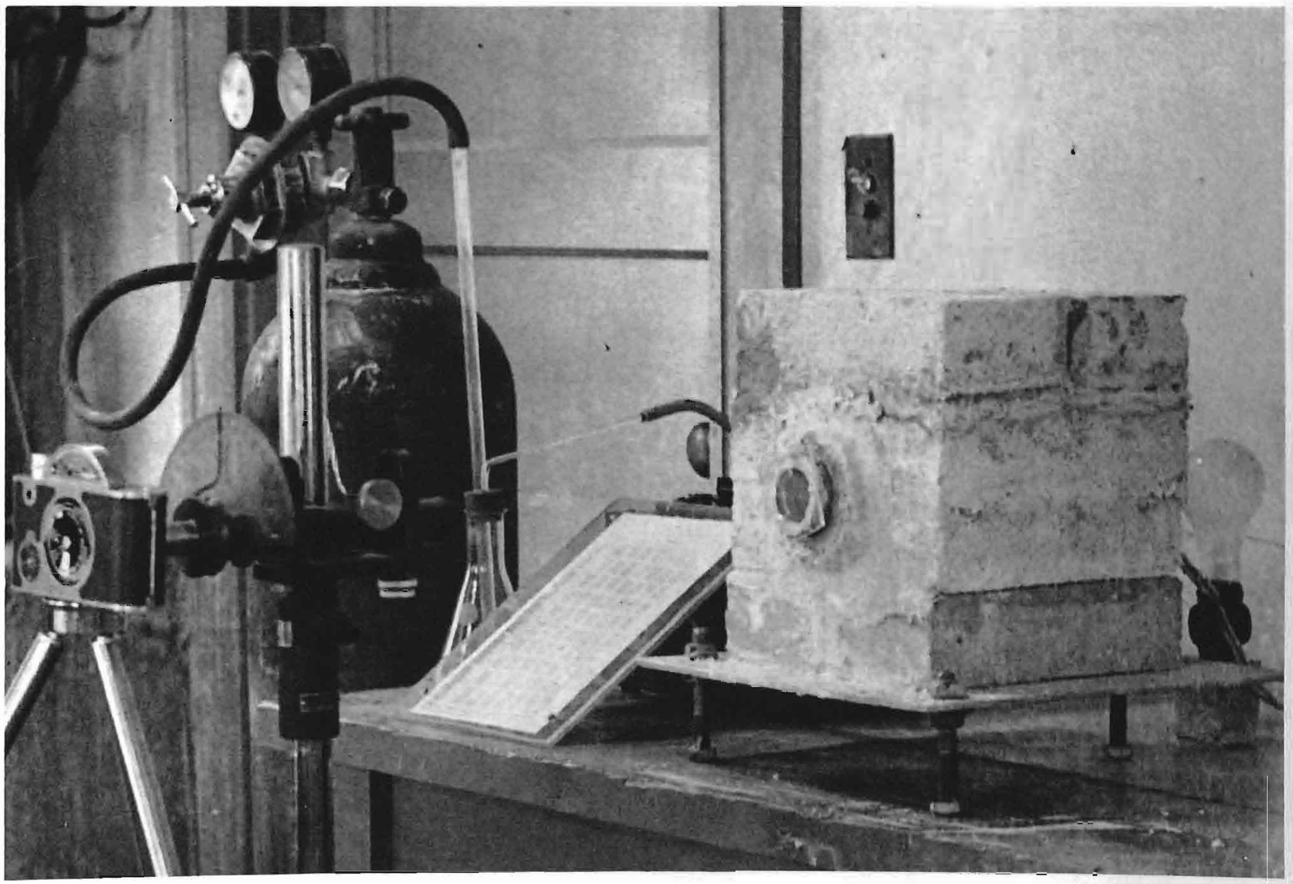

Figure 2.

An Experimental Set-up For the Measurement of Contact Angle.

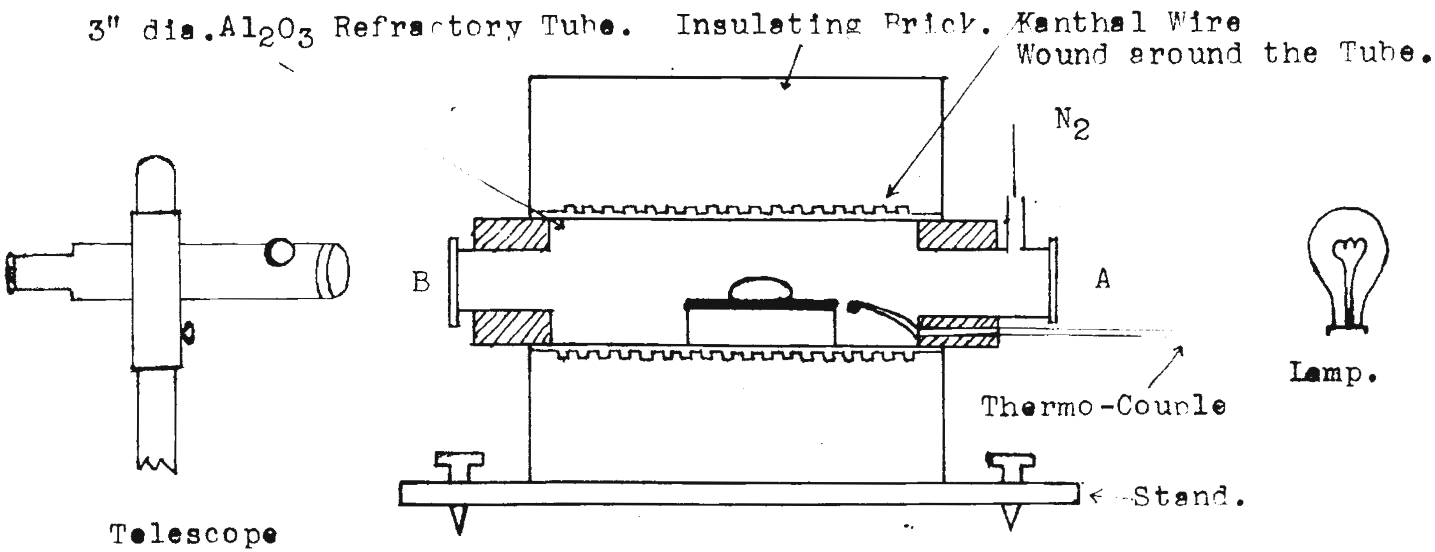

Figure 3. A Schematic Diagram of the Experimental Set-Up.

was also equipped with a glass window. This end was closed tightly while running the experiment. The furnace was kept on a levelling stand, C. Current was passed to the furnace through the variac R.

Furnace Atmosphere:

As oxygen reacts with the metal surface forming iron oxide layer which is supposed to aid adherence,[41] it was planned to stop this iron oxide formation by keeping nitrogen atmosphere in the furnace. According to Iradale[42] furnace atmosphere has no influence on surface tension and he says that any gas may be used so far as it is not too soluble or it does not react with the surface.

Pellet Preperation:

About fifty grams of frit from each representative samples was dry ground to pass 60-mesh sieve with less than 6-8% retained on it. Plankenhorn,[43] believes that the particle size have practically no influence on the fusion temperature or fluidity of pellets. Even so, particle size was controlled in this investigation so as to be

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41. Lord J.Q., "A Critical Analysis of Some Statements and Experiments on the Adherence of Sheet Steel Ground Coats." J.Am. Ceram. Soc., 20(9), pp.288-95 (1937.

42. Iradale T., "Adsorptioj from the Gas Phase at a Liquid Gas Interface". Phil. Mag. (6), 48, 1924, pp. 177-93; (6), 49, pp.603-627, 1925.

43. Plankenhorn W.J., "Factors Affecting Reproducibility of Flow Button Test" J.Am.Ceram. Soc., 31(12),pp. 338-44 1948.

on safe side. Pellets of each different frits were formed in a mold. The mold cavity was 0.5 inches in diameter and had a sufficient depth to hold 2 grams of unpacked frit particles. For holding these particles together, no organic binder was used in the preparation of pellets, as these binders would not oxidize in nitrogen atmosphere and may remain in the pellets even at higher temperatures. This presence may become objectionable. Three drops of distilled water were added in the previously weighed powdered frit and the moist frit was placed into the mold. With a little pressure on the top punch of the mold, pellets were easily made in uniform sizes. These pellets were dried before they were used for surface tension tests.

Cleaning of Metal:

$2\frac{1}{2}$ x $3\frac{1}{2}$ in. pieces of sheet steel were cleaned in a cleaning solution containing 2 percent sodium carbonate, 2 percent sodium hydroxide, and 1 percent sodium phosphate. The solution was kept at boiling temperature because of the fact that oil is less viscous at higher temperatures and also the activity of the cleaning solution increases with the increase in temperature.[44] The reason for increase in chemical activity with increase in temperature is the increase ionization of solution at higher temperature. Heat is also valuable in expanding the surface of the metal and

44. Andrews A.I. "Metal Preparation", Enamels, Twin City Printing Co., Illinois, pp. 75-121, 1935.

opening the pores, so that the cleaning solution may effectively remove the oil and grease from metal.

Metal was kept into the boiling solution for about fifteen minutes. After cleaning, water rinse was given and rinse was followed by pickling. Pickling consists of the removal of all rust from the ware. The pickling solution was made by dissolving 6% of concentrated sulphuric acid and 1% chemically pure sodium chloride in water. The sheets were allowed to remain in this solution for fifteen minutes so that all scale and rust were completely removed. Staley[45] believed that roughening caused on the metal surface due to pickling aids the adherence, but King[46] showed experimentally that even on black metal and also on polished metal, adherence is possible; so in this investigation the question of adherence caused by pickling is out of point.

Pickling was followed by rinsing and finally by neutrallizing. Neutralizing solution had 0.5% Na_2O in it. About five minutes were sufficient for neutralization. Cleaned metal pieces were immediately transformed from the neutralization bath to the dryer.

<u>Description of Test Method</u>:

A pellet was placed in the center of a cleaned metal piece and this was then placed into the furnace through the

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45. Staley H.F., "A Critical Analysis of Some Statements and Experiments on the Adherence of Sheet Steel Ground Coats, Discussion of Lord Paper". J.Am. Cer. Soc., 20(4) pp. 121-24, 1937.

46. King R.M., Ibid, 124-125.

end B. With the help of levelling screws of the stand C, metal piece was made to lie in a perfect horizontal position. End B was sealed after this. An electric bulb at the end A of the furnace brought some light in the furnace so that the pellet was distinctly seen through the telescope. A camera was adjusted behind the telescope to take the pictures of the angle pellet makes at higher temperature with the metal. Figure 2 shows the whole set up of the apparatus.

Temperature of the furnace was increased at the rate of six degrees per minute. Chrome-Alumel thermo-couple was placed in the furnace, and the potentiometer was joined to thermo-couple for taking the temperature reading. After a definite rise in temperature, the pellet started flattenning out. Photographs were taken at the regular interval of 25°C., rise of temperature after the pellet started to become shorter in length with the rise in temperature. This starts between the 630-650°C. This procedure was continued until the drop was completely flattened on the metal.

Height and Angle Measurement:

A photograph of a scale was made by placing the scale near a pellet in the furnace. This photograph of the scale was then enlarged along with the enlargements of the photos of the contact angles. This scale then was used to measure the heights of the drop at various temperatures. The contact angle was measured from the photographs by means of a simple protractor. Figure 4 shows an enlarged photograph of a drop at higher temperature.

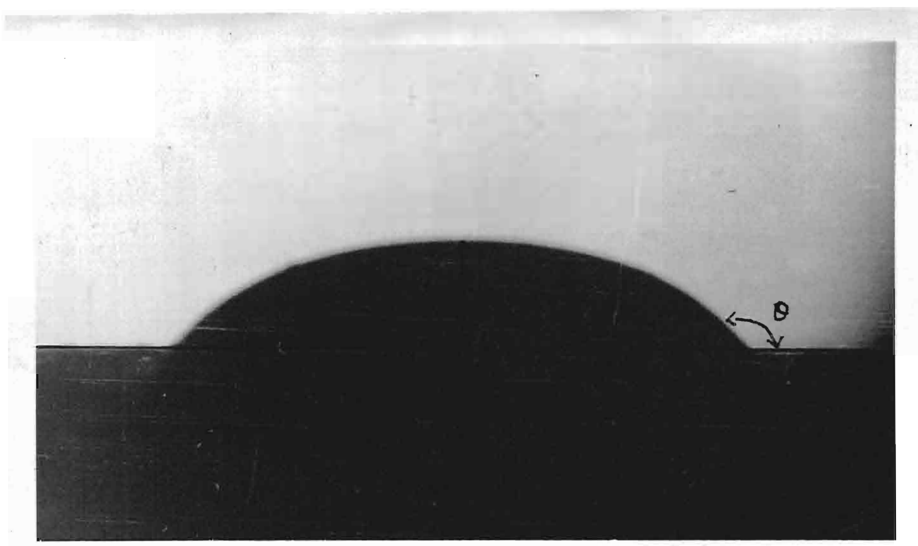

Figure 4.

Enamel Glass Drop.

Impact Test:

For impact tests to be made, frits were ground in a ball mill with 6% enameling clay and enough water to get 1.7 specific gravity of the slip. Slip was applied to the clean metal pieces by dipping method. After drying of the slip on the metal, all pieces were fired at 1550° F. temperature for 3 minutes. Nickel and arsenic containing enamel pieces were fired for 3½ minutes to get proper gloss. It may be said from this longer firing range of nickel and arsenic containing enamels that these two were more refractory than the rest. All the enameled pieces were then tested for adherence by the impact test method.[47,48,49,50] In these tests, the ball was dropped from successively higher levels, but each spot was impacted only once. The thickness of the coat was below .005" as recommended by the P.E.I.[51]

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47. Harrison W.N., and G.T. Thaler, "Test for Adherence of Vitreous Enamels to Metal," J.Am. Ceram. Soc., 11(11), 803-11, 1928.

48. Turk R.H., "Comparison of Results Obtained with an Impact Machine", Ibid, 13(11), 887-93, 1930.

49. Kinzie C.J. and J.B. Miller, "Method for Testing Adherence of Ground Coats to Metal", Bull. Am. Ceram. Soc., 14(11), 371-73, 1935.

50. McLaughlin J.L., "Evaluating Adherence of Blue Sheet Iron Ground Coats", J.Am. Ceram. Soc., 32(5), 166-70 (1949).

51. Porcelain Enamel Institute, "Impact Test for Laboratory Specimens of Porcelain Enameled Sheet Iron and Steel", Bulletin T-6, P.E.I., Washington D.C.

Fusibility Test:

For the measurement of fusibility of various enamel frits containing different oxides, the fusion block method test was made. The enamel frit was grinded and passed through 100 mesh sieve. Powdered frit was moistened with water containing organic binder and packed into the space above the incline of the block. The block then was dried and placed into the furnace. Furnace was heated up at the rate of 6°C. per minute till enamel reached the lowest intersection of the incline. The temperature at this point was taken as the fusion point of the frit. The temperature at which the flow started was also recorded and the difference in temperature between this start and the end point (when enamel flows up to the lowest intersection of the incline) was noted down to get an approximate idea about the viscocities of the various frits.

Density Measurement:

The densities of different frits used in this investigation was measured at room temperature by the picnometer method.

In order to evaluate the apparent surface tension of the glasses by Quincke's approximation formula, the density, contact angle, and the height of the drop should be known. Description of the measurement of the contact angle and the height of the drop is given previously.

Density is decreased with the increase in temperature[52,53,54] but there is such a little change that it may hardly affect the surface tension values if density at room temperature is used for all calculations.

Quincke's Approximation Formula:

Quincke[55] devised an approximation formula in 1868 to find the surface tension of the liquid in contact with the solid surface. This formula has been used by several investigators since then, and it is fairly accurate for the quick determination of the surface tension. As said before, this research does not claim to present the absolute values of surface tension, the approximation formula was taken to be good enough for evaluating the wetting properties of enamel glasses. Formula is:

$$T = \frac{g \sigma h^2}{2(1 - \cos\theta)}.$$

where,

T = Surface tension,
h = Height of the drop,
σ = Density of the glass,
θ = Contact angle.

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RESULTS and DISCUSSION

The photographs of the contact angles are included in the appendix of this thesis.

TABLE 4.
Contact Angle and Surface Tension

Adhering Oxide.	Temp. °C.	Height of Drop.	Contact Angle.	Cos θ	S.T. dynes/cm
Base	636	.420	90	0	212
"	650	.375	109.4	-.3322	127
"	675	.30	120	-.5000	72.2
"	700	.20	142.5	-.7934	26.8
"	725	.09	162.5	-.9537	5.0
"	750	neg.	neg.	neg.	neg.
Base + 3% CoO	650	.375	90	0	168
"	675	.34	126	-.5878	87.2
"	700	.198	153	-.8910	24.8
"	725	.14	161.6	-.9489	2.47
Base + 3% CuO	650	.45	90	0	238
"	675	.375	96	-.06976	176
"	700	.35	104.5	-.2504	115.5
"	725	.26	137.75	-.7408	45.8
"	750	.15	158.25	-.93201	13.6
"	775	.125	164	-.9613	9.39
Base + 3% MnO_2	636	.45	96	-.1045	241
"	650	.390	108	-.3090	193
"	675	.310	121	-.5150	83.7
"	700	.20	144.5	-.8141	29.1
"	725	.10	160	-.3969	6.79
"	750	neg.	neg.	neg.	neg.

Table 4 Continued.

Adhering Oxide	Temp. °C.	Height of drop.	Contact Angle	Cos θ	S.T. dynes/cm
Base + 3% As_2O_3	650	0.5	90	0	324
"	688	0.420	86.5	-.06105	244
"	700	0.375	91.5	-.02618	179
"	725	0.250	133	-.6820	48.2
"	750	0.235	137	-.7314	41.4
"	775	0.223	140	-.7660	36.5
"	800	0.218	141.5	-.7826	34.55
"	825	0.215	142.5	-.7934	33.40
"	850	0.210	145	-.8192	31.4
"	875	0.130	162.5	-.9537	11.4
"	900	neg.	neg.	neg.	neg.
Base + 3% WO_3	636	.4	89.75	-.00706	198
"	650	.35	101.5	-.1959	127
"	675	.25	111.0	-.3584	45.3
"	700	.18	147.0	-.8387	21.9
"	725	.11	163.5	-.9588	7.65
"	750	.08	169	-.9816	3.98
Base + 3% TiO_2	650	.45	90	0	246
"	675	.40	105	-.2588	154
"	700	.25	129.5	-.6361	46.5
"	725	.17	154.25	-.9011	18.45
"	750	.125	159.0	-.9335	9.80
"	775	neg.	neg.	neg.	neg.

Table 4 Continued.

Adhering Oxide	Temp. °C.	Height of drop.	Contact Angle	Cos θ	S.T. dynes/cm
Base + 3% MoO_3	636	.48	90	0	256
"	650	.370	93	-.05234	163.2
"	675	.300	104	-.2419	90.85
"	700	.200	145	-.8192	27.65
"	725	.100	155	-.9063	6.59
"	750	neg.	neg.	neg.	neg.
Base + 3% V_2O_5	640	.4	80	+.1736	249
"	650	.3	83	+.12187	132
"	675	.25	120	-.5	53.6
"	700	.19	140	-.7660	26.3
"	725	.15	156	-.9135	15.2
"	750	.075	169.25	-.9826	3.655
"	775	neg.	neg.	neg.	neg.
Base +3% NiO	675	.55			
"	716	.5	83.5	+.11320	381
"	725	.4	101	-.1908	181.6
"	750	.15	158.8	-.93232	15.8
"	775	.085	173	-.99255	4.90

TABLE 5.

FUSION TEMPERATURE AND FLUIDITY

Adhering Oxide in Frits.	Fusion Temperature. Start.	End.	Difference of Start & End.
Base	700	750	50
	709	752	43
	704.5	751	46.5 mean.
Base + 3% CoO	730	735	5
	728	732	4
	729	733.5	4.5 mean.
Base + 3% CuO	720	759	39
	725	756	31
	722.5	757.5	35 mean.
Base + 3% MnO_2	690	718	28
	688	720	32
	689	719	30 mean.
Base + 3% As_2O_3	718	886	168
	708	842	134
	713	859	151 mean.
Base + 3% V_2O_5	684	723	39
	686	721	35
	685	722	37 mean.
Base + 3% MoO_3	710	740	30
	708	750	42
	709	745	36 mean.
Base + 3% WO_3	676	738	62
	678	740	62
	677	739	62 mean.
Base + 3% TiO_2	711	752	41
	708	750	42
	709.5	751	41.5 mean.
Base + 3% NiO	736	820	84
	734	818	84
	735	819	84 mean.

TABLE 6.

DENSITY

ADHERING OXIDE POWDERED FRIT.		DENSITY CC.
Base	. . . .	2.450
Base + 3% CoO	. . . .	2.435
Base + 3% CuO	. . . .	2.400
Base + 3% MnO_2	. . . .	2.678
Base + 3% As_2O_3	. . . .	2.640
Base + 3% V_2O_5	. . . .	2.621
Base + 3% MoO_3	. . . .	2.550
Base + 3% WO_3	. . . .	2.521
Base + 3% TiO_2	. . . .	2.470
Base + 3% NiO	. . . .	2.764

TABLE 7.

ADHERENCE VALUES

Ground Coat of:	Thickness Inches.	Height* cm.	Adherence. erg/cm.
Base	.00380	26	5.82
CoO	.00391	52.5	11.8×10^6
MnO_2	.00181	30.5	6.77
NiO	.00340	20.0	4.54
As_2O_3	.00500	12.2	2.68
TiO_2	.00385	7.0	1.54
V_2O_5	.0055	9.1	2.06
MoO_3	.00490	20.5	4.56
WO_3	.00490	20	4.5
CuO	.0040	32.2	7.12

*Wt. of the ball = 226.7 gms.

TABLE 8

SLOPES OF CURVES AND ADHERENCE

Adhering Oxides.	Slope of Curves I.T. Temp.	Adherence ergs/cm.
Base	3.22	5.8×10^6
Base + 3% CoO	2.92	11.7×10^6
Base + 3% CuO	2.56	7.12×10^6
Base + 3% MnO_2	3.34	6.5×10^6
Base + 3% MoO_3	3.44	4.56×10^6
Base + 3% NiO	18.5	4.54×10^6
Base + 3% WO_3	3.91	4.5×10^6
Base + 3% As_2O_3	5.16	2.68×10^6
Base + 3% V_2O_5	4.12	2.06×10^6
Base + 3% TiO_2	4.16	1.54×10^6

I. T. = Interfacial Tension.

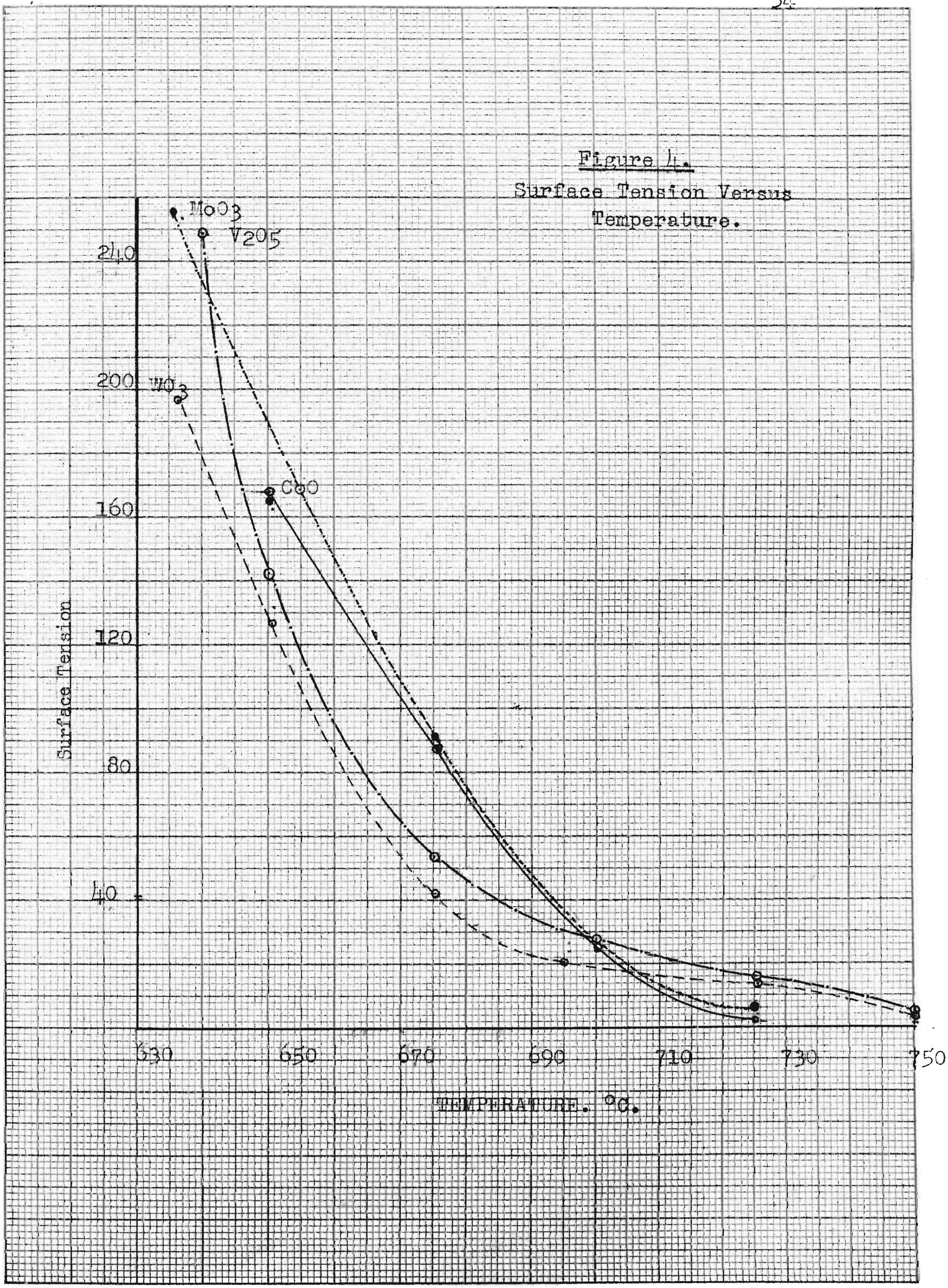
Figure 4.
Surface Tension Versus
Temperature.
MoO3
V2O5
WO3
CdO
240
200
160
120
80
40
Surface Tension
630
650
670
690
710
730
750
TEMPERATURE. °C.

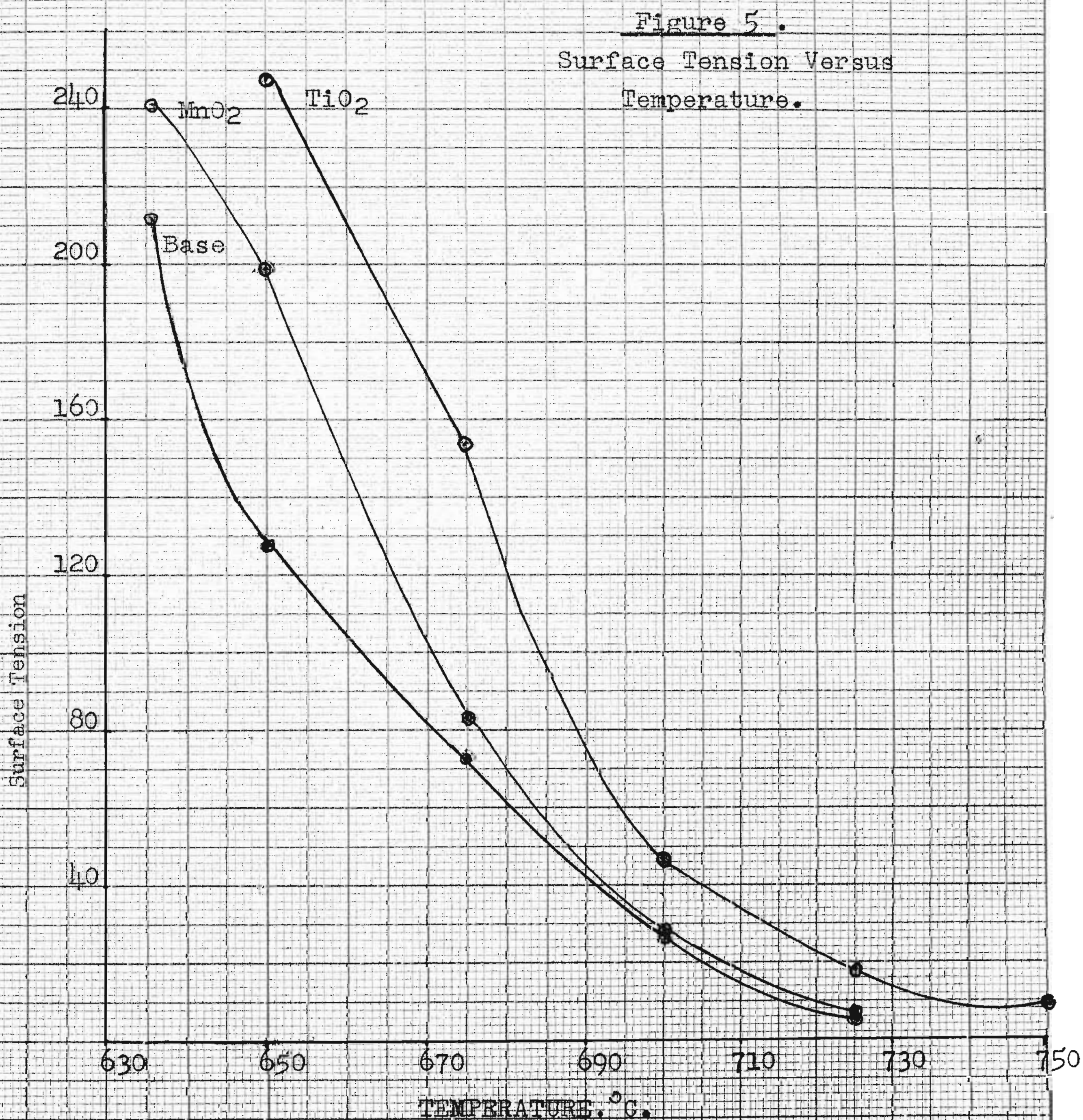
Figure 5.
Surface Tension Versus
Temperature.
240
200
160
120
80
40
MnO2
TiO2
Base
Surface Tension
630
650
670
690
710
730
750
TEMPRATURE. °C.

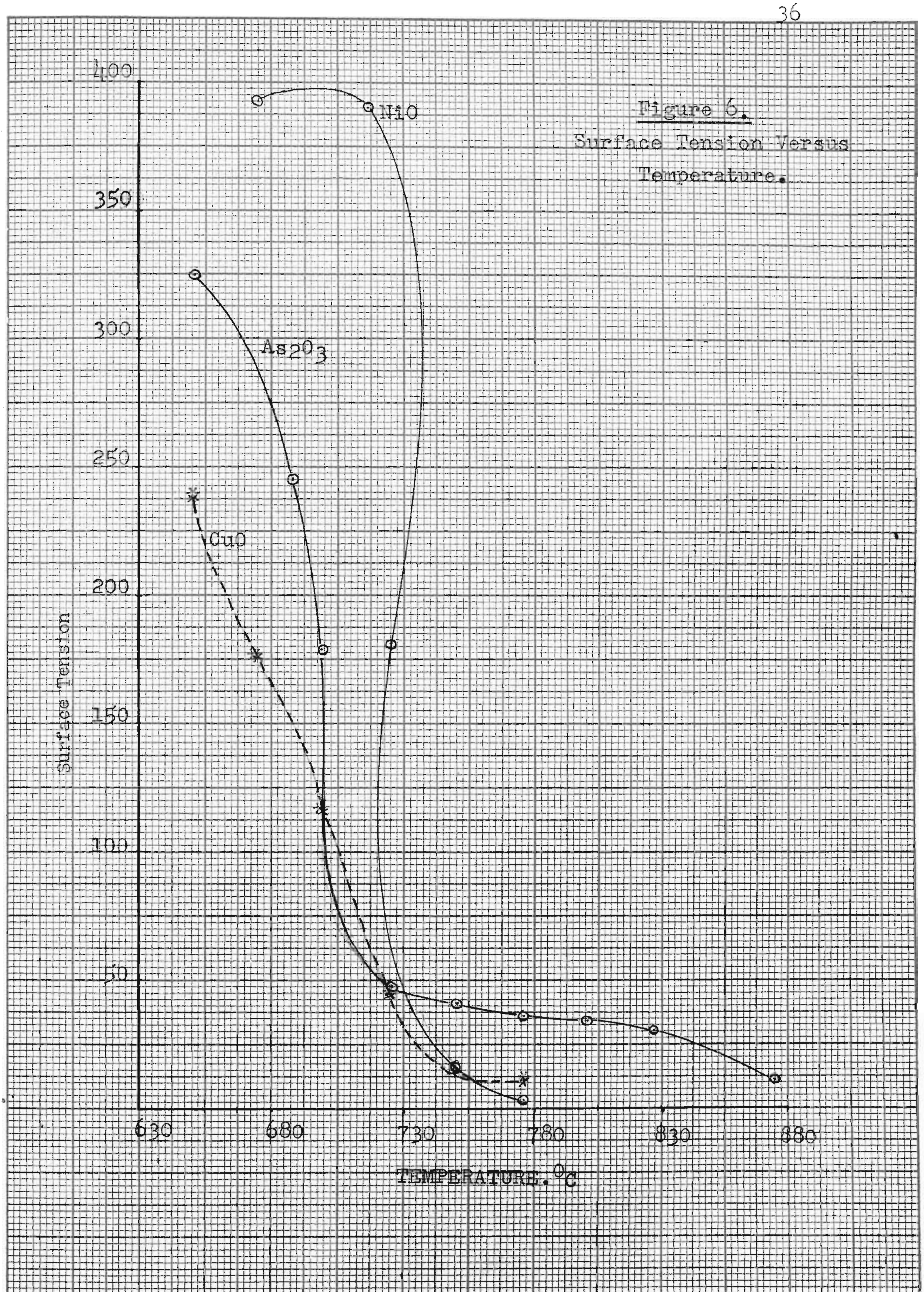
Figure 6.
Surface Tension Versus
Temperature.
400
350
300
250
200
150
100
50
Surface Tension
NiO
As2O3
CuO
630
680
730
780
830
880
TEMPERATURE. °C

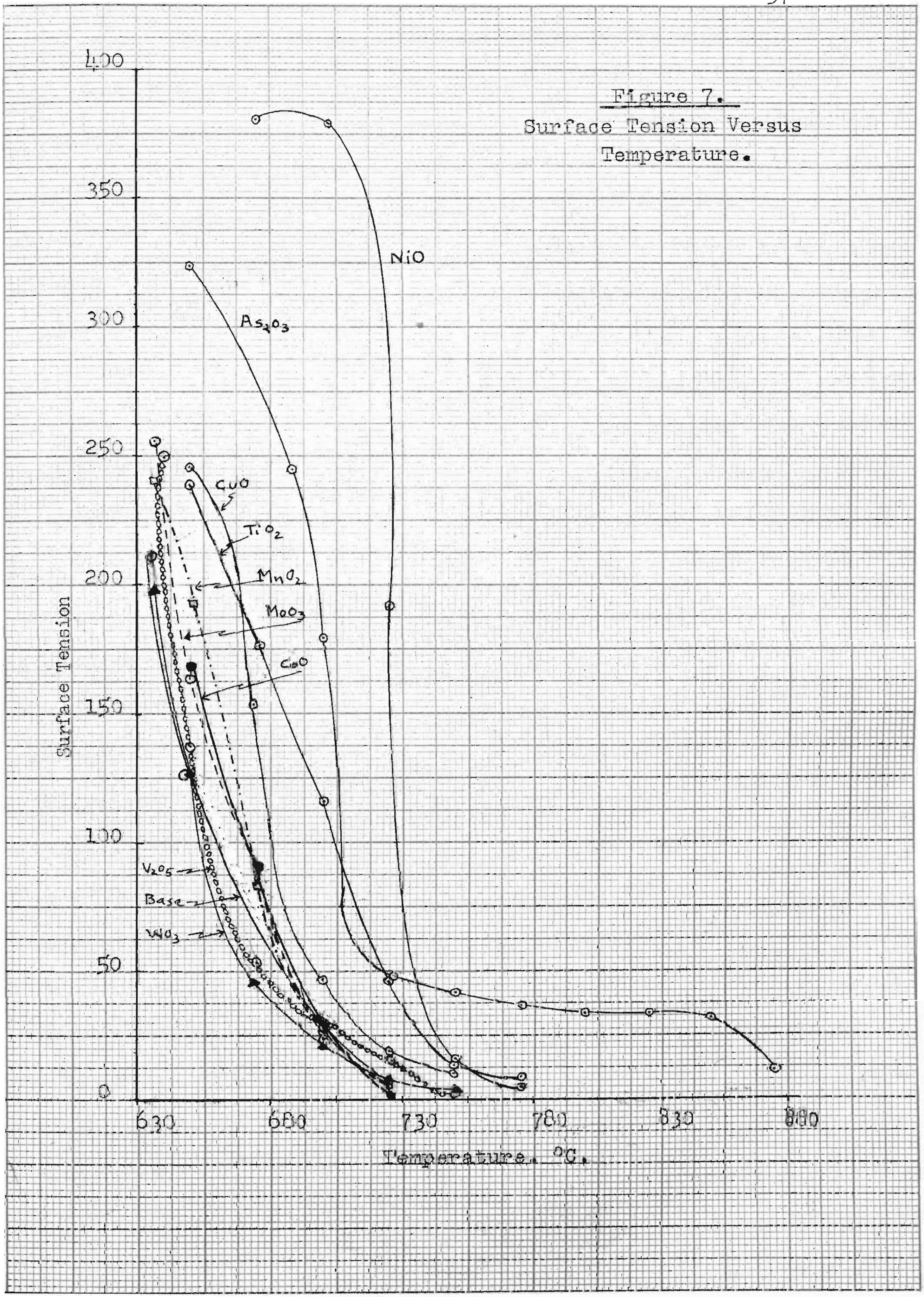
Figure 7.
Surface Tension Versus
Temperature.
400
350
300
250
200
150
100
50
0
630
680
730
780
830
880
Temperature, °C.
Surface Tension
NiO
As_2O_3
CuO
TiO_2
MnO_2
MoO_3
CoO
V_2O_5
Base
WO_3

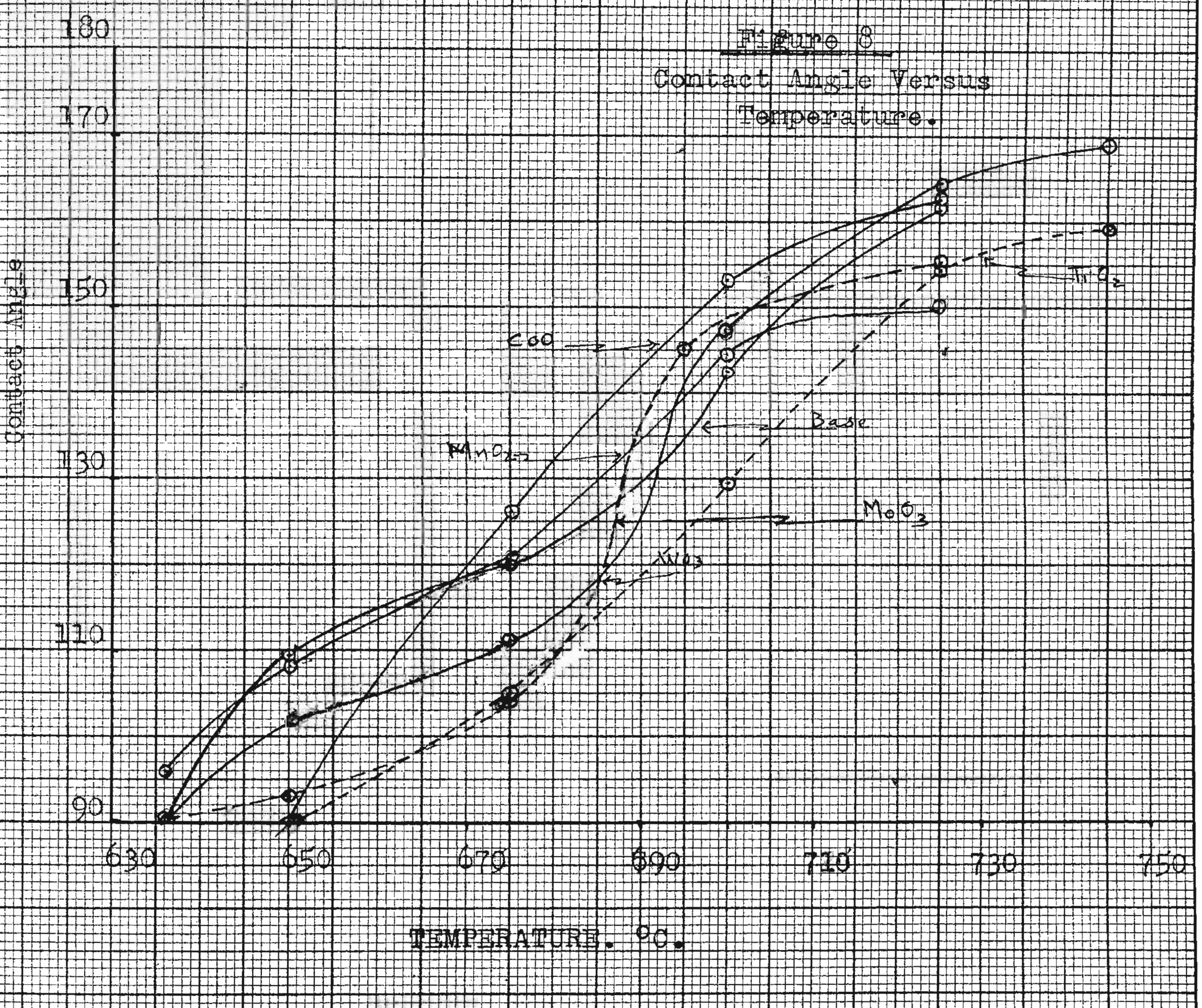
Figure 8
Contact Angle Versus
Temperature.
180
170
150
130
110
90
630
650
670
690
710
730
750
TEMPERATURE. °C.
Contact Angle
CoO
MnO2
Base
MoO3
WO3
TiO2

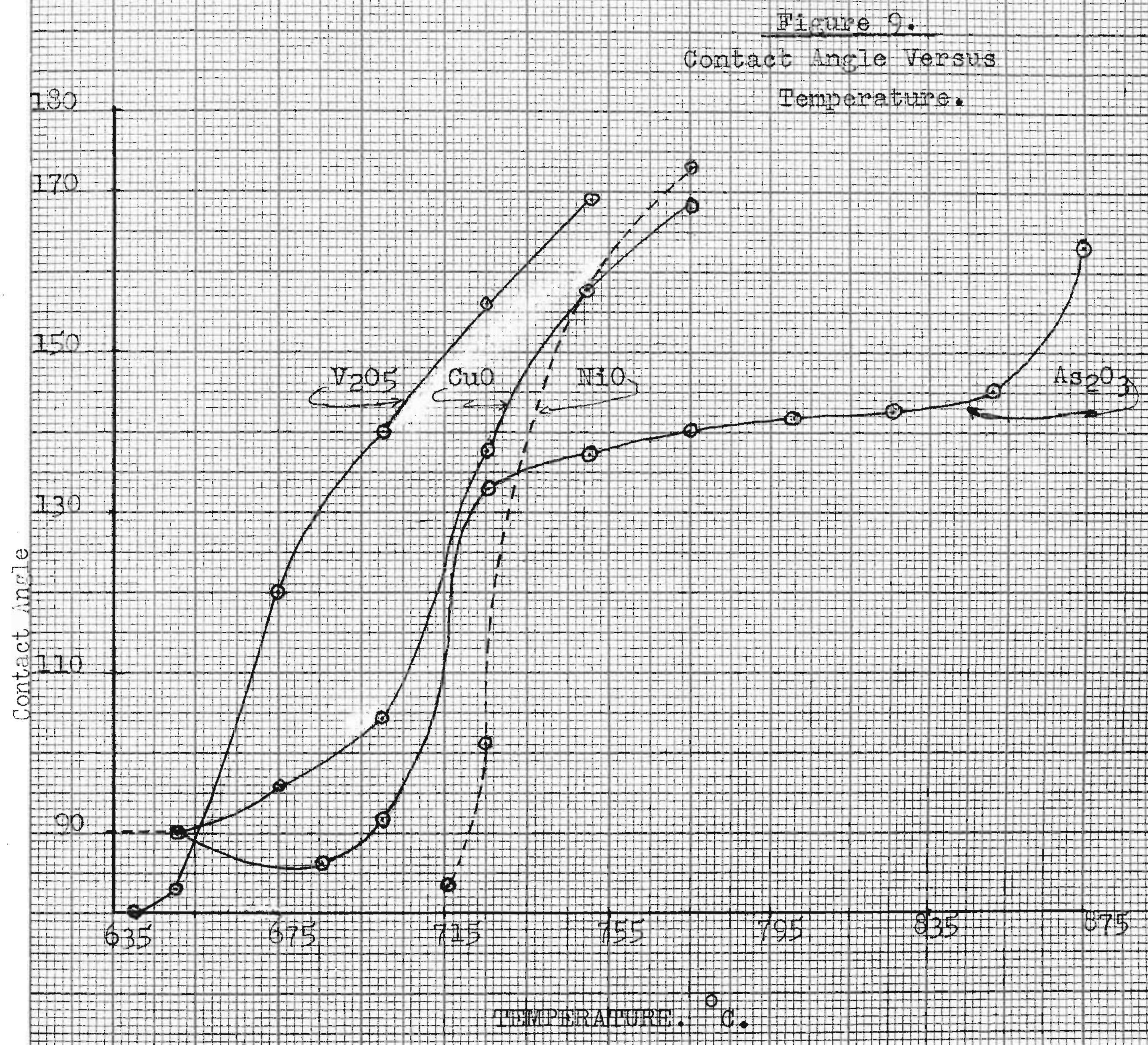
Figure 9.
Contact Angle Versus
Temperature.
180
170
150
130
110
90
Contact Angle
V2O5
CuO
NiO
As2O3
635
675
715
755
795
835
875
TEMPERATURE. °C.

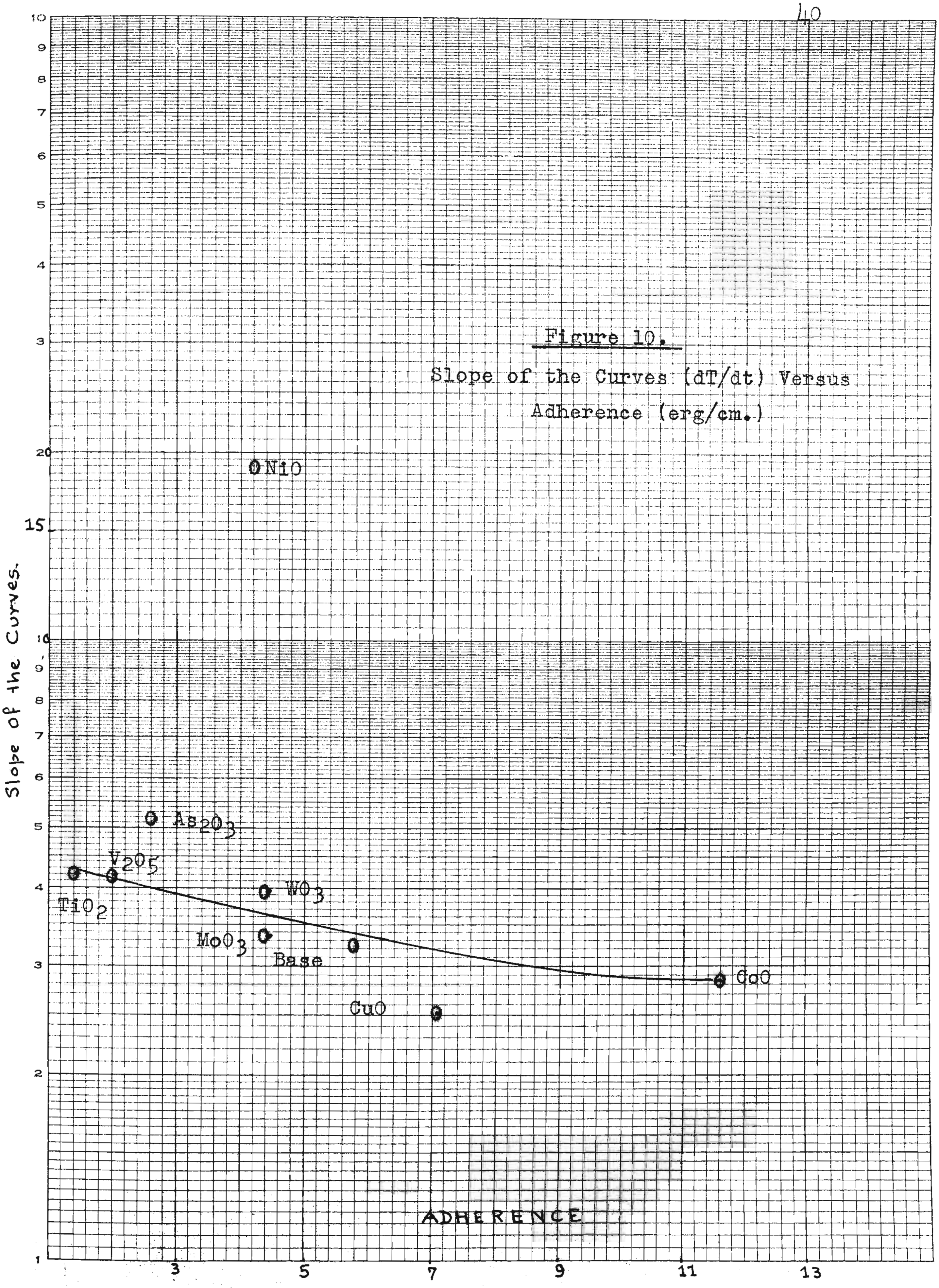

Figure 10.

Slope of the Curves (dT/dt) Versus Adherence (erg/cm.)

Discussion:

Table 4, includes the data on contact angle, θ, height of the drop, h, temperature, t, and surface tension, T, calculated with Quincke's Formula given on page 27.

Surface tensions obtained in this manner may be called apparent surface tension or the interfacial tension between the liquid and the solid surface. These values are termed "apparent surface tension" because the absolute values of surface tensions at elevated temperatures are obtained when the liquid glass attains equilibrium; however, since the purpose of this investigation was to find the wetting of enamel glasses at continuously increasing temperatures, and not to obtain the absolue values of surface tension, the attaining of equilibrium procedure was not followed.

The figures no. 4, 5, 6, and 7 are drawn to show the relation between the apparent surface tensions of the different enamel glasses and the temperatures. Each one of the figures 4, 5 and 6 contain three or four different curves of apparent surface tensions and temperatures. In figure 7 all the previous curves of figures 4, 5, and 6 are included.

From figure 7, it will be observed that with the increase in temperature there is a linear decrease in surface tension up to the certain point. After this point the decrease in surface tension is comparatively slower.

All the glasses, except arsenic oxide bearing glass, show apparent surface tension values less than 10 between the temperatures 625 and 675°C. Arsenic oxide glass attains low apparent surface tension at a relatively high temperature, 875°C.

To find out the reason why arsenic, nickel, and copper oxide bearing enamels have low interfacial tensions at higher temperatures than the other enamels, a seperate fusion block method test was ran to determine the refractoriness of each of these enamel glasses. From this fusion block method tests (table 5), arsenic nickel and copper oxides bearing enamel glasses were found to be more refractory than the other glasses, causing these three glasses to flatten on metal at relatively higher temperatures than the rest of the glasses.

In figure 7, it also will be found that the base glasses containing nickel and arsenic as the adhering oxides, show high surface tension and very steep slopes. Table 5, gives the temperature intervals between the starting and end point of glass flow in the fusion block method test. Arsenic and nickel bearing glasses show a large temperature interval in comparison with the other glasses. This indicates that the fluidity of these two glasses is much lower than the other enamel glasses.

Perhaps this greater refractoriness and lower fluidity of bases containing arsenic and nickel oxides as adhering agents may have delayed the wetting action of the glasses and brought out the different types of two curves. Except arsenic and nickel bearing glasses, all the other glasses show similar curves. When the slopes, dT/dt, of these curves were measured it was found that all had different slopes. For slope calculation, the linear portion of the curve was used and the change in apparent surface tension in a straight portion of the curve was divided by the temperature change. Nickel and arsenic oxides bearing glasses showed very high values of slopes, (Table 8); this may be due to the refractoriness and high viscocities of these two.

Table 8 also consists the adherence values computed by the impact test method. A comparison of these adherence values and the slopes of the curves, dT/dt, on figures 4, 5, and 6 was made and it was found that adherence was inversely proportional to the slopes of the curves. A possible explanation of the relation of this adherence and the rate of change of apparent interfacial tension may be developed by a consideration of glass wetting versus rate of heating. For glasses having small values of slope (see figure 1) that is to say, apparent interfacial tension decreasing slowly over a relatively long temperature range, wetting was initiated at relatively low temperatures. In the case of glasses showing large slopes, however, wetting was not realized until relatively high temperatures were obtained. Therefore, it is proposed that adherence may be promoted, in the case of an enamel glass showing a small slope, dT/dt, in figure 7, due to the greater temperature range over which the phenomena of wetting may occur.

The glass containing cobalt oxide shows the best adherence and shows a very low value of the slope. Thus the experimental results indicate that the slope of the curve, dT/dt, and the adherence values have an approximately linear relation, (see figure 10).

Nickel and manganese oxides bearing enamel frits are reported in the literature to have better adherence than the frits containing copper oxide, but in this research, copper oxide frit has shown better adherence than nickel and manganese oxides frits.

In the general practice, nickel and manganese oxides are added in a much smaller quantities than the amounts used in this research and this excessive quantity of oxides perhaps might have reduced the adherence. In the case of copper oxide, perhaps the higher quantity may have promoted adherence.

Table 7 includes the impact test values and the thickness of enamels. In the case of MnO_2 enamel glass, the thickness is very small and this small thickness may have contributed to the low adherence value of manganese oxide bearing glass as compared to glass containing copper oxide.

The densities of each frits was measured twice by means of picnometer method. The frits containing nickel, arsenic, and manganese oxides have shown much higher densities than the others.

It can be recalled from the theory of this investigation on page 4, that at zero interfacial tension, there will be perfect wetting, and that higher interfacial tension reduces the wetting and hence the adherence. All the ten samples in this investigation have a very low interfacial tensions at higher temperatures and because of this reason they all have good ability to wet the metal surface. All the frits have varying degree of adherence power but even then none have extremely poor adherence due to which popping off or chipping off effects may be observed.

In the theory discussion it was pointed out that the measurement of contact angle is necessary for the measurement of surface tension. Contact angles less than 90° do not wet the solid surface and do not show adherence. As the angle becomes greater than 90° the wetting ability gets better and better. At 180° there is a perfect wetting. All the different frits whose contact angles was measured at elevated temperatures do not have an angle less than 90° and hence none are non wetting in character. They all wet in a varying degree, but they do wet the solid metal surface. Figure 8 and nine shows the relation between the contact angles and the temperatures. In these figures there is an increase in contact angles with the increase in temperatures. The cobalt oxide curve has the minimum slope and from impact test results, it has shown the best adherence.

The curve is also very regular and almost linear. None of the other curves are so linear.

Lampman[56] has compared his adhering oxides bearing glazes on body by plotting contact angles versus temperatures of the glazes and he has shown graphically why cobalt oxide bearing glaze shows the best adherence. In our case the same reasoning can be applied and it can be shown that cobalt oxide has the best adherence because it has the least slope of the curve. Moreover, the data on surface tension of glasses indicate that glasses with the least slopes show the best adherence.

The experimental results also indicate that with the increase in contact angle there is a decrease in the surface tension. Moreover, if the graphs of contact angles versus temperatures and the surfaces tension versus temperatures are compared, it will be seen that these two types of curves have very close resemblance, and that they are similar in shape.

Finally, it may be said from the experimental results that the rate of wetting and the adherence values of the enamel glass are closely related and for good adherence rate of wetting should be low. The adherence shown by the different adhering oxides added in the base may be arranged in decreasing order; as: CoO, CuO, Base, NiO, MnO_2, MoO_3, WO_3

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56. Lampman C.M., "Effect of Different Bodies on Some Wetting and Flow Characteristics of Glazes", J.Am. Ceram. Soc., 252-258, (1938).

As_2O_3, V_2O_5 , and TiO_2. Slopes of the curves, dT/dt, are increased in the above order with exception of arsenic and the nickel oxides.

CONCLUSION

The experimental results indicate that:

1. Interfacial tension and contact angles of enamel glasses on metal are related to the adherence.
2. As the contact angle between the enamel and the iron increases, interfacial tension decreases.
3. A increase in the rate of change of interfacial tension, dT/dt, decreases the adherence; in other words, with the increase in a rate of wetting of the enamels to iron, the adherence decreases.
4. For best adherence, the slope of the curve, dT/dt, should be small.

SUMMARY:

For the evaluation of interfacial tension between the enamel glasses and the iron at elevated temperatures, the measurement of the contact angle and the height of the drop was made by taking the photographs of a sessile drop. From the contact angle, height and the density of the enamel glass, the interfacial tension was determined by the Quincke's approximation formula. The values of interfacial tensions were plotted against the temperatures, and slope of the curves, dT/dt, were determined. These slopes were compared with the adherence of enamels to steel. The relation, 'the adherence is inversely proportional to the rate of change of interfacial tension', was found to be existing by the above comparison.

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APPENDIX

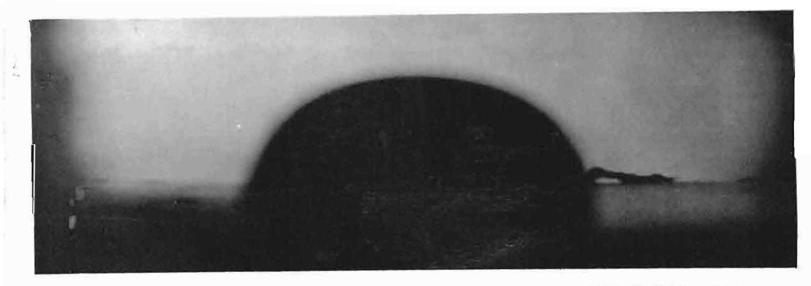
Abbreviations:

T = Interfacia Tension, Q = Contact Angle,

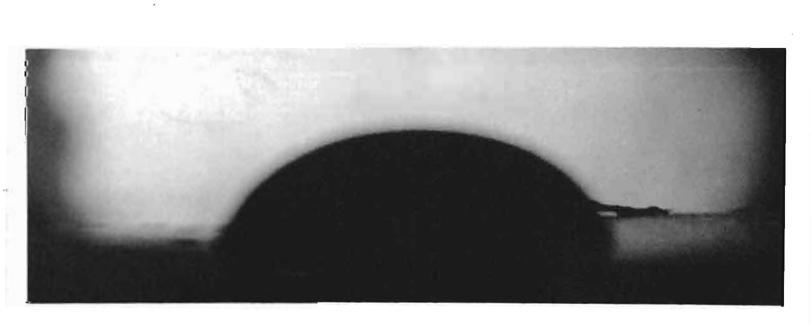
h = Height of the drop, t = Temperature

A = Kind of Frit.

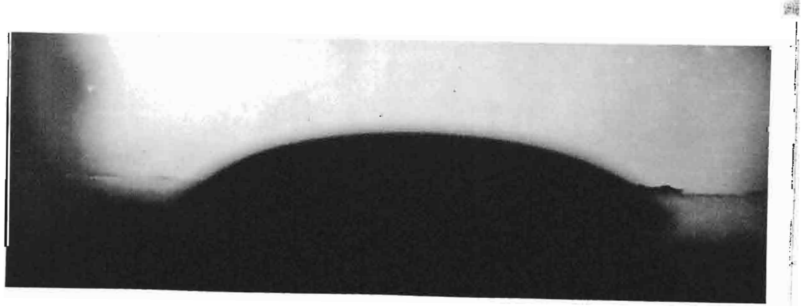
A = Base
Q = 90
h = .420
T = 212
t = 636



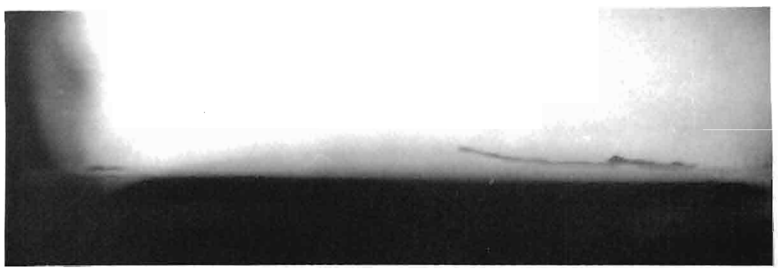
A = Base
Q = 109.4
h = .375
T = 127
t = 650



A = Base
Q = 120
h = .30
T = 72.2
t = 675

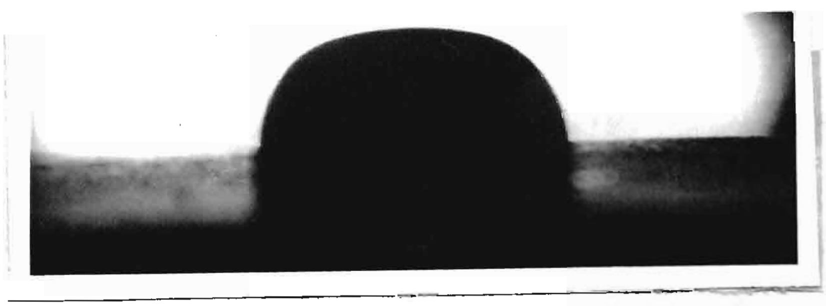


A = Base
Q = 142.5
h = .20
T = 26.8
t = 700

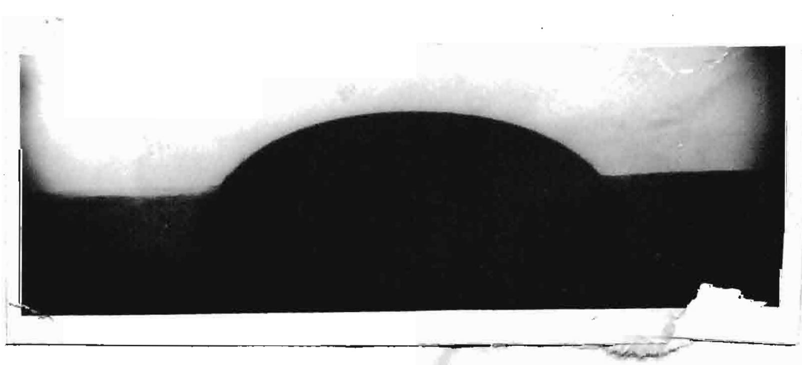


A = Base
Φ = 162.5
h = .09
T = 5
t = 725

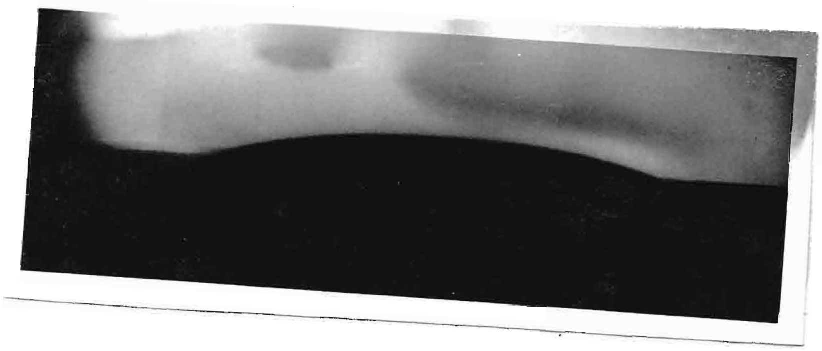
A = Base
Φ = neg.
h = neg.
T = neg.
t = 750



A = CoO
Φ = 90
h = .375
T = 168
t = 650

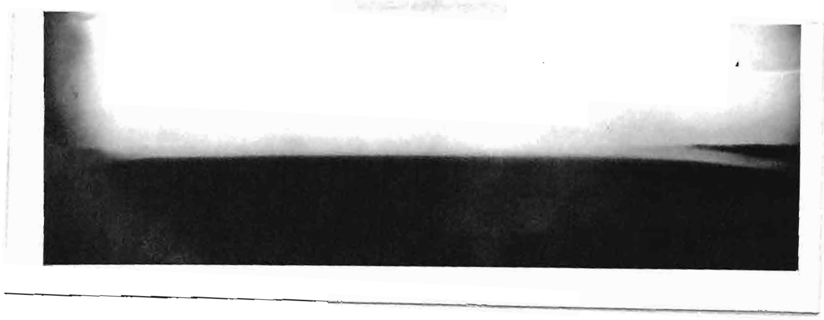


A = CoO
Φ = 126
h - .34
T = 87.2
t = 675

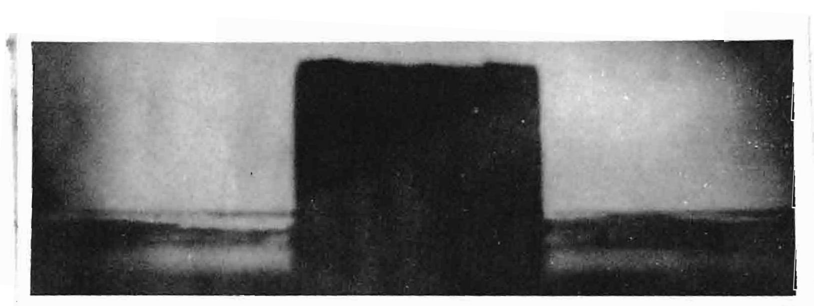


A = CoO
Q = 153
h = .198
T = 24.8
t = 700

A = CoO
Q = 161.6
h = 14
T = 2.47
t = 725



A = CoO
Q = neg.
h = neg.
T = neg.
t = 750



A = CuO
Q = 90
h = .45
T = 238
t = 650

A = CuO
Q = 94
h = .375
T = 176
t = 675

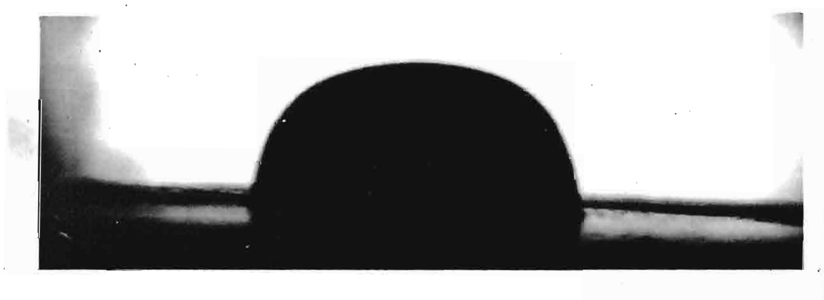
A = CuO
Q = 104.5
h = .35
T = 115.5
t = 700

A = CuO
Q = 137.75
h = 45.8
T = 45.8
t = 725

A = CuO
Q = 158.25
h = .15
T = 13.6
t = 750

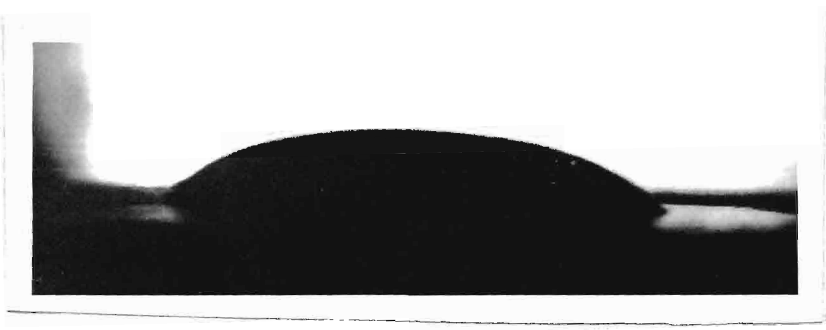
A = CuO
Q = 164
h = .125
T = 9.39
t = 775

A = MnO_2
Q = 96
h = .45
T = 241
t = 636

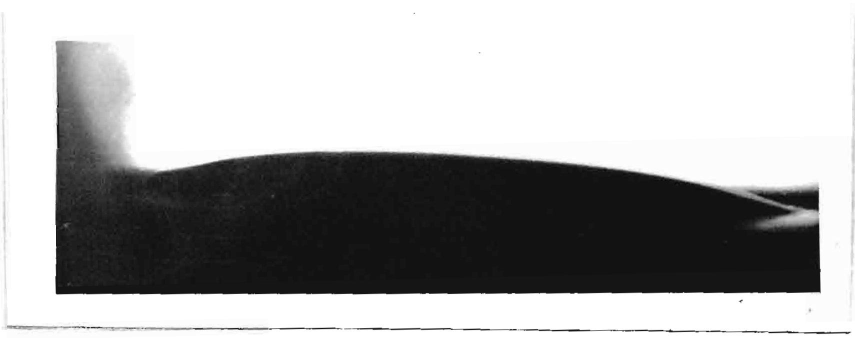


A = MnO_2
Q = 108
h = .390
T = 193
t = 650

A = MnO_2
Q = 121
h = .310
T = 83.7
t = 675



A = MnO_2
Q = 144.5
h = .20
T = 29.1
t = 700



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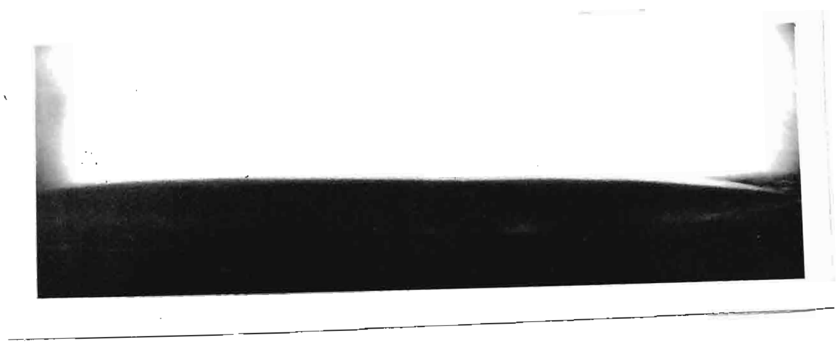
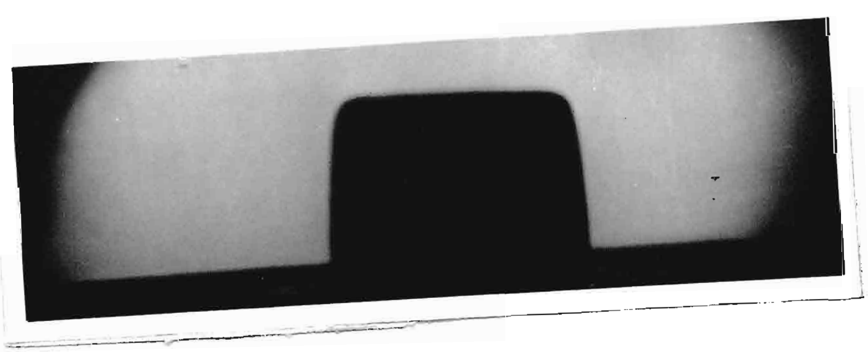
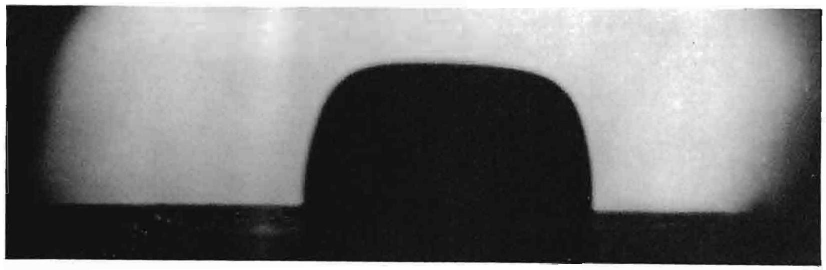
Q = 160
h = .10
T = 6.79
t = 725



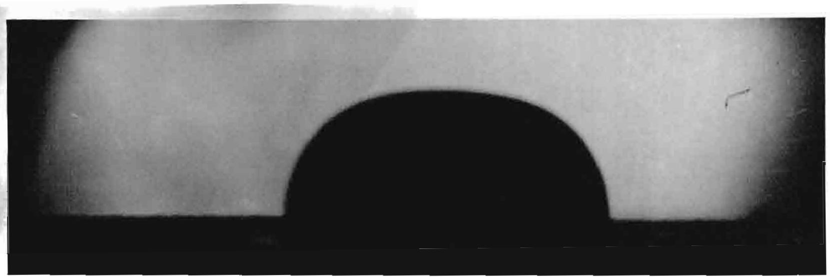
A = MnO_2
Q = neg.
h = neg.
T = neg.
t = 750



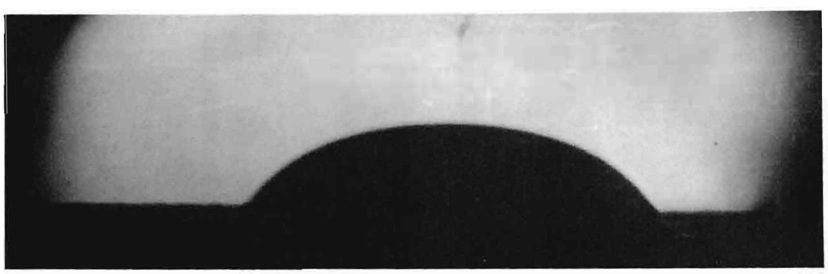
A = As_2O_3
Q = 90
h = .5
T = 324
t = 650



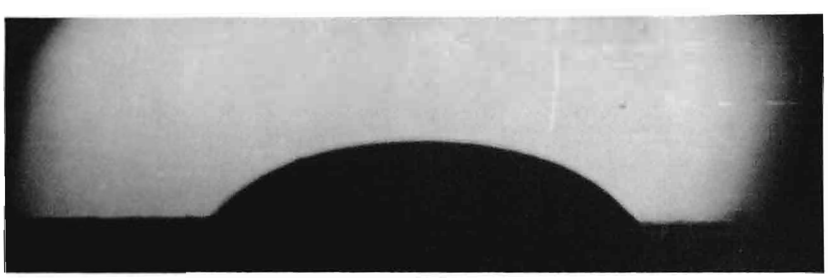
A = As_2O_3
Q = 86.5
h = .420
T = 244
t = 688



A = As_2O_3
Q = 91.5
h = .375
T = 179
t = 700



A = As_2O_3
Q = 133
h = .250
T = 48.2
t = 725



A = As_2O_3
Q = 137
h = .235
T = 41.4
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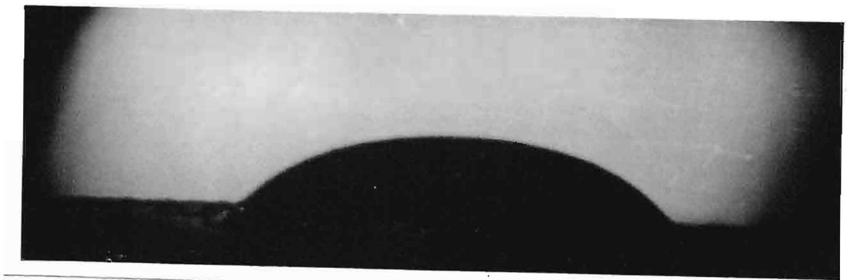

A = As_2O_3
θ = 140
h = .223
T = 36.5
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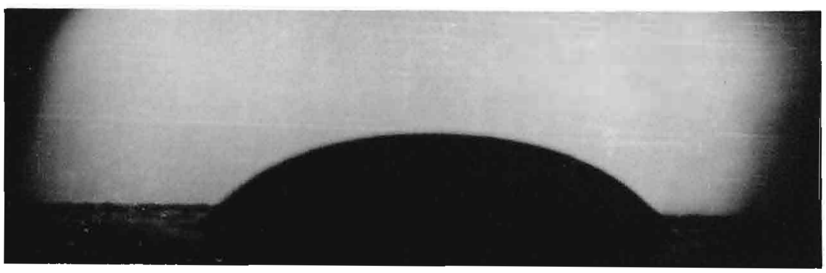

A = As_2O_3
θ = 141.5
h = .218
T = 34.55
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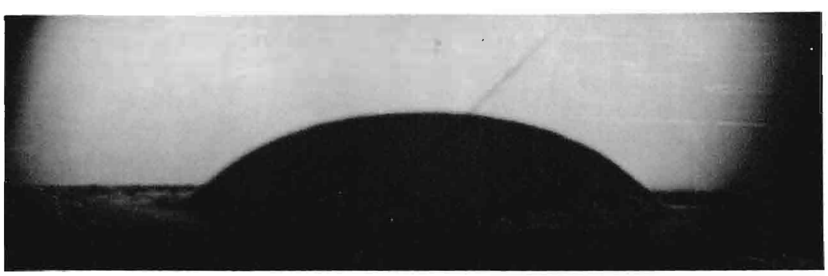
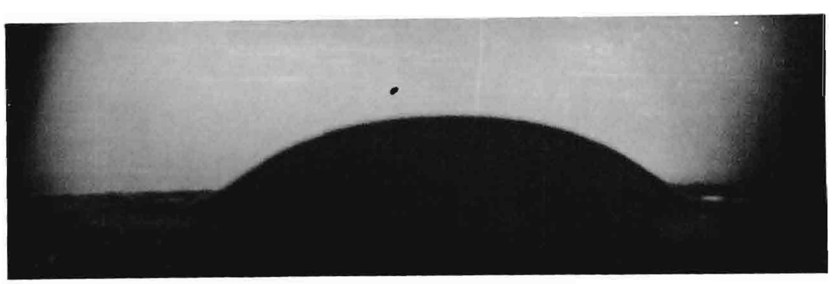
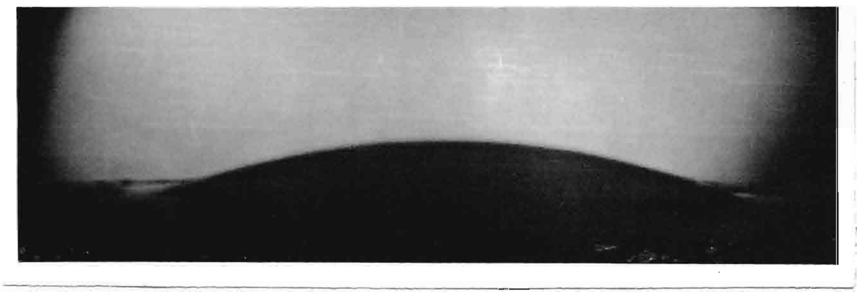


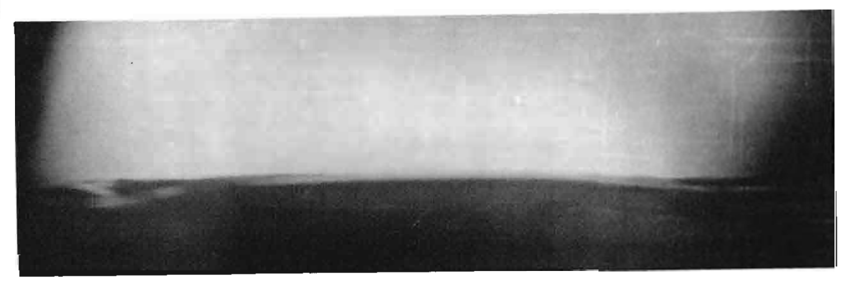
A = As_2O_3
θ = 142.5
h = .215
T = 33.40
t = 825



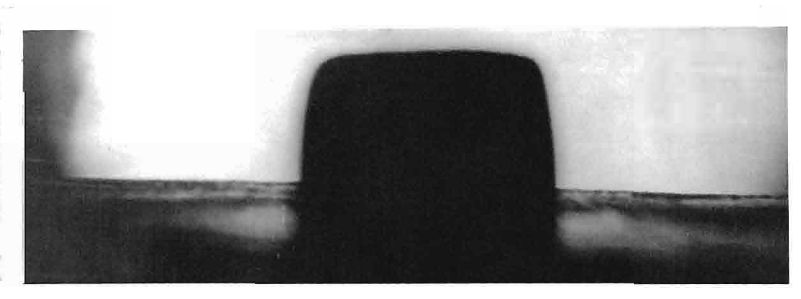
A = As_2O_3
θ = 145
h = 210
T = 31.4
t = 850



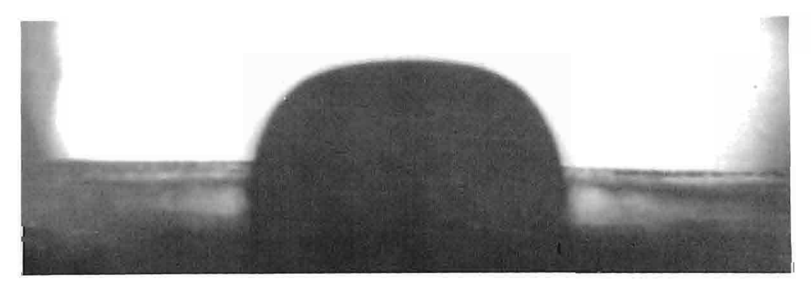
A = As_2O_3
θ = 162.5
h = .130
T = 11.4
t = 875



A = As_2O_3
θ = neg.
h = neg.
T = neg.
t = 900

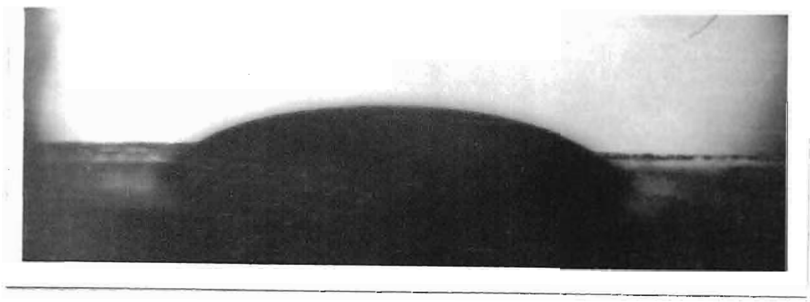


A = WO_3
θ = 90
h = .4
T = 198
t = 636



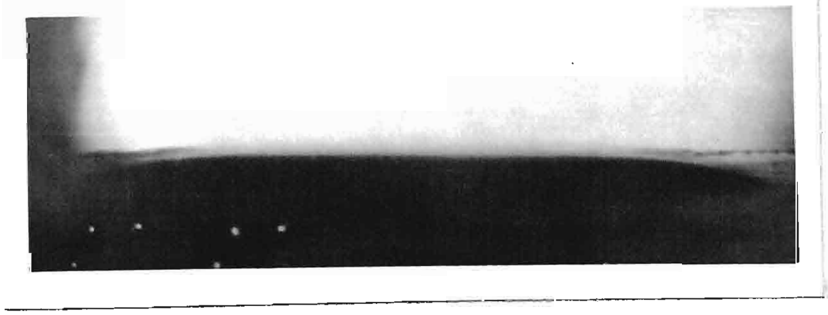
A = WO_3
θ = 101 25
h = .35
T = 127
t = 650

A = WO_3
Q = 111
h = .25
T = 45.3
t = 673



A = WO_3
Q = 147
h = .18
T = 21.9
t = 700

A = WO_3
Q = 163.5
h = .11
T = 7.65
t = 725



A = WO_3
Q = 169
h = .08
T = 3.98
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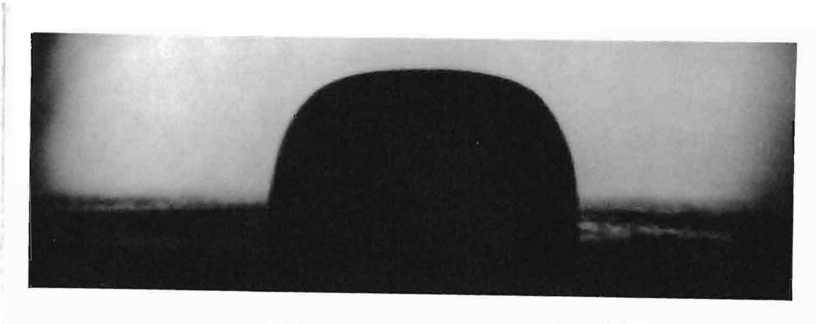
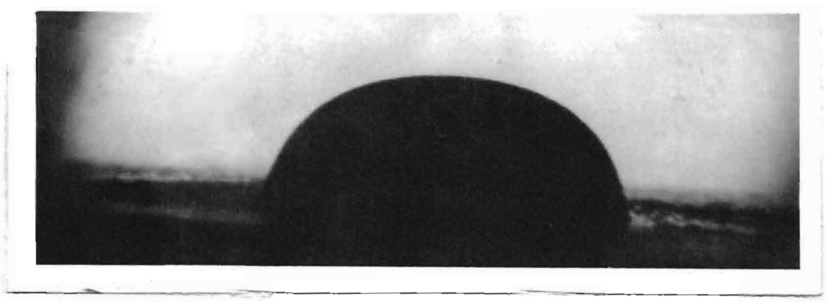
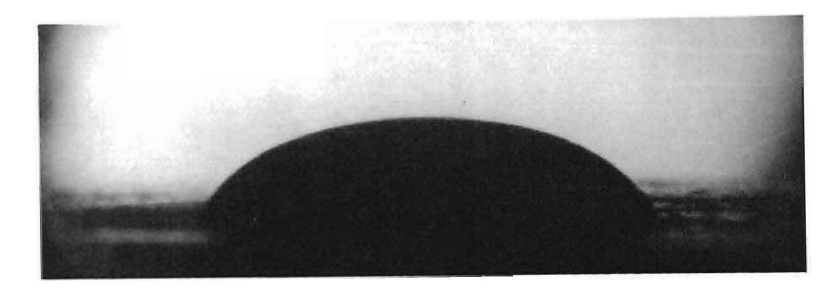


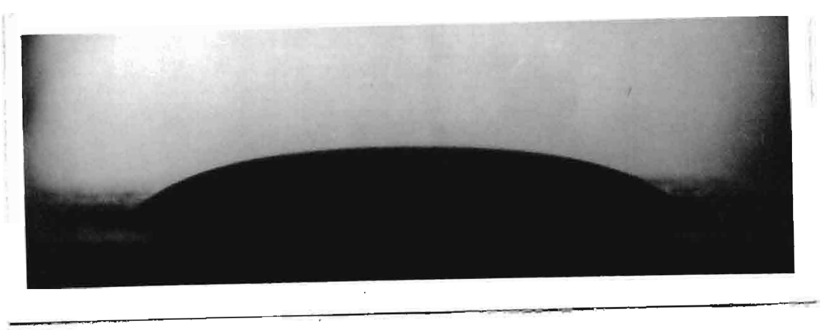
A = TiO_2
Φ = 90
h = .45
T = 246
t = 650



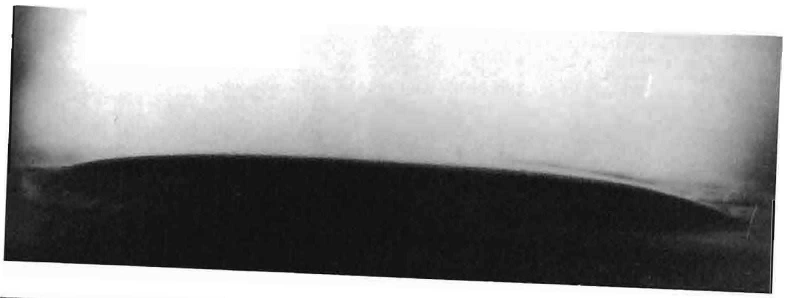
A = TiO_2
Φ = 125
h = .40
T = 154
t = 675



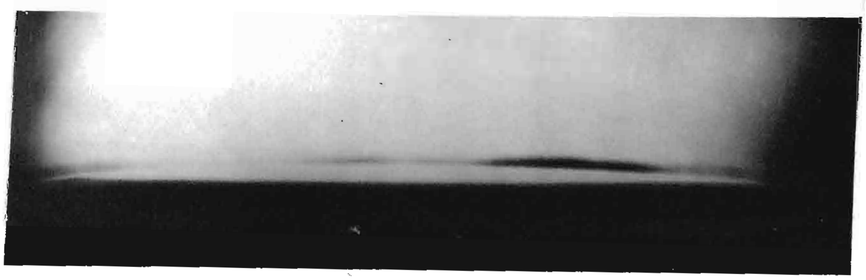
A = TiO_2
Φ = 129.5
h = .25
T = 46.5
t = 700



A = TiO_2
Φ = 154.25
h = .17
T = 18.45
t = 725

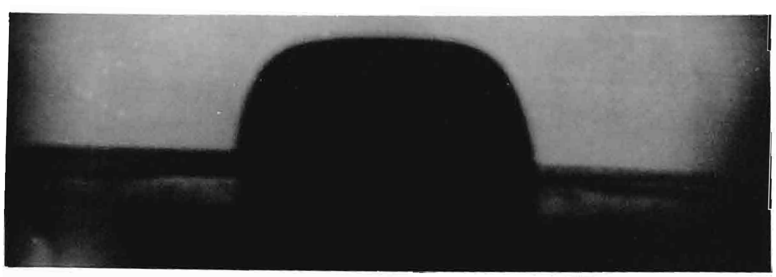


A = TiO_2
Q = 159
h = .125
T = 9.80
t = 750

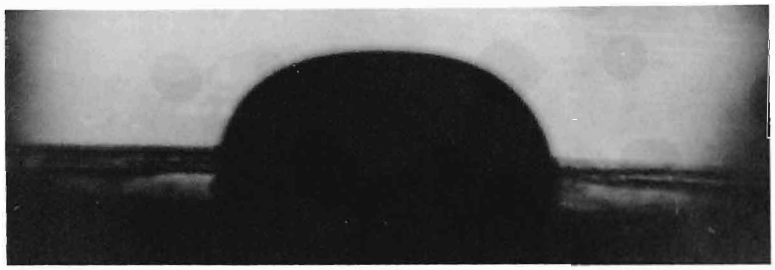


A = TiO_2
Q = 174
h = neg.
T = neg.
t = 775

A = MoO_3
Q = 90
h = .48
T = 256
t = 636



A = MoO_3
Q = 93
h = .370
T = 163.2
t = 650



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Q = 104
h = .300
T = 90.85
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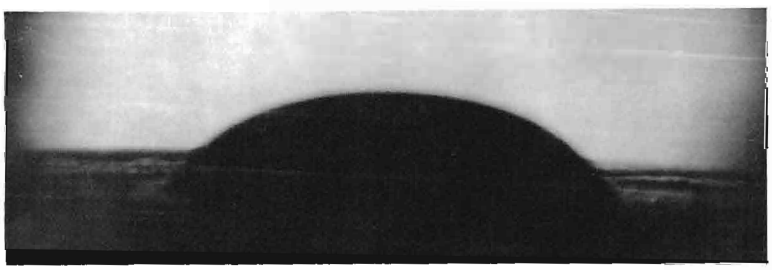
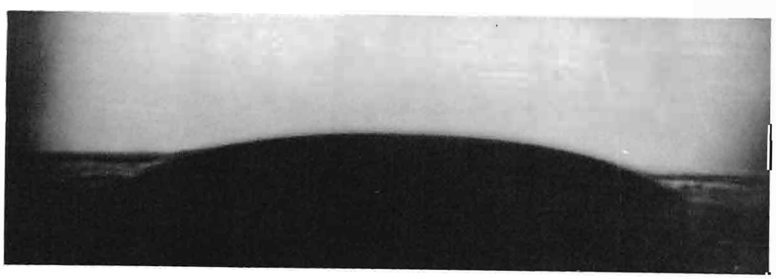
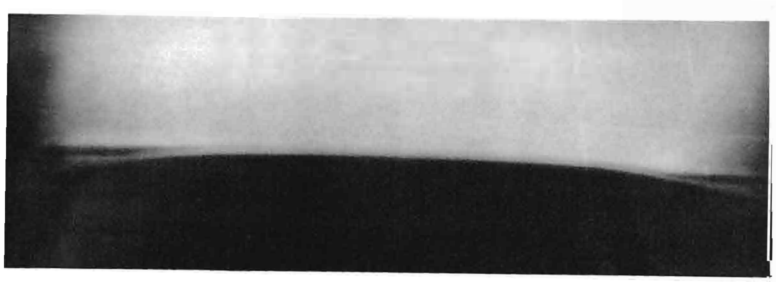


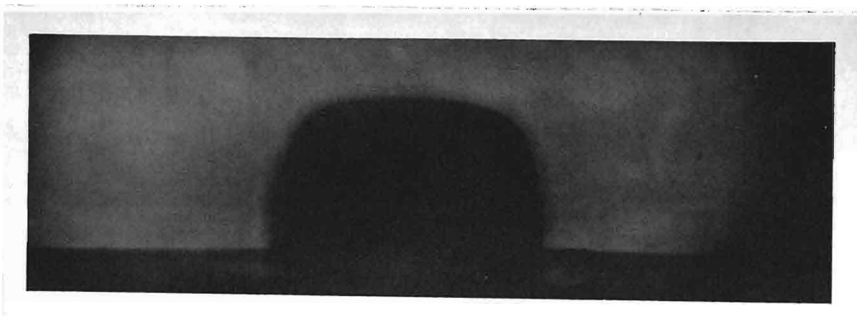
A = MoO_3
Q = 145
h = .200
T = 27.65
t = 700



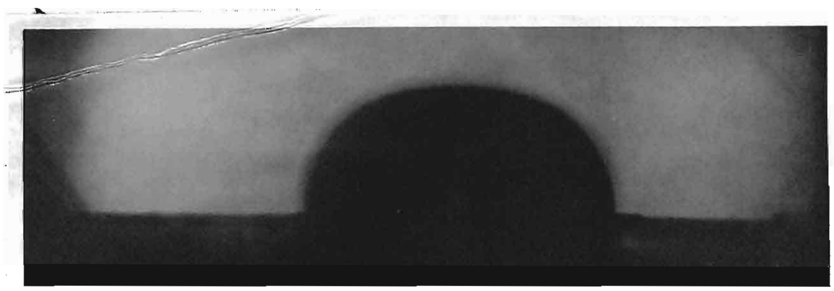
A = MoO_3
Q = 155
h = .100
T = 6.59
t = 725



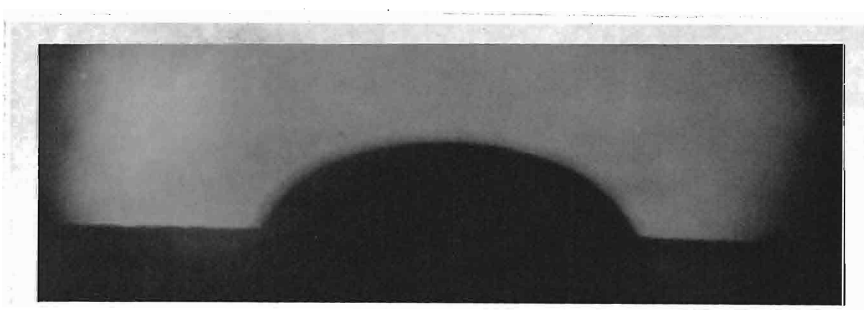
A = MoO_3
Q = 168.5
h = neg.
T = neg.
t = 750



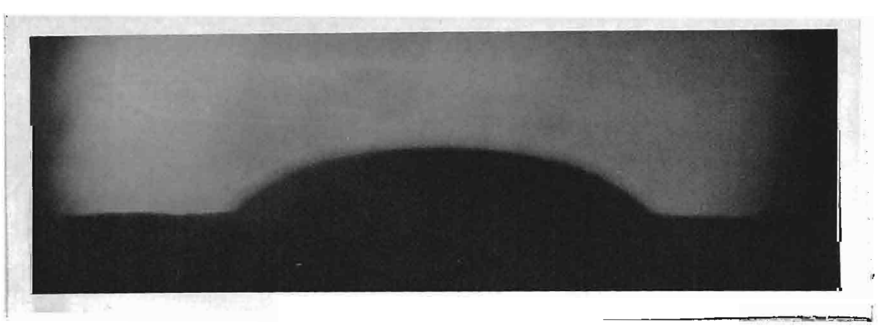
A = V_2O_5
Q = 80
h = .4
T = 249
t = 640



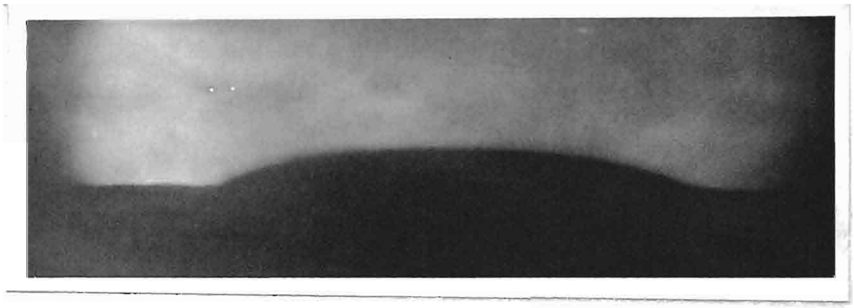
A = V_2O_5
Q = 83
h = .3
T = 132
t = 650



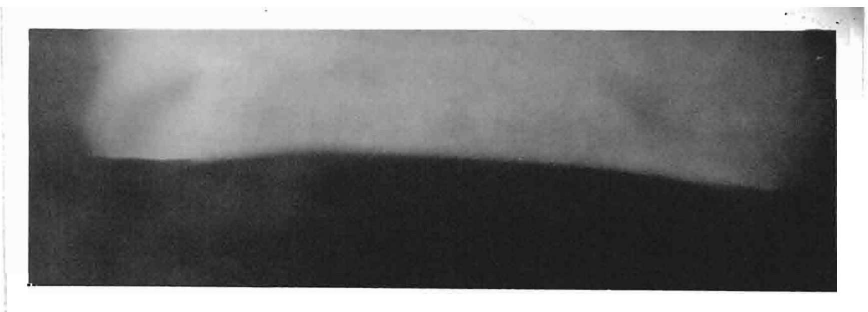
A = V_2O_5
Q = 120
h = .25
T = 53.6
t = 675



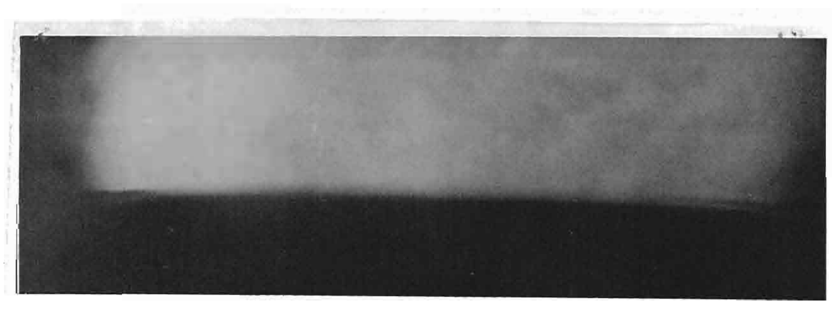
A = V_2O_5
Q = 140
h = .19
T = 26.3
t = 700



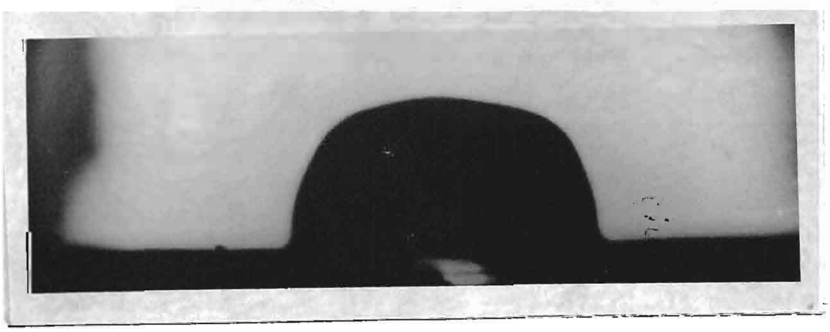
A = V_2O_5
Q = 156
h = .15
T = 15.2
t = 725



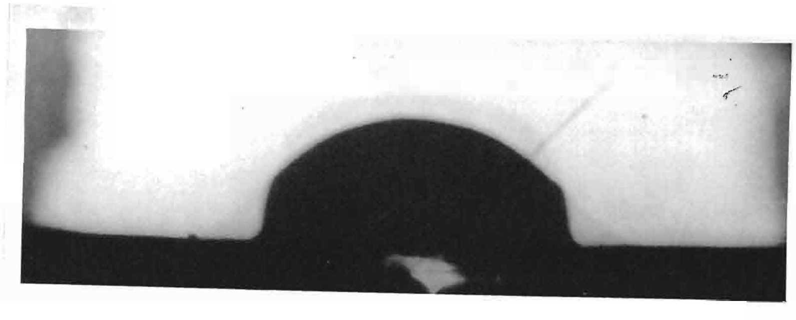
A = V_2O_5
Q = 169.25
h = .075
T = 3.655
t = 750



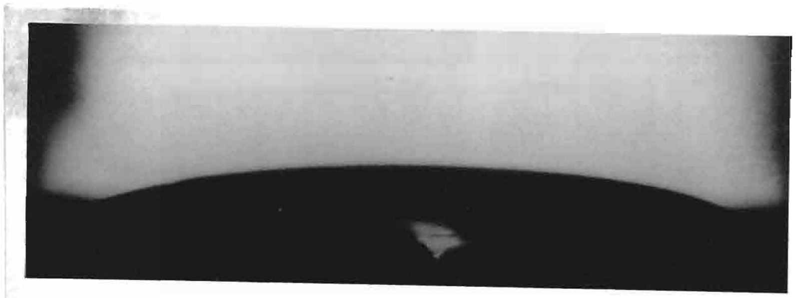
A = V_2O_5
Q = 172.5
h = .16?
t = 775
T = ?



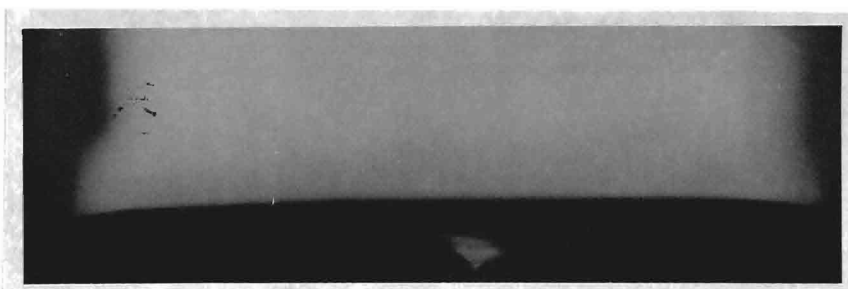
A = NiO
Q = 83.5
h = .5
T = 381
t = 716



A = NiO
Q = 101
h = .4
T = 181.6
t = 725



A = NiO
Q = 158.8
h = .15
T = 15.8
t = 750



A = NiO
Q = 173
h = .085
T = 4.90
t = 775

VITA

Chandrakant Chhotalal Shah was born in Ahmedabad, Bombay Province, India on June 17, 1924. He received his elementary schooling at Thole and Gujarat Vidyapith, Ahmedabad, India. He graduated from Navchetan High School in Ahmedabad City in 1942.

After graduating from the high school, he attended the Gujerat College in Ahmedabad for two years. He studied at the Wadia College, Poona in 1945 and got his Bachelor of Science degree in Chemistry and Physics from Bombay University in 1947.

The author joined the Missouri School of Mines and Metallurgy in February 1948 for his Master Degree in Ceramics.