THE SILICADIZING OF ALUMINUM

BY

EDWARD A SPEERS, P. ENG.

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THE SILICADIZING OF ALUMINUM

BY

EDWARD A SPEERS

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

DOCTOR OF PHILOSOPHY

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Edward A. Speers, P. Eng.
February 2, 1993

THE SILICADIZING OF ALUMINUM

ABSTRACT

This study examines the process of silicadizing aluminum. It optimizes the variables, characterizes the properties of the plated surface and determines the nature of the silicadized layer. The unique conditions are that first, silica can be plated out of an electrolyte; and second, that scintillations accompany the deposition process. Mechanisms are suggested to explain the plating process and the cause of the electroluminescence.

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THE SILICADIZING OF ALUMINUM

1.0 INTRODUCTION

Silicadizing is a technology to protect the surface of aluminum from corrosion. Patents have been obtained for silicadizing as far back as 1911, but the process has not been commercialized, nor has it been featured in the technical literature. The corrosion resistance and wear resistance properties of silicadized aluminum have been reported to be excellent,[1] but little is known concerning the nature of the surface coating. The reported properties of the silicadized surface and the process itself are commercially attractive and therefore this current research has been conducted with the objectives of investigating and optimizing the variables of the silicadizing process, characterizing the properties of the silicadized surfaces, and the nature of the silicadized surface layer.

The development of the base aluminum material, its uses, and the system currently used to protect the aluminum surface from corrosion are outlined and placed in Appendix A.

The alternate surface treatment for aluminum, called **silicadizing,** has been suggested in the following patents and in silicadizing manuals as being superior to anodizing in many respects. In silicadizing, the aluminum is made the anode as in anodizing, but potentials of several hundred volts and low amperage are utilized instead of the few volts used in anodizing with high amperage. Also, silicadizing uses alkaline silicate solutions which are environmentally more acceptable than the acid solutions used in anodizing and the silicadizing process has fewer steps in the procedure than has anodizing. The process investigated here is mainly the one called Undercoat, although some experiments were carried out on two others, called Hardcoat, and Super Hardcoat.

2.0 REVIEW OF THE LITERATURE

A computer search was undertaken through the following registered scientific literature search systems: SCISEARCH, ONTAP and COMPENDEX PLUS for the time period 1970 to August 1991. The words searched were "silicadizing aluminum'' and "alkali anodizing" and variants "silic", "alum", "anod" and "alk" through over ten million records. No relevant applicable references to aluminum were found.

Although many texts of the plating trade were consulted, only references to anodizing in acid solutions were found. No references to anodizing aluminum in an alkali silica were found except for one patent issued to S.S. Frey, U.S. Patent 2,780,591 (1957) where "A decorative finish is obtained on metal objects by first anodizing the surface in an alkaline solution containing colloidal silica to form a very thin invisible coating insulating film in certain areas, forming a pattern, and then applying over this a bright nickel plate which brings out the previously invisible pattern."

Reference Edition 4 of the Chemical Engineers' Handbook, gave no evidence of silicadizing in alkali solutions; however, Editions 2 and 3 described anodizing patents issued as follows:

Lewis W. Chubb's first U.S. Patent No. 999,749 issued in 1911 covered a method of forming edgewise-wound strap coils for electric apparatus and insulating them electrolytically in a bath of sodium silicate.

Chubb's second and third U.S. Patents Nos. 1,068,410 and 1,068,411 covered method and apparatus for coating electric conductors and wires respectively, again electrolytically in sodium silicate (or sodium borate in the former case).

In recent times the patent application of alkali silicate solutions to anodizing of aluminum has largely been due to the work of the late Rudolph Hradcovsky:

1962 Czechoslovakian Patent No. 104,927 to Hradcovsky and Belohradsky, as referred to in the 1974 Hradcovsky patent which follows, disclosed a coating on aluminum which had a weak breakdown voltage and a highly porous coating. The electrolyte was a "weakly alkaline aqueous bath composed of 10-15% sodium or potassium silicate and a hardener such as 3% ammonium molybdate."

1974 U.S. Patent No. 3,832,293 Hradcovsky, et al., devised a process for a durable coating on aluminum and magnesium by imposing a voltage "of at least 220 volts. . . .When the voltage exceeds about 220 volts, sparking occurs, causing deposition of the desired coating. However, depending upon the bath composition, voltages of up to 1,500 volts may be required to deposit a satisfactory coating." The electrolyte has a preferred concentration of 15 to 25 grams of potassium silicate per litre.

1974 U.S. Patent No. 3,834,999 to Hradcovsky and Kozak revealed the intent of providing a glassy, adherent, corrosion-resistant layer on "rectifier" metals, including aluminum, in contrast to the porous layer of the Czechoslovakian patent. Voltages of from 400 to 1500 volts were required to obtain a satisfactory coating and coatings up to 1 mm thickness may be readily obtained by this method The electrolyte bath contained " an alkali metal silicate and an alkali metal hydroxide," with an "alkali concentration of about 15% being desired to achieve the hardest coating."

1976 U.S. Patent No. 3,956,080, Hradcovsky, et al., is a similar process for forming a silicate coating on metal.

1978 U.S. Patent No. 4,082,626 to Hradcovsky describes a process for coating rectifiable metals at a voltage of up to 300 volts. Here the process is called a relatively low voltage one with an electrolyte of an aqueous solution "of pure potassium silicate (or a mixture of potassium silicate and a peroxide, e.g. sodium peroxide)." Here again, a spark is discharged at the surface of the rectifier metal at the start of coating. The voltage is then increased to about 300 volts and held there until the desired coating thickness is reached.

1980 U.S. Patent No. 4,184,926, Otto Kozak, covers ''Anti-corrosive Coating on Magnesium and its Alloys," again using an alkali silicate-based solution. The magnesium is first treated with a dip into aqueous hydrofluoric acid to form a fluoromagnesium layer on the metal surface. The metal thus coated is then immersed in an electrolyte. "The preferred electrolyte is an aqueous solution of alkali metal silicate and an aqueous metal hydroxide. An electric current is then applied between the magnesium metal anode and the container or cathode until a visible spark is discharged across the surface of the metal. This potential is maintained for a few minutes until a coating of the desired thickness is formed on the fluoromagnesium layer."

In 1985 the author was approached by the president of an American firm to verify two patents: Kozak (1980) U.S. Patent No. 4,184,926 and Hradcovsky (1978) U.S. Patent No. 4,082,626, in which the company had an interest. As mentioned above, the computer literature search showed that there had been no technical papers on the subject of anodizing in alkali silicates, nor on "silicadizing" of aluminum/magnesium during the last thirty years. The American company supplied manuals purporting to cover the methods delineated in the existing patents, plus further information not yet disclosed by patents.

During the contract a postdoctoral surface chemist, D. Khanangara, Ph.D., assisted me. This work was done in my company, INRAD Industrial Research and Development Ltd. in Winnipeg. It soon became apparent that the three different manuals supplied had variations and inconsistencies. It was learned that the originators of the patents were not prepared to divulge all the information on the process to the American company. "Verification" of the two patents was completed, but independent research has continued, resulting in this study.

3.0 EXPERIMENTAL AND TEST EQUIPMENT

3.1 This section describes the components required to execute the silicadizing of aluminum: the electrolyte which is a silicate, and its container(s), the electrodes: the anode and cathode, and the rectifier.

3.2 THE ELECTROLYTE

There is a great similarity between silica and water, as first pointed out by Bernal and Fowler[2] who referred to different intermolecular arrangements postulated for water at different temperatures, for instance:

"(1) Ice-tridymite-like (four coordinated) at low temperatures below 4°C.

(2) Quartz-like (four coordinated) between 4-200°C, roughly."

This similarity has also been pointed out by Iler:[3]

> As water is a unique liquid, so is amorphous silica a unique solid. They are much alike, both consisting mainly of oxygen atoms with the smaller hydrogen or silicon atoms in the interstices . . . [a]s pointed out by Weyl and Marboe . . . [s]ome propertiesof water and silica are so similar that the transition between hydrated silicic acids and the aqueous matrix is a gradual one.

The base electrolyte is a silicate: a syrupy, water-white, alkaline solution. Being similar to a sugar solution in appearance and in viscosity, the industry standard to measure the density of silicate solutions is by the Baumé scale. A graph comparing the Baumé scale to specific gravity is shown in Appendix B. Figure 1 shows the Potential-pH Diagram for the Silica-Water System at 25°C.

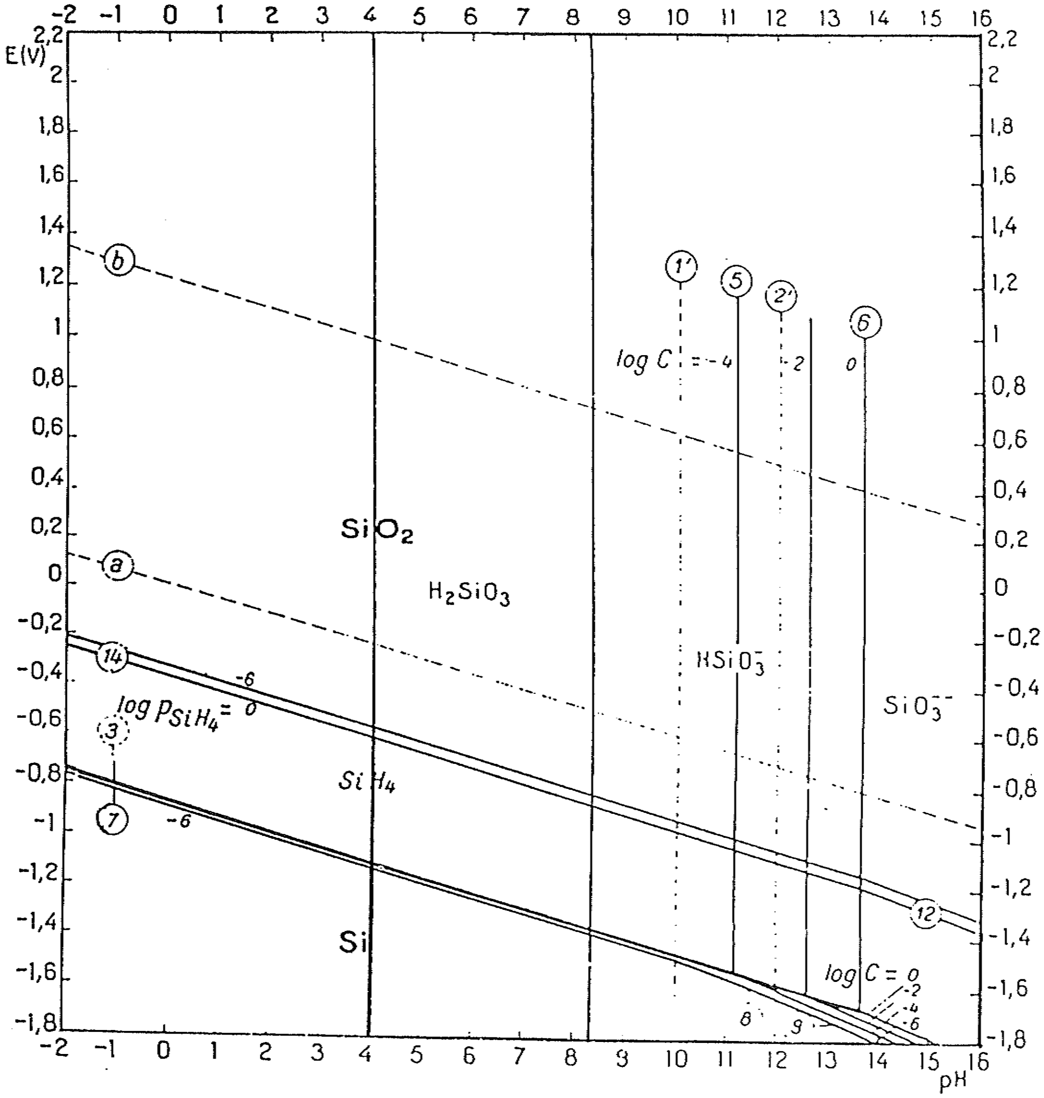


Figure 1

POURBAIX DIAGRAM - POTENTIAL VS pH for SILICA-WATER SYSTEM at 25°C

Throughout this report the terminology used in discussing silica is that used by Iler[4]:

> "Silica" is used as a short convenient designation for "silicon dioxide" in all its crystalline, amorphous, and hydrated or hydroxylated forms. This word does not occur in many languages, which generally use the term "silicon dioxide." However the latter implies only the composition SiO_2. In analysis, the term "silica" indicates only that the silicon content is given in terms of weight of SiO_2, regardless of the form in which it is actually present.

Above pH 9 monosilicic acid [$Si(OH)_4$] is ionized first to $(HO)_3SiO^-$ or at still higher pH to $(HO)_2SiO_2^{2-}$. The first equilibrium constant at 25°C based on the formulae:

$$Si(OH)_4 + OH^- \rightarrow H_3SiO_4^- + H_2O \rightarrow (OH)_3SiO^- + H_2O,$$

is approximately:[5]

$$\frac{[(HO)_3SiO^-]}{[OH^-][Si(OH)_4]} = 1.5 \times 10^4$$

or

$$\frac{[(HO)_3SiO^-\ [H^+]}{[Si(OH)_4]} = 10^{-9.8}$$

Huang[6] has proposed that $HSiO_3^-$ is the major reacting species above pH 9, as shown in the above equation.

In contrast to the above historic chemical analysis, research by Guth and Caullet,[7] by Harris and Howarth,[8] McCormick and Bell[9] and by Jianchong Yang, and Alon McCormick[10] using Nuclear Magnetic Resonance (NMR) has shown in analyzing alkaline silicate solutions in the study of the formation of Zeolites, that the predominate species is the monomer $SiO_3^=$at all pH levels. Oligomers are made up from the monomers in dimers, and trimers, etc., but at high pH the monomer predominates. The bond strength of the oligimers decreases as the oligomer size increases.

The electrolyte solutions covered by patents listed above are considered open literature. Basically, the formulations therein are silicate solutions and, while sodium silicates will work, the potassium salt is preferred because of ease of solubility, compatibility with other ingredients, and lack of efflorescence. Potassium silicates are a family of chemicals with a wide range of physical and chemical properties. The various characteristics of potassium silicates permit their use in applications as diverse as welding rods, soaps, detergents, coating materials, and electronics. In flux coatings for welding electrodes, potassium silicate provides a smooth arc and quiet burning. High solubility and compatibility with other ingredients also make potassium silicate preferable. Potassium silicate does not effloresce (i.e., does not form the white dust of minute crystals as sodium silicate is prone to do when used to coat basement floors, for instance) and is therefore ideal for use in paints and other types of coatings and bindings.[11] Industrial potassium silicates include a percentage of sodium silicates in solutions.

Potassium silicate solution is not a controlled product under the Workplace Hazardous Materials Information System (WHMIS). It is completely soluble in water. It is a non-flammable, stable aqueous liquid. However, on long contact with some metals, such as aluminum, tin, lead or zinc, flammable hydrogen gas may be produced. The amphoteric nature of aluminum and zinc allow these metals to dissolve in an alkaline solution with the evolution of hydrogen, and the formation of metal ions:

$$Zn + 2OH^{-} + 2H_2O \rightarrow Zn(OH)_4^{=} + H_2.$$

Therefore, steel drums or other non-reactive containers only must be used. It gels on mixing with acid. The solutions used in silicadizing are dilute. For example, K88 Potassium Silicate came as a 30° Baumé solution (now replaced by K 6 at 40° Bé) which is diluted with other ingredients to give a 5° to 10° Baumé commercial solution. The pH of the electrolyte should be around 12 for most effective silicadizing applications.[12]

It should be noted that during the silicadizing of aluminum, some dissolution and precipitation of the aluminum oxide surface occurs occasionally and the resulting product may appear as a deposit in the electrolyzing container. This is in line with the findings of Lewis and Plumb,[13] that

> [T]he principal material transported through the oxide film during anodizing is aluminum and not oxygen. This result is consistent with work which indicates that, under forming conditions, barrier type oxides are nonstoichiometric, containing excess aluminum.

Also, Young[14] has suggested that the metal is mobile and thus excess metal ions are "frozen into" the aluminum oxide when acid anodizing is stopped.

3.3 THE ELECTRODES

The preferred cathode is stainless steel, although other metals will do providing they are electrolytically insoluble. Nickel and iron were also used successfully.

The anode is the aluminum or aluminum alloy product that is to receive the silicadized coating. The aluminum sheet used in the laboratory was supplied by Reynolds Aluminum Company and consisted of the following:

0.020″ #3003 H 14 aluminum sheet
0.016″ #1100 mill finish aluminum sheet
0.040″ #5052-0 mill finish aluminum sheet

Other aluminum sheets coated included schedule #2024 and #6061-T6.

3.4 THE TANK

In the laboratory it was common practice to use beakers where the test pieces were small. While volumes of 2, 6, and 22.5 litres readily handled these small pieces, larger ones were treated in fibreglass or acrylic tanks or steel drums. As the voltage used ranged above 250 volts with relatively small amperage, often under one ampere, considerable heat was generated when the heavier coatings were required. Thus, sufficient solution volume or a cooling system is needed to keep the temperature < 60°C over the deposition time period of approximately 5 to 10 minutes. Industrially, cooling coils will be required for high production rates along with temperature monitoring and control. Here, the tanks should be sized to match the products to be treated. It is noted that should the article be of an outsize such as a commercial lamp standard, facilities can readily be prepared by digging a suitably shaped hole in the ground, lining it with polyethylene sheeting, adding a cathode electrode of a size 1.5 to 2 times the area of the anode lamp standard surface to be treated, suspending the standard in the silicadized solution, and proceeding by supplying the power.

3.5 THE RECTIFIER

The silicadizing process requires a high voltage rectifier compared to the rectifier used for acid anodizing. For instance, there are many anodizing rectifiers having voltage capacities of 5 to 40 volts, or 15 to 20 volts for castings, with current draw up to 88 amps/sq.m.[15] In silicadizing, the initial current is ramped up to 10 amps at 25 to 50 volts for a few seconds, to break the natural oxide layer, followed by a buildup of the silicadized coating causing the amperage to decrease due to the coating resistance and necessitating a rise in voltage to over 250 volts (at low amperage) to continue the formation of the desired coating thickness. A 100 KVA unit will coat approximately 4.5 to 6 m^2 every 10 minutes. Safety precautions need to be taken because of the high voltage. Plastic decking or similar insulated flooring must be supplied. The rectifiers supplied to the industry for anodizing generally range up to 100 volts with amperage from 250 to 10,000 amperes (Rapid Electric Company, Brookfield, CT literature). Custom designed DC power supplies ranging from 6 to 1,000 volts and 15 to 50,000 amperes are available on special order. A rectifier design of 100 KVA would cover most commercal applications when silicadizing. The higher amperage is required at the initial ramping time while processing often continues at under 1 amp for small parts and generally in the range of 250-500 ma/dm^2 by adjustment of the voltage.

(For rectifier data see Appendix F).

4.0 PROCESSING FACILITIES

4.1 LABORATORY SET-UP

The laboratory set-up used in this research consisted of a Powerstat® controlling the incoming AC power,then a rectifier converting the power to DC, with gauges showing the voltage and amperage being used during the experiments, as shown in Figures 2.

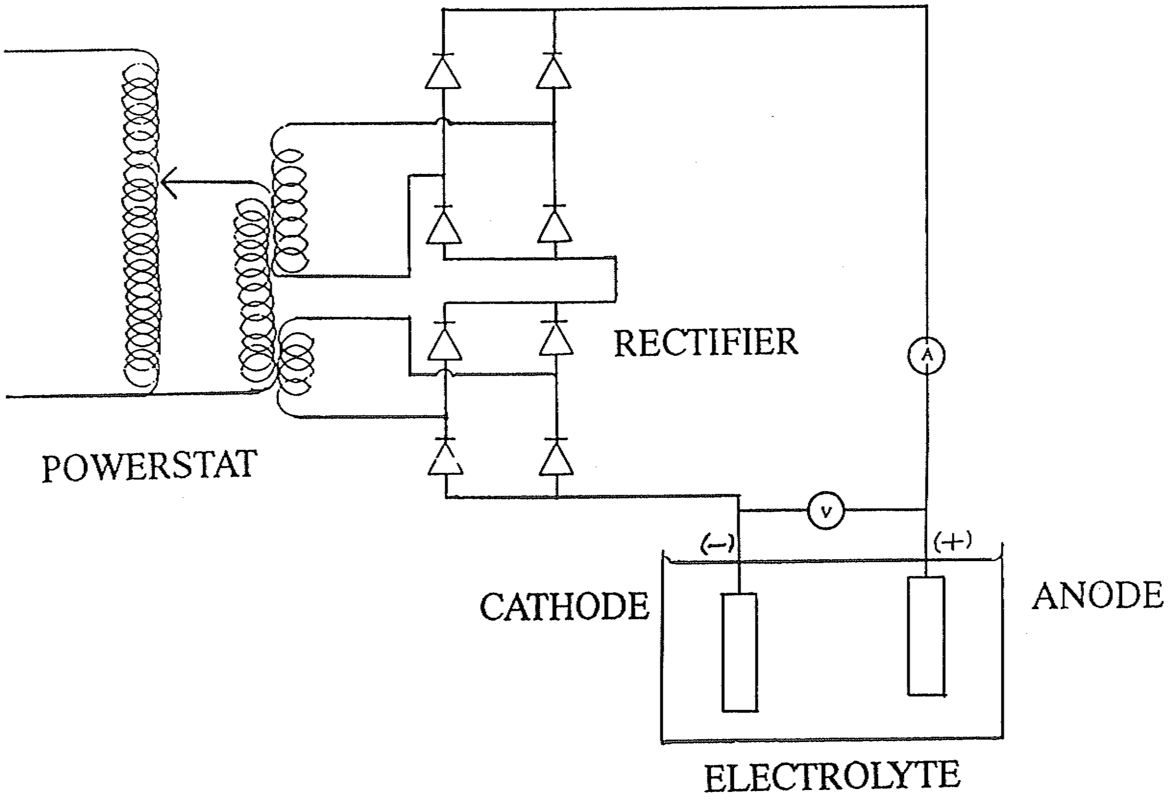


Figure 2 LABORATORY SET-UP FOR SILICODIZING

4.2 INDUSTRIAL SET-UP

In industry it should be possible to run a processing facility with four tanks: one for the Undercoat solution, one for the Hardcoat, and one for the Decorative coat, or Super Hardcoat. A cleaning tank may be necessary which would precede the processing tanks In the laboratory testing it was found that the initial ramping voltage applied tended to remove the normal aluminum oxide and thus clean the samples before, the silicadizing started. Temperature control of the bath, as mentioned above will be necessary, which will involve the installation of a heat exchanger with an attendant cooling system. (Appendix G illustrates an industrial tank layout).

Sources of power, water and air are required. In the laboratory, use was made of the flow of forced air in the fume hood to dry samples. As the samples come from the solution at a temperature above room temperature, the drying time was short. Forced air drying may be required in industry.

5.0 TEST RESULTS

This section describes the experimental results obtained in researching the latest patents mentioned above. Subsequently, further experimental results are presented which appear to have overcome some of the experimental difficulties experienced with the patent procedures, at least in the laboratory tests. Some comments are made with regard to the use of, and need for, hydrofluoric acid when silicadizing.

5.1 UNDERCOAT

As mentioned above, undercoat experiments were carried out in baths of three sizes:

(a) a 600 ml beaker
(b) a 6 litre bath
(c) a 22.5 litre bath

One of the typical recipes for the Undercoat is the following:

Potassium silicate, 30°Bé	150 grams
Potassium Peroxide	20 grams
H_2O	1000 grams

A 50 x 50 x 1 mm aluminum sheet is placed in the bath made from the above ingredients, at ambient temperature of 25°C. The aluminum sheet serves as the anode and an iron sheet is immersed into the bath as a cathode.

On application of power to the cell a coating of white silicate is formed on the anode material at a voltage above approximately 250 volts. The interesting accompanying phenomenon during the deposition phase is the generation of sparks over the surface of the immersed anode along with gaseous hydrogen and oxygen at the cathode and anode respectively. These factors are described and analyzed in greater detail later in this thesis.

All Baumé readings were taken with a Baumé hydrometer which was washed with water after each test, dried and stored until the next test. Periodically the hydrometer was checked against distilled water, and if required the reading was adjusted linearly in accordance with the graph in Appendix B showing the relationship between the Baumé and Specific Gravity readings. The undercoat was easy to obtain in under 7 minutes, depositing a coating thickness between 0.012 mm to 0.025 mm depending on the time and concentration of the solution used. The colour was off-white to

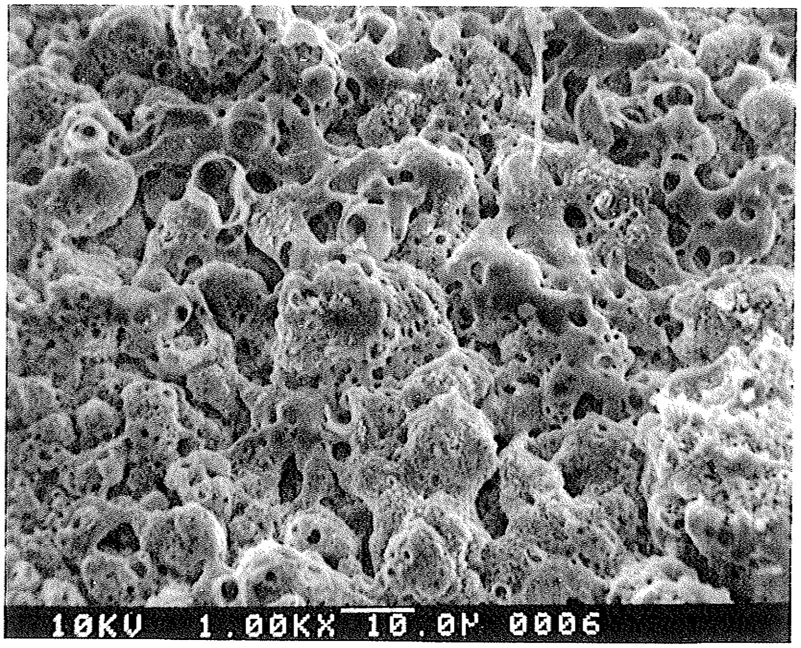


Figure 3 SURFACE BY SEM (1000X)

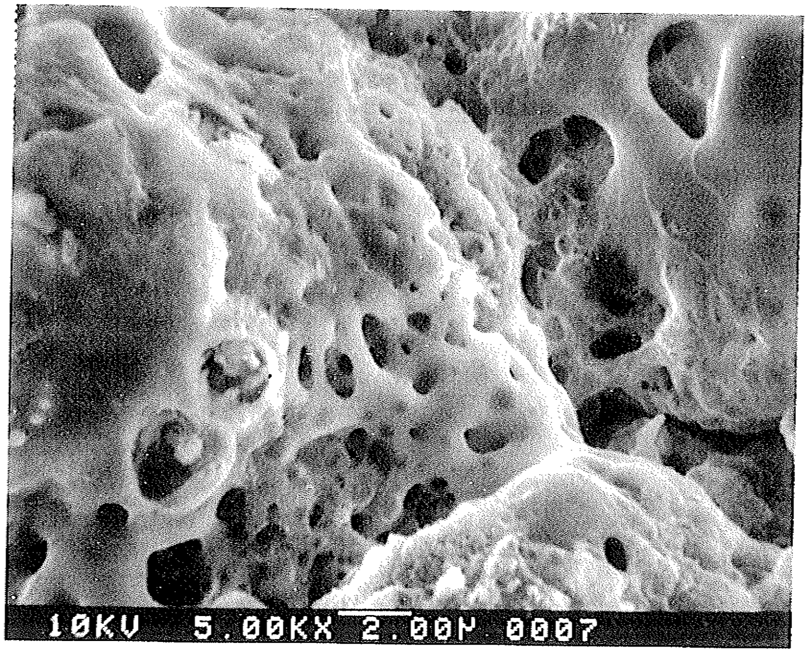


Figure 3A SURFACE BY SEM (5000X)

SEM MICROGRAPHS OF SURFACE

light grey and the surface appeared smooth to the eye. In the scanning electron microscope the surface consists of nodules, rounded, porous, having a ridged sponge-like appearance (Figure 3 and 3A, Undercoat, at 1000x and 5000x by SEM).

Figure 3B shows the cross-section of the silicadized coating by SEM as mounted, and polished in a Bakelite matrix. The white area at the base is the aluminum substrate. On top of the aluminum is a layer of aluminum oxide, followed by the plated silicate layer. The black area at the top is the Bakelite.

The interaction of Temperature-Voltage with Time is shown in Figure 4. Initially the voltage is ramped up to about 50 v, while the amperage goes to 8-10 amps depending on the concentration of the electrolyte. The amperage falls quickly as the surface oxide builds up. The voltage is increased to 200+ volts, and the silicate coating starts to plate out. This process can also be obtained by a programmed increase in voltage.

The graph of Undercoat Thickness vs Time (Figure 5) shows that at 7.6° Bé and a pH of 12 the silicadized coating does not start to build until the voltage reaches in excess of 200 volts and that the higher the voltage the faster the surface layer grows.

The result of a study of Potential vs Time at Constant Current Densities for an Undercoat solution is shown in Figure 6. This figure shows

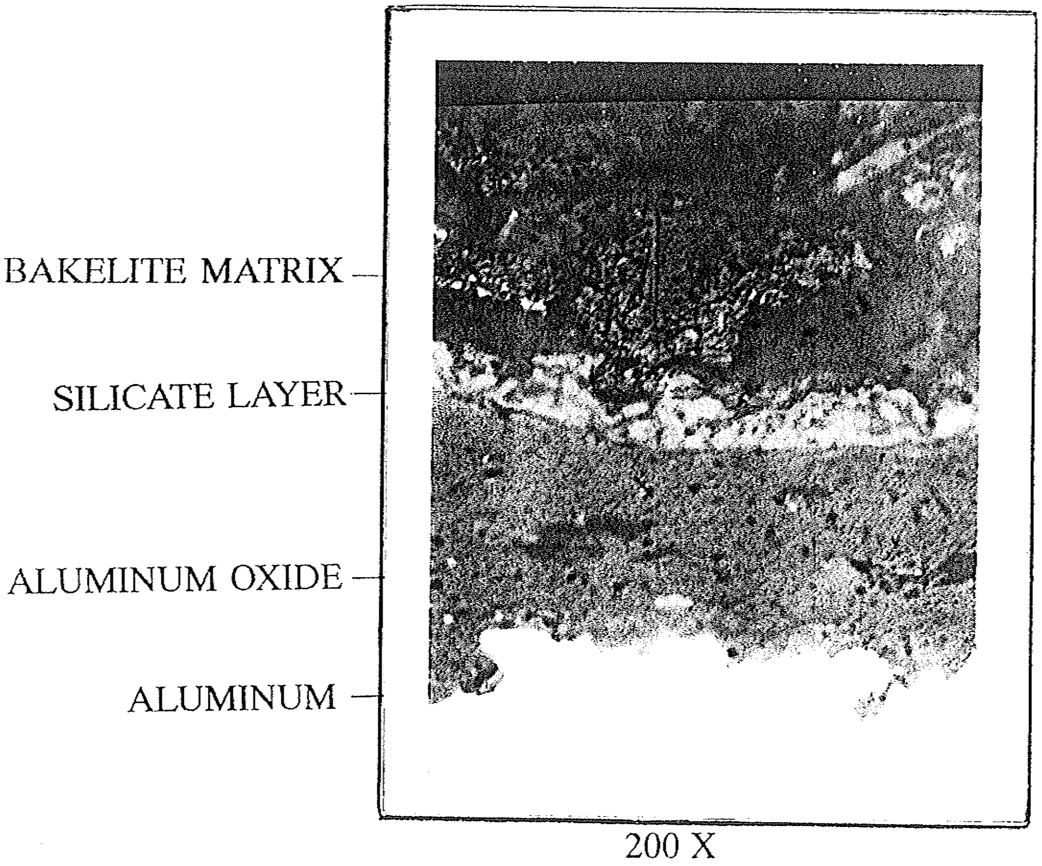


Figure 3B **CROSS-SECTION OF SILICADIZED COATING**

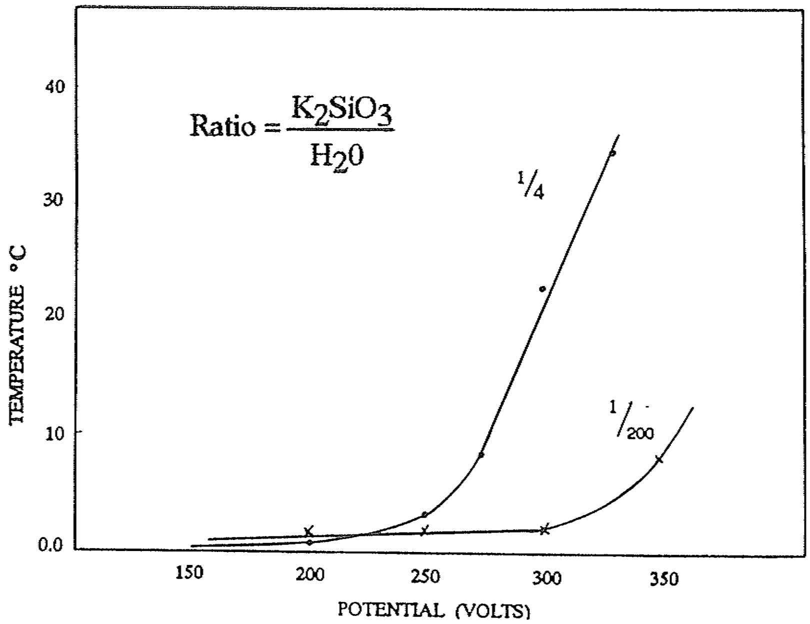


Figure 4 **TEMPERATURE VS POTENTIAL**

Showing the rise in temperature of the concentrated solution over that of the dilute solution taken from room temperature during 2 minute trial runs.

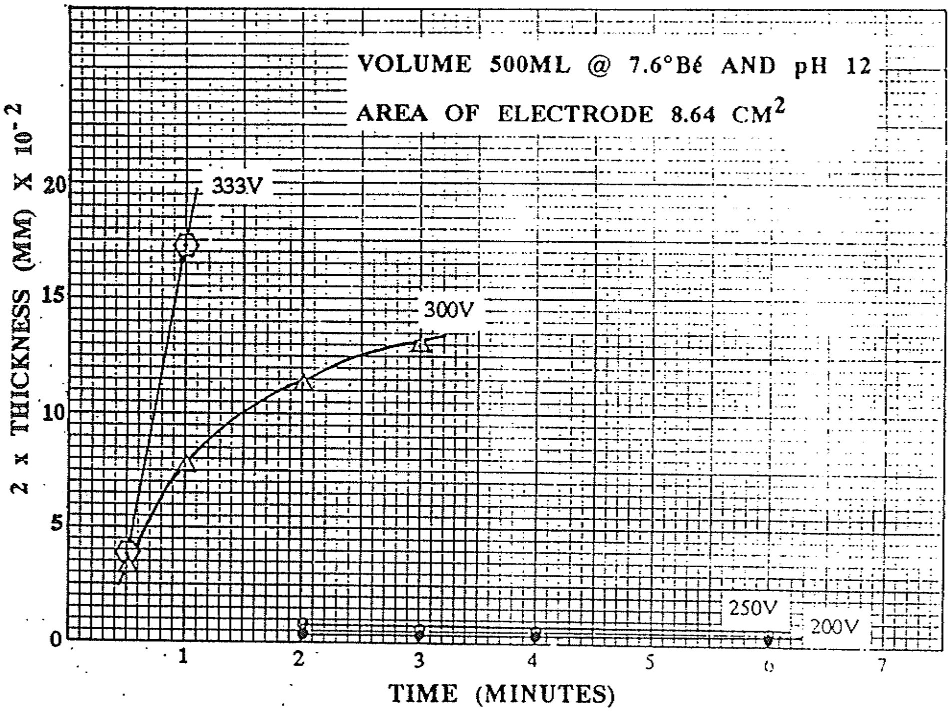


Figure 5 UNDERCOAT: COATING THICKNESS VS TIME

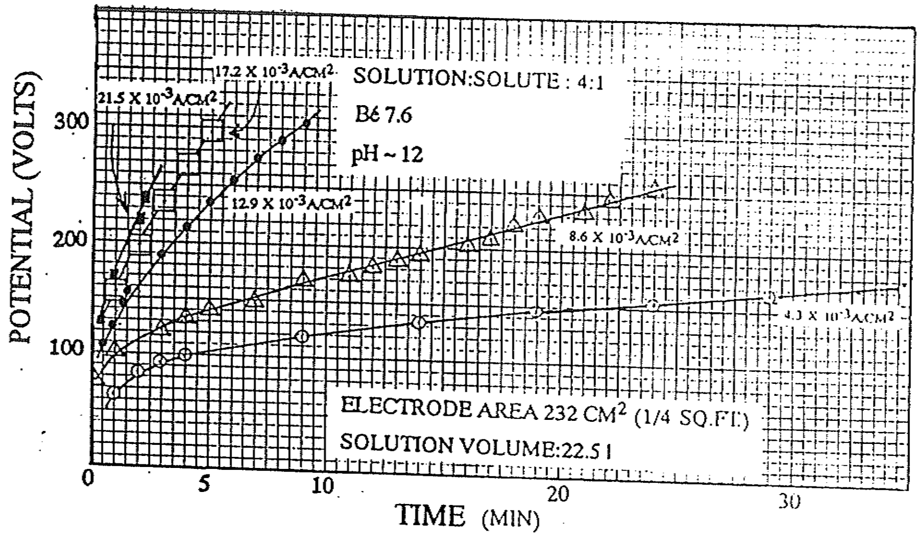


Figure 6 UNDERCOAT
POTENTIAL VS TIME @ CONSTANT CURRENT

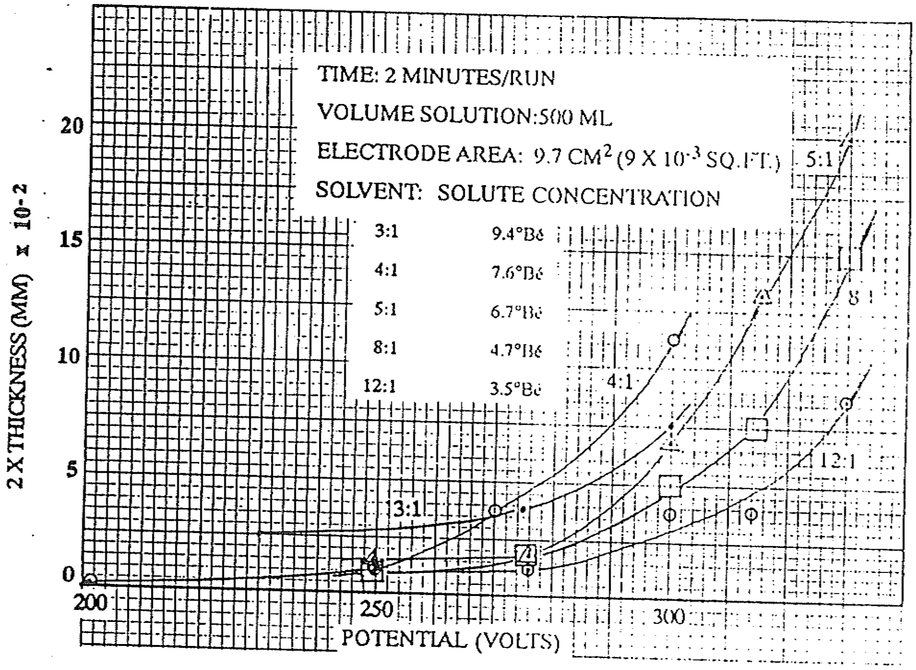


Figure 7 UNDERCOAT
THICKNESS VS POTENTIAL (VOLTS)

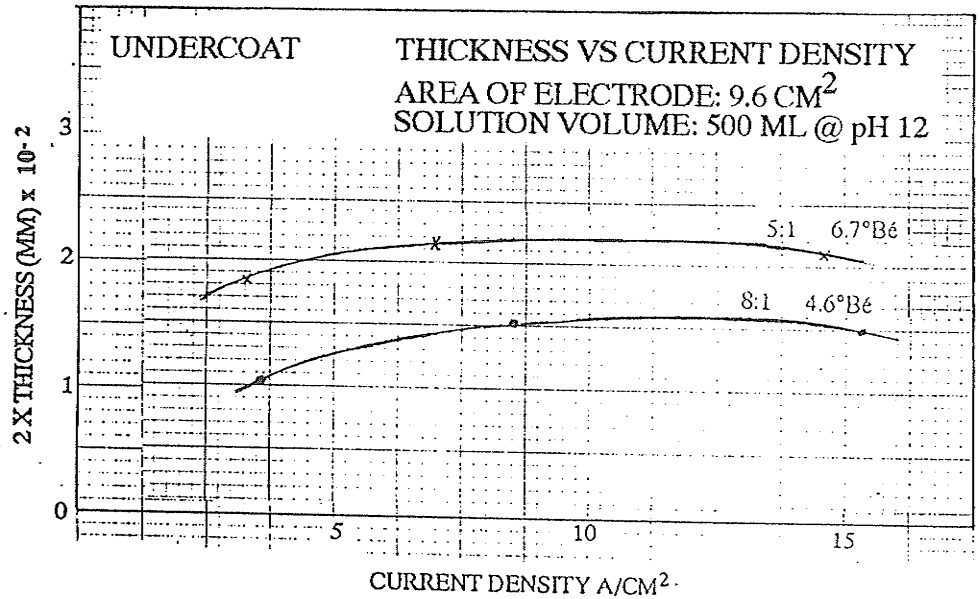


Figure 8 UNDERCOAT
THICKNESS VS CURRENT DENSITY

that the greater the power input the shorter the processing time. Each point represents a separate test. The higher the current density, the higher the applied potential to maintain the current density level, and the shorter the time required to reach a given thickness.

Figure 7 shows the Applied Voltage vs Thickness of deposit for Undercoat solutions of varying Baumé readings. The time of the applied voltage was kept constant at 2 minutes. It is evident that deposition at over 300 volts gives the most rapid buildup of surface thickness (measured with a micrometer). Dilution down to 12:1 gave a Baumé reading of 3.5°, and still gave satisfactory results when the voltage was increased to 325 volts. The higher the solution concentration the less time was needed to reach a given coating thickness.

Figure 8 shows Thickness vs Current Density with various Undercoat solution concentrations. Additional tests were run which confirmed the form of the graphs as shown for 4.6° and 6.7° Bé. Each point on the graph represents a separate plating out from separate solutions. Note that a maximum thickness is obtained and does not increase with increased current density. That is, the thickness of the deposit is independent of the current density when the potential reaches the limiting value. The reason is due to the build-up of Al_2O_3 on the aluminum and then the silicate coating following on top of the Al_2O_3 creates a resistance to the passage of current at any given voltage. The temperature variations for this graph were +2°,-3° C from 25°C, room temperature.

Similarly, Figure 9 shows the results obtained at the limiting voltages on a plot of Potential vs Time at constant current densities in an Undercoat solution volume of 500 ml at readings of 4.6° Baumé (white) and 6.7° Baumé (black). Each point was a separate test. The rise in temperature per curve was 20°C for the longer curves down to 15°C for the shorter ones, from 25°C room temperature.

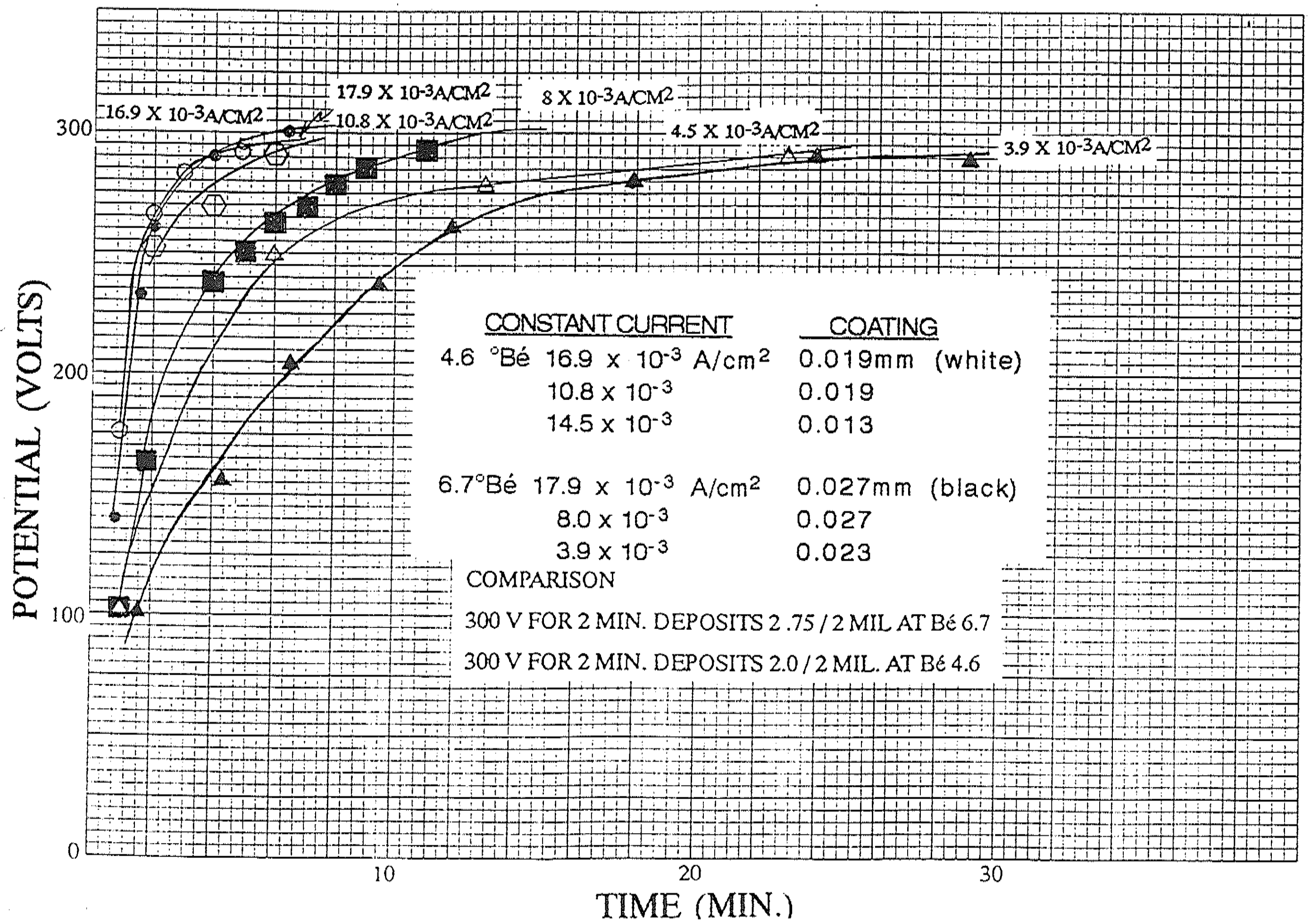


Figure 9 UNDERCOAT
POTENTIAL VS TIME AT CONSTANT CURRENTS

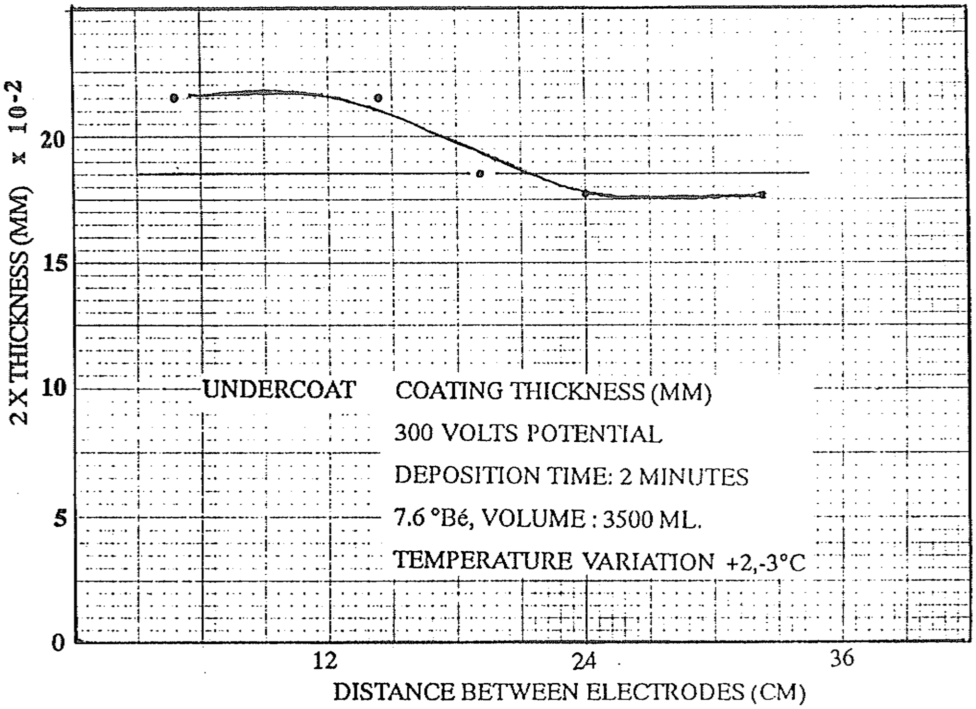


Figure 10 UNDERCOAT
THICKNESS VS DISTANCE BETWEEN ELECTRODES

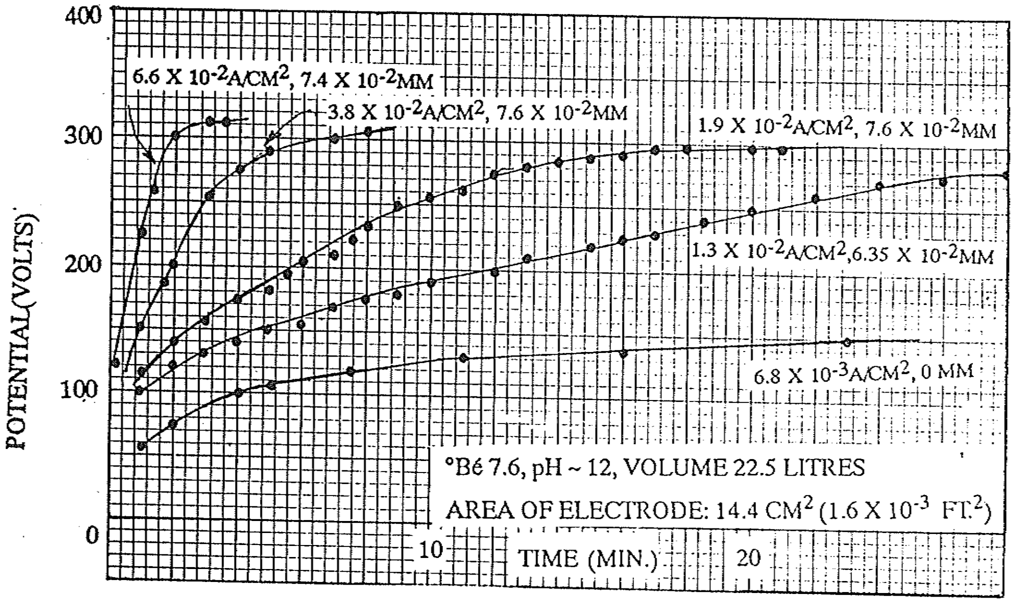


Figure 11 UNDERCOAT
POTENTIAL VS TIME @ CONSTANT CURRENTS

Figure 10 shows a plot of Coating Thickness vs Distance between electrodes at 300 volts potential in a 7.6° Bé Undercoat solution. The volume of the bath was 3500 ml. Deposition time was 2 minutes per reading. The coating thickness applied during a two minute run lowers slightly with the distance between the electrodes.

Figure 11 Potential vs Time at constant current densities in an Undercoat solution volume of 22.5 litres shows the limiting values reached. The pH was approximately 12 and the density 7.6° Baumé. This plot again confirms that the thickness of deposit is independent of the current density when the potential reaches the limiting value.

Figure 12 shows the Undercoat variation of Coating Thickness vs Time for various potentials. The solution volume was 22.5 litres at 7.4° Baumé. The temperature was 25°C,-0,+2°, essentially at constant temperature. Each point represents a separate test. The area of the electrode was 14.8 cm^2 x 0.037 cm. It is evident from the straight lines of this graph that the thickness of deposit is easier to control via the applied voltage rather than by control of the current which tends to decrease as the surface layer resistance builds up. It should be noted that while not shown, all lines on Figure 12 would go through the origin at zero time, and be brought up to the respective voltages immediately after the first 10 seconds ramping of the current.

The difference between Figure 9 and Figure 11 may be due to the temperature effect in 500 ml solution volume (15°-20°C rise) compared to the negligible temperature rise in 22.5 litres of solution (0°C to 1°C) for the data in Figure 11.

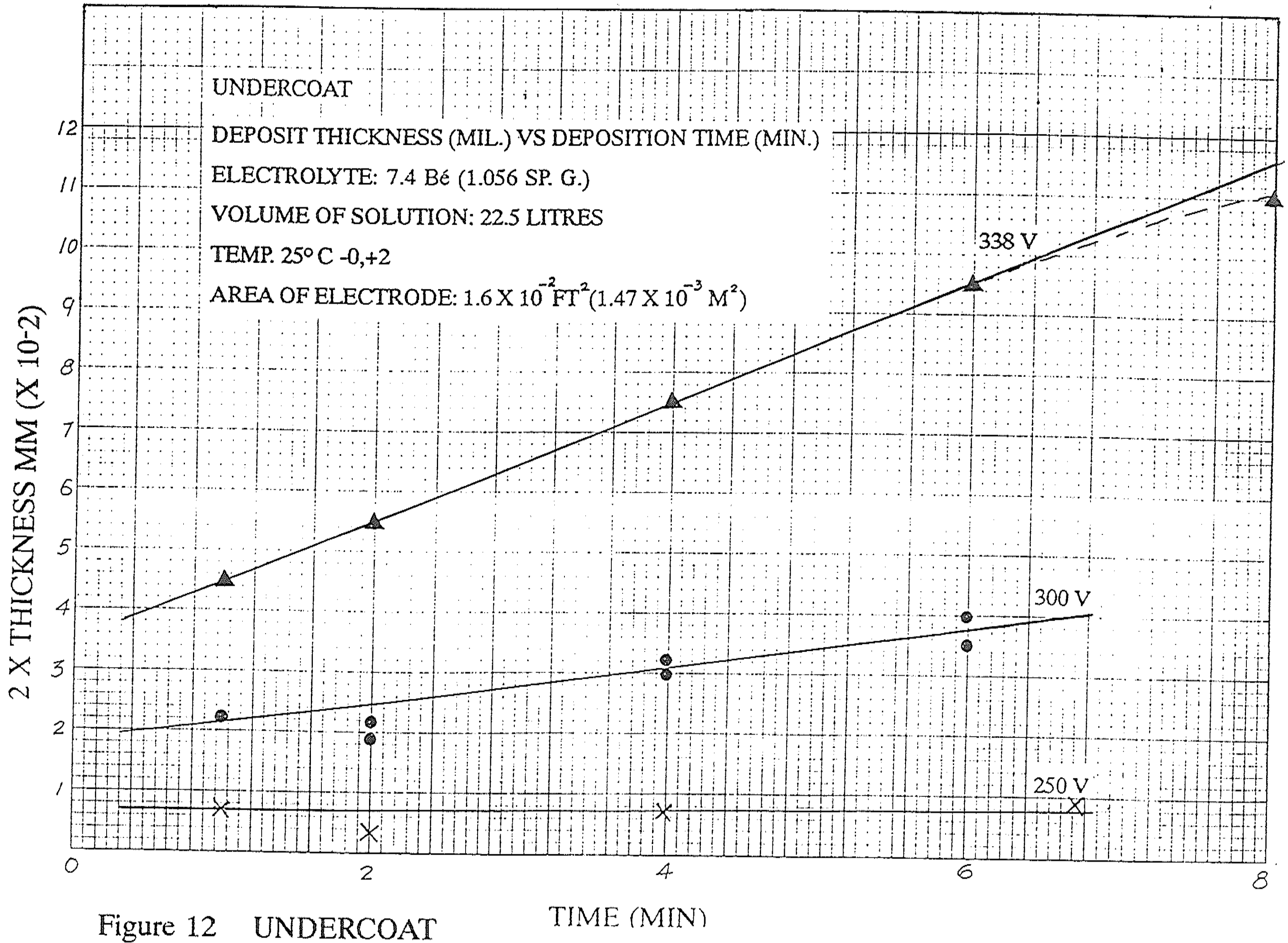


Figure 12 UNDERCOAT
EFFECT OF POTENTIAL ON THICKNESS VS TIME

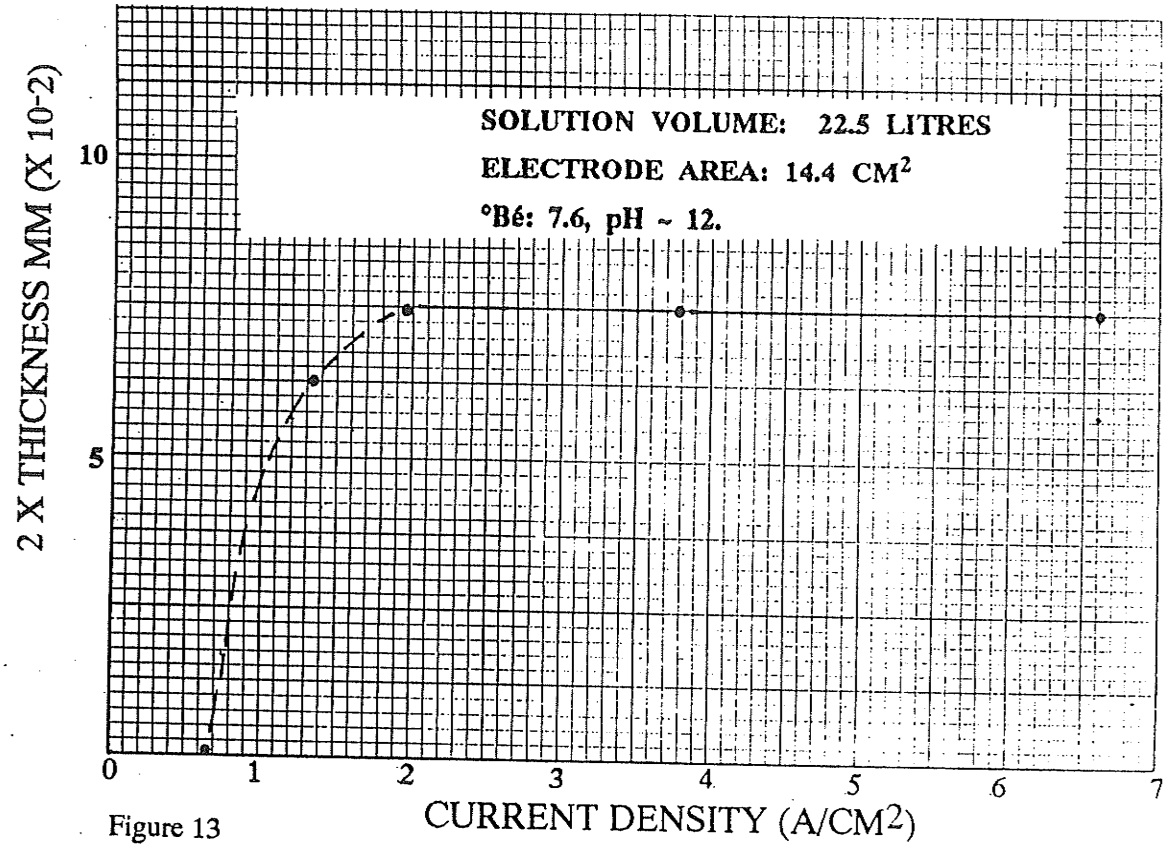


Figure 13

UNDERCOAT: THICKNESS VS CURRENT DENSITY

Figure 13 Undercoat, Thickness vs Current Density is a replot of the data from Figure 12. This plot confirms that the thickness of deposit is independent of the current density when the potential reaches the limiting value. The plot in Figure 13 does not go through the origin because there is no silicate deposit until the voltage reaches about 200 v with the current density, in this case at 0.65 amperes.

In summary, the Undercoat can be readily obtained in various thicknesses. If damaged, testing showed it was easily healed by repeating the process. The silicadizing electrolyte solutions for the Undercoat were reusable after standing for over a month.

5.2 ADHESION, SALT SPRAY, AND HUMIDITY TESTS

Because the Undercoat surfaces have a somewhat porous structure, similar to the surface of a petrified sponge, botryoidal in structure, as shown in Figure 3, it has been recommended as an undercoat for improving paint adherence to aluminum. Samples prepared for Flyer Industries Ltd. were sent for testing to the Sherwin Williams Paint Company in Chicago. Laboratory tests consisted of a 96-hour humidity (adhesion tested immediately and after 1 hour recovery) and 240-hour 5% salt spray (ASTM.B117).

The Sherwin Williams report comments:

> Uncoated panels with just the Silicadized process performed well in both Salt Spray and Humidity.. . [T]he Humidity test is a good indicator of long term adhesion.

The complete Sherwin Williams report is attached as Appendix C.

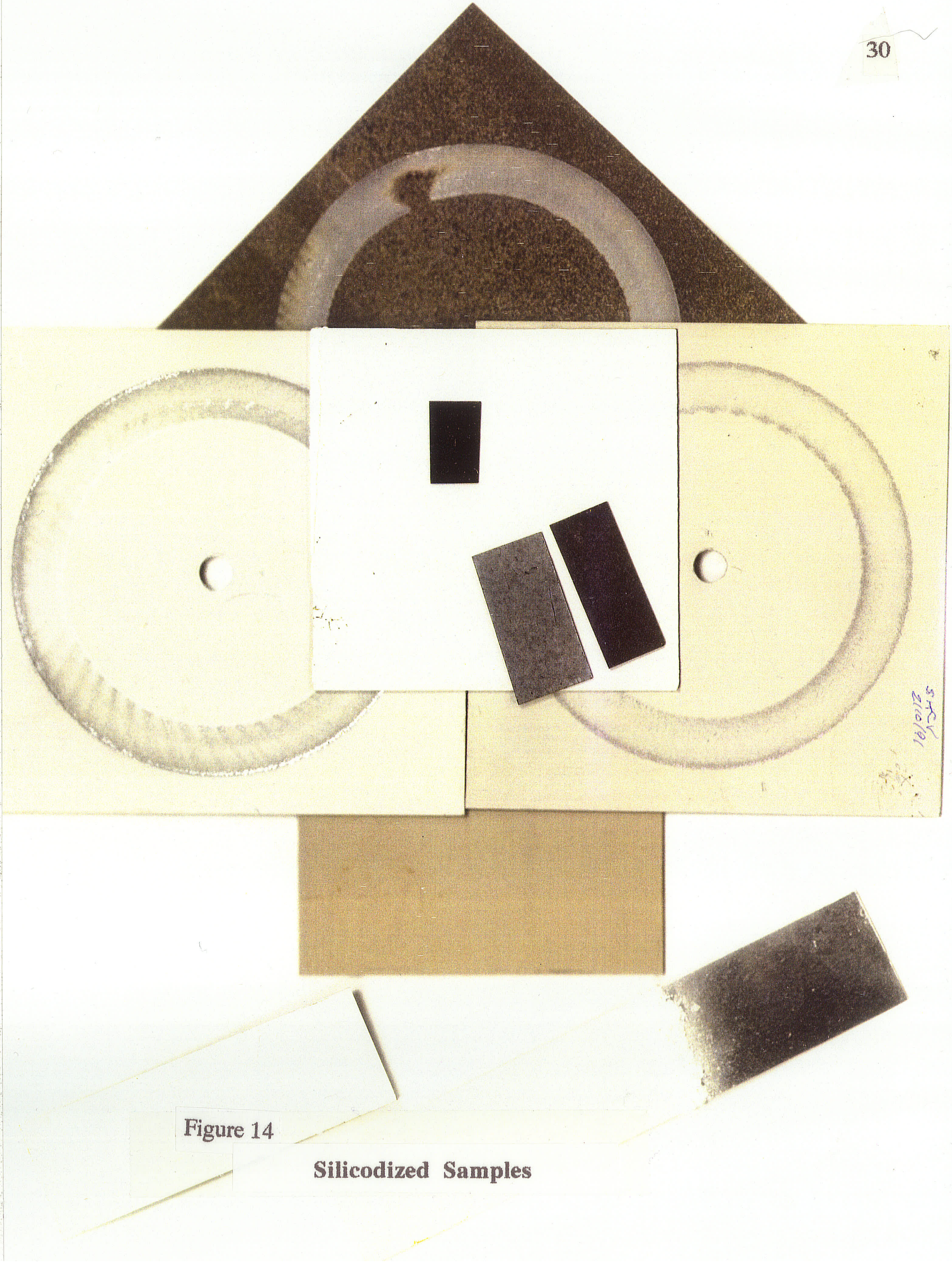


Figure 14

Silicodized Samples

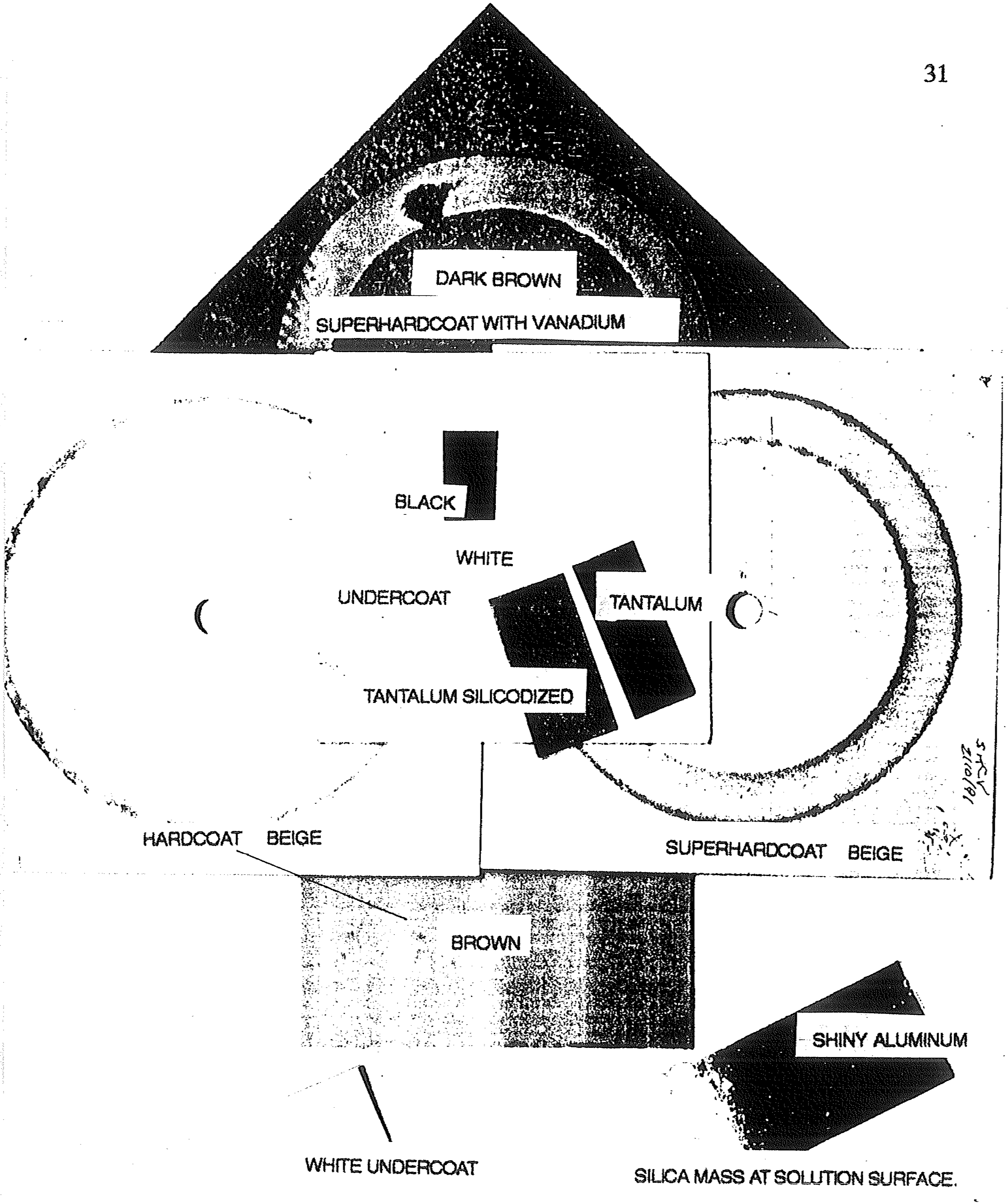


Figure 14A Nomenclature Code to Samples

On request, aluminum sample plaques (#2024 and #6061-T6)(7.5 x 15 x 1.5 mm) from a Minneapolis company were Undercoat silicadized with a coating of 0.025/2 thickness, and returned to the company, where they were tested. The salt spray tests were run to meet ASTM B-117 specifications for 336 hours at 95°C (a double run), with a loss in weight of 0.01 g. All tests passed military standards. The samples were silicadized for 7.5 minutes and had fine hard deposits. The test report is attached as Appendix D.

Three Undercoat silicadized plaques (#3003-H14) having the dimensions 75 x 100 mm x 0.51 mm (3 x 4 x 0.020 inches) were immersed in distilled water (pH 7) for eight days at a temperature of 75°C to check for solubility weight loss. (Meta and orthosilicates are reported to be soluble in both cold and hot water).[16] The average data follows:

Table 1: Solubility

Initial weight of 3 Al. plaques	30.973 g	Average weight: 10.324 g
Final weight after silicadizing	31.301 g (dried)	Average weight: 10.434 g
Weight after immersion and drying	31.206 g	Average weight: 10.402 g
Plate weight (coating)	0.328 g	Average weight: 0.110 g
Weight of plate loss	0.095 g	Average weight: 0.032 g
Percent loss	0.032/0.110=28.8%	

Drying of the plaques was by forced dry air at 54 linear meters per minute at 30°C for a day.

A further solution test was undertaken wherein 7/10 of sample plaque #13, Undercoat, which had participated in the above test, was again immersed in distilled water for 25 days at a room temperature of 25°C. The weight before immersion was 7.787 g and the weight on removal from the water and after drying in the air stream described above, was 7.788 g. The reason for the difference between the two tests is that the first test removed all that was soluble from the silicate (28.8%), leaving 71.2% as insoluble under the test conditions.

This result is interesting in that it shows some water solubility when in 100% total immersion. The salt spray test showed less than 1% loss, while the Florida weather test (see below) had very little loss experienced after six months exposure. Both of these tests were as plated without a water wash following plating. (Rather, there was no water wash following plating in our laboratory and no water wash has been confirmed for the Florida exposure. The ASTM salt test does not require prewashing of the test plaque.)

5.3 CORROSION TESTS

Three aluminum plaques (#3003-H14) 75 x 100 x 0.508 mm having average weight 10.340 g were silicadized with Undercoat (coating thickness averaged 0.0127 mm), and were then immersed in sulphuric acid (pH 2.8-3.8) for eight days at a temperature of 75°C.

Table 2: Solubility in H_2SO_4

Average silicadized weight	10.429 g
After acid treatment, weight	10.397 g
Average weight loss	0.032 g per plaque after drying

The average weight loss was 26 x 10^{-5} $mg/mm^2/day$.

Drying was by forced air at 75°C for one day. Silicadizing aluminum provides considerable protection from the effects of acid solutions. On the same surface area and time basis as above, aluminum alloy 3004 H14 without silicadizing (Figure A3, Appendix A) had a weight loss of 0.0505 g.

Three Undercoated silicadized plaques (3003-H14), sized as above, were immersed in NaOH (pH 10.8-11.7) for a period of ten days, after which the measured weight increase of the aluminum and coating averaged 4.5%. This weight gain was caused by considerable corrosion as both the silicadized coating and the base aluminum metal were attacked by NaOH. There was a loss of the integrity of the aluminum panel as holes appeared through the silicadized layer.

In both the above alkali and humidity tests there was one plaque excluded from the data. These plaques were "burnt" when the silicadizing voltage passed the stage where small scintillations cover the anode (in the electrolyte) as the deposit developed. As the voltage increased, larger scintillations appeared until there occurred a progressive line of heavier illumination, which most often ran in curves. The heavy sparking occurred at the next stage as the voltage was further increased. This process is described below under Section 9. The result left heavier concrete-like, dome-shaped accretions on the surface where the sparking occurred. In the alkali test the result of the NaOH immersion on this plaque with "concretions" caused a gain of 11.8% in weight due to excessive corrosion, while in the humidity test the burnt plaque showed a loss of 0.97%, and since both these weight changes are well outside the average of the related tested plaques, these figures have not been included in the results given above. Both plaques had been dried in an air stream, as above. These data on alkali testing are not surprising as silica, silicon dioxide and aluminum are reported to be soluble or subject to corrosion in high pH solutions.[17]

5.4 WEATHERING TESTS

Ten test plaques (#3003-H14)(75 x 100 x 0.508 mm) of the Undercoat were sent to Florida in October 1991 for weathering effects on silicadized aluminum over a six months period. The plaques went to Florida in October 1991 and were mounted outside. The Florida sun and rain would cause expansion and contraction of the plaques and give a measure of the adhesion of the coatings under environmental conditions. In April 1992 they were weighed on receipt in Winnipeg and the results showed an average loss of weight of 0.005 g per plaque which averaged 10.44 g. As these samples were handled several times after reaching Florida and were returned interleaved with paper in a light cardboard container which showed evidence of crushing, it may be that some of the slight loss in weight may not have been due to environmental conditions, but to handling. The globular silicate surface of the Undercoat is softer than the Hardcoat surface, and consequently more subject to damage. It is, however, this condition that serves to grab and hold paint when applied. The appearance of the samples was the same as when they left, except for one which had what appeared to be a brownish water stain.

5.5 HARDCOAT, SUPER HARDCOAT AND DECORATIVE COAT

The recipe for the Hardcoat was in two parts, for example:

A: 1700 ml H_2O distilled
400 ml K_2SiO_3 (30° Bé)
45 g Na_2O_2, and

B: 30 ml CH_3COOH (concentrated)
180 ml H_2O distilled

First mix solution A, wherein the Na_2O_2 is added slowly, in small quantities with constant stirring, "so that free oxygen will not escape." Next, B is slowly added while the bath is stirred. The fully mixed bath is then tested for pH and adjusted with the peroxide and acid to achieve a pH of 12. The bath should then be allowed to stand for 24 hours, and again adjusted to 4° Baumé, and a pH of 12.

The Super Hardcoat also has two parts; the first part A, is the same as the Hardcoat above, while the B part has changed quantities as follows:

B: 30 ml CH_3COOH concentrated
20 ml H_2O distilled

To prepare the solution, slowly pour solution B into A while stirring. The well stirred bath is allowed to rest for one hour. Then "3-6 g of Na_2O_2" is to be added with stirring. The adjustments after this are the same as for Hardcoat.

Initial solutions for Hardcoat and for Super Hardcoat were prepared in accordance with manuals supplied by the clients. Adjustments were necessary to reach the recommended Baumé readings for the Super Hardcoat. This was done by the addition of distilled water and acetic acid as recommended. Smooth coatings were obtained at pH 12 and around 5°Bé. Coloured coatings were obtained by the addition of 5 g vanadium oxide per litre of solution. The more vanadium oxide that is added, the darker the colour in developing beige, brown and black decorative coatings.

Unlike the Undercoat solutions, the solutions for Hardcoat/Decorative coat were found to be unstable. By comparison, the Undercoat solutions were reusable after standing for more than a month. Hardcoat and Super Hardcoat solutions gave clear solutions and good deposits as long as the temperature did not rise over 60°C. Beyond this temperature cloudy solutions developed, resulting in "burnt" deposits. (For "burnt" see Scintillations, Section 8.) All prepared baths, irrespective of whether they were clear or cloudy, precipitated within two days even before adding acetic acid. The addition of Na_2O_2 as recommended, made the solutions unstable. Attempts to stabilize the bath using 20 g Na_2O_2 rather than 45 g as indicated in the procedure for Hardcoat resulted in stability for more than a week, but the deposits were inferior--uneven and friable. A run with 30 g Na_2O_2 remained clear for about three weeks, then a precipitate formed. It is known that silicate solutions absorb CO_2 from the atmosphere, and while precautions were taken to prevent this while the solutions were not being used, a precipitate of Na_2CO_3, could have occurred(Reference 1). Generally the precipitates returned to solution on the addition of NaOH, indicating the precipitate was likely Na_2SiO_3.

Stable baths were obtained by changing the Hardcoat formula to the following:

1400 ml H_2O
400 ml K_2SiO_3 30°Bé.
20-25 g Na_2O_2

The bath was mixed as before to achieve a 9° Baumé solution. The bath was formed by letting it work with a normal cathode and aluminum anode for about one hour at 50% of the normal initial current (about 4 amperes). Stable baths were achieved.

In using the Hardcoat the Baumé readings changed from day to day. The cause was traced to the obvious loss, on electrolysis, of hydrogen and oxygen as components of the water solvent. This loss during electrolysis, combined with the evaporation due to the high temperature of the anode and thus the solution (over 80°C), means that the solution was becoming more concentrated with use. The effect on plating was as follows and as illustrated in Figure 15:

Table 3: Hardcoat, Solution Losses during Silicadizing

ph	°Bé	Time (min)	Voltage	Day 1 (mil)	Day 2	Day 3
13	5.0	2	250	0.00125		
		10		0.03		
	5.4	2	250		0.005	
		10			0.0125	
	6.0	2	190			0.013
		10				0.021

Figure 15 shows Hardcoat, Thickness vs Time with the results obtained two and three days after preparing the bath, using various voltages. The solution was made up of 1400 ml H_2O plus 100 ml K_2SiO_3 plus 20 g of Na_2O_2 which was diluted to 4000 ml to obtain the desired 5° Baumé density. The pH was > 13.

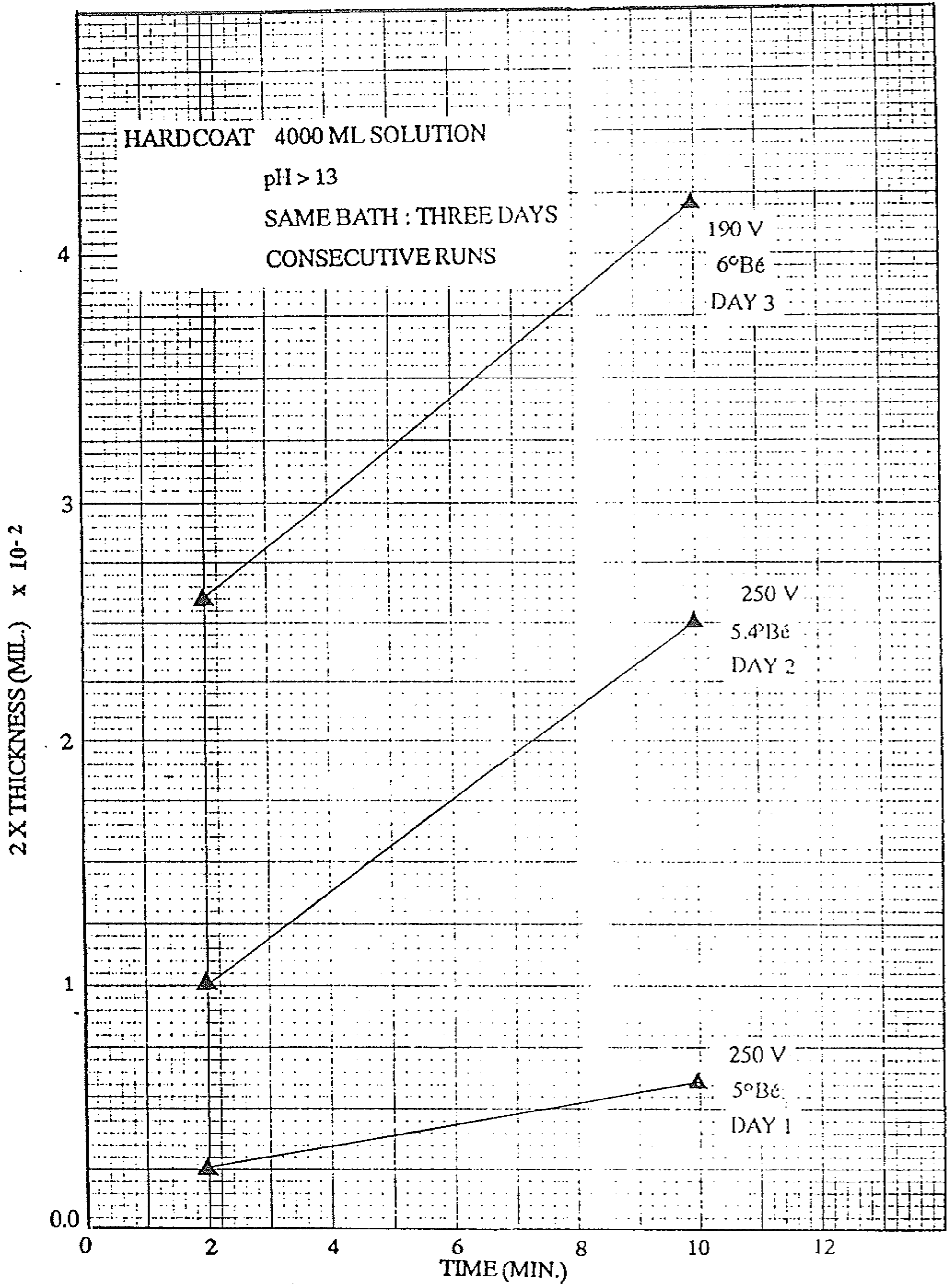


Figure 15 HARDCOAT
THICKNESS VS TIME

To ascertain if these anomalous conditions carried over to Super Hardcoat, additional tests were run. Figure 16 shows a graph of Thickness vs Time for Super Hardcoat at a voltage of 250 volts for different solution densities on three consecutive days. The 250 volts was at or just above the sparking voltage where scintillations appear on the anode, which, in general, appeared to coincide with the deposition of silicate on the anode. To be more exact, the procedure was to ramp the voltage to 50+ volts for 10 seconds and then to 250 volts for the number of minutes listed. Initially the amperage would rise to about 10 amperes and fall off as the voltage went to 250 volts.

Table 4: Super Hardcoat, Solution Losses during Silicadizing

Day	Volume (ml)	°Bé	pH	Time (min)	Thickness	Temp. change
1	3150	7.4	11.9	2	0.015/2	23-30°C
				10	0.015/2	30-40°C
	3385	6.1	11.4	2	0.005/2	35-37°C
				10	0.005/2	34-36°C
2	3385	6.1	11.4	2	0.008/2	
				10	0.008/2	
3	3385	6.1	11.4	2	0.005/2	
				7	0.005/2	
				10	0.005/2	
				15	0.005/2	
	5200	5.6	11.4	2	0.003/2	33-39°C
				10	0.005/2	33-39°C
				15	0.005/2	33-39°C

Figure 17 on Super Hardcoat, Coating Thickness vs Time for Super Hardcoat at a constant potential of 300 volts, shows very unusual results from experiments carried out two days after preparation of the bath. The 4000 ml bath was prepared at 5° Baumé and step-wise diluted to 6000 ml with deionized water to give the other Baumé readings to the final 2° Baumé solution. Two possible explanations for this unusual behaviour follow.

The increase in Baumé readings from day to day, as stated above, is due to hydrogen and oxygen being liberated at the electrodes and to evaporation. In a manner anomalous to the normal Faraday process, the gas production increases as the voltage increases (amperage decreases). (The possibility of an anomaly to Faraday's law has been pointed out before by Palit[18] in several interesting papers wherein he reported "electron glow," with both hydrogen and oxygen being given off from both electrodes in liberal quantities yielding up to 500% over that expected on the basis of Faraday's Laws).

Tests were run on aging of the solution alone to ascertain whether chemical conditions within the solution, such as polymerization, could change the density of the solution. Aged solutions of known density were used, and also fresh solutions in capped bottles. Two of nine Baumé tests follow for Undercoat: (solution: 80 ml of K_2SiO_3/litre of H_2O, deionized). The room temperature was constant as indicated during the tests. The aged solution was Hardcoat: (solution: 200 ml K_2SiO_3 /700 ml H_2O, 10.7 Na_2O_2, formed one hour), pH 12.8, 8.5°Bé. No change in density under these conditions was evident.

Table 5: Specific Gravity Tests

Fresh Solution		Aged Solution (1991/11/01)	
Date 1990/05/01	Reading @ 28°C 2°B	Date 1991/04/25	Reading @ 30°C 9.3°B
05/03	2.1	04/27	9.4
05/07	2.2	05/03	9.4
05/14	2.2	05/07	9.2
05/17	2.1	05/17	9.2

Viscosity tests were also run using a Fisher #100-52 Viscosimeter tube:

Table 6: Viscosity Tests

Undercoat#1, 22° C Time (14.2°Bé)	Undercoat #2, 22° C Time (10.7°Bé)	Super Hardcoat, 22° C Time (10.7°Bé)
94.5 sec.	81.8 sec.	91.1 sec.
94.8	82.0	90.7
94.9	82.4	90.5
94.9	82.8	89.1
94.5	82.8	89.0
94.4		89.3

Twelve other tests for viscosity change were run also without sufficient variation to indicate a composition change.

Iler[19] mentions the effects of organic compounds on solubility:

> Broadly speaking, organic compounds can either retard dissolution by covering the silica surface with a strongly sorbed film or accelerate dissolution by removing the soluble $Si(OH)_4$ that is in equilibrium with the surface by converting it to a soluble complex.

The condition shown in Figure 17 only happened once out of over twenty Hardcoat/Super Hardcoat tests. It may be that the suggestion from Iler accounts for the variance observed; in any case it is evident that further work is needed to stabilize the Super Hardcoat for commercial use.

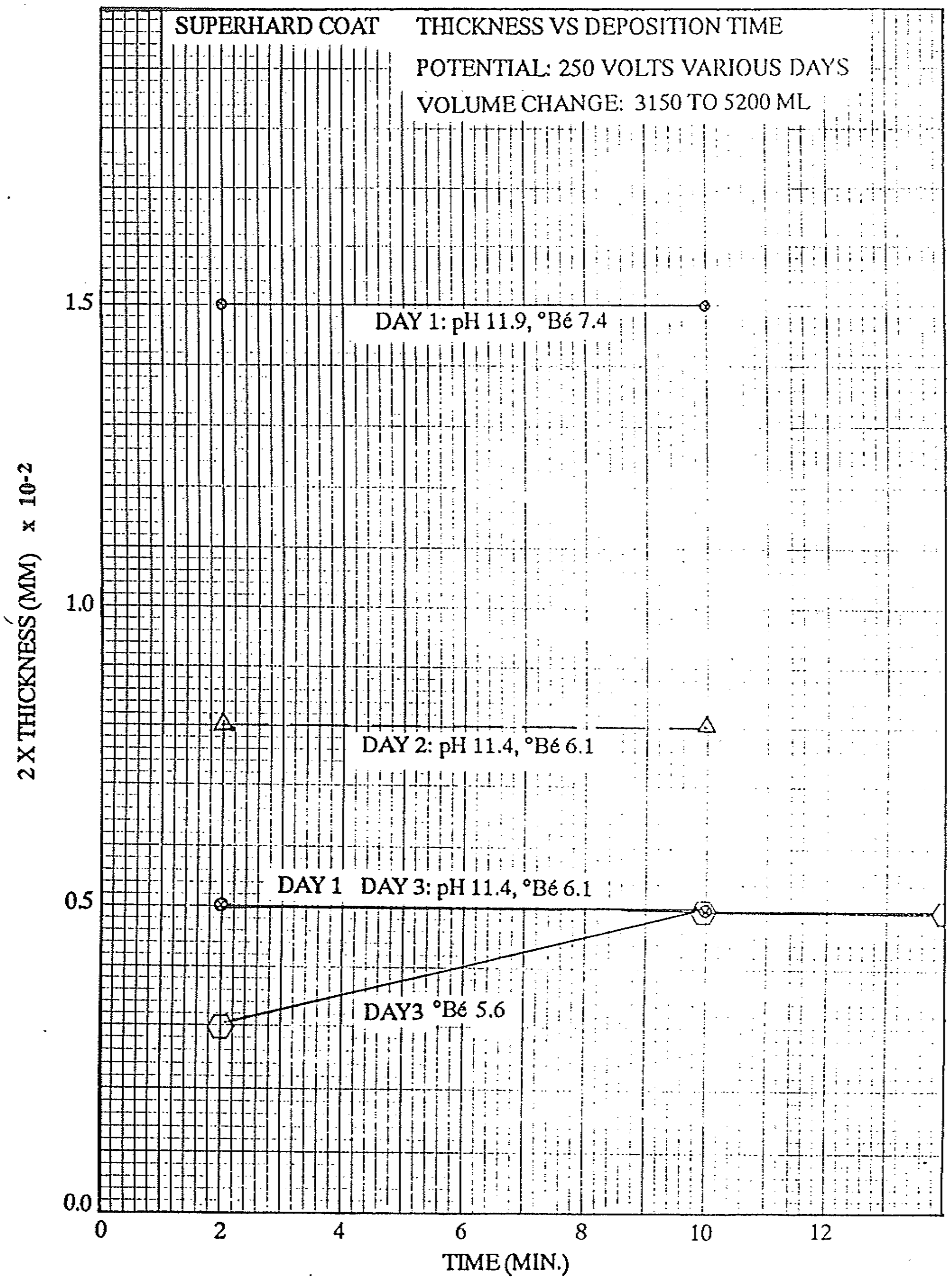


Figure 16 SUPER HARDCOAT
THICKNESS VS DEPOSITION TIME

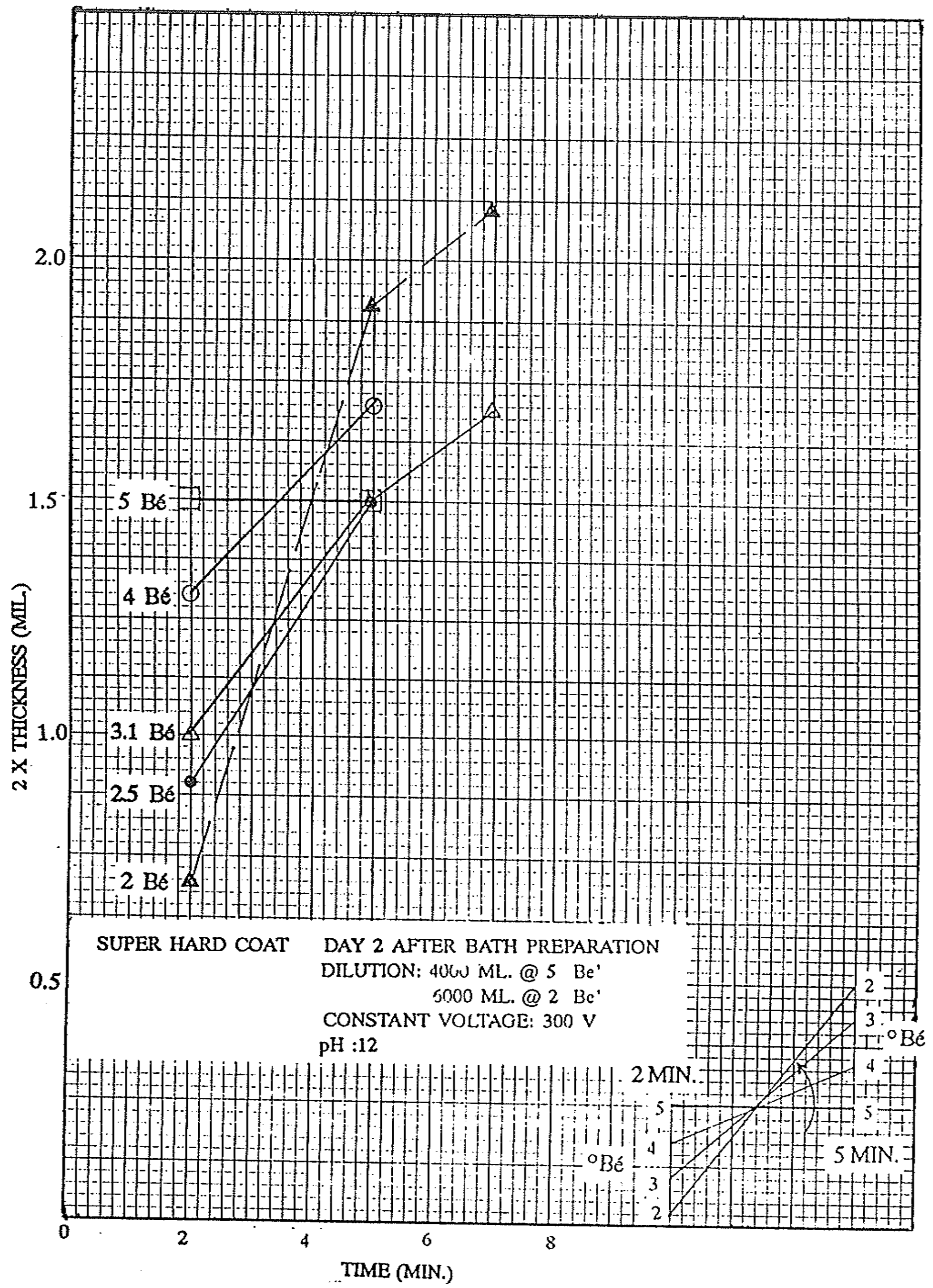


Figure 17 SUPER HARDCOAT

THICKNESS VS DEPOSITION TIME

6.0 COATING ANALYSES

An important aspect of success in securing satisfactory coatings is the condition of the substrate. Most aluminum sheets were silicadized directly without prior cleaning. The abrasion tests which follow were on aluminum that was etched in KOH before silicadizing. A condition not readily evident has to do with porosity. Porosity is covered more fully in Section 8.0 Castings.

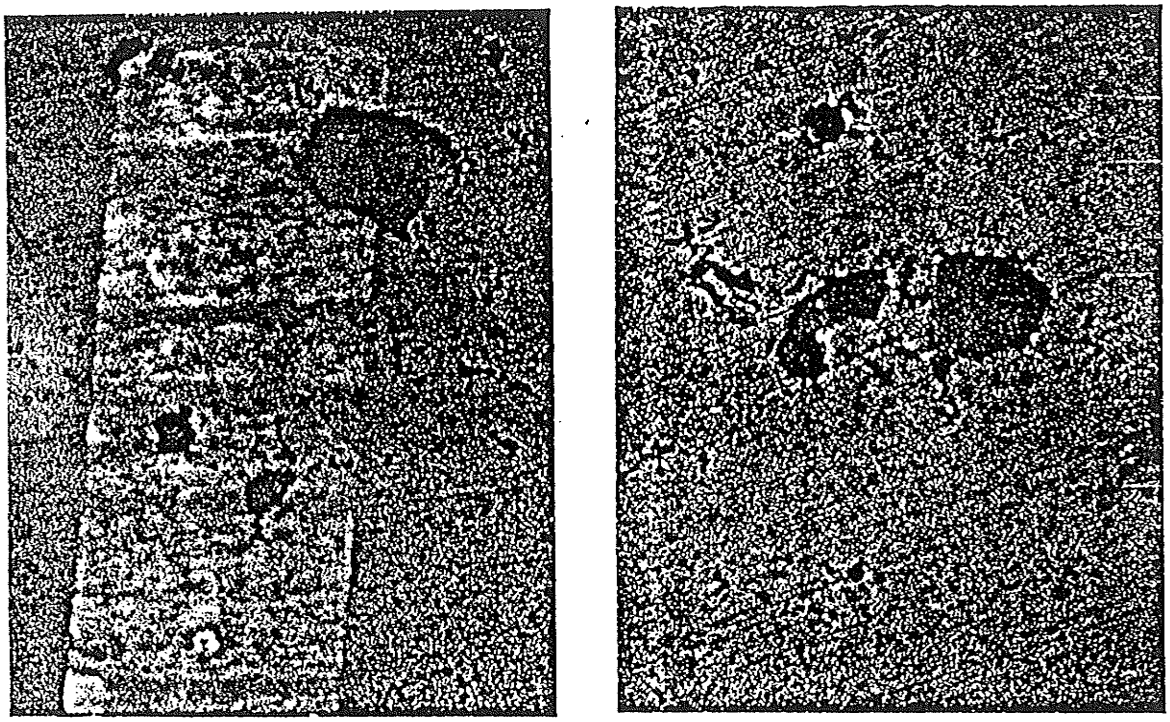


Figure 18 **CAVITIES IN COMPUTER CASTINGS**

SEM MICROGRAPHS OF SURFACE

6.1 COMPOSITION

Figure 3B entitled "A Cross Section of the Undercoat" shows the silicadized layer over a layer of aluminum oxide on the aluminum substrate, surrounded by the Bakelite matrix material used to hold the specimen while grinding and polishing the specimen.

Initial tests to analyze the Undercoat were undertaken using a Joel JXA840 Scanning Electron Microscope to obtain back scattering electron images (BSE) of the Undercoat silicadized surface (Figure 19). The related analyses are shown in Figure 21 and are summarized as follows:

Table 7: Summary of EDS from Figure 21 by JOEL JX840 SEM

wt % Al	wt % Si	wt % K	wt % Ca
8.99	76.86	12.81	1.34

The calcium came from the Kasil 88. The factory confirmed 10-12 ppm as standard, but not listed in the company literature.

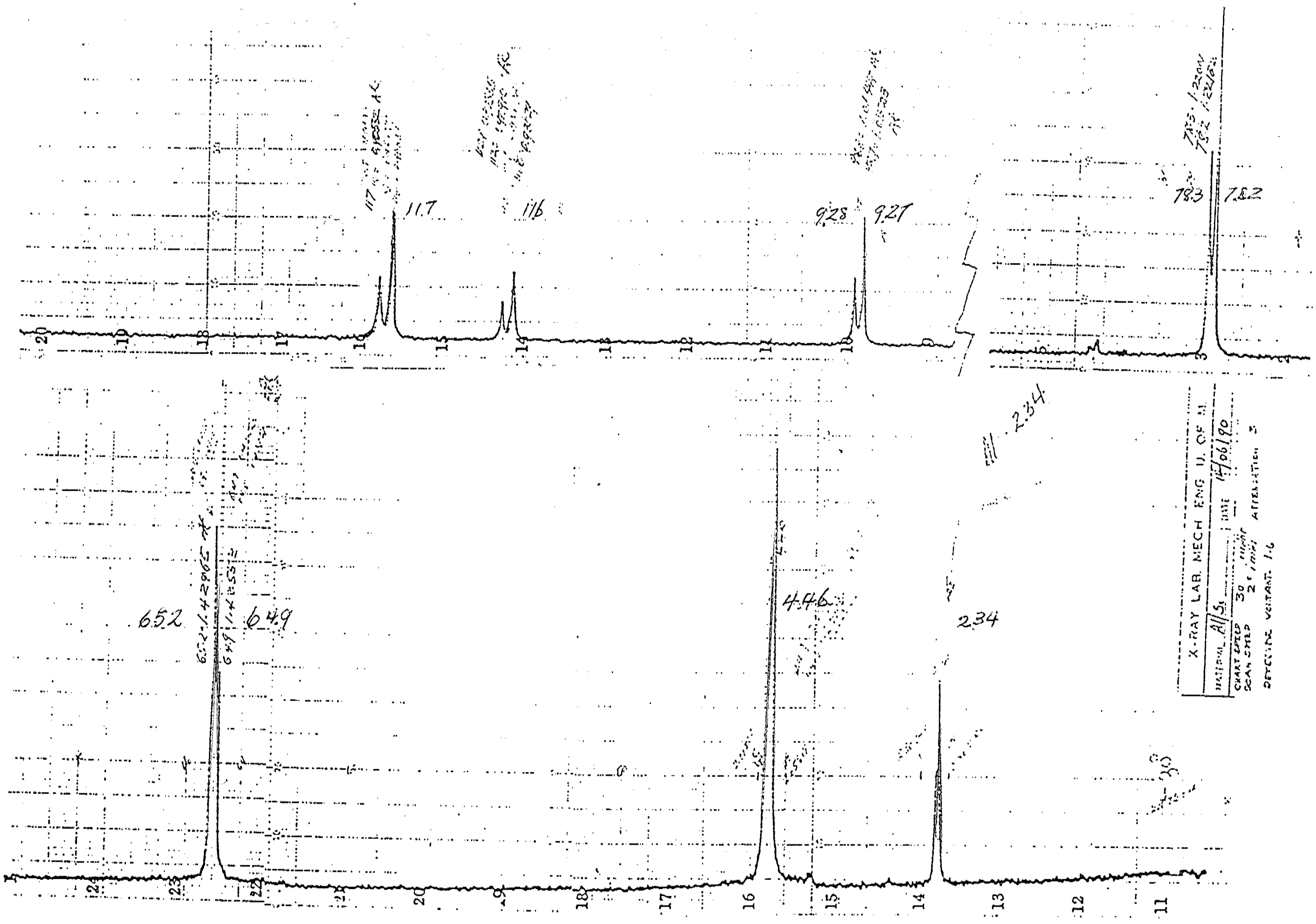


Figure 20

X-RAY ANALYSIS OF SILICADIZED COATING ON ALUMINUM BY PHILIPS X-RAY SPECTROMETER MATCHED TO A PHILIPS CHART RECORDER SHOWING PEAKS FOR ALUMINUM, BUT NO EVIDENCE OF CRYSTALLINE SILICA

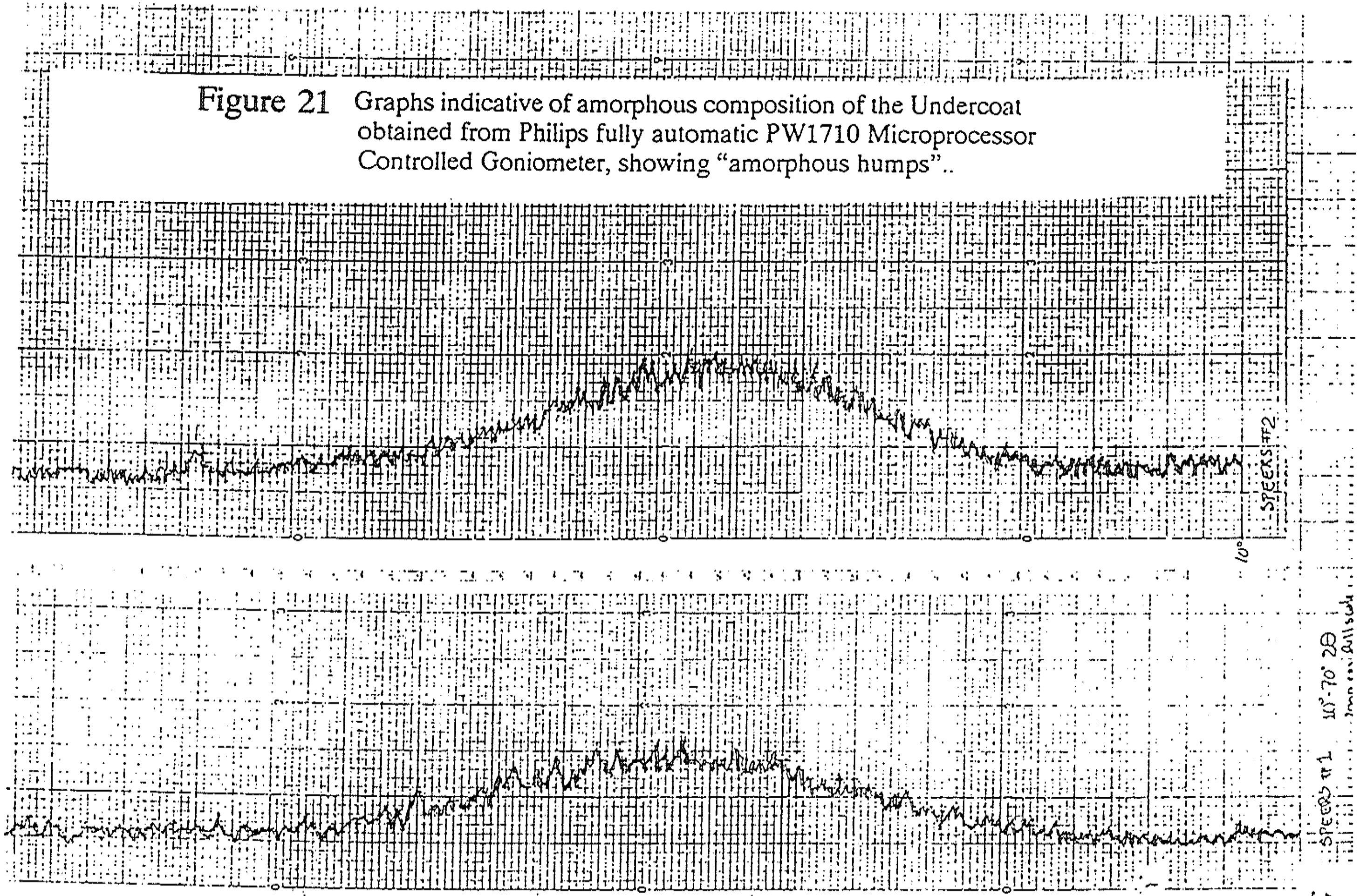


Figure 21 Graphs indicative of amorphous composition of the Undercoat obtained from Philips fully automatic PW1710 Microprocessor Controlled Goniometer, showing "amorphous humps"..

Figure 21

X-ray analysis by Philips X-ray Diffractometer matched to a Philips chart recorder showed peaks for aluminum, which were assumed to be from the base aluminum. There was no evidence of crystalline SiO_2, an indication that the silicadizing coating is most likely amorphous, or may have micro crystallite particles (Figure 20).

A study of two samples of the Undercoat surface using a Philips fully automated PW1710 Microprocessor Controlled Goniometer showed the very diffuse and weak peaks indicative of an amorphous composition (Figure 21).

A study was undertaken on scrapings from the silicadized aluminum surface which were put through a 325-mesh screen, then encapsulated in a 5 mm glass capillary and placed in the centre of a Philips Debye-Sher camera. Then, using X-ray analysis, two samples were measured twice. The results showed diffused rings and the readings obtained could not be identified through the Fang and Bloss reference, or through the Department of Geology Computer Library, University of Manitoba, reinforcing the evidence of the plated surface being amorphous or having only a very small degree of crystallinity.

Analysis by electron probe by back-scattered electrons and by reflection on a similar sample, showed confirmation of the Si, Al, and K peaks with a few percent Na. Figure 22 shows the surface under scanning electron probe by back-scattered electrons (BSE) where the medium to dark areas are mainly Al or Al/Si mixtures with K, while the bright area is due to Si with a few percent of Al and K, while under reflection the bright areas are Al with a few percent Si, and the darkest areas are Si with a few percent K.

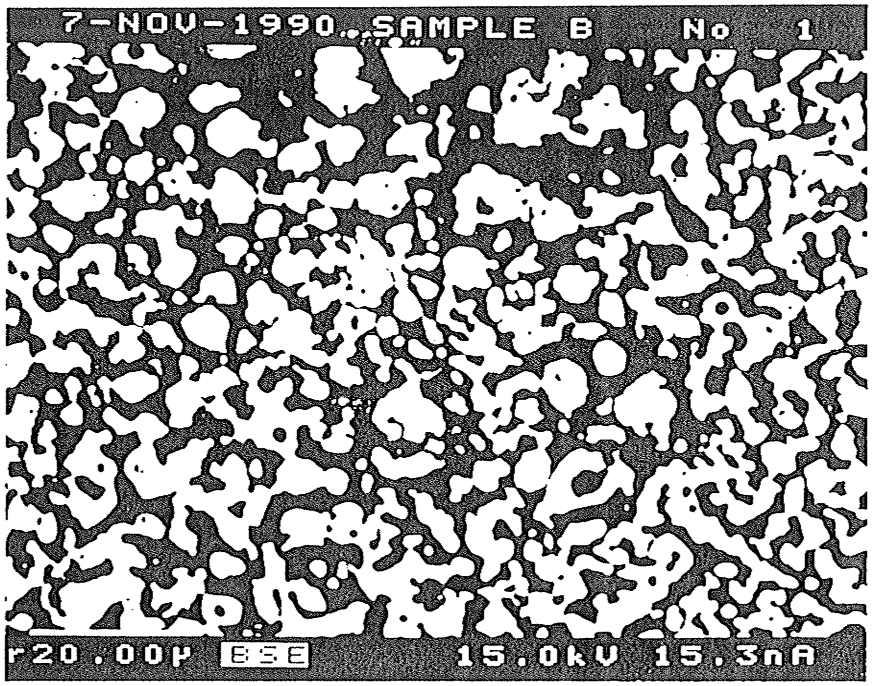


Figure 22 UNDERCOAT

SEM PROBE STUDY OF SILICADIZED COATING

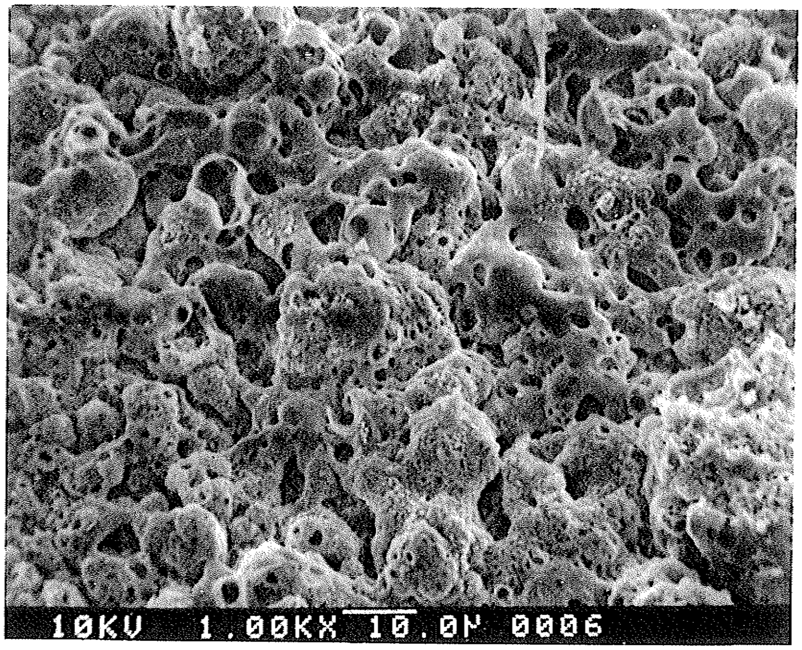


Figure 23 **UNDERCOAT (1000X)**

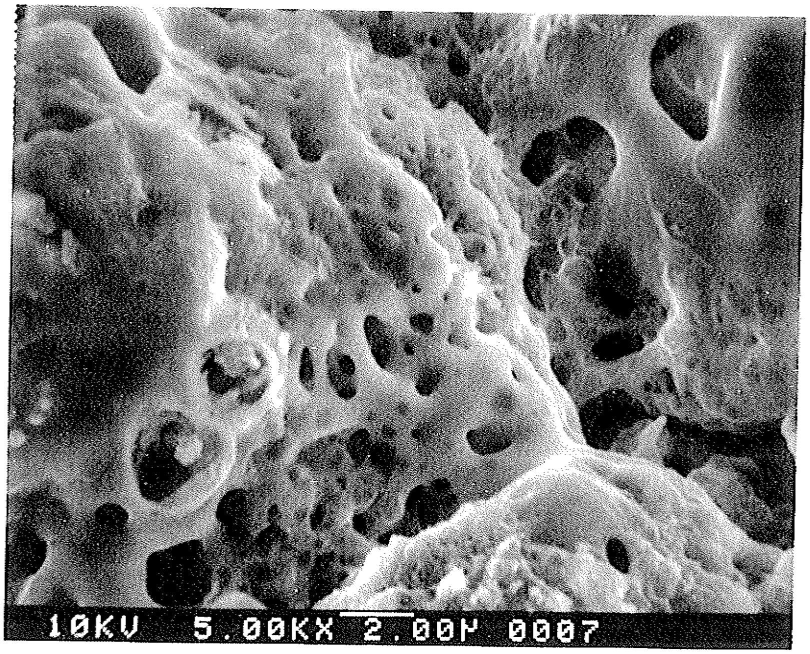
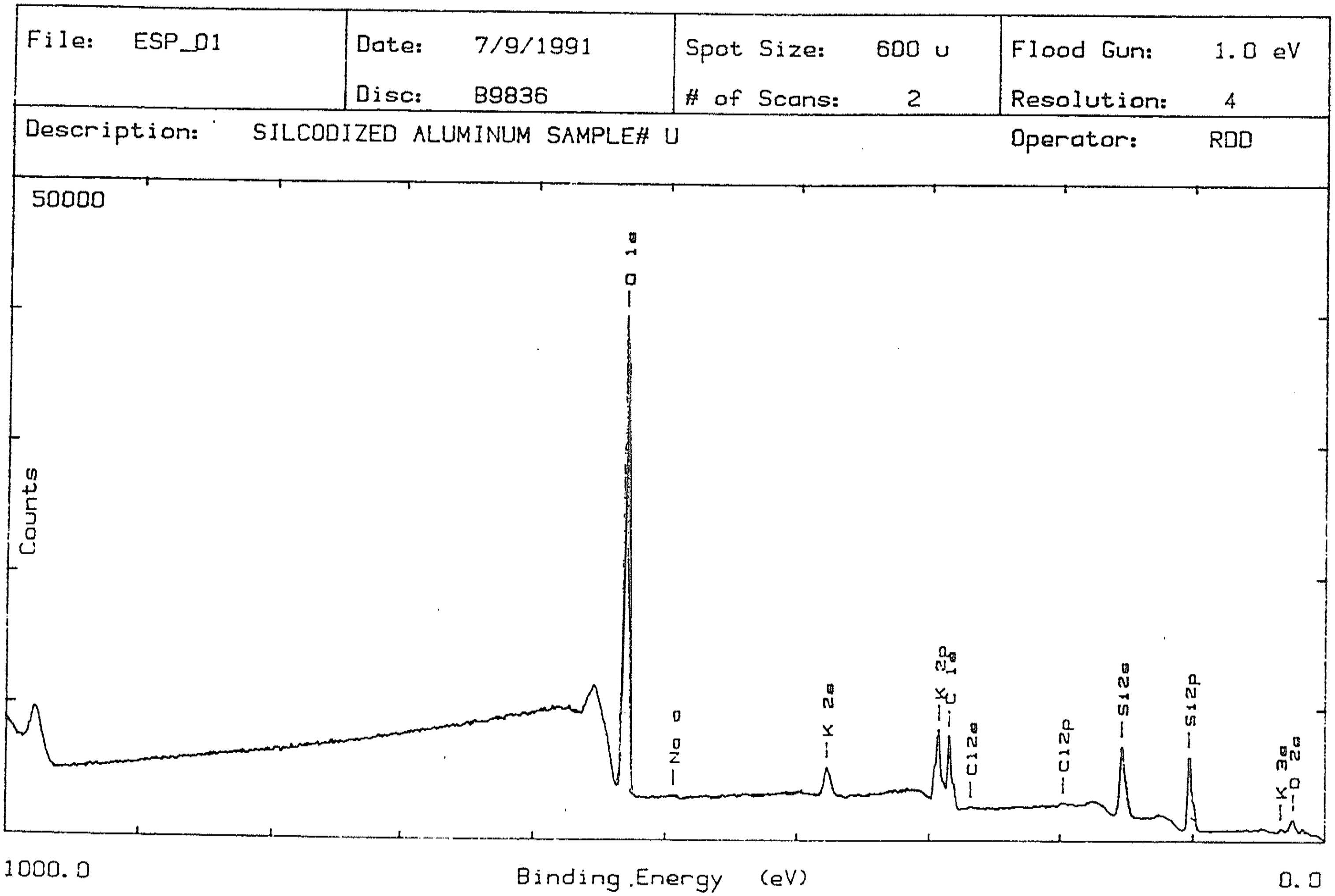


Figure 24 **UNDERCOAT (5000X)**

SEM MICROGRAPH OF SURFACE



File: ESP_01	Date: 7/9/1991 Disc: B9836	Spot Size: 600 u # of Scans: 2	Flood Gun: 1.0 eV Resolution: 4
Description: SILCODIZED ALUMINUM SAMPLE# U			Operator: RDD

SURFACE SCIENCE WESTERN

Figure 25 UNDERCOAT
X-RAY PHOTOELECTRON
SPECTROSCOPY SURVEY SPECTRA.

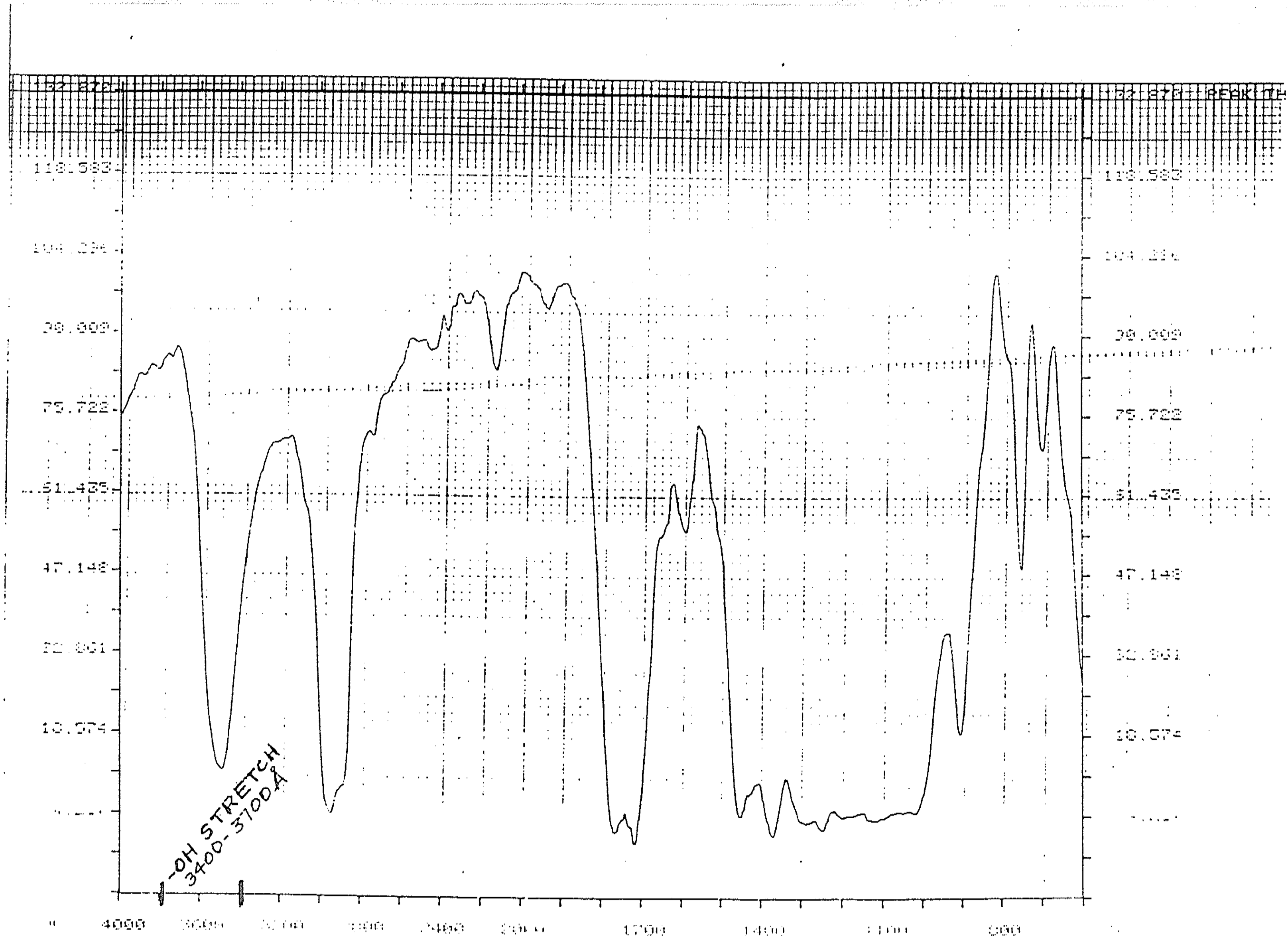
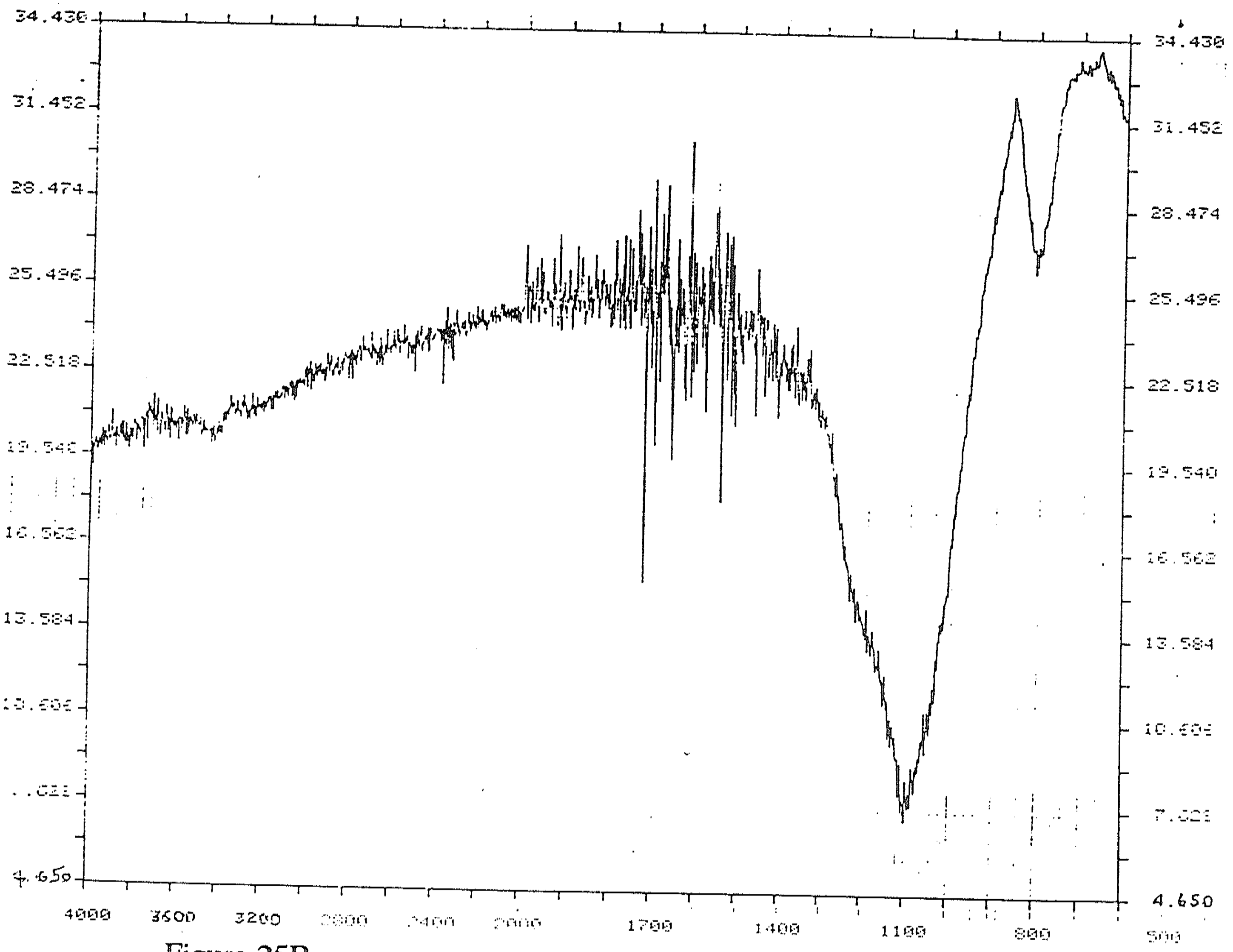


Figure 25A

INFRARED SPECTRA BEFORE DEHYDRATION



```
PEAK THRESHOLD =
          CM-1

        3423.0
        2501.0
        2370.0
        2325.0
        1984.0
        1961.0
        1937.0
        1924.0
        1917.0
        1905.0
        1892.0
        1877.0
        1864.0
        1849.0
        1832.0
        1805.0
        1797.0
        1784.0
        1776.0
        1772.0
        1760.0
        1750.0
        1739.0
        1734.0
        1721.0
        1717.0
        1713.0
        1708.0
        1697.0
        1687.0
        1681.0
        1670.0
        1657.0
        [illegible]
        [illegible]
        [illegible]
```

Figure 25B

INFRARED SPECTRA AFTER DEHYDRATION

Further analyses of the surfaces were undertaken at the Surface Science Laboratory, The University of Western Ontario. Referring to Figures 23 and 24 which show SEM micrographs of the Undercoat at magnifications of 1000 X and 5000 X, giving views of the surface as plated out (same as Figures 3 and 3A), X-ray Photoelectron Spectroscopy (XPS) was carried out using a modified SSL Model SSX-100 small spot XPS. An Al Kα monochromatized X-ray source focused to a 600 μm spot size was used to survey the spectra. Figure 25 shows the XPS survey spectra for Undercoat. The XPS technique provides elemental information for the outer 5 nm (50Å) of the surface. Note the high count for oxygen in the spectra shown as Figure 25.

Infrared spectroscopy data for silica from Hair,[20] show evidence of low levels of hydration by sharp bands appearing at 3660 and 3540 $cm^{-1.}$ Figure 25A shows the IR spectra of silicate scrapings mounted in KBr, as produced, revealing a band in the -OH stretch region of 3500 to 3700 Angstroms.[21] When the silicate scrapings and the KBr were dehydrated at temperatures to 300°C for 24 hours the IR spectra shows no bands in the -OH stretch region, possibly indicating that heating the silicadized sheets would result in greater resistance to solubility in water (Figure 25B).

From the data up to this point, and in view of the amount of oxygen surrounding and liberated at the anode, it is assumed that the product being deposited is in the form of oxides: Al_2O_3, SiO_2, and possibly K_2O, and Na_2O.

Iler[22] has written:

> There is no evidence of a hydrated silica being crystallized directly from a solution of silica and water. Yet there is the peculiarity that certain hydrates, once formed, exhibit what seems to be a

characteristic solubility, implying that since an equilibrium is reached, silica must pass from solution to the solid phase as well as the reverse. However, the data are conflicting.

Figures 26 and 27 show the surface of the Hardcoat by SEM at 1000 X and a selected spot on the surface enlarged to 5000 X to show sodium-rich crystallites in dendritic form. The survey spectra as determined by X-ray Photoelectron Specroscopy (XPS) is shown in Figure 28.

Figures 29 and 30 show the surface of the Super Hardcoat (SHC) again at 1000 X and at 5000 X by the same SEM techniques as above. Note that the nodules become smaller and close packed as the images go from the Undercoat to the Hardcoat to the Super Hardcoat, and that no crystallites are evident other than those shown in the Undercoat. The size of the globular nodules in the SHC and HCV coatings approximated 3-5 μm. The corresponding SHC survey spectra by XPS is shown in Figure 31.

A further variation of the Hardcoat (HC) is the HCV with vanadium as shown in the SEM Figures 32 and 33. The nodules are even smaller here. In this form there is a colour change from the white-grey to brown and black. The XPS analysis is shown in Figure 34. A summary of the XPS survey spectra from the above silicadized samples is shown in Table 9.

A further study using Scanning Electron Microscopy and Energy Dispersive X-ray (EDX) analysis was undertaken, and the EDX spectra from the corresponding silicadized samples, Hardcoat, Super Hardcoat and Hardcoat with vanadium, each with a particle analysis, are shown in Figures 35, 36, 37, 38, 39, 40 and 41 respectively. The results as shown are fairly uniform in analysis for Undercoat (Figure 35), Hardcoat and Hardcoat (crystals) (Figures 36,and 37), showing high silica peaks, small Al, K/Na, and oxygen peaks. Figure 38, Super Hardcoat, shows a high aluminum peak on the substrate with a small silica peak, while the Figure 39 on a particle of the Super Hardcoat shows in Figure 39 a high silicate peak and a small aluminum peak. Similarly, Figures 40, Super Hardcoat with Vanadium shows a high peak of aluminum in the substrate and small silica, while the particle analysis (Figure 41) shows high silica, with a small aluminum peak. This turn-about in between aluminum and silica in Figures 38 to 41 is believed due to the coating not completely covering the whole substrate, thus revealing high aluminum. The iron shown in the latter is believed to be from the clamp holding the anode which tended to disintegrate in the alkali electrolyte.

Figure 33A shows the "burn" concretions on silicadized aluminum as the effect of too high a voltage applied before coating thickness (i.e. resistance) has built up.

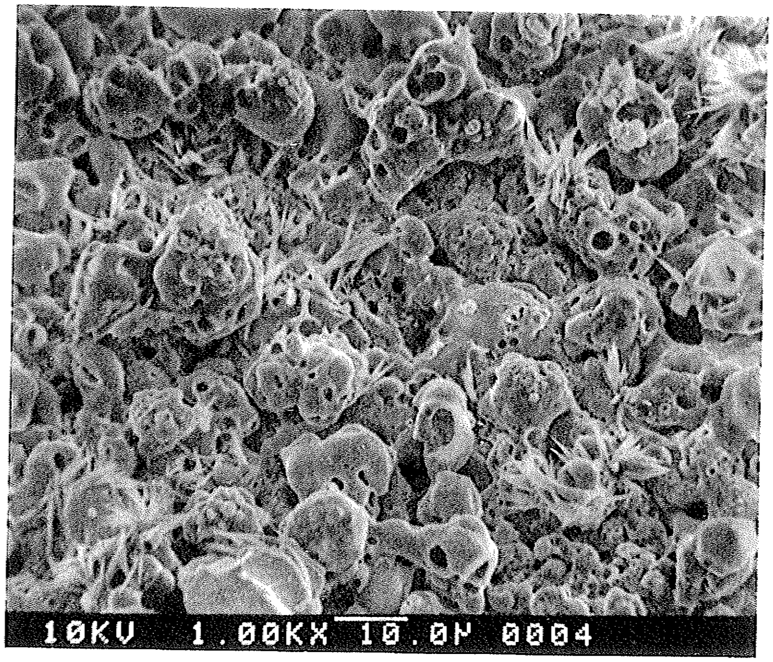


Figure 26
HARDCOAT (1000X)

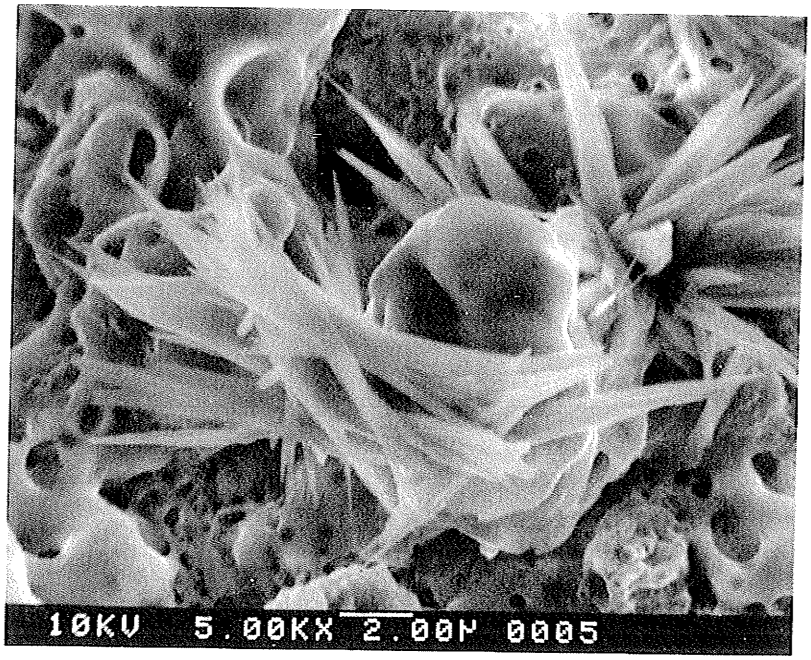
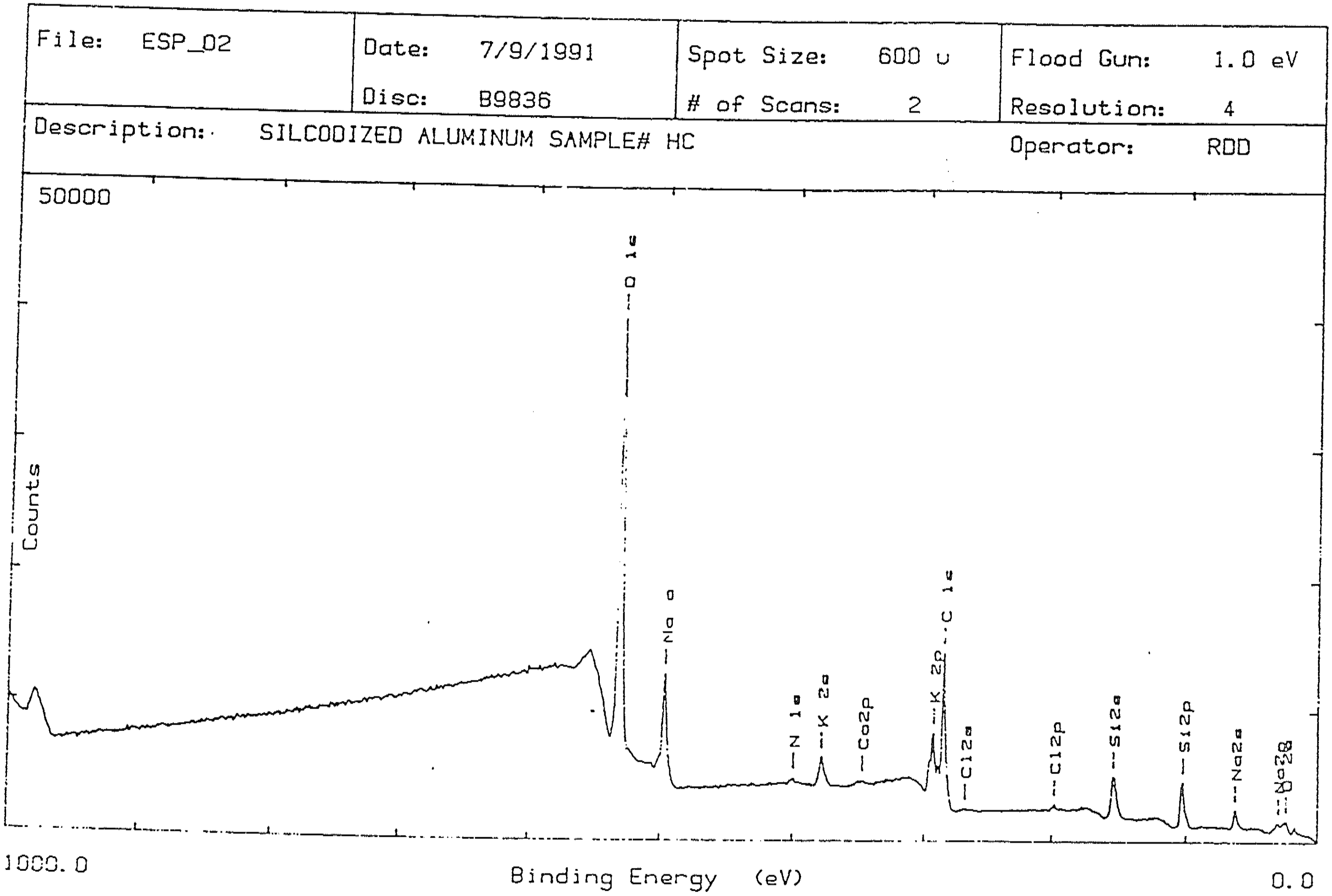


Figure 27 HARDCOAT (5000X) SHOWING SODIUM-RICH CRYSTALLITES

SEM MICROGRAPHS OF SURFACE



File: ESP_02

Date: 7/9/1991

Disc: B9836

Spot Size: 600 u

# of Scans: 2

Flood Gun: 1.0 eV

Resolution: 4

Description: SILCODIZED ALUMINUM SAMPLE# HC

Operator: RDD

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Figure 28 HARDCOAT

X-RAY PHOTOELECTRON
SPECTROSCOPY SURVEY SPECTRA

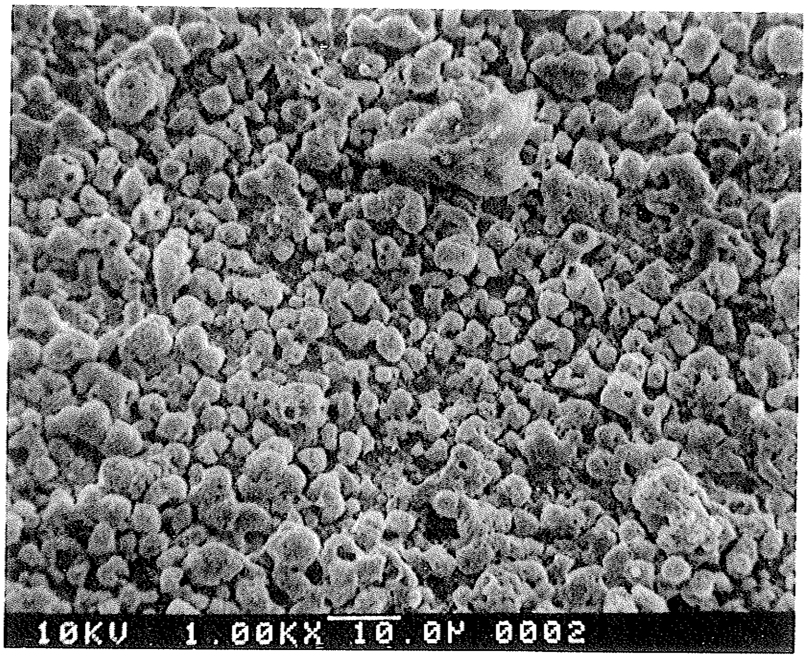


Figure 29 SUPER HARDCOAT (1000X)

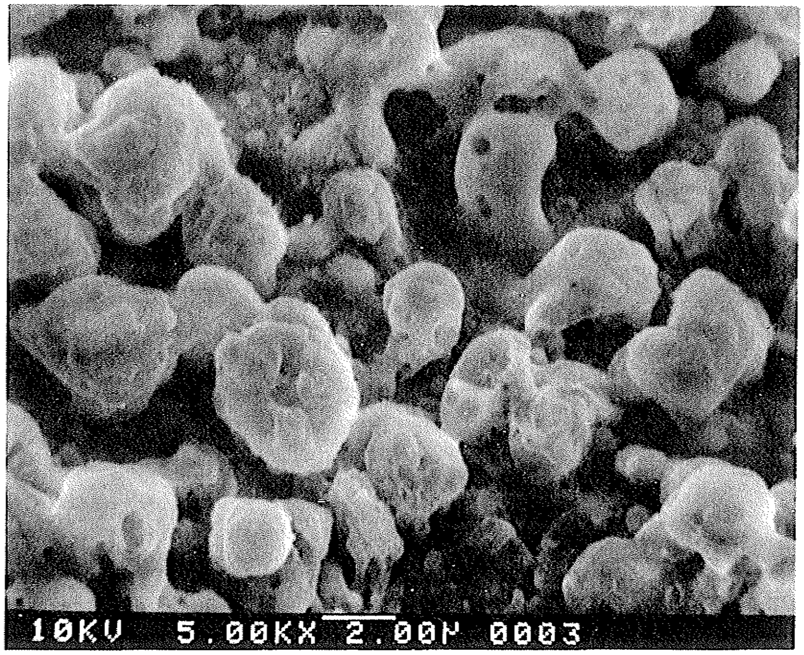
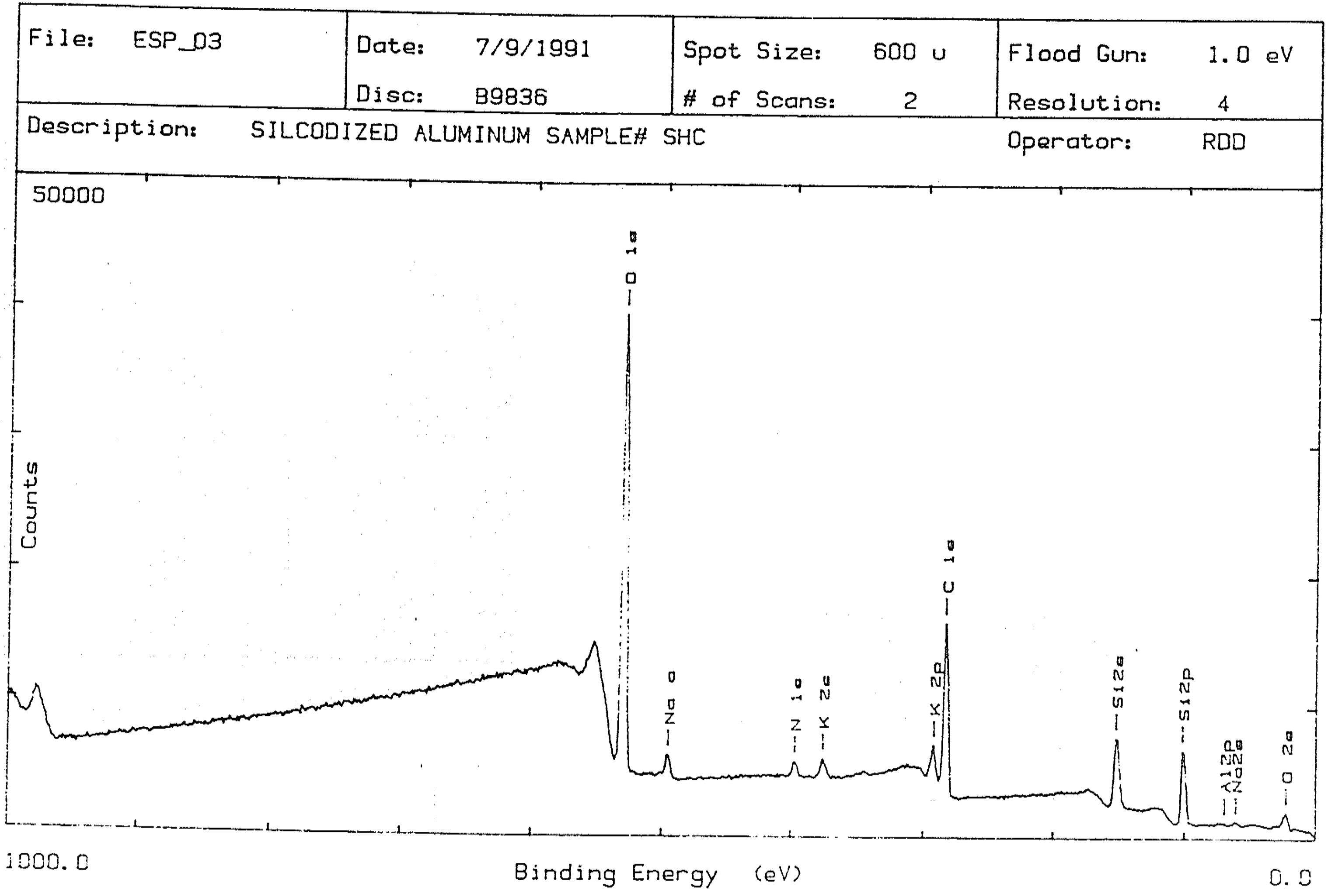


Figure 30 SUPER HARDCOAT (5000X)

SEM MICROGRAPH OF SUPER HARDCOAT SURFACE



File: ESP_03

Date: 7/9/1991

Disc: B9836

Spot Size: 600 u

# of Scans: 2

Flood Gun: 1.0 eV

Resolution: 4

Description: SILCODIZED ALUMINUM SAMPLE# SHC

Operator: RDD

SURFACE SCIENCE WESTERN

Figure 31 SUPER HARDCOAT

X-RAY PHOTOELECTRON
SPECTROSCOPY SURVEY SPECTRA

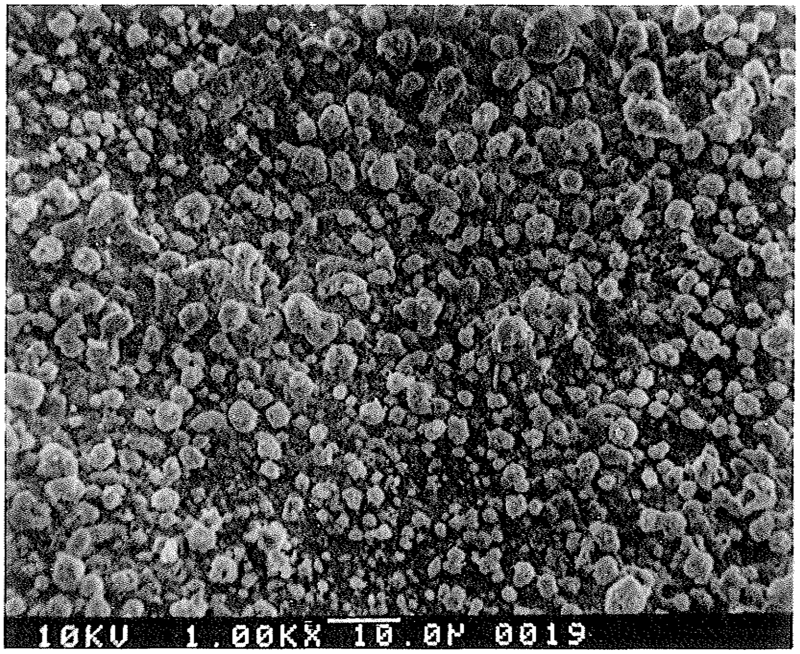


Figure 32 SUPER HARDCOAT WITH VANADIUM (1000X)

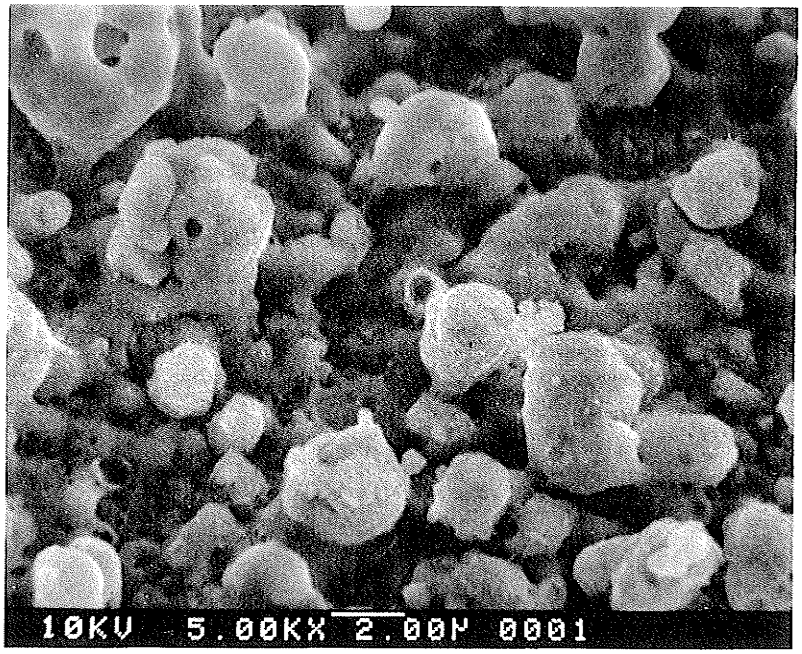


Figure 33 SUPER HARDCOAT WITH VANADIUM (5000X)

SEM MICROGRAPHS OF SURFACE

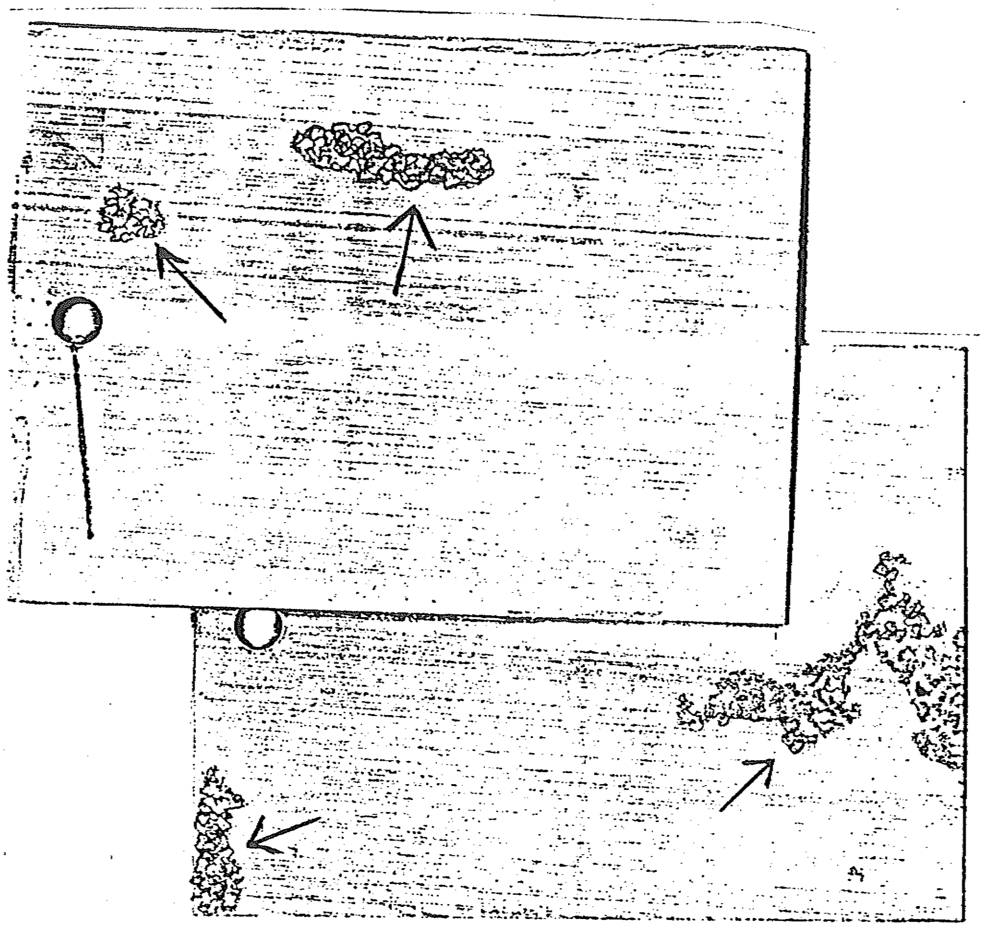
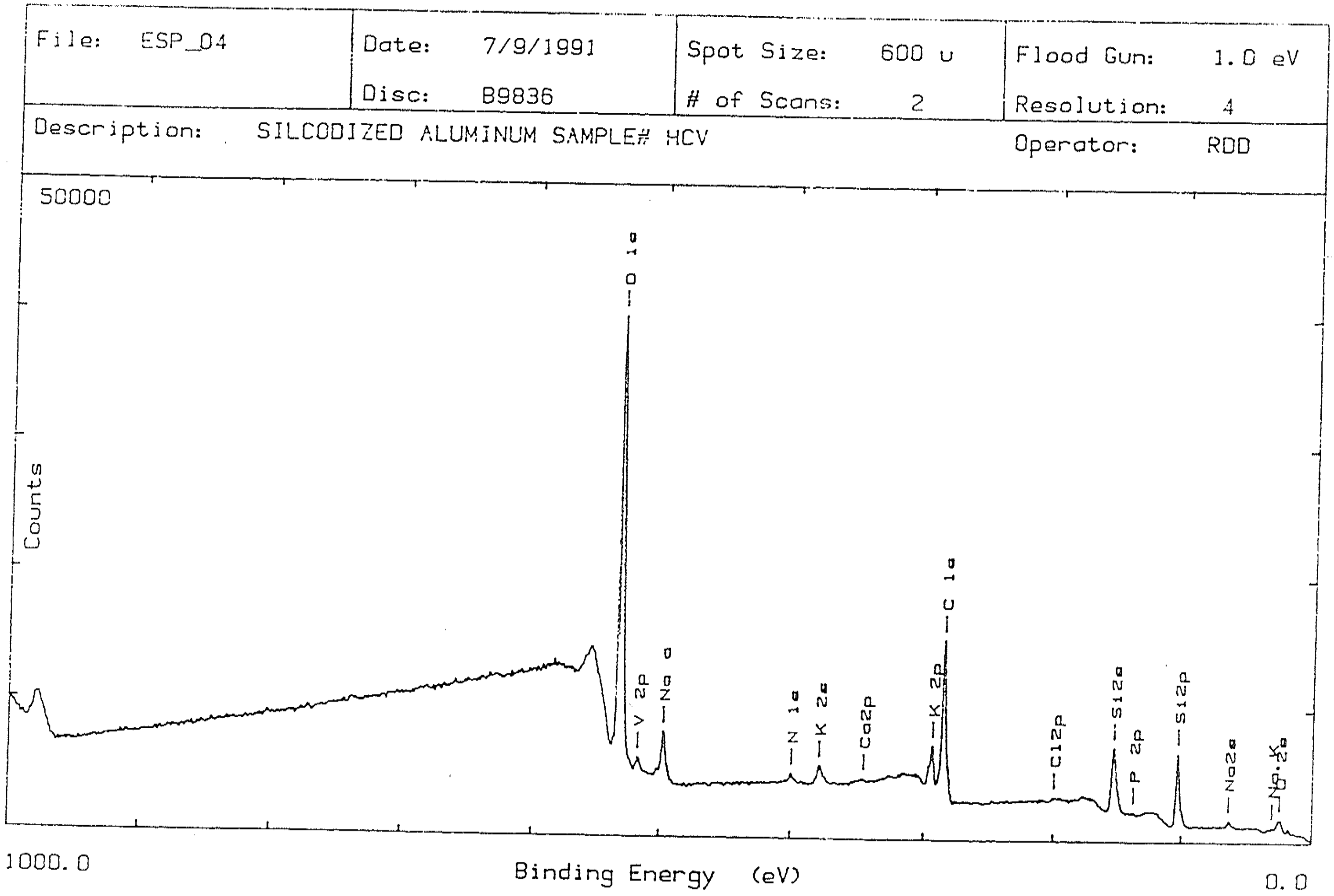


FIGURE 33A

CONCRETIONS SHOWING ON SILICODIZED ALUMINUM DUE TO "BURN " EFFECTS



File: ESP_04

Date: 7/9/1991

Disc: B9836

Spot Size: 600 u

\# of Scans: 2

Flood Gun: 1.0 eV

Resolution: 4

Description: SILCODIZED ALUMINUM SAMPLE# HCV

Operator: RDD

SURFACE SCIENCE WESTERN Figure 34 HARDCOAT WITH VANADIUM

X-RAY PHOTOELECTRON
SPECTROGRAPHY SURVEY SPECTRA

Table 8: Surface Composition (at.%) of Silicadized Coatings

Sample	O	C	Si	K	Na	Cl	Ca	V
U	56.1	13.4	24.6	5.0	0.5	0.4	--	--
HC	46.6	25.5	13.4	3.4	9.9	0.3	0.2	--
SHC	41.1	34.1	17.8	1.8	1.9	--	0.2	--
HCV	42.8	31.9	17.1	1.8	4.5	0.3	0.2	0.3

The **X-RAY PHOTOELECTRON SPECTROSCOPY** provides elemental information for the outer 5 nm of the surface. The **ATOMIC PERCENTAGES OF THE SURFACE COMPOSITIONS** for each sample are shown in the table.

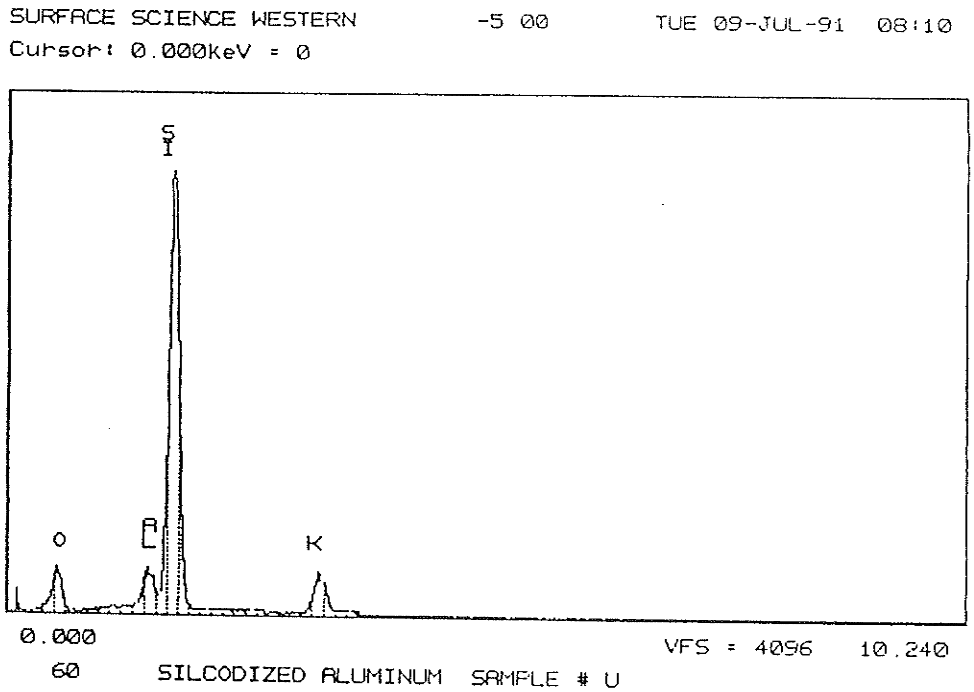
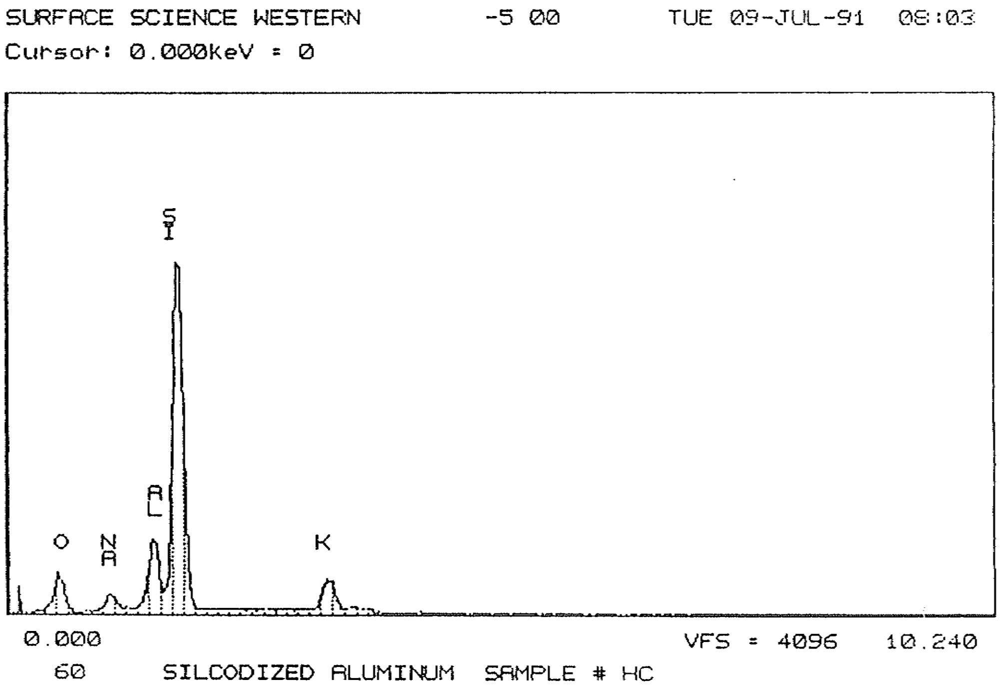


Figure 35 UNDERCOAT

ENERGY DISPERSIVE X-RAY ANALYSIS



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SURFACE SCIENCE WESTERN          -5 00        TUE 09-JUL-91   08:03
Cursor: 0.000KeV = 0
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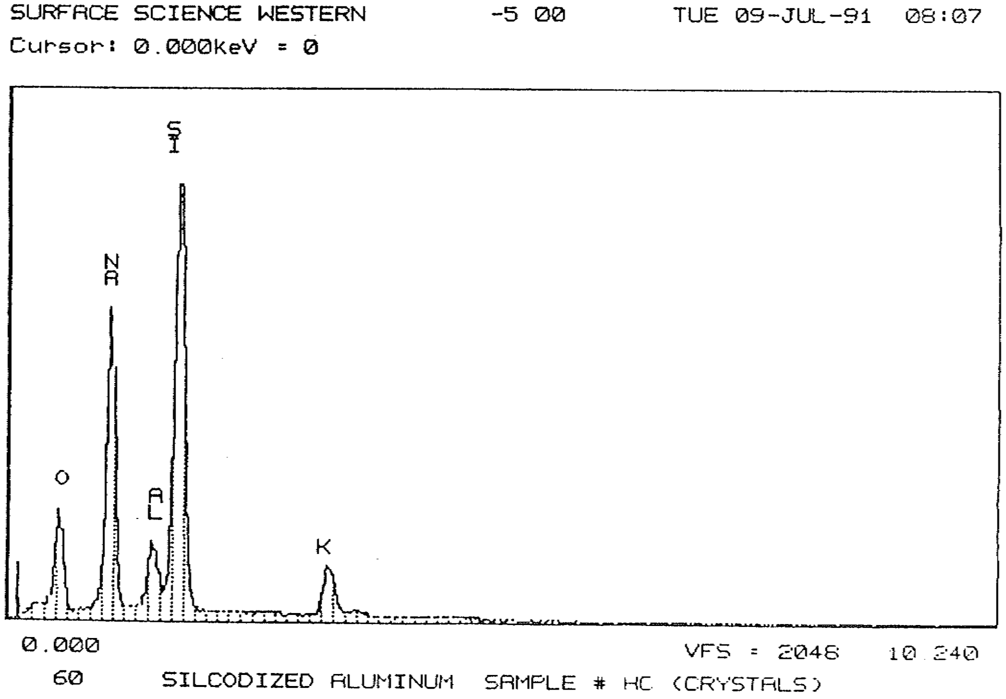
```
0.000                                        VFS = 4096    10.240
  60      SILCODIZED ALUMINUM   SAMPLE # HC
```

Figure 36 HARDCOAT



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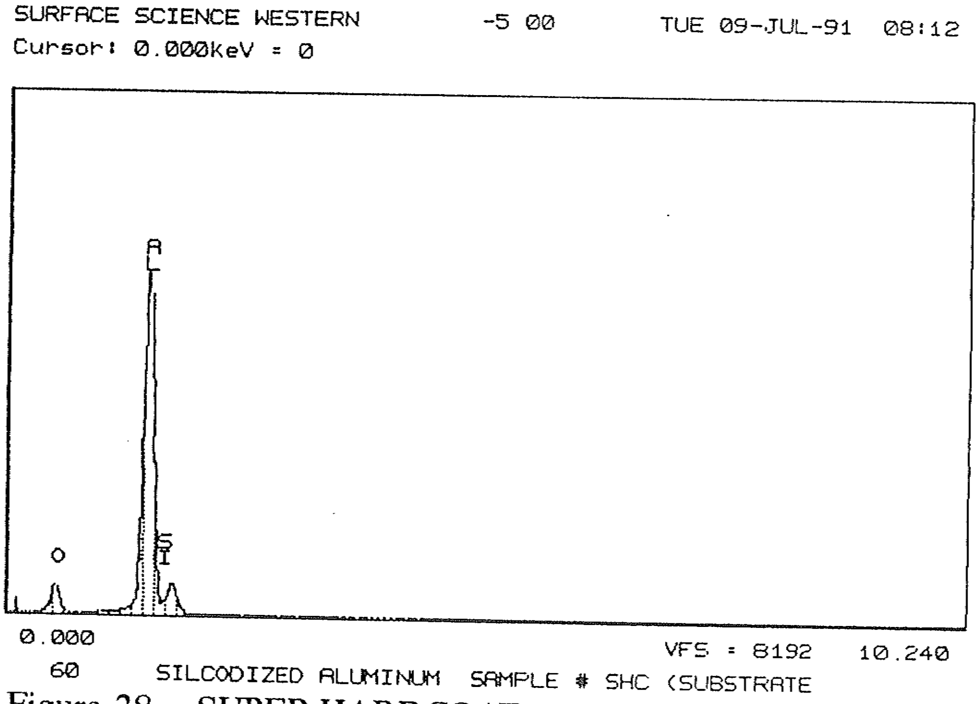
SURFACE SCIENCE WESTERN          -5 00        TUE 09-JUL-91   08:07
Cursor: 0.000KeV = 0
```

```
0.000                                        VFS = 2048    10.240
  60      SILCODIZED ALUMINUM   SAMPLE # HC  (CRYSTALS)
```

Figure 37 HARDCOAT (CRYSTALS)

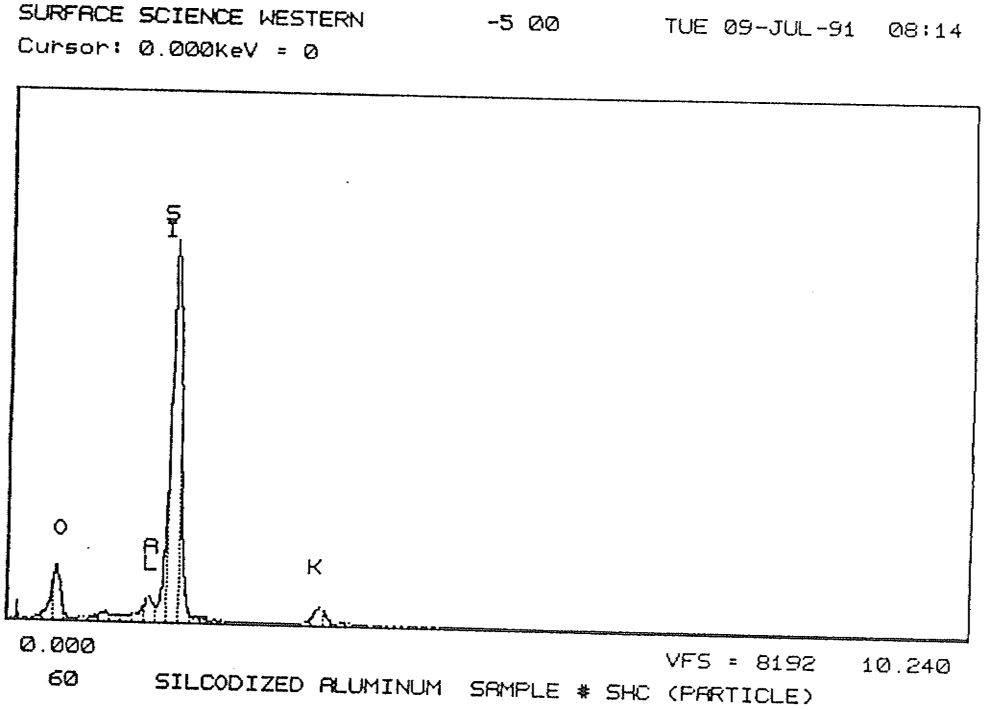
ENERGY DISPERSIVE X-RAY ANALYSIS



SURFACE SCIENCE WESTERN -5 00 TUE 09-JUL-91 08:12
Cursor: 0.000KeV = 0

0.000 VFS = 8192 10.240
60 SILCODIZED ALUMINUM SAMPLE # SHC (SUBSTRATE

Figure 38 SUPER HARDCOAT



SURFACE SCIENCE WESTERN -5 00 TUE 09-JUL-91 08:14
Cursor: 0.000KeV = 0

0.000 VFS = 8192 10.240
60 SILCODIZED ALUMINUM SAMPLE # SHC (PARTICLE)

Figure 39 SUPER HARDCOAT (PARTICLE)

ENERGY DISPERSIVE X-RAY ANALYSIS

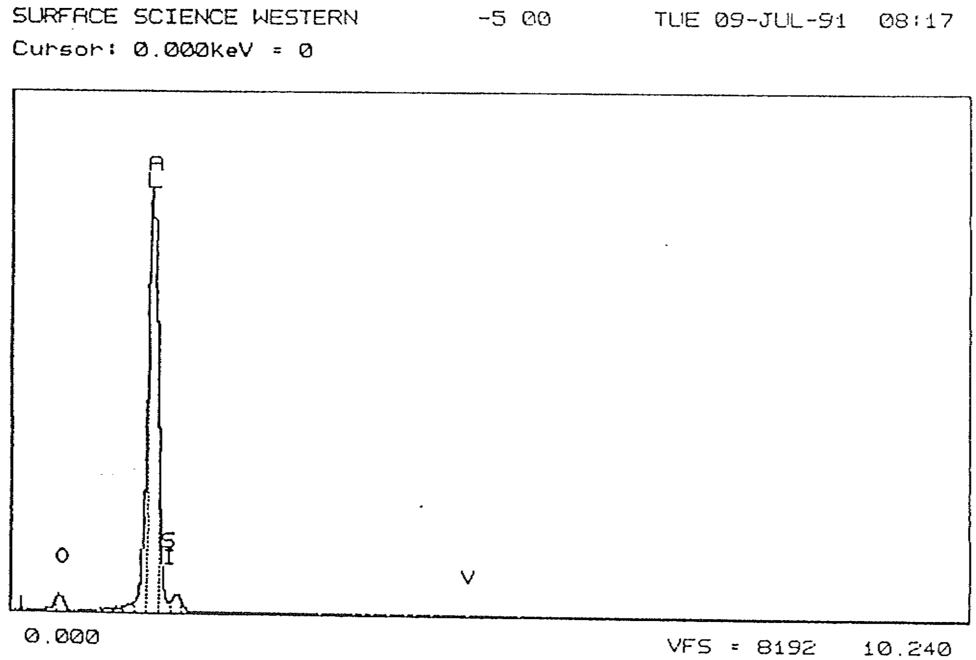


Figure 40 SUPER HARDCOAT WITH VANADIUM

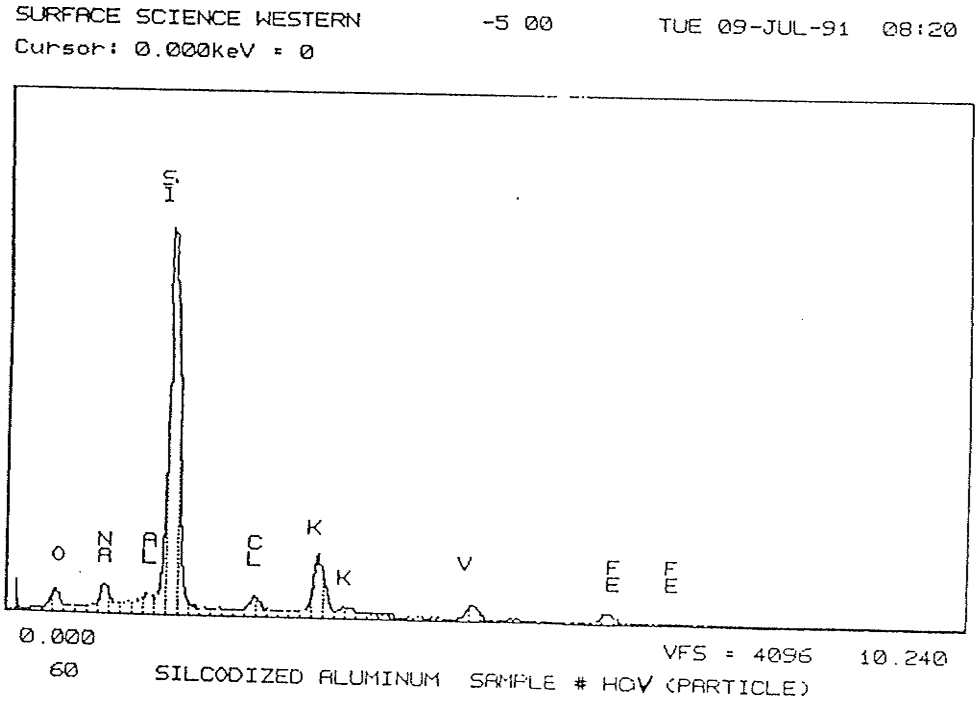


Figure 41 SUPER HARDCOAT WITH VANADIUM (PARTICLE)

ENERGY DISPERSIVE X-RAY ANALYSIS

6.2 MELTING POINT

An attempt was made to determine the melting point of the silicadized Undercoat on aluminum. Initial tests overran the melting point of aluminum and left the metal in a porous purse of silicate/aluminum oxide. A subsequent test, of three Undercoat samples encapsulated in argon was run on the floor of the furnace up to 680°C. At this temperature the two outer samples had started to turn a darker colour while the centre sample remained unchanged. The units closest to the walls received heat from the floor as well as the walls, while the centre unit received most of its heat from the floor of the furnace. Figure 42 shows a darkened background as the aluminum melted into the silica surface. The Undercoat was not a low melting silicate.

Because the melting point of aluminum (660°C) is well below that of the ortho silicate(1018°C) or meta silicate (1088°C) it was necessary to select a metal substrate with a much higher melting point. Tantalum (MP 2850°C) was chosen and was silicadized with the Undercoat. Figure 43 is an SEM photo of the surface at 1000 X, while Figure 44 shows the surface at 4500X. The coated sample was encapsulated in an argon atmosphere and the temperature was raised to 1020°C. By this temperature the silicadized surface had started to melt, as shown in Figure 45 at 1000 X magnification and in Figure 46 at 4500 X magnification. It appears that the silicadized surface melts at about 1018°C, which is the melting point of orthosilicate of composition Na_4SiO_4, or $Si(OH)_4$, or, since the plating out occurs at pH 12, the solution formula could be $(HO)_2SiO_2^{2-}$ or $HSiO_3^-/SiO_3^{2-}$. The corresponding SEM analysis of the coating is shown (Figure 47). The first sodium orthosilicate (Na_4SiO_4) is soluble in hot and cold water.[23] The silicadized coating has shown a resistance to going into solution, up to 75°C (at least 71%) and to be able to withstand a humid atmosphere in the salt test (Appendix B). This may be due to the (OH) and the H_2O being absent from the formulation because of the temperature of forming, leaving the formula as Na_2SiO_3 or K_2SiO_3, dehydrated. A further conclusion from the above tests is that to obtain a smooth silica (melted glass) coating on aluminum it will be necessary to develop a lower melting point silicate composition from which to silicadize the aluminum, because at present the aluminum melts before the current silicadized coating.

Before leaving this section on melting one further experiment should be mentioned. A narrow strip of aluminum 25 x 75 mm was silicadized with Hardcoat for 5 minutes at 234 v, 0.24 amps (orange sparks) resulting in a rough surface. The temperature went from room temperature (25°C) to 55°C. The same strip was then placed in a concentrated borate solution and power supplied for 5 minutes at 280-285 v, 0.5-0.4 amps. The solution surface was 2/3 of the way up the silicadized strip. Again orange sparks were observed on the submerged portion of the strip, while at the solution surface a variable blue strip of light occurred across the silicadized surface. The solution temperature went from 25°C to 75°C. On subsequent examination, the area under the blue light was a strip of transparent, smooth glass. Immediately above this glass the silicadized area showed stress cracking presumably from differential expansion of the aluminum vs the silicadized surface, while below the glass line the borate deposit was smooth. The base aluminum did not appear to be affected.

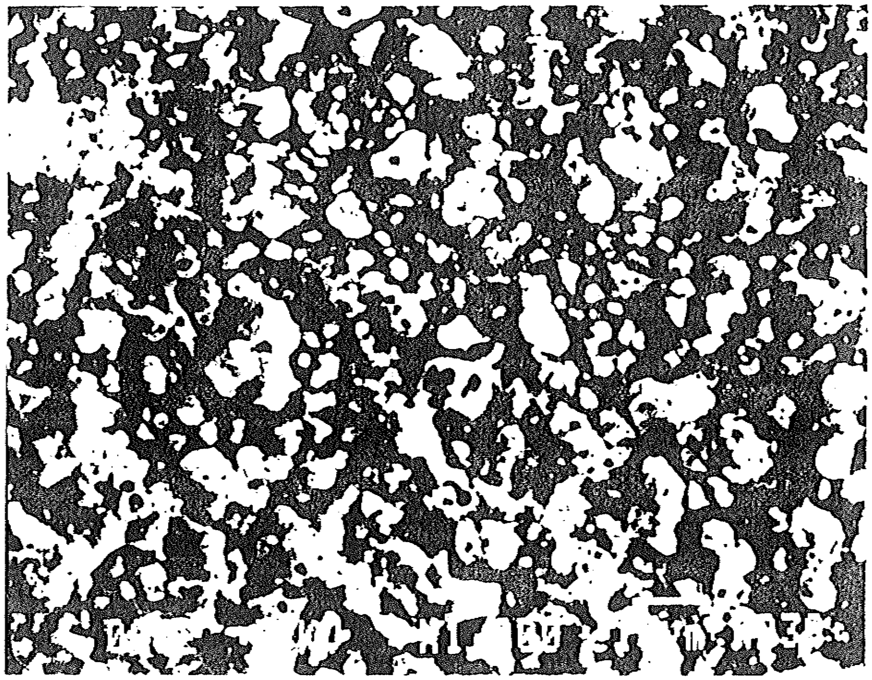


Figure 42

SILICADIZED ALUMINUM HEATED TO 680°C

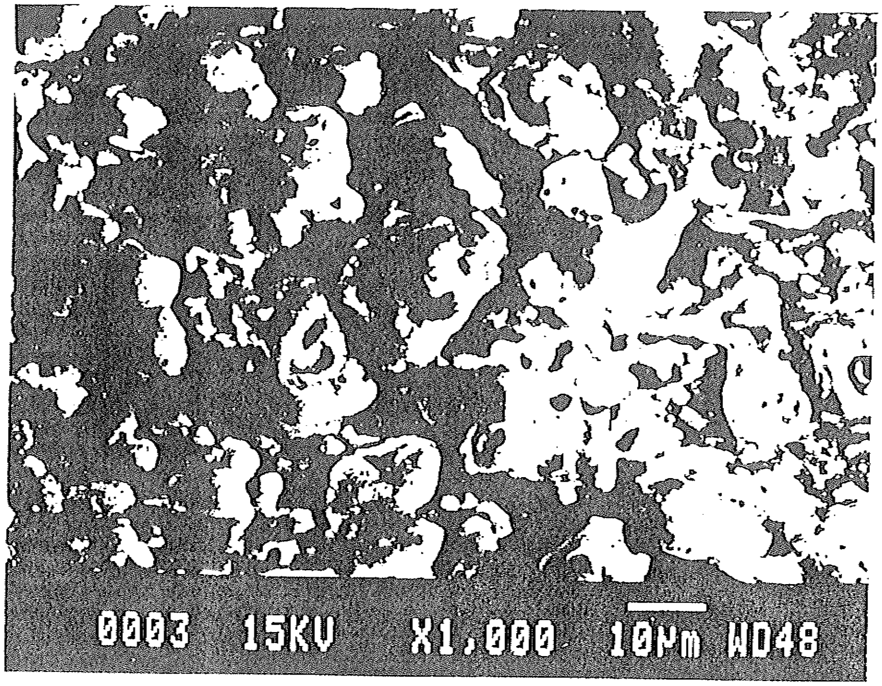


Figure 43 SEM (1000 X)

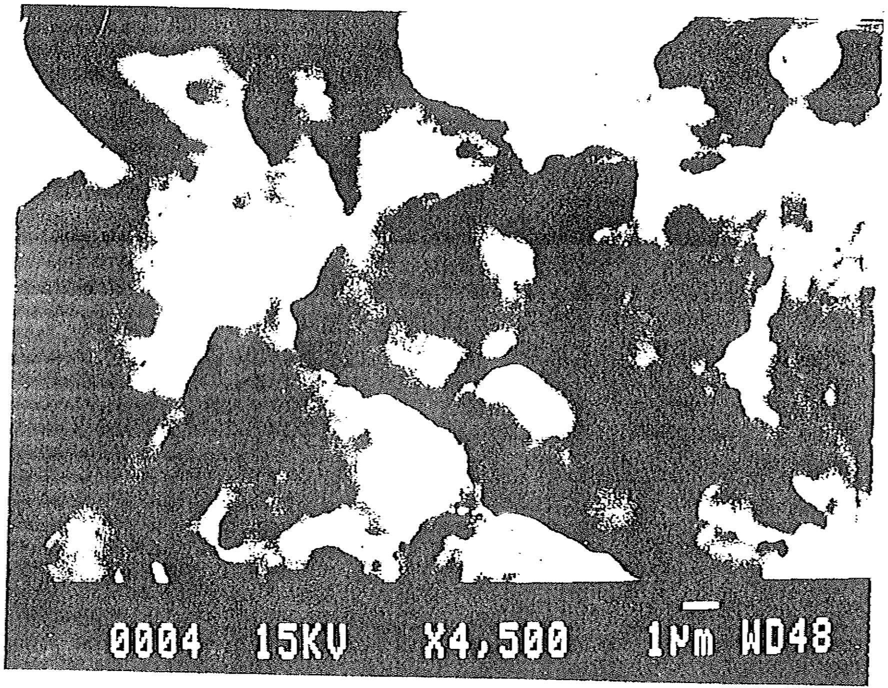


Figure 44 SEM (4500 X)

SILICADIZED TANTALUM

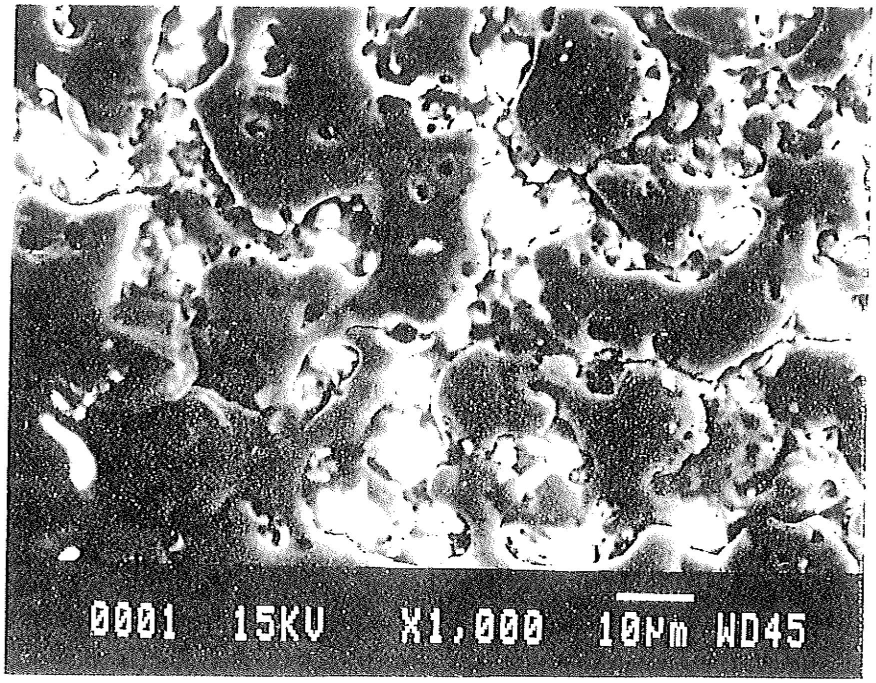


Figure 45 SEM(1000X)

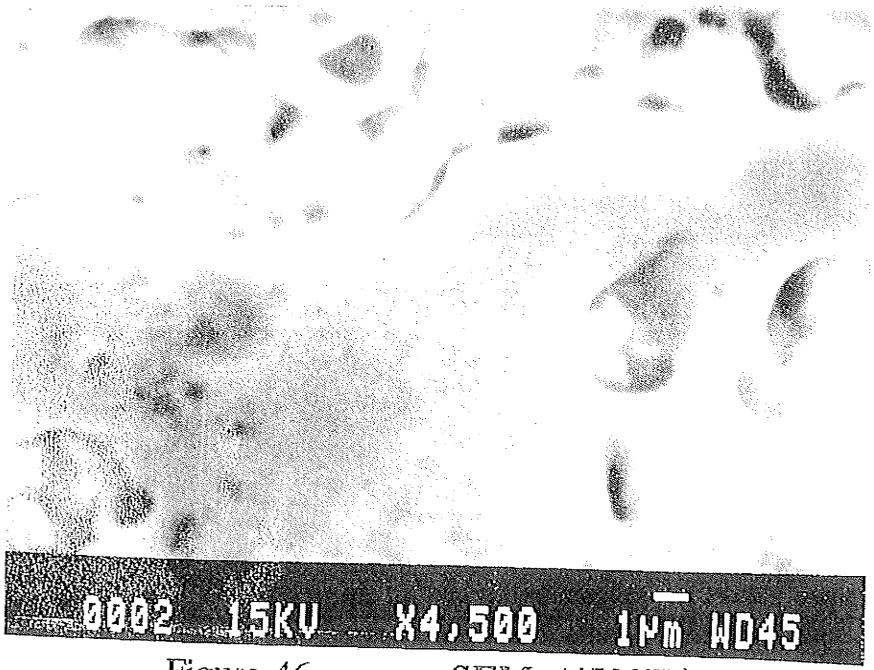


Figure 46 SEM (4500X)

SILICADIZED TANTALUM HEATED TO
1020°C IN ARGON ATMOSPHERE

```
ZAF CORRECTION          15.00 KV        41.61 Degs
No. of Iterations  3
----      K        [Z]       [A]       [F]      [ZAF]    ATOM.%    WT.%
SI-K    0.600     0.897     1.146     0.999     1.029     86.98    54.34
CL-K    0.000     0.960     1.474     0.999     1.414      0.00     0.00 ,G *
V -K    0.013     1.023     1.070     0.994     1.089      1.17     1.32
K -K    0.008     0.939     1.262     0.993     1.184      1.01     0.88
TA-L    0.377     1.325     0.993     1.000     1.316     10.84    43.56
 * - High Absorbance
```

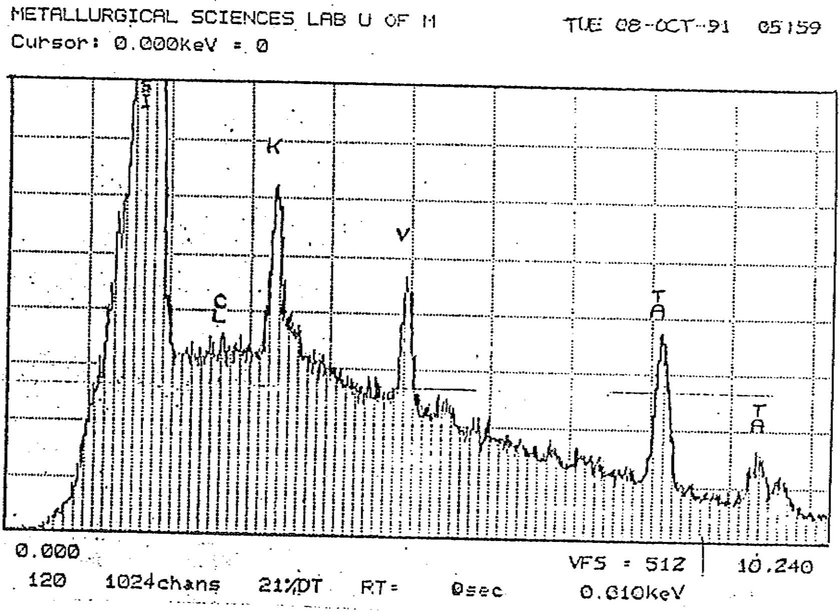


Figure 47 **SEM SPECTROSCOPY ANALYSIS**

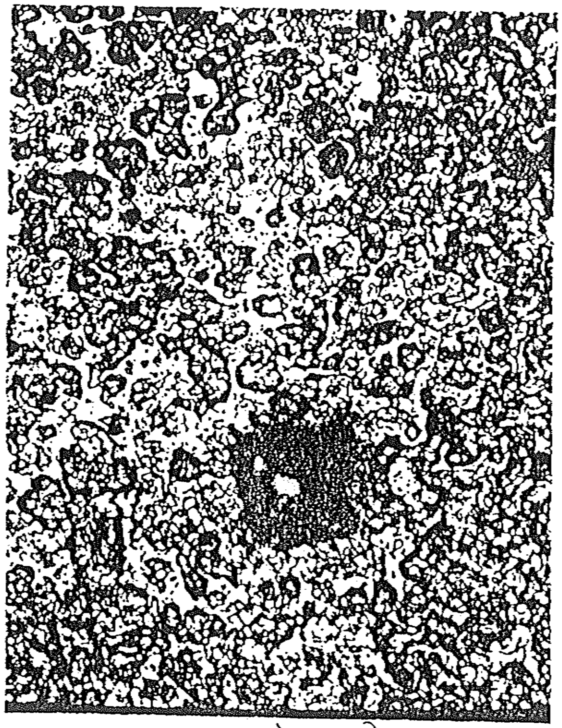
6.3 HARDNESS

Tests run to determine hardness of the Undercoat under the Vicker's Hardness Test were not conclusive, giving hardness readings too close to that of the aluminum being coated (Figure 50A). The thickness of the silicadized coatings tested was in the order of 0.012 to 0.025 mm. Here the measurements were by micrometer with an accuracy of approximately 1/10,000.

Abrasion tests were run using H38 Calibrade wheels, two per trial and a 250 g tread load on a Taber Abrasion machine made by the Custom Scientific Company. The results were as follows:

Undercoat	10 cycles
Superhardcoat	180
Anodized aluminum	20
Hard Anodized Aluminum	80
Aluminum with natural oxide	5

These tests, while comparative, are somewhat subjective as to when the coating is abraded equally. The Superhardcoat even at 180 cycles had one area of the coating not reduced to the aluminum oxide.



X.210

Figure 48

INDENT ON UNDERCOATED ALUMINUM USING VICKER'S HARDNESS TESTER

7.0 FLUORIDE SOLUTIONS

In the manuals for Super Hardcoat the use of fluoride ions was recommended for use in the bath and, while it does react with aluminum to give a complex ion AlF_6^{-3}, there are several cases of fluorine atoms acting as bridges and being two coordinate rather than the usual one, for instance:[24]

> [I]n BeF_2 glass BeF_4 tetrahedra are joined together by shared fluorine atoms, and in SbF_5, a viscous liquid, polymeric species also occur. The best documented cases of fluorine bridging occur in $K^+[(C_2H_5)_3Al\text{-}F\text{-}Al(C_2H_5)_3]^-$, in which the Al-F-Al group is linear and symmetrical and the Al-F distance is equal to 1.80 ± 0.06 Å, and in BeF_2.

The use of hydrogen fluoride is not desirable if SiF_4 evolves as a gas during silicadization. Hydrogen fluoride attacks glass (SiO_2),

$$SiO_2 + 4HF \rightarrow SiF_4 \uparrow + 2H_2O$$

The product SiF_4 is a gas. In addition, the potential at which F^- discharges is higher than that where water decomposition starts (1.23v):

$$F2\uparrow + 2e^- = 2F^-, (E^\circ{=}2.87)^{25}, \text{ or}$$

$$F^- = 1/2\,F2 + e^- \ (E^\circ = 2.85)^{26}, \text{ or}$$

$$\text{HF aqua} = 1/2\,F2 + H^+ + e^- \ (E^\circ = 3.03)$$

> These potentials are so high that water is decomposed by fluorine with evolution of oxygen and ozone. In the electrolysis of aqueous fluorine at high anode current density the oxygen evolved may be shown to contain small concentrations of ozone; recently, however, it has been suggested that the formation of ozone on electrolyzing hydrogen fluoride at very low concentrations, are discharged at lower potentials than fluoride ions.[27]

A discussion of the dangers possible in using hydrogen fluoride in the silicadizing reaction is contributed in Appendix E.

When sodium fluoride was used in the decorative coating experiment a black coating was obtained which was rough and not satisfactory. It was found, however, that without the fluoride, a satisfactory black coating could be obtained. Smooth coloured coatings, beige, brown, to black, were obtained by the addition of vanadate or molybdenate compounds to the Super Hardcoat. The intensity of the colour of the deposit varied with the amount of the addition, the potential applied, and the deposition time.

8.0 CASTINGS

The first aluminum casting silicadized was a part for the base of a heated mirror for the outside of a Motor Coach Industries Ltd. bus. The part was shaped like a cup with a side hole. All surfaces silicadized evenly.

Subsequently, a computer part with an American Society of Metals designated composition AZ91D, mainly magnesium with 0.9% zinc, was submitted for silicadizing. Many attempts were made, including plating with only a 1°C temperature rise, resulting in a powdery base. All proved unsuccessful. Examination of the part under scanning electron microscopy (SEM) showed the part to be quite porous (Figure 18), which proved to be one reason for failure. As the coating was applied the part increased in temperature due to the power supplied. With the increase in temperature the trapped air in the voids expanded and burst through the coating, leaving a pitted surface. A picture showing a similar surface appears in The Handbook of Thin Film Technology, although here high current densities are cited as the cause.[28] No picture of the surface before plating appears in the handbook so one can only conjecture that the casting shows porosity and that the entrapped air is the actual cause of the vent forms shown as a result of the high current density heating the air. The reason given in our case is the porosity, in theirs it was the high current density. (Our current density is low).

Other magnesium and tantalum sheets were coated without difficulty. The presence of zinc in the AZ91D magnesium casting may have been a contributing factor as the manuals received indicated that if the combined content of copper, zinc, tin or iron is over 3% the results are rather poor. These percentages did not apply, but the reason for inadequate coating has not been resolved.

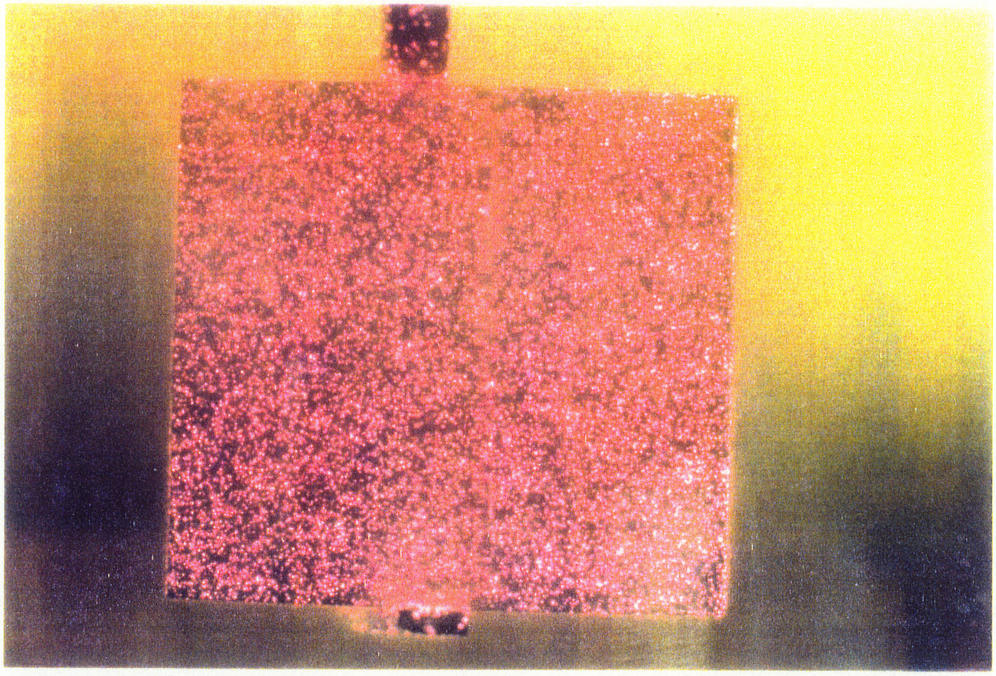
9.0 SCINTILLATIONS

Figure 49 shows the scintillations appearing on the aluminum silicadized coating as the voltage reaches and exceeds the so-called "sparking voltage." At voltages up to the time that the scintillations appear, the DC energy supplied largely goes to electolyze the aqueous silicate solution, producing hydrogen and oxygen; building up the Al_2O_3 undercoat. (These gases were verified by the glowing splinter technique and also by Gas Chromatography).

Figure 49

EQUIPMENT USED TO DETERMINE SPECTRA OF SCINTILLATIONS

A) RECTIFIER
B) JARRELL-ASH MONOCHROMATOR WITH AMPLIFIER AND PEN RECORDER. TANK OF ELECTROLYTE SHOWING RECTANGULAR SILICADIZED PANEL IS ON THE LEFT.



photograph by John Mathews

Figure 50 SCINTILLATIONS AS THEY APPEAR ON SILICADIZING ALUMINUM.

The scintillations were examined by concentrating the emitted light on the receiving slit of a Jarrell Ash 82-41, 0.25 metre Ebert Monochromater having a grating with 2360 grooves per mm, with the resulting analysis recorded on a Hewlett Packard Pen Recorder 17172A (Figure 51 shows the equipment layout).

The yellow-orange scintillations showed a radiation peak at approximately 589 nanometers using a slit width of 50 μ. Concentrating the light was necessary, as the scintillations alone would not register in the monochromater. To allow more light in, a 500 μ slit was employed. With a slit width of 500 μ two peaks became apparent at about 589.0 and 589.6 nanometers, indicative of sodium.

Many confirming tests were run to study the sodium output, and to identify what appeared to be an initial white-violet smaller scintillation occurring in advance of the yellow-orange. This white-violet scintillation would go to the yellow light after a few minutes. Concentrating the emitted white light at a slit width of 500 μ revealed additional details. Now peaks occurred at 400-435 nanometers and at 760-770 nanometers and were thus identified as potassium where the specific main lines are 404.5 and 404.7 nm, 766.5 and 769.9 nm (Figure 50).

In <u>Anodic Oxide Films</u>, under the heading Electroluminescence, Young[29] suggests

> The emission of light during the polarization of the anodic film on tantalum and aluminium at fields too low to produce growth and, in particular, on changing the potential from anodic to cathodic values has been reported in many papers. (Schulze, 1906; Lavaux, 1919; Forrest, 1930; Güntherschulze and Betz, 1932, 1935; Rummel, 1936; Guminski, 1936; Anderson, 1943; Smith, 1957, 1959; van Geel et al.,1957). The spectrum depends on the impurities, as does the intensity. Smith found that the electroluminescence of aluminium was

> greater with aluminium which had been prepared for anodizing by etching rather than electropolishing. This shows that weak places in the film are important. It would appear, in fact, that electroluminescence may be largely due to faults in the film rather than to recombination at impurity centres in a homogeneous film.

(None of the above references quoted by Young identified the wavelength or source of the light observed.)

Mikho et al.[30] reported that the luminescence of Al_2O_3 films placed in an electrolyte was observed "in the absence of an exciting voltage," while in further work Mikho and Denisova [31] attempted to resolve the cause, noting

> . . . an increase in the intensity of the luminescence . . . as the temperature of the electrolyte was increased. However, degradation of the surface of the oxide film occurs in this case with an increase in its rate of dissolution, and this phenomenon can produce a significant contribution to the luminescence in the form of so-called lyoluminescence, i.e. luminescence accompanying dissolution.

The results of their investigation, they suggest,

> . . . attest to the fact that the appearance of the luminescence of Al_2O_3 films in contact with an electrolyte in the absence of excitation and under the effects of weak electric fields occurs with the participation of ions of the electrolyte of both signs: the ions of one sign form impurity levels of an acceptor nature with holes localized in them, which are capable of ionizing the luminescence centers, and the ions of the other sign form impurity levels of a donor nature. The recombination of the electrons supplied by the latter with the ionized luminescence centres is accompanied by the emission of light.

In the above report, an aqueous solution of oxalic acid and tartaric acid was used with a 3% aqueous solution of NaCl (pH 7.5) serving as the electrolyte with tin-oxide field electrode and the Al_2O_3 film as the sample. The light is not identified by colour or by wavelength. Could the light have come from the sodium contained in the electrolyte, as described in the current research in this section.

One test was run using a weak NaCl solution as electrolyte, but no scintillations were observed.

G. Dearnaley[32] of Atomic Energy Research Establishment, Harwell, England, has developed a phenomenological model, based on the development of conducting filaments to explain electron emission and light emission occurring from small scintillating centres. The behaviour of oxide-coated thermionic cathodes and SiO negative-resistance elements is explained. H. Kanter and W. A. Feibelman[33] have also reported on scintillating centres, as has K. Vijh,[34] relative to solid state science. Waring and Benjamini[35]

> observed sparking during the anodization of silicon in a solution of KNO_3 in ethylene glycol. To help determine the region in which the sparks were generated they bubbled neon against the sodium wafer. When these bubbles passed near a spark they gave a brilliant red-orange flash characteristic of a neon discharge. From this they concluded that the sparks were associated with a strong field that extended into the solution.

Fowkes and Burgess, according to Iler,[36]

> showed that the surface of silica traps sodium atoms. Even the purest quartz collects 10^{13} cm^{-2} [sodium] atoms within 100 Å of the surface. This creates a negative oxide ion charge at the surface. If the surface is etched off with HF it becomes uncharged, but after some weeks at room temperature more sodium comes from the interior.

10.0 A SUGGESTED SCINTILLATION MECHANISM

Sodium, one of the most electropositive elements, having one electron per atom to transfer, readily becomes a powerful reducing agent. It combines vigourously with water, producing NaOH and liberating hydrogen. This is frequently evident when performing the silicadizing operation and the anode being treated has undercuts, the hydrogen accumulates briefly in these areas and the resultant banging and bumping as the hydrogen ignites is somewhat alarming:

$$2\,Na + 2\,H_2O = 2\,NaOH + H_2\uparrow$$

Early in the experiments it was determined that hydrogen readily pours off the cathode on electrolyzing and, besides being liberated at the solution surface, also flow near the surface in the direction of the anode as shown by streams of bubbles. It was also determined that oxygen is the gas liberated from the anode, largely through the electrolysis of water.

However, when the scintillations appear at and above the sparking voltage, elemental metal is being ionized, and this is the cause of the sparkings. The first sparking that appears as white-mauve scintillation is due to potassium (I=100.1 kcal/mole), an alkali metal more active than sodium (I=118.5 kcal/mole). Secondly, the sparks become yellow as the voltage increases and the sodium ionizes, masking the white-mauve light from the ionizing of potassium. It is possible that the sodium/potassium ions pick up electrons at the cathode to become elemental sodium and potassium, and then are transported to the anode where they ionize. This travelling does not seem likely because both elements would almost immediately combine with the water molecules to release hydrogen and create more alkali. There is a substantial localized increase in temperature of the solution around the anode due to the glow discharge. It appears that the Na ion, fully hydrated with four OH ions surrounding it, still has a positive field and as a complex is drawn toward the anode by convection and the attraction of the outer Helmholtz layer of negative ions surrounding the anode. Here the Na complex comes under the influence of the anode glow discharge and the high ionizing field which increases directly with the applied voltage. This field is thought to be the source of energy to electronically excite the OH^- ions surrounding the Na^+ ions, causing a rearrangement of the OH^- ions with the release of four electrons, as follows:

$$4\,NaOH \rightarrow 4\,Na^+ + 4\,(OH^-) + 4\,e^- \qquad (1)$$

Simultaneously the free electrons react with the Na^+ ions elevating them to an exciting energy level, $E_{n,p}$ to $E_{(n+q)p}$ which, on falling back to their base state, give off the light observed as sparks or electroluminescence occurring all over the anode:

$$Na^+ + e \rightarrow Na^* \rightarrow Na + h\mu$$

Thermodynamically, the above reaction (1) will go to completion:

$$\Delta G° = [\Delta G°(4\,Na+) + \Delta G°4\,(OH-)] - \Delta G°(4\,NaOH)]$$

$$\Delta G° = 4(-261.87) + 4\,(-157.30) - 4\,(-379.78)$$

$$\Delta G° = -157.55 \text{ kj/mole}$$

and the reaction: $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$

$$\Delta G° = \Delta G°[2(-90.77) + 0] - 2[0 + (-56.687)$$

$$\Delta G° = -\,68.17 \text{ kcal/mole } (-\,285.22 \text{ kJ/mole}).$$

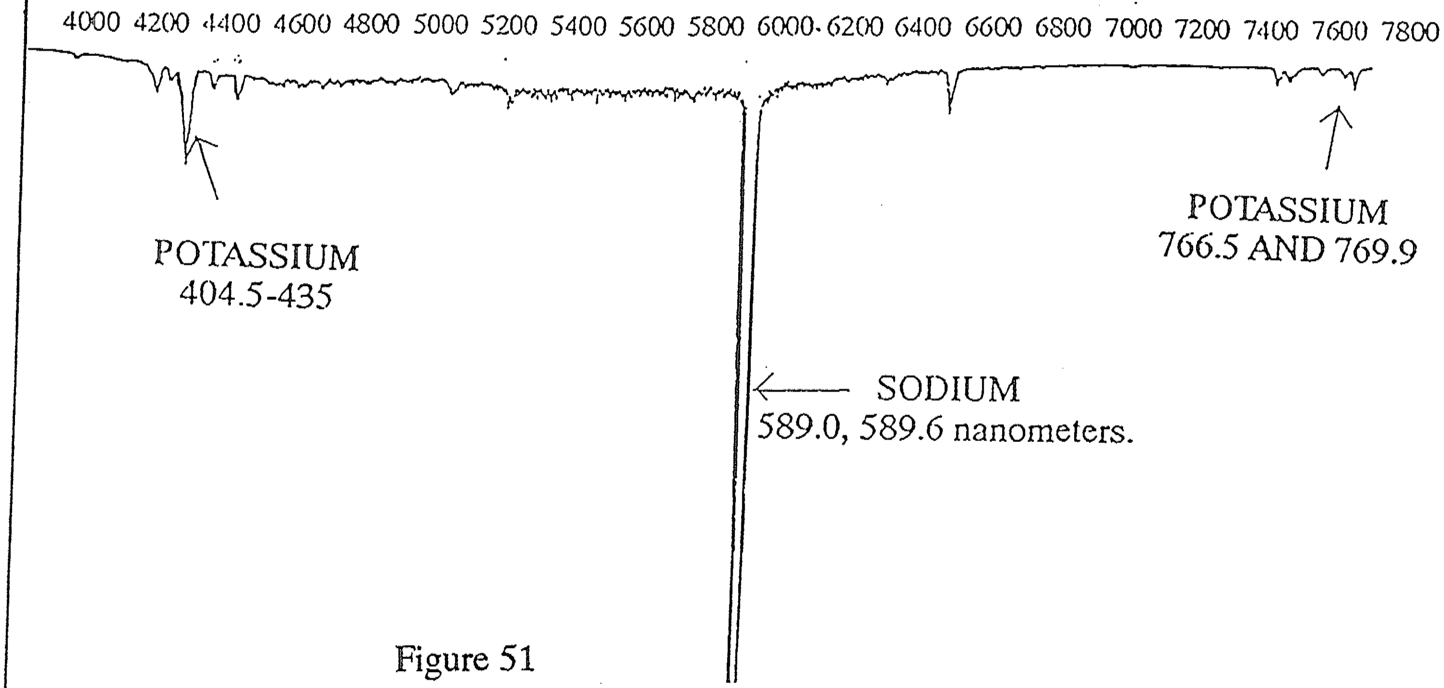


Figure 51

SPECTRA OF SCINTILLATIONS
using a 500 μ SLIT WIDTH
IN A JARRELL-ASH MONOCHROMATOR

A favoured, alternative mechanism suggested by Conway (Reference 55) for the origin of the light flashes may be the electronic excitation of Na^+ or K^+ ions within the solution, as when salt (Na^+ and Cl^- ions within the crystal), is thrown into a flame the Na D-lines are excited, (thermally in this case), giving the familiar yellow colour.

Here, thermionic electrons having a negative charge the same as ionized particles, but with mass 1/1800 that of the hydrogen ion could be expelled from the anode during the glow discharge, resulting in a plasma of electrons surrounding the electrode. The electrons in the aluminum anode have kinetic as well as potential energy. In Figure 52, which is the Energy Diagram for an Electron at the Surface of a Metal the work necessary to extract the fastest electron from the surface and leave it with zero kinetic energy outside the surface is the difference beween U and k, that is ω, the work function. In the equation $h\upsilon = \omega$, from Einstein's equation for kinetic energy of the free electron T and the frequency of radiation υ: $T = h\upsilon - \omega$, when the $T = 0$, the equation determines the photoelectric threshhold frequency. Electrons which receive enough energy to escape the metal surface have potential energy equivalent to U. They may now collide with the K/Na atoms causing them to absorb quanta, elevating the elements to excited states from which they may reradiate energy as fluorescent radiation in wavelengths characteristic of the absorbing atoms, or they may pass energy on to other elemental particles on collision. With the evidence of the glow discharge plasma existing this appears to be a reasonable explanation, although all the above suppositions may be existing.

11.0 A SUGGESTED SILICADIZING MECHANISM

The following general comments are preparatory to a suggested silicadizing mechanism, and are presented to help explain events as observed during this research:

Swann[37] reports, "In aqueous solutions high concentrations of the salt [sodium or potassium] are favorable to coupling. . . . Side reactions are promoted in aqueous alkaline electrolytes."

Iler[38] stated that

> [t]he nature of the silica in silicate ions in any alkaline solution cannot be determined by a chemical measurement that involves any change in the concentration of silica or alkali, electrolyte content, or temperature because these all shift the equilibrium between monomeric and various polymeric species.

He suggested that sodium acts as a bridging factor where the adsorbed cations of the salt act in the coagulation of silica, similar to the coagulation of the basic ferric or aluminum salts. Iler conjectures,

> When a sodium ion is adsorbed on the surface of a silica particle, one or more of the oxygen atoms of the water of hydration can be displaced by the oxygens of the surface silanol groups (SiOH), which thus become linked directly to sodium . . . . There is no apparent way to determine whether the adsorbed cations in the flocculate are concentrated at the particle to particle areas of contact, as might be expected if the cations form the bridges . . . .

Iler advises:[39]

> Under almost all conditions, soluble silica comes out of solution as spherical, amorphous particles that, depending on the concentration,

> temperature, and pH, remain as sol, are aggregated into a gel network, or are coagulated as a precipitate.

This is the reverse of dissolution (except at lower pH where acid-induced polymerization is irreversible).

Sugar and Guba [40] reported from an SEM study that fine pore silica gel was made up of a thread or fibre-like network wherein the fibres were made up of chains of spheres.

Usher[41] commented :

> that the aggregation of particles into chains was first explained on the basis that a single particle would preferentially aggregate with a neighboring pair of particles to overcome the repulsive force of only one of the particles of the pair.

Spectrographic studies of silicate solutions indicate that the $Si(OH)_6^{2-}$ does not exist in solution.[42]

In the area of the work undertaken here at pH 12, both aluminum and silica are in the double charge state: AlO_2^{2-} and SiO_3^{2-}.[43] Infrared studies by Hair[44], have shown that while aluminum is much more reactive, both aluminum and silica surfaces contain hydroxyl groups. The greater activity, according to Hair, has been attributed to the presence of a second type of acid site of the electron-abstracting or Lewis acid kind.

Florke's studies in solid state electrolysis and Holmquist's phase studies on systems Na_2O-SiO_2 and K_2O-SiO_2 led to the conclusion that tridymite (Na $[AlSiO_4]$) is not a phase in the pure SiO_2 system, but instead requires alkali or hydrogen ions to balance the charges resulting from minor replacement of Si^{+4} by Al^{+3}, as reported by Liebau.[45]

In this work silica coatings form a resistant layer, bonded to the aluminum oxide surface. The low solubility of sodium/potassium aluminosilicate minerals, such as clays, illustrate the strong specific interaction between the respective oxides. Both aluminum and silicon form comparable coordination numbers of 4 or 6 to oxygen under suitable conditions, and both have the same atomic diameter. Since $Al(OH)_4^{-1}$ is structurally similar to $Si(OH)_4$, the ion can fit into the SiO_2 surface, creating an aluminosilicate with a fixed negative charge. Iler[46] points to the work of Milliken, Mills and Oblad[47] which shows that the anion is stable only in the presence of a cation other than hydrogen, the free acid being unstable.

By this current work it is suggested that sodium/potassium is that ion and that the pH is an important factor in the reaction.

To describe the reaction: First the rectifier is turned on and as the current is ramped up to about 10 amperes, the potential reads about 50 volts, and this is held for 10 seconds. The solution is being electrolyzed, with hydrogen and oxygen being liberated at the cathode and anode respectively, although some of the hydrogen is observed streaming toward the anode through the top layer of the solution. As there is a dilute sodium/potassium silicate solution between a stainless steel cathode and an aluminum anode the anions of SiO_3^{2-} combine with water to form various ionic forms in the aqueous alkaline solution changing toward the right as the pH increases to pH 12 in the following (Pourbaix)[48]:

$$H_2SiO_3\ aq \rightarrow H_2SiO_3 + H_2O \rightarrow HSiO_3^- + H^+ \rightarrow SiO_3^{=} + H^+.$$

Other reactions that take place at the same time in this solution are:

$$H_2O \rightarrow H_2 + 1/2\ O_2,\ \text{by electrolysis, or}$$

$$2\ H_2O \rightarrow 2\ H_2 + O_2.$$

Attempts to determine silica coming off with the steam or vapour using a cold mirror, did not result in a residue of silica. However, when silicadizing with the electrolyte in glass beakers frequently it was found that dendrites of silica would form from the top of the anode over to the edge of the beaker, indicating that a certain amount of current leakage was travelling on the surface of the glass and that silica was coming up with the oxygen bubbles into the immediate surface atmosphere.

The equation

$$SiO_3^{=} + 2H^+ = SiO_2 + H_2O,$$

is of interest. Thermodynamically,the Free Energy of this reaction is

$$\Delta G^\circ = \Delta G^\circ_{SiO_2} + \Delta G^\circ_{H_2O} - \Delta G^\circ_{SiO_3^=} - 2\Delta G^\circ_{H^+}$$

where $\Delta G^\circ_{SiO_2}$ = -192 kcal/mole

$\Delta G^\circ_{H_2O}$ = -56.69 kcal/mole

$\Delta G^\circ_{SiO_3}$ = -212 kcal/mole

$\Delta G^\circ_{H^+}$ = 0.0 kcal/mole

$\Delta G^\circ = (-192) + (-56.69) - (-212) - 2(0).$

$\Delta G^\circ = -36.69$ kcal./mole.

(Data ex Latimer(1923), Ref. 48, generally U.S. Bureau of Standards data) (Data updated to Gesser (1974), Ref. 24,: $\Delta G^\circ = -40.69$ kcal/mole where $\Delta G^\circ_{SiO_2}$=-196 kcal/mole, U. S. Bureau of Standards data.)

The Free Energy value represents the maximum available work required to go from the initial to the final state, and in the above reactions the negative values indicate that the reactions will proceed spontaneously, as the equation: $\Delta G = \Delta H - T\Delta S$ (equivalent) combines the effect of the two important factors, the enthalpy (ΔH) and entropy (ΔS) changes, which, taken together, control the direction of a chemical change.

The amperage drops as the aluminum surface oxidizes, increasing the resistance to the current flow. The voltage must now be increased to maintain a flow of current, and then, as the surface oxide again increases in thickness it again increases the resistance to current flow. Increasing the voltage to 200-250 volts, the current is at 2 to 4 amperes, depending on the concentration, and at about this potential small spark discharges appear on the surface of the anode. The initial sparks are small and white-violet in colour. The spectroscopic analysis shows a reaction in the range of 400-435 nanometers and at 766.5 and 769.9 nanometers. This is due to potassium (ionization potential 4.339 ev)[49] As the solution temperature and voltage increases, varying with the solution used, the sparks become yellow-orange, masking the former scintillations due to potassium. The colour of the orange sparks under water have been determined as due to sodium (ionization potential 5.138 ev) showing absorption spectra at 589 and 589.6 nanometers.

As the sparking voltage is reached, a silica coating starts to form on the aluminum. As it forms, the resistance to the current passing increases, and as a consequence, the current declines further. It may go below 0.8 amp and, as the sparking starts to diminish, it is reinstated by increasing the voltage and thus increasing the plating thickness. The amperage stays low due to the buildup of the coating resistance.

By serendipity, in one test a high external resistance was accidentally introduced to the circuit when the connection to the cathode was not properly tightened. The voltage went up to 285 volts with the amperage at 0.1 amps and lower, and sparking occurred without the build-up of a coating. The sparks were small. Thus, it appears the electroluminescent effect is a separate phenomena not necessarily associated with the silicadizing process per se at this stage. (Note: The wattage went from 28.5 watts to about 3.0 watts as the amperage went from 0.1 amp to approximately 0.01 amp during this display.)

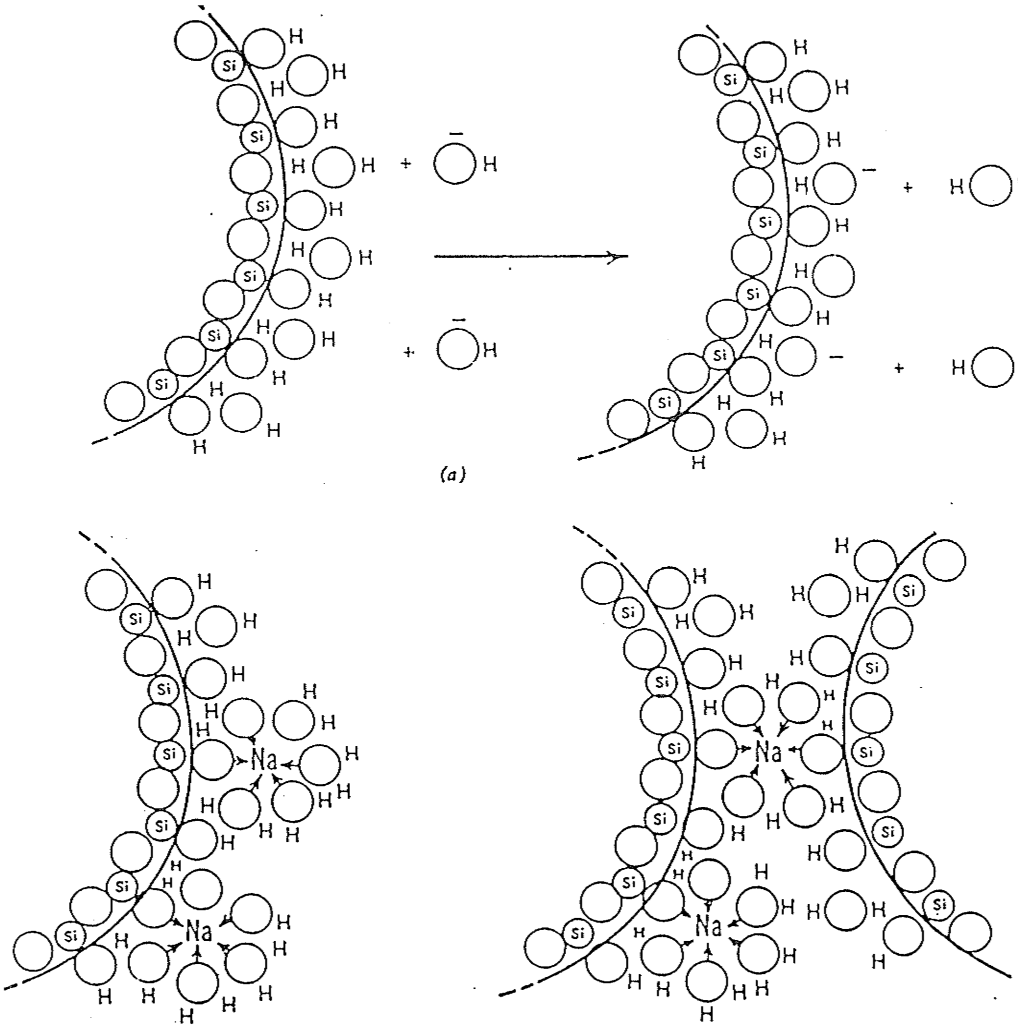
NaOH is the solvent for the silica in the silicate being used. When a weak solution (1/200) of sodium silicate is electrolyzed, the anode, when viewed in the dark has initially a faint red glow discharge at 200 volts which, as the voltage is increased, shows small, fine scintillations of a light colour. It may be possible for the Na^+ to pick up an electron as discussed above, be elevated to a higher energy level.and then drop back to a lower level releasing a quantum of light.

The NMR research[50] indicates groups of $SiO_3^=$ abound at the higher pH.

In the normal set-up the scintillations occur as the silica is being plated out onto the aluminum surface. To quote Hunt (Reference 49, his p. 7):

> Although positive or negative ions can have a separate existence in the gas phase, in solution the total number of positive charges is always equal to the total number of negative charges simultaneously present. This makes it very difficult to assess the properties of individual ions in solution, since one is always dealing with a mixture.

Let us also assume, as Iler has suggested, the possibility of bonding between the silica particles through coordination with coagulating alkali metal cations.



(a)

Figure 53 (b)

(c)

ILER'S HYPOTHESIS: SHOWING POSSIBLE BONDING BETWEEN SILICA PARTICLES THROUGH COORDINATION WITH FLOCCULATING METAL CATIONS.

a) Hydroxyl ion absorbs hydrogen and transfers negative charge to water layer hydrogen bonded to silanol groups on particle surface;

b) Hydrated Na ion is absorbed at the negative site forming neutral complex;

c) Collision with an uncharged area of a second particle permits the sodium ion to coordinate with oxygens of silanol and surface-bonded water, forming a cordination link between the particles.

First there would be a negative ion charge transferred to the water layer hydrogen-bonded to the silanol groups on the particle surface. (This is the equivalent to the adsorption of a hydroxyl ion.) Then a hydrated sodium ion is adsorbed at a negative site, forming a neutral complex. The collision of this system with an uncharged area of a second particle permits the sodium ion to coordinate with oxygens of silanol and surface-bonded water, forming the coordination link or links between the particles. This is essentially Iler's proposal. Figure 53 shows Iler's bonding illustrations.[51]

Depasse and Watillon[52] advise that above pH 11 only Li and Na of the alkali ions continue to act as bridging ions; the larger K ion does not.

However, there is another phenonemon at work here, that is the method of electrophoresis involving the of the displacement of dissolved molecules under the influence of an electrical charge. The development of electrophoresis as a quantitative tool dates from the Ph. D. thesis of Arne Tiselius in 1930. His subsequent work in this field resulted in chromatography and adsorption analysis, and the Nobel prize in 1940. We are probably more familiar with the process through the separation of blood serum into its protein components: albumin, α_1-globulin, α_2-globulin, β-globulin and γ-globulin.

The evidence of electrophoresis occurring in this research is as follows: When the scintillations occur with increased voltage in the area of 285-300 volts, the sparks increase in size and frequency. They sparkle randomly, not generated from apparent fixed points as do CO_2 bubbles in a carbonated beverage. However, as the voltage is increased further, a second effect is evident as the scintillations now grow from their first site in a curved position of successive sparks, as though the deposit associated with the initial spark was the end of a linear string which is pulled in and deposited on the coating.

On increasing the voltage further, there is a third effect, during which the "burn" areas travel in a bright curving form over a relatively broad area. More than one burn patch may occur at one time, or the burn fades and starts in another area. The deposit under these conditions leaves raised nodules of "concrete" above the coated surface. From the alkali tests undertaken it is assumed that this burning action destroys the adhesion of the main coating as the areas so affected disintegrate and allow the aluminum to be attacked. This is not a desirable effect.

The sodium/potassium ion may thus act as a bridging agent because under normal silicadizing conditions the deposit does not start until the potential reaches the discharge point of the energized sodium. The sodium sparks in random fashion, while the glow discharge acts as a sintering system as the silica plates out from solution. The rounded globular forms shown in the SEM photographs appear flame-treated by the heat being generated. The second stage, outlined above, where the sparks enlarge and briefly deposit silica with curving scintillations, appears to represent a chain of connected particles. Up to this stage all evidence indicates that the bonding is strong and the coating obtained resists the attack of weather, acid and salt solutions. In the third stage, where the sparks extend over areas as though the ionization potential serves to attract a raft of particles with their sodium-bridging agents, the heat then generated is sufficient to break the bond of the coating to the aluminum, probably by expanding the aluminum under the coating. These effects appear to lend support to Iler's hypothesis, in that sodium appears linked to silica which is deposited when the ionization potential is reached and the sodium absorbs energy sufficient to affect the electronic, vibrational and rotational levels of the atom leaving it in a high energy state that under certain conditions leads to a decomposition of, or modification of, the electronic energy state leading to a photochemical reaction. It is apparent that as the voltage is increase, larger and larger colloidal silica groupings of molecules are attracted to the anode and deposited there, starting from small point sources of illumination, to "strings", to rafts or clumps, indicative of electrophoretic migration of colloidal silica.

The NMR studies[53] report not only monomeric $[Si(OH)_{4-x}O_x]^{x-}$ anions but a spectrum of oligomeric anions differing in both molecular weight and extent of ionization wherein $-Si-O-Na^+$ groups abound. Anions having charges as high as 4^- were detected but at pH 12 the largest fraction had a charge of 2^-. The data lends credence to Iler's hypothesis, and to the mechanism proposed here.

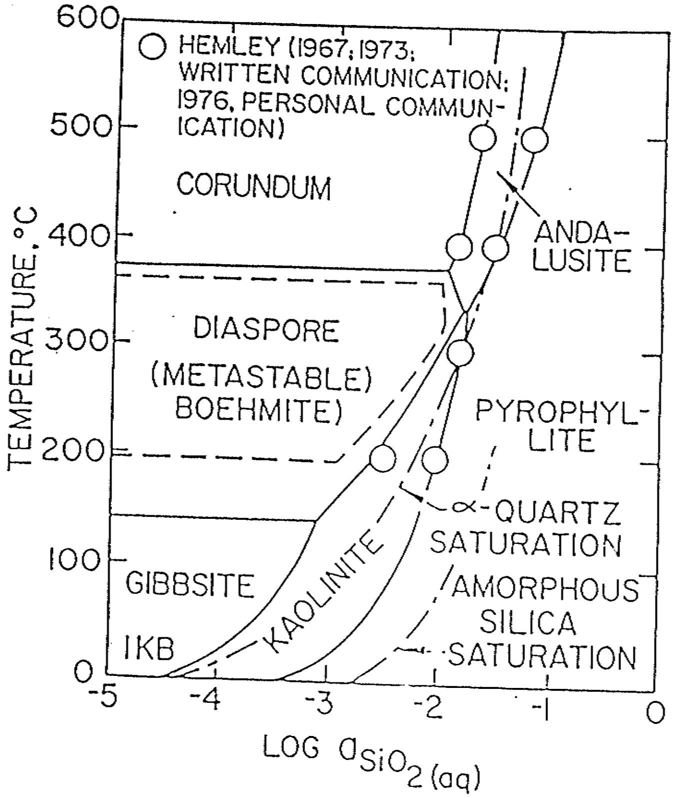


Figure 54

EQUILIBRIUM ACTIVITY DIAGRAM for the SYSTEM Al_2O_3-SiO_2-H_2O

The coating from the various silicate solutions appears basically to be a sintered form of amorphous Na_2SiO_3 (28.8%) plus SiO_2 (71.2%) with some evidence of K_2O plus Al/Al_20_3 occasionally evident, with some crystallites.

Figure 55 shows the Equilibrium Activity Diagram for the System: Al_20_3-SiO_2-H_2O at 1 kb and temperatures to 600°C generated from thermodynamic data for minerals.[54] Note that the amorphous silica deposition occurs in the area of dilute silicate concentration, as has been found in this research.

The term "sintering" has been mentioned as the energy term allowing the silica to be deposited. Thermodynamically, flame temperatures can be determined, but, as yet, there is no way of determining the temperatures of sparks,[55] especially those that occur under water.

Pourbaix has stated:

> Silicon cannot be separated from aqueous solutions of its salts by electrolysis; it is usually obtained by the reduction of silica or silicates using alkali or alkaline earth metals, magnesium or aluminium.[56]

Silicon is obtained by electrolysis of $SiCl_4$ from organic solvents. In the research undertaken here it is possible to extract silica in one form or another from aqueous solution by electrolysis .

12.0 COST ADVANTAGE OF SILICADIZING

As the number of functions required to silicadize aluminum products is substantially reduced over that required when an anodized coating is prepared, the number of tanks required will vary from one to four depending on the variety of coatings to be offered, as explained above. The tanks will be sized according to the articles to be processed, allowing 400 litres per square metre of surface area to be treated. The investment in capital equipment is substantially reduced by the reduction in the number of tanks required over that required for anodizing (See Appendix A). The coatings can be put on in a matter of 5 to 7 minutes processing time; thus the power costs and labour costs are also correspondingly reduced per unit of production relative to anodizing.

The chemicals required are sold in concentrated form. The concentrate is mixed at a rate of 1 gallon to 4 gallons of distilled or demineralized water. A gallon of concentrate thus prepared will coat up to 2000 square feet at 0.5 mils thickness. The cost of the basic solution for silicadizing is less than the sulphuric acid required for anodizing.

The cost of the required rectifier for silicadizing will be marginally higher than the rectifiers currently available from stock standardized for the acid anodizing of aluminum. Thus while no fixed costs are quoted, the economies in capital equipment, electrolyte costs, reduced production time and labour, all predicate an over-all reduction in cost relative to anodizing for basic coating protection of aluminum, magnesium or tantalum.

13.0 CONCLUSIONS

The conclusions reached as a result of this research are that silica can be easily deposited from an aqueous solution of silicates onto aluminum, magnesium, or tantalum, resulting in a glass or ceramic-like surface which, on the application of heat, can be made smooth, opaque, and possibly transparent with the right chemical mix. The optimum conditions for the silicadized Undercoat occur at pH 12 with a solution of around 5° to 10° Baumé, and temperatures in the range of 25°C to 60°C. Quality control of the plating from silicate solution for a given repetitive thickness can be obtained through control of the applied voltage rather than by current, as used in acid anodizing.

The coatings appear to be of amorphous compositions with the inclusion of some micro crystallites. Chemically, the coatings are a mixture of Na_2SiO_3/SiO_2 with occasionally some K_2O and Al/Al_2O_3 within the structures--in effect a glass or ceramic. The surface of the undercoat has been shown to be of a sintered appearance as though fire polished, being of a rounded, botryoidal form, yet having an evident porous structure highly suited to holding additional surface coatings such as epoxy paints. The coatings have shown resistance to corrosion of the underlying metal, partly through generation of a new oxide coating on the metal before the silica coating is deposited.

In addition, a mechanism has been developed to explain the observed scintillations that appear during the process, and it has been shown that this process can occur separately from the silicadizing under special circumstances wherein an outside resistance is added to the circuit. Further, that the high voltage used results in a highly ionized field with thermionic emission (glow discharge) serving to vapourize potassium/sodium and thus to provide the scintillations observed.

A mechanism to explain the silicadizing process has also been presented. It has been suggested that potassium/sodium ions act as bridging ions between silicate particles, which, with the vapourizing of the elemental sodium, allow deposition of silica onto the aluminum oxide surface. The heat generated from the plasma is responsible for the sintered look of the resultant coating when viewed under SEM conditions.

While successful silicadized coatings have been obtained with the various coatings described, it is clear that more information must be gathered to obtain a better understanding of the silicadizing process. Most of the available information has been found to be empirical. The ultimate mechanism of silicadization, the effect of Na_2O_2 on the hardness of the deposit, the effect of acetic acid on the smoothness of the deposit, temperature effects on the hardness and smoothness of the deposit and the aging effects of the bath have to be better understood to obtain a clearer picture of the silicadizing process. The colour coatings are currently restricted in choice of colour, and experiments which seek to increase the strength between the silicadized layer and the adsorbed colour layer are required. Many chemicals to colour the anodized coatings have been used in the acid anodizing process. Experimenting with these chemicals in the Super Hardcoat formulation may prove worthwhile.

The silicadized Undercoat has proven to be easily obtained, economical, and satisfactory as a base for holding paint on aluminum. In addition, the Undercoat has proven to be resistant to salt spray, humidity, and to acid environments, showing promise for commercial application.

It is anticipated that the Hardcoat and Super Hardcoat, being basically of the same material, will pass the same tests. For these latter, commercialization requires that further research be undertaken.

In Anodic Oxide Films Young[57] states,

> It is evident that the behaviour of aluminum is very complicated and that much systematic investigation is required under a wide variety of experimental conditions.

Silicate is very similar to aluminum oxide and matches it in complexity. By suggesting in this paper a mechanism to explain the scintillations observed, and a mechanism to explain how silica can be deposited from an alkali solution, further horizons for research appear to be opened.

14.0 SUGGESTIONS FOR FURTHER STUDY

While some suggestions have been indicated in the Conclusions above, there are other areas which merit attention. The matter of glow discharge plasma reactions in solutions has not been dealt with extensively in the literature although physically it appears to be a very active area in physics and chemistry.

The work mentioned at the end of the Section 6.2, Melting Point, indicated a melting of the silica coating in conjunction with a second coating of a borate solution, resulting in the production of a line of transparent glass occurring at the solution surface interface, with production of a very smooth coat of borate on top of the silica coating. This phenomenon needs further study to see if a smooth resistant coating can be developed at a lower temperature.

Several existing studies have indicated aluminum, which has no known biological function in higher animals, is involved in two of the characteristic pathological features--senile plaques and neurofibrillary tangle bearing neurones--of brains of patients with Alzheimer's disease.[58] A two-year study by Dr. Donald McLachlan, Director of the University of Toronto's Centre for Research in Neurodegenerative Diseases has indicated that if the high level of aluminum in Toronto's drinking water (200 mg/l) was reduced to 50 mg/l, it might cut the rate of Azheimer's disease by 40%. Today 300,000 Canadians are affected, and by 2033 almost a million Canadians are expected to suffer from memory loss and disability so severe that they are unaware of their lives. The aluminum in drinking water mainly comes from the use of alum by the guardians of municipal drinking water for purposes of clarification. However, one of the most common sources of additional dietary aluminum referred to in the literature is aluminum cookingware. The cooking of acidic foods in aluminum dissolves the aluminum and increases its concentration in the foods. Even scrubbing the pots releases aluminum particles, exposing fresh surfaces. Many additives to food involve aluminum; for example, sodium aluminum phosphate is a source of acid in raising agents, while sodium aluminum silicate is an anti-caking agent. If some of the aluminum can be prevented from dissolving into the foods by silicadizing the utensils, it may assist in reducing the onset of Alzheimer's disease.

Most of the silica-aluminum infrared studies have started from an acid position; similarly, zeolites are presumed to have highly acidic surfaces similar to those of the silica-alumina gels. It may therefore be of interest to examine the aluminum-silica derived from alkali sources, as in silicadizing, through infrared studies in greater depth as a further research project, and also relative to its use.as possible catalysts.

The question of whether the silanol complex disintegrates as a result of a thermionic-electrolytic reaction may possibly be answered if H_2SiO_4 were to be used instead of K_2/Na_2SiO_4 to give silicate coatings without scintillations.

Today fibre optics are being produced with aluminum and with gold exteriors to reduce the possibility of light losses through increased reflectivity of the surface layer. In the case of gold, the melting point is too low to adequately silicadize the surface. However, it should be possible to silicadize the exterior of the aluminum-coated optic fibre and thus increase its resistance to abrasion, to acid and salt, and to water corrosion, a practical application of silicadizing.

Tantalum fibres are also produced, and it should be possible to silicadize these fibres, and possibly make the coating transparent by fusion in an argon or nitrogen atmosphere. Thus, it may be possible to reduce corrosion of the tantalum through silicadizing.

With regard to colours of silicadized surfaces, only a limited range of white, grey, beige, brown and black have been achieved. Work with a limited number of dyes has not been successful. Baking with various metal oxides may be effective in adsorbing the colours into the silica surface, as has been done with sapphires.

Because silicadized aluminum has been shown to be resistant to acid, salt, and water corrosion to a degree, and also to be able to take paint for further finishing, there are possibilities of commercial development in several areas:

Aluminum boats, canoes and buoys are in use on inland lakes. On silicadizing the aluminum, the application could be broadened to include sea use, with or without epoxy coatings. Research is required. In addition sailboat fittings could be made of aluminum and silicadized, reducing the weight compared to bronze fittings, although not to plastic.

Electric cars need to be as light as possible. Silicadized aluminum or magnesium panels, exhaust piping, mufflers, and hub caps would reduce the weight relative to steel, with the additional advantage of acid and salt resistance. Colour, where required, could be added by epoxy painting.

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APPENDIX A

DEVELOPMENT AND ANODIZING OF ALUMINUM

Since 1886, when aluminum was first extracted electrolytically by an American, Charles M. Hall, and independently by a Frenchman, P.L.T. Heroult, this metal has found increasing applications in a variety of industrial and household uses. Aluminum comes from the electrolytic extraction industry in ingots which are then melted and alloyed in electric furnaces and cast into billets or sheets. The billets are extruded into strips, bars, rods and structural members, or forged into utensils, containers and hardware. For exterior and structural use, experience had to be gained in alloying to impart sufficient strength to the panels. The light weight, ease of construction and good corrosive resistance of aluminum and its alloys make it suitable in a multitude of applications, including outdoor cladding, road signs, and structural members in motor vehicles and aeroplanes.

Aluminum owes its resistance to corrosion to the aluminum oxide film that forms naturally and bonds tightly to its surface. It quickly re-forms if damaged. This oxide film is approximately 7.5 nm thick and gives a limited protection from corrosion. The thermodynamic conditions illustrating the stability of the oxide film are shown in Figure A1, the Pourbaix diagram of Potential vs pH,[1] which shows that aluminum has a passive nature over the range shown. Figure A2[2] shows the weight loss of alloy 3004-H14 after exposure of one week in distilled water and in solutions of various pH values.

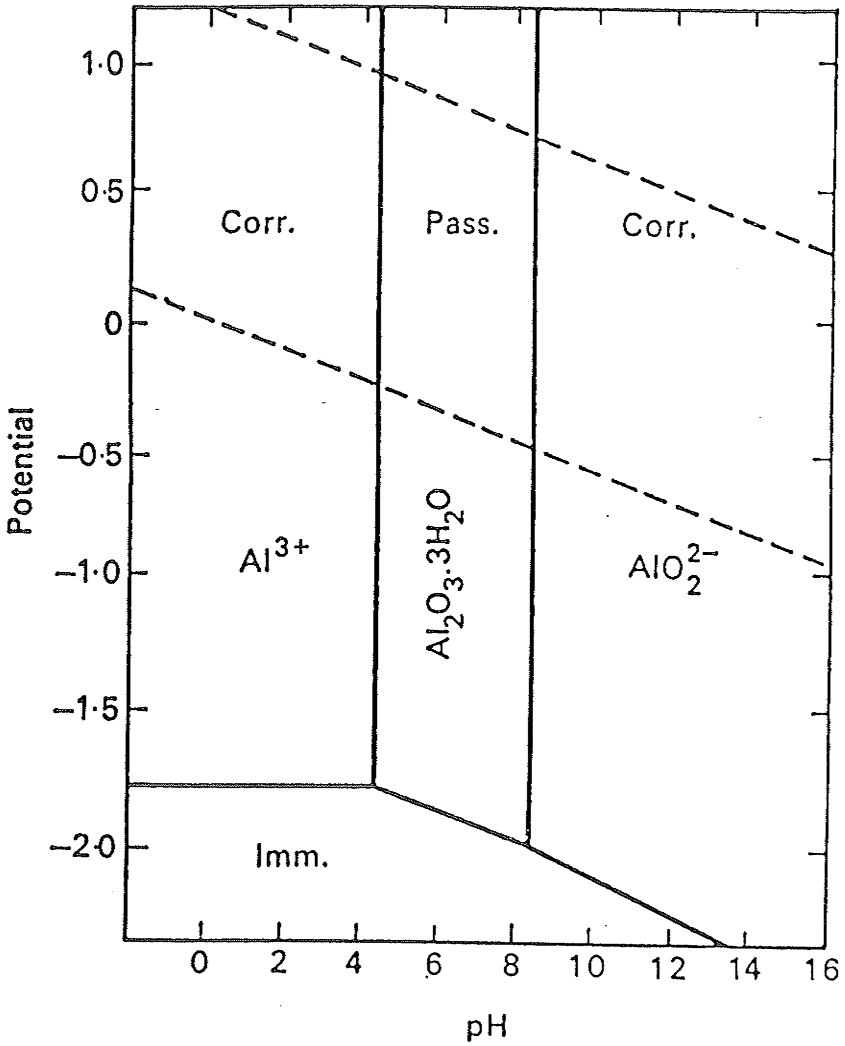


Figure A1 **POURBAIX (POTENTIAL VS pH) DIAGRAM FOR ALUMINUM AND BAYERITE ($AL^2O^3.3H_2O$) FORMATION.** [1]

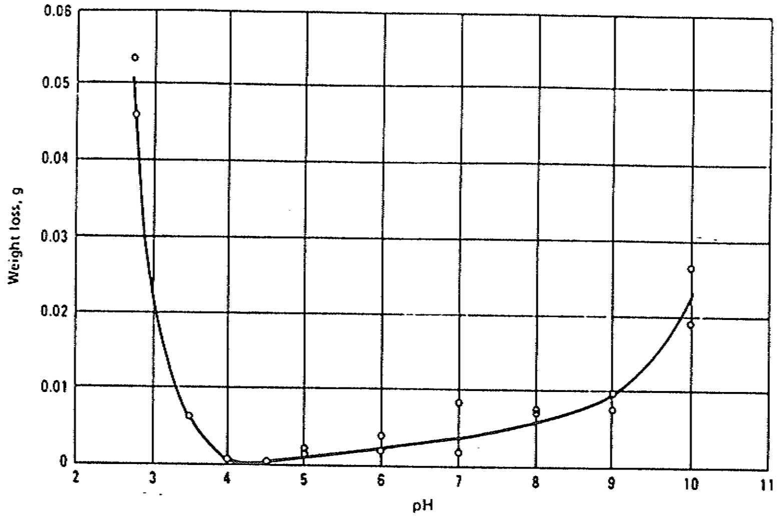


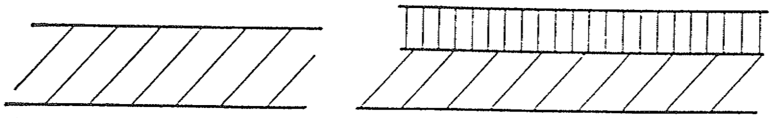
Figure A2 **WEIGHT LOSS OF ALLOY 3004-H14 EXPOSED 1 WEEK IN DISTILLED WATER AND IN SOLUTIONS OF VARIOUS pH VALUES. SPECIMENS WERE 1.6 X 13 X 75 MM. TEST TEMPERATURE WAS 60°C**

Historically, for exterior use, the natural oxide coating was not enough. Paint and other coatings adhered poorly to it and deterioration under the effects of temperature and acid rain dictated that better protection be sought. This was obtained through anodizing the aluminum in a variety of acid solutions. Anodizing is an oxidation process which deposits an oxide layer on the metal that is thicker than the naturally occurring oxide layer.

In **anodizing,** the articles are the anode in a dilute **acid** solution--not the cathode as in electroplating--and the oxygen liberated at the anode face results in the formation of the coherent oxide film which is very adherent to the metal. The diagrams in Figure A3 show how the film is formed in acid anodizing on the surface of the aluminum.[3] The main processes in use employ solutions of sulphuric acid, chromic acid or a mixture of sulphuric acid and oxalic acid as electrolytes.[4] All are damaging to the environment .

The anodized layer is built up from the base of the film, but the acids used for the anodic oxidation processes have a solvent action on the aluminum oxide film so that a porous cell structure, as shown, is formed. About half the aluminum converted to aluminum oxide is dissolved by the acid anodizing solution under normal conditions. High current densities give thicker films and when a certain critical thickness is reached, depending on the alloy being anodized, the rate of film formation balances the rate of film dissolution by the solution and the film will not grow thicker. However, the overall dimension of the aluminum article will be reduced.[5]

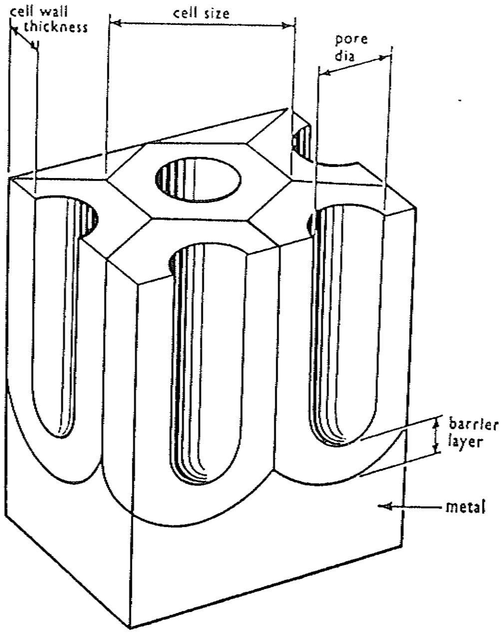
The thickness of the cell walls and the barrier layer are proportional to the voltage applied. The size of the pore or cell is dependent on three main interrelated factors: solution concentration, solution temperature, and applied current density. By varying these factors, anodizing film can be produced for different purposes; for example, the use of a more concentrated



Aluminium surface before anodic oxidation.

Anodised aluminium surface showing oxide layer.

During the anodic oxidation process the surface of the aluminium is converted to aluminium oxide. The thickness of the oxide layer is approximately twice that of the aluminium removed.



Microsection of an anodic film showing porous cell structure.

Figure A3 **MICROSECTION OF AN ANODIC FILM SHOWING POROUS CELL STRUCTURE ABOVE NON-POROUS BARRIER LAYER, WHICH DEVELOPS DURING ACID ANODIZATION OF ALUMINUM**[3] sulphuric acid solution and a higher temperature gives a more open structure suitable for dyed, decorative aluminum. Conversely, the use of a lower acid concentration and a lower operating temperature results in a smaller pore size and a harder film suitable for engineering applications.[6]

Most acid anodic films must be sealed, involving treating the anodized or the anodized and dyed articles in boiling water, salt solutions, or in low pressure steam and, under these conditions, hydration of the amorphous oxide is believed to occur, becoming the crystalline oxide $Al_2O_3 \, H_2O$. This change is accompanied by a volume increase which swells the cell walls closing the pores while preserving the cell structure.[7] The film thickness is usually between 25 to 100 microns (0.001 to 0.004 in.), depending on the specification, but thicker films can be obtained on suitable alloys.[8]

The minimum normal sequence in all the above anodizing processes in acid solutions are the following:[9]

1. Preparation of sheet to be anodized (e.g., degreasing if needed)
2. Anodizing
3. Cold rinse
4. Neutralising
5. Cold rinse
6. Dye
7. Rinse
8. Seal

The following list, while not exhaustive, represents some of the efforts of prior workers in the field of acid anodizing of aluminum:
3,003,933; 3,275,537; 3,355,368; 3,445,349; 3,532,607; 3,672,964; 3,899,400; 3,996,115; 4,113,579; 4,128,461; 4,170,525; 4,440,606; and 4,502,925.

These patents show the significant role which the electrolytic solution plays in the anodizing process in providing aluminum and its alloys with a protective coating. In general, the nature and properties of the coating depend on the composition of the anodic bath. In the above patent list, most of the anodic solutions are acids: sulphuric, oxalic, chromic, hydrofluoric, potassium permanganate, malonic, nitric, and hydrochloric, although sodium carbonate, sodium bicarbonate, borax, and mixtures of ammonia and ammonium sulphide are also recommended. For instance, in addition to the above patents, Loeb (1899) U.S. Patent No. 690,210 uses hydrofluoric acid with sodium carbonate; Mershon (1913) U.S. Patent No. 1,065,704, borax; Presser (1914) U.S. Patent No. 1,117,240, sodium carbonate and bicarbonate; Abernethy (1919) U.S. Patent No. 1,323,236, potassium permanganate; Flick (1923) U.S. Patent No. 1,526,127, ammonia and ammonium sulphide; Bengough and Stuart (1923) U.S. Patent No.1,771,910, chromic acid; Walls (1985) U.S. Patent No. 4,502,925, nitric, hydrochloric and hydrofluoric salts.

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[1] The Canning Handbook, Surface Finishing Technology, 798 ff (1982).

[2] ASM Metals Handbook, Vol. 2, American Society of Metals, (1979) 205.

[3] Ibid., 797.

[4] The Canning Handbook, 797, (1982).

[5] Ibid., 798.

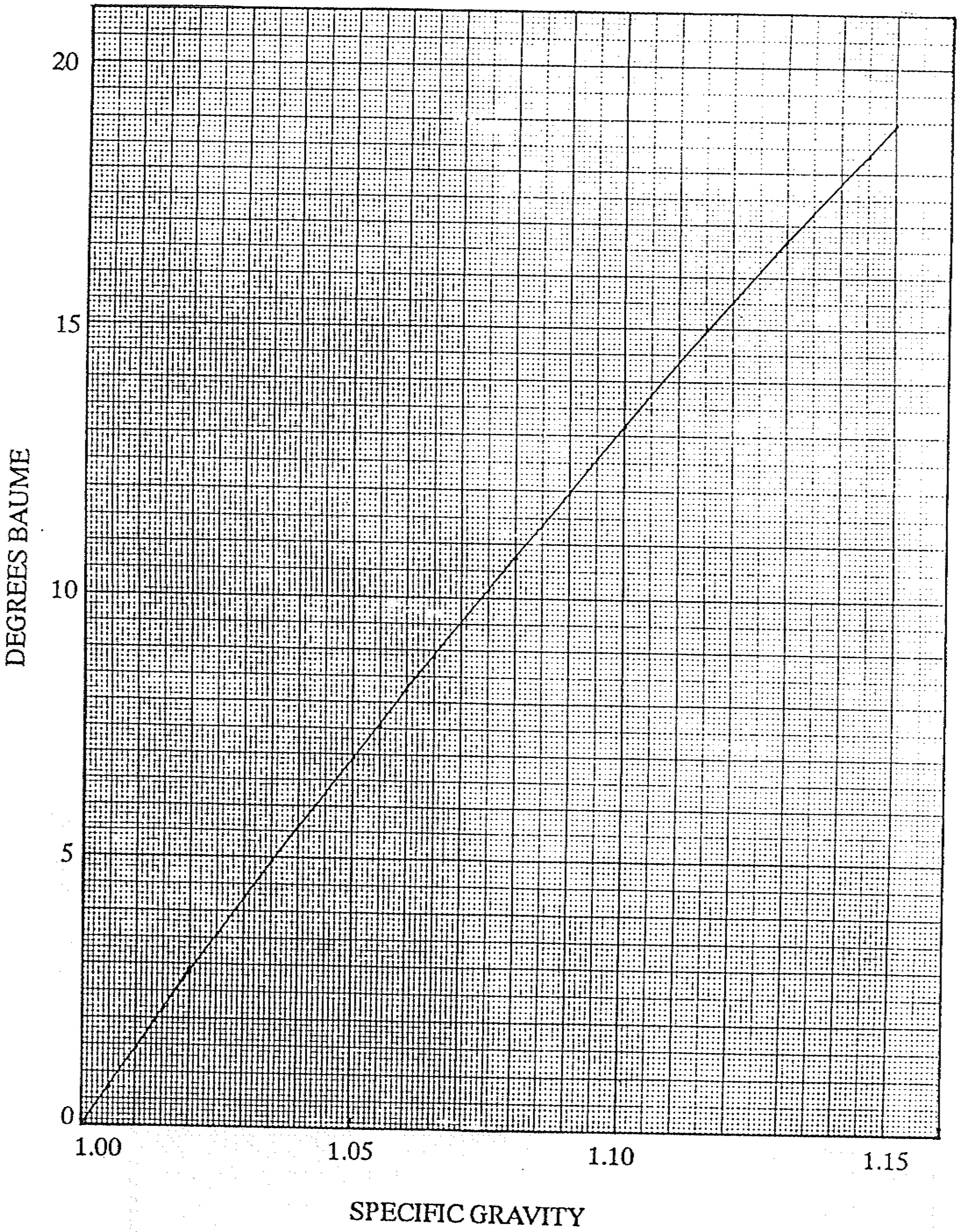
[6] Ibid., 823.

[7] Ibid., 798.

[8] Ibid., 820.

[9] Ibid., 822.

APPENDIX B



US NATIONAL BUREAU OF STANDARDS

APPENDIX C

SHERWIN WILLIAMS

INTRA-COMPANY CORRESPONDENCE

RECEIVERS LOCATION AND DEPARTMENT
Winnipeg, Man.
TO (INDIVIDUALS NAME)
Richard Kozicki
REPLY TO LETTER OF

DATE
June 26, 1985
SENDERS LOCATION, DEPARTMENT, AND TELEPHONE NUMBER
AWSTC-Automotive Aftermarket - 3469
SUBJECT
Flyer Industries

We finished lab testing on the aluminum substrates for Flyer Industries. Both SUNFIRE 421 and Acrylic Enamel with POLASOL were the topcoats. Various pretreatments and primers were tested over both aluminum substrates (non-pretreated and the Silicordizing process). Lab tests were 96 hour Humidity (adhesion tested immediately and after 1 hour recovery) and 240 hour 5% Salt Spray.

The best performing systems are:

Acrylic Enamel with POLASOL
Fleet Epoxy (E2 R 978)

and

SUNFIRE 421
Fleet Epoxy (E2 R 978)

The SUNFIRE 421/Epoxy system was predictably better than Acrylic Enamel. Uncoated panels with just the Silicordizing process performed well in both Salt Spray and Humidity.

We had to cut the panels up into smaller test panels to allow us to test all the variables. If you need larger panels to show, please send additional pieces (2 for each topcoat system).

The Silicordizing process seems to give better performance than the nonpretreated process. However, topcoats do not adhere directly, even when scuff sanded. This pretreatment must be primed. Our tests show the Humidity test to be more critical than the Salt Spray.

The Humidity test is a good indicator of long term adhesion.

Once again, the best system appears to be: Silicordizing Process Pretreatment, Fleet Epoxy, E2 R 978, SUNFIRE 421.

Kenneth Leluga

Kenneth C. Lelugas
Automotive Aftermarket

KCL:dam

cc: MIH, JAK, BWilliamson

APPENDIX D

CIE INDUSTRIAL CHEMICAL & EQUIPMENT CO.
COMPLETE METAL FINISHING EQUIPMENT & SUPPLIES

2205 E. HENNEPIN AVENUE
MINNEAPOLIS, MINNESOTA 554
TELEPHONE: (612) 378-7581

SALT SPRAY TEST REPORT

REPORT NO. 11268 P.O. NO. 7791

DATE January 14, 1991 B/L NO. ______

CUSTOMER: Nor-Ell, Inc. 851 Hubbard Avenue - St. Paul, MN 55104

PARTS DESCRIPTION: 1 Aluminum Test Panel

TEST SPECIFICATIONS: ASTM Specification B-117

A. Testing Media: 5% Sodium Chloride Sp. Gr. 1.04 pH: 7.2

B. Cabinet Temperature: 95° F. Tower Temp. 119° F.

C. Fog Collection Data: 1.6 cc/hr. Sp. Gr. 1.03

D. Method of Cleaning Before: None

E. Method of Support: Rack mounted, 6% from vertical

F. Description of Protection: Special

G. Exposure Period: 336 Hours

H. Interruptions: None, other than for testing media replenishment

I. Results: ( ) In our opinion, parts tested are Satisfactory, XXXXXXXXXXXXXX, with no evidence of excessive corrosion of basis metal.

(X) Parts tested are returned for your examination.

INDUSTRIAL CHEMICAL & EQUIPMENT CO.

Nicholas C
Nicholas Corriere, Jr.

State of Minnesota, County of Hennepin
Subscribed and sworn to by N. Corriere, Jr.
this 14th day of January, 1991

Mary E. Kohls

MARY E. KOHLS
NOTARY PUBLIC—MINNESOTA
HENNEPIN COUNTY
My Comm. Expires Mar. 13, 1994

APPENDIX E

POSSIBLE DANGERS IN THE USE OF FLUORIDES IN SILICADIZING

In silicadizing with HF present, it is important to understand how fluoride ions react at high voltage electrolysis in alkali aqueous solutions if such a bath is to be considered indispensable in the silicadizing process. In the light of using HF and related compounds as "an essential feature of the present invention"[1] wherein Na_2O_2 is used with the potential of free oxygen, along with anodic oxygen production, and where continuous sparking is evident as in Super Hardcoat silicadizing, substantial care and continual vigilance are essential.

The potential at which F^- discharges is higher than that where water decomposition starts (1.23 v):

$$F^- = 1/2\,F_2 + e^- \quad (E^\circ = 2.85\text{ v})^2$$

$$\text{HF aqua} = 1/2\,F_2 + H^+ + e^- \quad (E^\circ = 3.03\text{ v})$$

For electrolytes such as LiF, NaF, KF. NH_4F or KFHF there is a break at about 1.5 v, which is believed to be associated with the decomposition of H_20 (1.23v), and a second at a higher voltage which varies with F^- concentration and may be associated with the primary electrode process involving discharge of the F^- ions.[3]

The gaseous compound having the formula OF_2 has been found among the products of electrolysis of a slightly moist F_2-generator bath at 100°C or lower. Because NaOH is the solvent used in the preparation of silicate solutions then, according to Cotton and Wilkinson[4],

[o]xygen fluorides (OF_2) are prepared by passing fluorine gas rapidly through a 2% sodium hydroxide solution, by electrolysis of aqueous HF-KF solutions, or by the action of F_2 on moist KF. . It is a pale yellow poisonous gas (bp 145°C). It is relatively unreactive and can be mixed with H_2, CH_4, or CO without reaction, although sparking causes violent explosion. Mixtures of OF_2 with Cl_2, Br_2, or I_2 explode at room temperature. It is fairly readily hydrolized by base:

$$OF_2 + 2OH^- \rightarrow O_2 + 2F^- + H_2O$$

It reacts more slowly with water, but explodes with steam:

$$OF_2 + H_2O \rightarrow O_2 + 2HF$$

and it liberates other halogens from their acids or salts:

$$OF_2 + 4HX(aq) \rightarrow 2X_2 + 2HF + H_2O$$

In silicadizing, the generation of steam has been experienced occurring around the anode. With the sparking that occurs in silicadizing and the possibility of free oxygen the danger of explosions is present. OF_2 is only slightly soluble in water, but its oxidation power towards aqueous solutions is very high. The further danger is to the personnel engaged in silicadizing with OF_2 present.. It is said to be more dangerous to lungs than fluorine itself because it passes the bronchia and dissolves in the delicate tissues, producing a delayed oedema.[4]

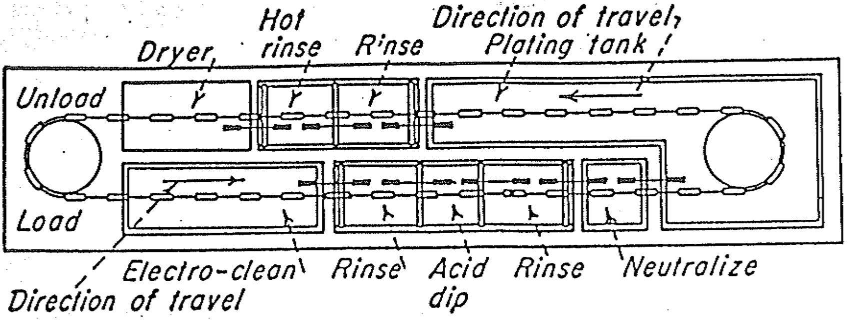
APPENDIX F

RECTIFIER DATA

Input:	550-600 V, 3 phase
Output:	600 V 100 KW 0-166 Amperes
Details:	Duty Cycle 500% overload for 30 sec. 125% for 2 hrs.
Regulator:	Automatic constant current Automatic voltage stabilizer +/- 1% Starting AC magnetic contactor (protection short circuit limit fuses) Peak inverse voltage 10x rated DC output.
Transformer:	Cu-Coil insulating material to 220°C Maximum temperature rise 80°C above 40°C ambient
Cooling:	Forced air
Meters:	DC voltage Dc amperage
Shunt:	50 millivolt

APPENDIX G

INDUSTRIAL SET-UP



THE DIAGRAM SHOWS A PLAN VIEW OF A RETURN-TYPE PLATING MACHINE, CONTAINING RELATIVELY FEW OPERATIONS. THIS TYPE OF MACHINE MAY BE EXPANDED TO EMBRACE ALMOST ANY NUMBER OF OPERATIONS. OR TWO SEPARATE AND DISTINCT OPERATING ROUTINES MAY BE BUILT INTO ONE OF THESE MACHINES, THUS SERVING THE PURPOSE OF TWO UNITS: I.E., THE RACK MAY BE LOADED ON CONVEYOR AT ONE END, PASSED THROUGH VARIOUS OPERATIONS AND BE REMOVED AT THE OTHER END FOR COLOUR BUFFING, THEN AGAIN RACKED AND REPLACED ON CONVEYOR FOR RETURN TO THE STARTING POINT THROUGH THE PRESCRIBED PROCESSES. THE ADAPTABILITY OF THIS MACHINE IS ALMOST UNLIMITED. IN SILICODIZING, THE UNDERCOAT AS WELL AS HARDCOAT PLATING, COULD BE DONE ON THE ONE AUTOMATED MACHINE.

LARGE QUANTITIES OF SMALL OBJECTS ARE PLATED IN PERFORATED STAINLESS STEEL BARRELS WHICH ROTATE IN THE PLATING SOLUTION

Adapted from the Chemical Engineer's Handbook, 3rd. Edition,

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