TANTALUM PRODUCERS INTERNATIONAL STUDY CENTER

QUARTERLY BULLETIN ISSUE No 28 DECEMBER 1981 FOURTH QUARTER

## T.I.C. Activities

The Sixteenth General Assembly was held in the dignified surroundings of the Cercle Royal Gaulois in Brussels on October 29th 1981, chaired by the President of the T.I.C., Dr George Korinek.

Three companies were elected to membership, bringing the total number of members to sixty-one.

Production statistics for the first two quarters of 1981 were circulated, and showed that tantalum supply continues steadily. Figures had been reported by all twenty-two of the member companies engaged in the production of tantalum. Production totalled 1,286,497 lbs. $Ta_2O_5$ contained, for the first six months of 1981, being 841,423 lbs. in slags and 445,074 lbs. in concentrates.

Mr Conrad L. Brown, Vice President and General Manager of Fansteel Inc., North Chicago, Illinois, U.S.A., was elected to the Presidency for the coming year, succeeding Dr Korinek at the end of the current meeting. Mr René Van Achter, representing Sabemin, was elected to the Executive Committee following the retirement of Mr Paul Leynen; Mr Van Achter is of Belgian nationality. The other members of the Executive Committee were re-elected to a further term of office.

Dr Korinek, Mr Brown and Mr Becker-Fluegel visited Mr Leynen after the meeting to present to him an elegant tantalum plaque, specially made in appreciation of his service to the T.I.C.

Mr Henri Simonet, Professor at the Université Libre de Bruxelles, formerly Foreign Minister of Belgium, very kindly consented to address the meeting, after the formal business of the T.I.C. had been concluded. He gave a well-informed and penetrating survey of « Recent Developments in African Affairs », and the wide range of his observations proved to be of great interest to the delegates.

## 1980 U.S. Shipments of Tantalum and Columbium Products

Even though the shipments of tantalum and columbium products in the U.S. by domestic producers in 1980 decreased by 11.2 % from 1979, they equalled the shipments of 1978. The comparison from 1976 through 1980 follows : (1,000 lb. units of contained tantalum and columbium)

| *PRODUCT* | *1976* | *1977* | *1978* | *1979* | *1980* |
|---|---|---|---|---|---|
| TANTALUM | | | | | |
| Oxides and salts | 55.4 | 62.8 | 38.2 | 35.4 | 48.7 |
| Alloy Additive | 13.2 | 12.2 | 4.4 | 23.7 | 8.1 |
| Carbide | 93.3 | 113.5 | 116.9 | 190.1 | 125.7 |
| Powder and Anodes | 759.0 | 759.2 | 840.0 | 928.2 | 852.9 |
| Ingot | 7.7 | 8.0 | 7.2 | 6.6 | 23.0 |
| Mill Products | 238.5 | 292.4 | 321.9 | 365.2 | 318.8 |
| Scrap | 130.7 | 168.3 | 184.1 | 151.0 | 130.9 |
| Other | — | 2.0 | 2.1 | — | 1.7 |
| Total | 1,297.8 | 1,418.4 | 1,514.8 | 1,700.2 | 1,509.8 |
| % Change | 50.0 | 9.3 | 6.8 | 12.2 | (11.2) |
| COLUMBIUM | | | | | |
| Compounds | 791.8 | 872.4 | 1,611.0 | 1,627.8 | 1,066.6 |
| Metal | 101.6 | 189.3 | 223.7 | 329.5 | 344.7 |
| Miscellaneous | 41.0 | 16.6 | 12.5 | 64.2 | 18.5 |
| Total | 934.4 | 1,078.3 | 1,847.2 | 2,021.5 | 1,429.8 |
| % Change | (12.3) | 15.5 | 71.3 | 9.4 | (29.3) |

### T.I.C. SIXTEENTH GENERAL ASSEMBLY

**The Sixteenth General Assembly of the Tantalum Producers International Study Center was convened at the Cercle Royal Gaulois, Brussels, Belgium, on Thursday, October 29th 1981, chaired by Dr George Korinek, President. 44 of the 58 member companies were represented.**

**The General Assembly conducted the business of the T.I.C., including :**

- **The election of 3 new members;**
- **A review of the production statistics for the first two quarters of 1981;**
- **Election of officers.**

**Mr Conrad L. Brown of Fansteel Inc was elected President for the coming year. Mr René Van Achter of Sabemin was elected to the Executive Committee on the retirement of Mr Paul Leynen.**

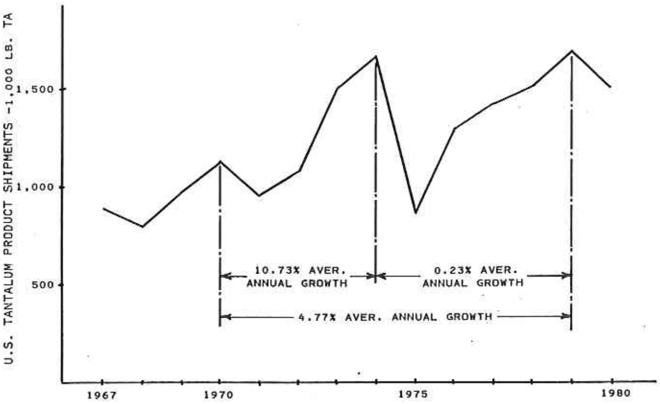
**The business of the meeting having been concluded, Mr Henri Simonet, Professor at the Université Libre de Bruxelles, formerly Foreign Minister of Belgium, addressed the assembled delegates on « Recent Developments in African Affairs ».**

**The Seventeenth General Assembly of the T.I.C. will be held on June 7th to June 9th 1982 in Tulsa, Oklahoma, U.S.A. Fansteel Inc. will be the host company. The meeting will include a visit to the Fansteel basic-processing plant in nearby Muskogee, Oklahoma.**

**For further details of the meeting or information on the T.I.C., please contact Mrs. J.A. Wickens, Secretary, Tantalum Producers International Study Center, 1, rue aux Laines, 1000 Brussels, Belgium; cable address : Tictan Brussels.**

Since most of the decrease in 1980 can be attributed to economic conditions, there again does not appear to be any significant effect of reduction in demand resulting from efforts to eliminate the use of tantalum or substitute other metals for it. The larger decrease in carbide than in other products may indicate some effects of conservation in the cutting tool industry. Since these reported shipments do not include carbide imported or recycled, it is hard to draw firm conclusions.

The U.S. shipment trend for the 1970 decade can be best visualized graphically. The compounded average annual growth rate from 1970 through 1979 was 4.77 %, but if 1980 is included for a full ten years, the rate was only 3.05 %. It is interesting to note, however, that the peak in 1979 was almost identical to the peak in 1974, indicating that the rapid growth of the first four years of the decade was not repeated in the last half of the decade. Without economic-cycle effect, the market could be considered to have levelled.



The shipments by U.S. producers of capacitor powder and anodes shows an average annual growth rate of 5.51 % for the decade through 1980. The actual growth, however, is certainly greater as there were no significant imports of capacitor powder at the beginning of the decade. Powder imports are now quite sizeable. In addition, exports of capacitor powder in comparison to the total production are now less than ten years ago when there was practically no powder production outside the U.S. There are now sizeable suppliers in both Western Europe and Japan.

Based on the reported shipment of products, an estimate can be made of the source material usage, allowing for unrecoverable losses in processing and for the scrap purchased by the processors for recycling. Calculation provides the following estimates of the tantalum and columbium content of ores and slags consumed each year by the processors (1,000 lb. units):

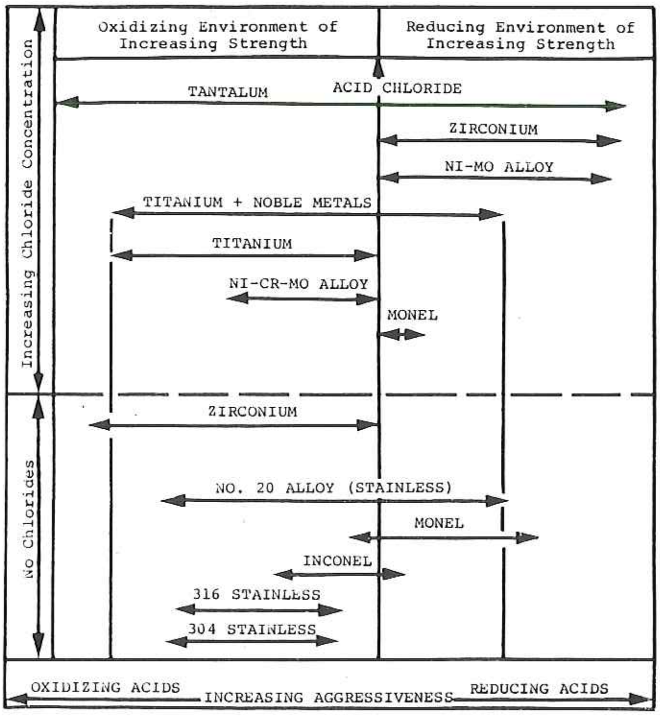
| *Year* | *lb.* $Ta_2O_5$ | *lb.* $Cb_2O_5$ | $Ta_2O_5 : Cb_2O_5$ |
|---|---|---|---|
| 1976 | 1,740 | 1,490 | 1.17 |
| 1977 | 1,910 | 1,720 | 1.10 |
| 1978 | 2,040 | 2,950 | 0.70 |
| 1979 | 2,260 | 3,220 | 0.70 |
| 1980 | 2,020 | 2,280 | 0.89 |

The increase in the ratio of tantalum oxide to columbium oxide in the ores and slags used probably indicates a reduction in the use of columbites of the low ratio tantalum content. Both the decreased demand for columbium products and the introduction of lower priced refined columbium oxide made from pyrochlor sources have probably contributed to the shift. The latter situation is also considered to be the cause of a large part of the drop in columbium compounds by domestic tantalum processors as pyrochlor sources have begun to provide high purity columbium master alloys.

## Corrosion resistance of tantalum - Introduction

*The source material for this article has been obtained primarily from the extensive « Corrosion Data Survey on Tantalum » written by M. Schussler, Senior Scientist of Fansteel, Inc., as published in May 1972. It is intended that future articles will be published covering more specific corrosion characteristics of tantalum - Editor.*

The corrosion resistance of tantalum is phenomenal in comparison with other corrosion resistant metals and alloys, as illustrated in the following diagram which indicates the useful range of various commercial metals and alloys in oxidizing and reducing environments in either the presence or the absence of chlorides :



Oxidizing-type environments are those containing nitric acid, ferric chloride, aqua regia, cupric chloride, hydrogen peroxide, and sodium hypochlorite. Reducing-type environments include hydrochloric acid, sulphuric acid, phosphoric acid, oxalic acid, acetic acid, and aluminium chloride. Tantalum has the greatest range of resistance to all conditions, even with chloride ions present. The second best material, which approaches but does not equal tantalum, is a titanium-palladium alloy. Other metals and alloys are suitable only under limited conditions. As an example, zirconium is suitable in reducing media in the presence of acid chlorides but only in the absence of acid chlorides if the environment is oxidizing.

Long lists have been published covering the resistance to corrosion of tantalum by acids, salts, and miscellaneous corrosion reagents. These lists are all characterized by almost universal « no attack » designations. There are some few exceptions. The principal non-resistant reagents are :

| | *Concentration* | *Temp., F* |
|---|---|---|
| ACIDS | | |
| Fluoboric acid | 5-20 % | Elevated |
| Fluorosilicic acid | 10 % | Room |
| Hydrofluoric acid | 5-48 % | Room |
| Hydrofluoric acid (anhydrous) | 100 % | Room |
| Hydrofluoric acid vapour | — | Room |
| Hydrofluoric-Nitric | 1 : 15 | Room |
| Sulphuric acid | Concentrated | Boiling |
| Sulphuric acid | Fuming | Room |
| SALTS | | |
| Aluminium fluoride | 5 % - saturated | Room |
| Ammonium fluoride | 10 % | Room |
| Potassium hydroxide | 5 % | Room |
| Potassium hydroxide | 27 % | Boiling |
| Potassium pyrosulphate | — | Molten |
| Sodium bisulphate | — | Molten |
| Sodium fluoride | 5 % - Saturation | Room |
| Sodium hydroxide | 10 % - Saturation | Room-boiling |
| Sodium pyrosulphate | — | Molten |
| MISCELLANEOUS CORROSIVE REAGENTS | | |
| Air | — | Above 575° |
| Borax | — | Fused |
| Fluorine | — | Room |
| Lye (caustic) | 34 % | 230° |
| Nitre cake | — | Fused |
| Potash | Solution | Hot |
| Sulphur trioxide | Dry | Room |

The unique characteristics of tantalum are emphasized by the fact that these listed reagents were the only ones in lists of 55 acids, 140 salts, and 116 corrosive reagents. The areas of corrosion attack are limited to various types of fluorine acids and salts, sulphuric acid, and the more corrosive sodium and potassium salts. Even sulphuric acid, in all concentrations, below its boiling temperature does not affect tantalum.

These wide ranges of types of reagent, concentration, and temperature of the media to which tantalum exhibits excellent corrosion resistance have led to one of the major tantalum applications — as a material for the construction of chemical equipment.

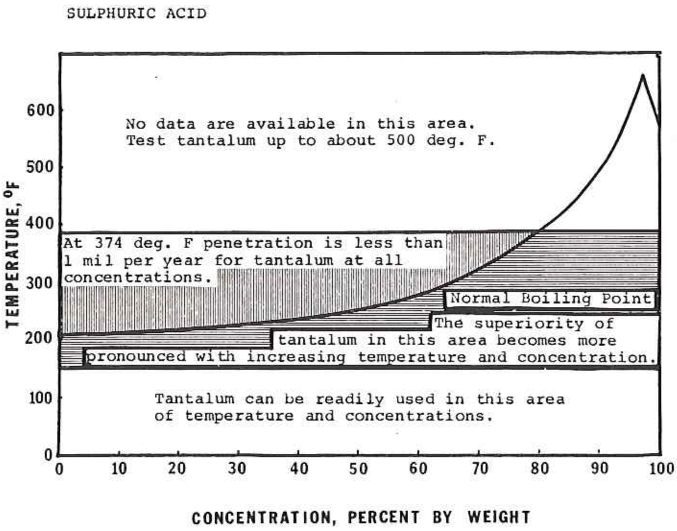
In general, the overall chemical properties of tantalum are characterized by inertness at ordinary temperatures and by the exact opposite at elevated temperatures. Above 300 °C tantalum reacts with all of the common gases except argon and helium. The rate of reaction increases with increasing temperatures. It reacts with carbon, sulphur and iodine at temperatures above 1200 °C.

Tantalum is not attacked, however, by fresh water, mine waters (usually acidic) or sea water, either hot or cold. But when used with boiler waters and condensates, the alkalinity must be controlled. The pH should be less than 9 as a maximum and preferably no more than 8.

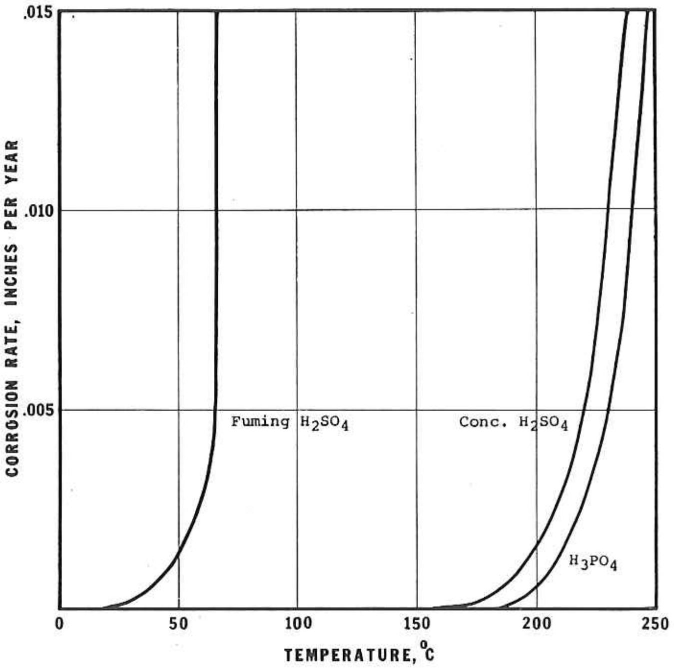
Tantalum is completely inert to body fluids and tissues. Bone and tissues do not recede from tantalum which makes tantalum very attractive as an implant material for the human body. However, the great weight of tantalum is a disadvantage in this application. Once used in artificial parts for the human skeletal structure, it has been generally replaced by other metals, alloys and plastics which are not only lighter but which can be cast directly into shapes without the extensive and costly machining required to use tantalum. There is still extensive use, because of the superiority of tantalum over other metals, for surgical clamps. These clamps can be safely left in the body cavities indefinitely without fear of reaction.

When corrosion resistance to acids is considered, the characteristics of tantalum are quite similar to those of glass in that both are immune to attack by almost all acids except hydrofluoric. For this reason, processes piloted in glass equipment in the laboratory can be transferred to the plant operations in tantalum equipment with complete assurance that the equipment will be free of corrosion, that the product will not be contaminated and that undesired side reactions will not occur. A typical case can be seen by considering sulphuric acid reactions with tantalum.

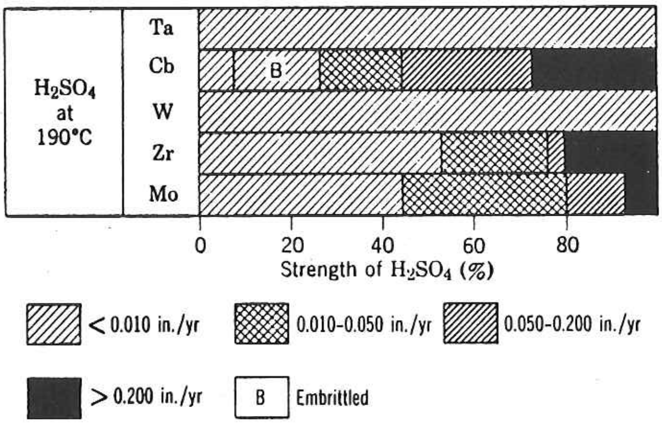
Tantalum is highly resistant to corrosion by sulphuric acid in all concentrations. It is inert to dilute acid even at boiling temperatures and it is not attacked by concentrated acid at temperatures below 150 °C. A slow, uniform attack begins at about 175 °C but without deep grain-boundary penetration or pitting. As a result, tantalum can be used successfully with 98 % acid at temperatures as high as 200 °C. The relationship between acid concentration and the use of tantalum is clear in this diagram.



Fuming sulphuric acid, however, attacks tantalum much more rapidly than the concentrated sulphuric acid.



The attack on tantalum by either form of sulphuric acid is uniform to the extent that the life of the tantalum, measured in years, can be predicted accurately. Compared to other reactive and refractory metals, tantalum has the widest range of application. Even though the following chart indicates that tungsten is the equal, practical considerations of the ease of fabrication of tantalum compared to tungsten rules out tungsten as a competitor to tantalum for chemical equipment involving sulphuric acid.



## APPLICATIONS WHERE CORROSION RESISTANCE IS APPLIED

In chemical industry equipment, tantalum is widely used for sulphuric acid concentrators and condensation of acids and acidic chemicals. It is also used in the manufacture of pharmaceuticals and fine chemicals where contamination cannot be tolerated. Tantalum is used in generally hostile environments and sometimes to permit minimizing equipment volume. And for over 30 years, tantalum has been used to produce hydrochloric acid from hydrogen chloride gas by absorption. Tantalum can be found in the manufacture of insecticides, explosives, dye stuffs, plastics and in the condensation of phosgene derivatives.

Tantalum equipment as used by the chemical industry is of wide variety. It ranges from simple thermowells to complex heat exchangers and reaction vessels. It has been configured into intricate shapes such as impellers for pumps and as simple plugs to repair defects in glass-lined steel tanks.

# U.S. stockpile acquisition of tantalum

After the passing of about twenty years without any purchase of tantalum source materials for the U.S. National Stockpile, acquisition has been revived. As a part of the new policy recently established by the U.S. Government, President Reagan announced on March 13, 1981 that « It is now widely recognized that our nation is vulnerable to sudden shortages in basic raw materials that are necessary to our defense production base. I am today directing the Federal Emergency Management Agency to begin a purchase program for the National Defense Stockpile of strategic and critical materials. These purchases, estimated initially at $ 100 million, are a step to restructure the existing $ 15 billion stockpile in critical areas of deficiency. This overdue addition to our stockpile constitutes a necessary hedge against disruption of supply ».

The Strategic Materials Act of June 7, 1939 included provisions for initiation of stockpiling for seven strategic metals. After the U.S. entry into World War II, the program was expanded to include all critical commodities including columbium and tantalum ores. After World War II, stockpiling was extended under the Strategic and Critical Materials Act of 1947. The avowed purpose was to provide for the industrial and essential civilian wartime needs, not just those of a military nature.

Both the basic and maximum objectives for columbium and tantalum bearing materials were achieved by 1959. The tantalum reached a peak of about 5.0 million lb. contained in tantalites and columbites. From 1965 through 1970 columbite was considered to be excessive and it was sold which diminished the tantalum inventory to 3.9 million lb. Another revision of policy led to the disposal of tantalites from 1972 through 1975, further reducing the inventory to a little more than 2.5 million lb. It has remained at this level ever since.

Revisions in strategic concepts and in the intended use of the Stockpile have led to changes in the quantitative objective for tantalum on several occasions. In the early 1960's the objective was reduced from the original level to 2.9 million lb. and then again to only 0.3 million lb. in 1973. Then in 1976 it was raised to 5.5 million lb. with the intent that most of it should be in an advanced form, not just ores and concentrates. The most recent re-evaluation of strategic objectives has led to a new level, announced in May 1980, of 7.2 million lb. recoverable in ores and concentrates only (actually 8.4 million lb. in the ores and concentrates). Thus, at present, the Stockpile is about 6.0 million lb. short of objective.

The purchased ores and concentrates (probably including artificial concentrates produced by upgrading tin slags) will be made to a new specification, P-113a, issued by the U.S. Department of Commerce on August 3, 1981 and it provides for two grades of concentrates :

**Tantalum natural mineral and concentrates, synthetic concentrates, and chemically processed materials and concentrates :**

| | *Percent by Weight Dry Basis* | |
|---|---|---|
| | *Grade 1* | *Grade 2* |
| Tantalum Pentoxide ($Ta_2O_5$) | 25.0 Min. | 19.0 Min. |
| Tantalum Pentoxide + Columbium Pentoxide | 55.0 Min. | 40.0 Min. |
| Titanium Dioxide ($TiO_2$) | 6.0 Max. | — |
| Stannic Dioxide ($SnO_2$) | 6.0 Max. | — |
| Titanium Dioxide and Stannic Oxide combined | — | 20.0 Max. |
| Antimony (Sb) | .01 Max. | .01 Max. |
| Thorium ($ThO_2$) | ** | ** |
| Uranium ($U_3O_8$) | ** | ** |

** — to be determined and reported.

On September 25, 1981, the General Services Administration released a solicitation for offers to sell to the Government « up to 61.050 pounds tantalum contained » to « Grade A » of the specification (assumed to mean Grade 1), packed in containers, delivered f.o.b. to the Government Strategic Materials Depot in Hammond, Indiana. There is no specified delivery date. Offers are to be received by the Government no later than at 5 : 00 p.m. on October 26, 1981. (The results of this purchase will be reported in a future edition of the T.I.C. « Bulletin ».)

At this time, plans for future acquisitions are not being made public in order that the stated policy will not be violated, « The Stockpile purchase program will strive to be a stabilizing force in the market. Therefore, purchases made at any given time will be in moderate amounts. The Strategic and Critical Materials Stockpiling Act provides a 5-year time frame for spending appropriated funds in order to avoid market disruptions ».

# Anodizing tantalum for art purposes

*(Since the publication of the article « Tantalum and Niobium Jewellery » in issue No. 25 of the T.I.C. « Bulletin », there have been several inquiries concerning the anodizing of tantalum. This article provides the basis of a « do-it-yourself » activity as explored by the Editor.)*

When the surface of metal is cleaned to the extent that it is free of any compounds, the fresh surface attracts oxygen from the air and becomes covered with a layer of metallic oxide. In most metals the reaction is rather rapid, taking place before a controlled technique can be applied to obtain particular effects. Using reactive metals (titanium and zirconium) or refractory metals (tantalum or niobium), however, permits the application of controlled techniques to build the oxide layer precisely as desired. Also, with these metals, the oxide layer can be kept very thin so that it remains transparent. It can then be thickened by heat or electrochemical means to any amount desired.

When white light is reflected from a film of transparent material, interference occurs between the light reflected from the top and bottom surfaces. When the light reflected from the bottom surface returns to the top surface in phase with the light reflected from the top surface, reinforcement occurs and there will be a brilliant reflection. But, when the light is out of phase, the reflection will be very feeble. Since the various colour components of white light have different frequencies, reinforcement will occur when the thickness of the film is just right for the frequency of a particular colour. Therefore, the colour reflected depends entirely on the film thickness. A chart for tantalum oxide follows showing the colour as related to the film thickness and, of further importance, the applied voltage required to form that particular film thickness when the film is formed by anodizing :

| *Thickness of Film* | *Observed Colour* | *Final Filming Voltage* |
|---|---|---|
| | Metallic Grey | 0 |
| 225 Å | Deep Brown | 15 |
| 300 | Violet | 20 |
| 376 | Royal Blue | 25 |
| 600 | Grey Green | 40 |
| 675 | Light Yellow | 45 |
| 900 | Golden | 60 |
| 1,050 | Violet | 70 |
| 1,200 | Royal Blue | 80 |
| 1,350 | Blue Green | 90 |
| 1,650 | Golden | 110 |
| 1,800 | Violet | 120 |
| 2,250 | Yellow Green | 150 |
| 2,550 | Neutral Grey | 170 |
| 3,000 | Green | 200 |

The thin oxide film can be formed by heat. A small torch can be used to localize the effect. It is difficult, however, to control the rate of film build-up and to obtain uniformity. The threshold of film formation is about 250 °C but increases rapidly as the temperature increases. For best control, lower temperatures should be used, but the time to obtain the thicker films is quite long, a matter of several minutes. Better temperature-time control could be obtained by placing the tantalum in a furnace at a stabilized temperature, but such can be used only if the entire area is to be coloured. And, even then, uniformity is not assured at corners and edges.

(This article will be continued in Bulletin No. 29, giving practical details of possible methods of anodizing.)

## NEW MEMBERSHIP

The following companies were elected to membership by the Sixteenth General Assembly :

**Metallurgical Industries Inc.,**
1 Coldstream Way,
Tinton Falls,
New Jersey 07724, U.S.A.

**Centro Minero Penouta, S.A.,**
Plaza de Colon 2,
Torres de Jerez 1,
Madrid 4, Spain.

**Associated Mines (Thailand) Ltd.,**
1/1 Convent Road,
Bangkok 5, Thailand.
(Delegate in England.)