



The William Blum Lectures

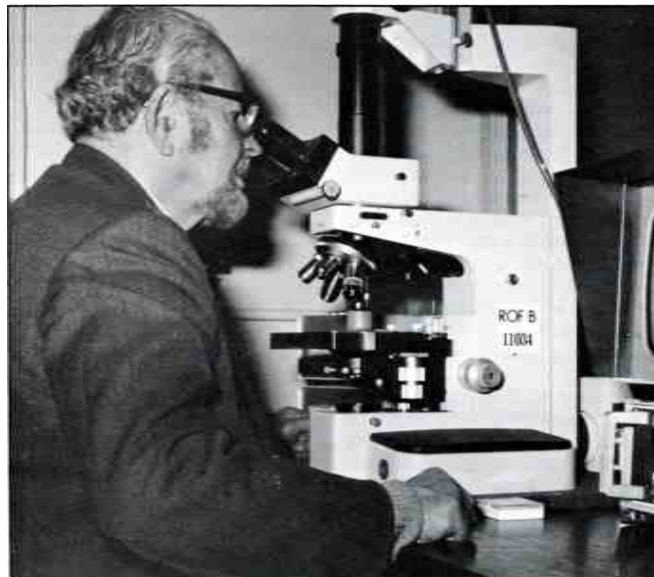
#28 - Simon Wernick - 1987



The 28th William Blum Lecture
Presented at the 74th AESF Annual Convention (SUR/FIN 1987)
in Chicago, Illinois
July 13, 1987

Anodizing of Aluminum: The Sealing Problem

by
Dr. Simon Wernick
Recipient of the 1986 William Blum
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Introduction

I am proud, indeed, to find myself now included in that select company of distinguished scientists who have been honored with the AESF Scientific Achievement Award. When I survey the list of previous recipients, I find it a humbling experience and one which, coming at the end of a long career in surface finishing, will be greatly cherished.

This lecture has been established in the memory of Dr. William Blum. I can claim to have had the privilege of knowing Dr. Blum through a valued friendship covering many years. Not only did we meet from time to time in the USA, but we kept up sporadic correspondence from which I learned a great deal about Bill and his family. Bill kept a written record of his family's activities and round about the end of the year, he would send me a detailed note of his travels (he was an avid traveler) and family events - all of which made fascinating reading.

However, I valued most the personal encounters with Bill during the time he was the doyen of metal finishing at the National Bureau of Standards, Washington, DC, where I had the pleasure of meeting him, and subsequently in other technical capacities. Particularly, I recall his attendance over 30 years ago on the occasion of the Fourth International Conference, held in London under the auspices of the International Council for Electrodeposition. This group was to become today's International Union for Surface Finishing (IUSF), now planning its 12th prestigious International Congress, October 4-7, 1988, in Paris, France. There is a full record of the 4th Congress when Dr. Blum and several other eminent American scientists were present. I will refer in greater detail later to events at this congress that had a bearing on an R&D project that has been close to my heart for many years.

England's Institute of Metal Finishing (IMF), in which I have taken a prominent part over many decades, together with AESF can fairly claim to have been pioneers in establishing media for the advancement of surface finishing for universal benefit. The two societies have enjoyed a cordial relationship for over half a century and, indeed, it was largely through their collaboration that the predecessor of IUSF was born.

With that foreword, it is time now to consider matters of more immediate moment, of technical not to say scientific importance. I will offer some remarks on a subject which engaged a great deal of my attention in the past and that I still find very fascinating today - anodizing of aluminum. In particular, I will review historical curiosities of the development of coloring processes, then proceed with the principal theme of this presentation - cold sealing.

Colorful memories

The concept of the erudite electrochemist developing some abstruse theory by carrying out laboratory experiments using the most up-to-date apparatus involving computers, lasers and the like has not always resulted in landmarks for anodizing research. By contrast, concepts and chance have sometimes produced remarkable results. That some of the great developments in



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anodizing have likewise come about not so much from theory and complicated and painstaking research is well illustrated by the invention of color anodizing.

This was undoubtedly achieved by Dr. Guy Bengough, inventor of chromic acid anodizing - differing from the uniform-voltage sulfuric acid process that came later, and necessitating, because of its low conductivity, a step-by-step voltage, which, in Bengough's original process, rose from 5 to 50 V. Despite this obvious drawback, the process or modifications of it are used to this day to obtain the highest degree of protection, especially in the aeronautical and armament industries.

Bengough was a modest character with a great sense of humor and I recall being present at one of his lectures when he described the manner in which color anodizing first came to light. He said he found it unnecessary to employ complex laboratory apparatus. The fact was, on that notable day, he had produced a number of panels of anodized aluminum and left them on the lab bench to be examined the following day. Fortunately, as the door was closed, the lab cat was locked in. Fortunately, too, near the anodized panels was a bottle of ink. Fortunately, the bottle had been left open. The rest is history! (I like to feel that the ink was red, so that during her life, the cat was strikingly identified from among her fellows as a benefactor to mankind and a veritable Madame Curie in anodizing technology!)

With rather less chance but with no immense sophistication, I believe I can claim to be an early if not the first researcher to detach the oxide film physically from its substrate base. This was achieved over half a century ago by using the great affinity that mercury has for aluminum to undermine the oxide film by quite a simple procedure.¹ An anodic sample was stripped physically of oxide on one small area, exposing the aluminum, then subjected to attack by a blob of mercury. The sample was next immersed in a solution of mercuric chloride. What happened is that the initial attack continued throughout the anodic area, undermining the oxide and producing a rather beautiful cascade of flakes of oxide. These could now be physically handled, dried, and examined - not only for thickness, but for other physical properties. Of course, since then, more sophisticated methods (*e.g.*, electrolytic) have been developed.

Returning to the Bengough discovery, the capacity for absorbing dyestuffs was to become one of the most important and exploited properties of anodized aluminum. The oxide film as it is formed initially is in a gel-like state and amenable to change according to its subsequent environment. The importance of sealing was early recognized, and the simplest method (still considered by some the most effective) was immersion in boiling water.

Apart from dyeing, a number of wax formulations were the first to be applied and some of these still find application. At the same time, the capability to absorb inorganic salts from aqueous solution was noted, and attention naturally turned to materials like chromates, dichromates and silicates because of their well-known beneficial effect in enhancing the corrosion resistance of aluminum.

Development of sealing

From the earliest times, it has been believed that in sealing, the anhydrous oxide is hydrated; it expands and fills out the pore spaces. As a result, the boehmite-type $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ crystal form is produced, with increased elasticity and decreased hardness and wear resistance. That anodic oxide coatings lose their absorptive power when in contact with steam was first recorded by Setoh and Metaya in 1929.² It was found that the hydration resulting from steam treatment was not only more effective than any wax or oil in sealing the surface, but that the reaction was irreversible; the oxide film became greatly more resistant to leaching or fading and the corrosion resistance improved.

It is doubtful whether anodizing would have achieved its present importance without its property of responding to sealing. Although the importance of the operation was understood from the start, a good 30 years were to elapse before one could discuss the mechanism with any great degree of confidence, and it continues to be a controversial subject to this day.

In hot water sealing, the aluminum oxide - both barrier layer and the porous coating - is at first hydrated. After a short time, however, the circulation of water through the pores is impeded, and only the surface layer of the coating continues to be hydrated until the upper portions of the pore channels are plugged. Hoar and Wood³ in 1961 studied the sealing mechanism by measuring the electrical impedance of sulfuric acid anodic oxide films on aluminum sealed in a variety of media and came to the

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conclusion that the pores become filled by inward movement from their sides at the same time they are plugged at the surface until the pore volume is about 99% filled (Fig. 1).

These investigators also found that allowing the coating to dry between anodizing and sealing may slow down the sealing action considerably. The sealing process may be summarized as a dissolution reaction at the film and pore wall surfaces with release of the anion, then reprecipitation of this material on the pore walls to give a boehmite gel, followed by conversion of the gel to crystalline boehmite at the film surface (Fig. 2).

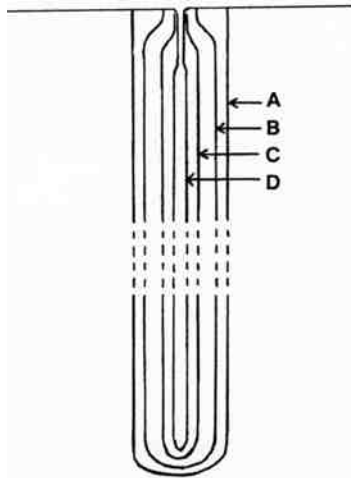


Figure 1 - Diagram depicts progress of sealing. A represents wall of unsealed pore; B, C and D, successive stages of sealing.

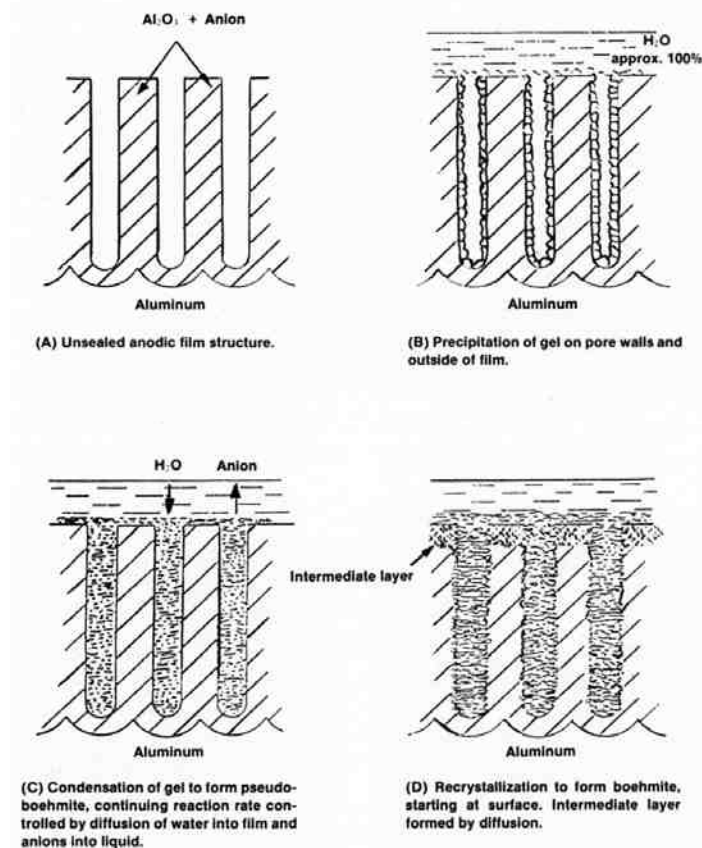


Figure 2 - Stages illustrate general mechanism of water sealing anodic oxide coatings



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A feature to be noted in Fig. 2 is the presence of a so-called intermediate layer. This layer near the outer surface of the anodic coating is very important and was first described by Wefers⁴ in 1973. Studies two years later using very long sealing times (up to 72 hr) on phosphoric acid anodized films gave direct evidence of the presence of the intermediate layer, as did the work by Thompson, *et al.*⁵ These authors found that the protection value of the intermediate layer depends primarily on its thickness, which increases with sealing time.

In one study of an anodic film sealed for 24 hr, electron micrographs showed that the original pore structure is completely lost and that there is a clear line of demarcation between the intermediate layer and the remaining pore structure. The intermediate layer continues to grow for many hours in the sealing solution and becomes several micrometers thick; but, of course, with practical sealing times, it is usually less than a micrometer in thickness.

Its importance, however, may be very great, as recent work indicates that some of the short-term weathering effects that may be seen on colored anodic coatings (*e.g.*, iridescence) may be due to the presence of the intermediate layer.

The most convincing demonstrations of the sealing process have come from electron micrographs of replicas of the film surface. Such replicas of the unsealed coating show a clear pattern of the pore openings, and these are still clear after about a 1-min seal and visible but less clear after 10 min in boiling water. But after 30 min of sealing, the porous structure is completely obliterated, to be replaced by a crystal-like arrangement. After 24 hr, a needle-like structure is observed above this.

The importance of this observation is that the crystalline material seen on the surface of the film (boehmite, of course) is in fact the smut or bloom that occurs as a result of conventional sealing.

From the work of Thompson *et al.* on phosphoric acid anodized films, a replica electron micrograph of a fractured anodic film sealed for 72 hr in boiling water clearly showed the outer boehmite crystals, the intermediate layer, the pore filling, and the texture changes in the original cell material.

Cold sealing

The use of much lower seal temperatures reduces energy costs significantly. As long ago as 1969,⁶ a Japanese process claimed to produce acceptable sealing in 5 min and perfect sealing in 10 min at room temperature by using an aqueous solution containing ferricyanide, phosphate, and calcium chloride at a pH controlled at about 4.5 with an organic acid. The inventors at the time compared it favorably with other systems, including those based on nickel or cobalt acetates.

Alcoa in 1980⁷ described sealing at a minimum of 60°C in a solution containing a hydrolyzable metallic salt (*e.g.*, nickel acetate or nickel sulfate), an ethanalamine, and a soluble sulfate. Sealing smut is produced in this solution and is later removed by dipping the sealed work into a mineral acid bath. Later patents by Alcoa call for much lower temperatures for sealing in ammonia vapors.⁸ Samples sealed in this way are said to be smut free, and both sulfuric acid anodized and integral color work are said to be successfully sealed.

More recently, a great deal of work by what might be called the "Italian School"⁹⁻¹⁴ has led to the development of highly practical cold seal systems. These are used at about 30°C and appear to be based on solutions that contain fluoride or silica compounds in the presence of nickel salts, and often in a water/alcohol mixture. The water/alcohol solvent apparently lowers the solubility of the salts and facilitates precipitation within the pores of the anodic film. It is clear from these conditions that conventional hydrothermal sealing is not involved in these processes and that pore plugging by nickel salts, fluorides or silicates represents the mechanism of sealing. For this reason, there have been some objections to the term "cold sealing," and "impregnation" has been suggested as being more appropriate instead.

In the Italian work, a typical formulation is quoted as 6.5 g/L of a nickel compound, 2 g/L of a fluorine compound, and 50 g/L of 2-butanol. Sealing for 10 to 15 min at about 30°C is recommended. Work sealed in this way has been shown by Strazzi to have good corrosion resistance and good seal quality, and is considered equivalent in performance to that produced by conventional sealing.

There is still concern, nevertheless, particularly for exterior architectural applications, about long-term properties. As the sealing mechanism does not depend on normal boehmite or pseudoboehmite formation, there is also controversy over whether the



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normal corrosion and seal quality tests can be applied to work sealed in this way. Certainly, the mechanism is very different, as work tested soon after sealing will usually give very high admittance and weight loss values, and it is only after 24 hr or more that they fall within normal accepted limits. This creates problems in terms of online production evaluation of seal quality. To overcome this, some plants first use a cold seal, then follow up with a short treatment in a warm rinse - say, 10 min at 45°C.

The Italtelco work¹¹ is based on the use of salts such as nickel acetate or nickel fluoride (6-7 g/L) in the presence of ethyl silicate (1 g/L), a suitable silane such as aminopropyl triethoxysilane (0.3 g/L), and an alcohol such as iso-butyl alcohol (15 g/L). These solutions are used for about 10 min at 30°C and a pH of 5.5-6.5. Again, the work cannot be tested for seal quality immediately, but experience in Italy and America with products sealed in this way has been satisfactory.

Grace¹³ uses a similar combination of a nickel salt and a surfactant for cold sealing, the preferred surfactants being fluorocarbon esters, fluorinated ethers or polysiloxanes. Again, a temperature of 20 to 30°C and a pH of about 6 for 30 min have given acceptable performance.¹⁴

Mechanism debate

While it has been established that the mechanism of cold sealing differs fundamentally from that of thermal sealing, this fact has perhaps not been taken sufficiently into account in the controversy that currently affects the testing of the efficiency of the sealing process. It is true that cold-sealed anodized aluminum soon after its production often fails the admittance or impedance test, although it does so after some time elapses. The advocates for cold sealing point out that this fact arises from the nature of the cold seal mechanisms, and furthermore that this activity represents a benefit rather than a drawback in the long run.

It is worth examining this claim. With a cold seal product, there is a water presence and an "uncondensed" hydrated oxide within the pore and correspondingly an absence of the normal plugging at the mouth of the pore, which aids conductance but which is inimical to the admittance test. Nevertheless, this alters with the passage of time and indeed eventually results in a more (rather than less) complete seal through progressive condensation within the pores.

In short, the failure to pass a production-line admittance test may be considered of little practical significance in the long run. There is thus something of an impasse on the real value of the admittance test regarded as sacrosanct by those responsible for ensuring quality in production. Of late, additional heat treatment has been resorted to by some users of cold sealing to accelerate the aging process with encouraging results.

On the other hand, it is true, of course, that failure to pass the acceptance test could be due to causes other than inadequate sealing (*e.g.*, below-standard anodizing). An effective way to ensure that sealing is adequate is to make use of a test panel accompanying each production batch, subjecting it after cold sealing to a short immersion (say, 10 min) in hot water (60°C).

Other notable work

Let me now turn to some of the interesting work being carried out in the UK on the complex structure of the anodic layer on aluminum. Using tools unknown to us in the laboratory in the old days, fascinating pictures of the architecture of the structure have come to light. Some of the most notable work has been undertaken by Dr. David Arrowsmith and was recently described in his Hothersall Memorial Annual Lecture¹⁵ at an IMF meeting.

Using a stereoscan scanning electron microscope with magnification up to 10⁶, it was possible to view deeply into the shape and structure of the anodic layer. Figure 3, for example, is an SEM of phosphoric acid anodized aluminum, although work was also conducted on chemically polished, etched, and conversion-coated specimens. At higher magnification, Fig. 4 vividly shows the detail of pore branching and the inclination of divergent pores. Using these techniques, any progressive changes with time of processing readily become apparent and greatly aid subsequent interpretation.¹⁶

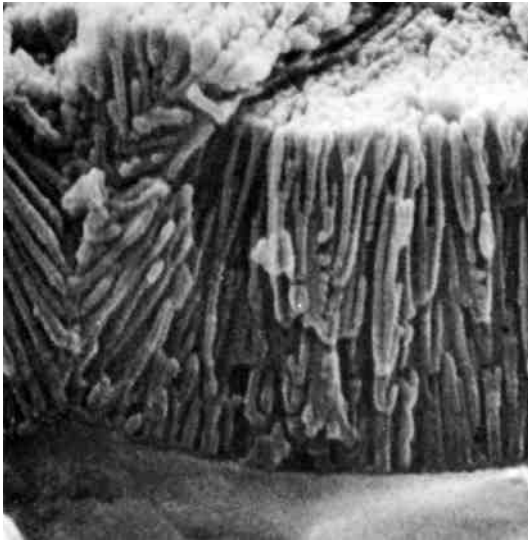


Figure 3 - SEM photo of phosphoric acid anodized aluminum at high magnification. Lab tools like stereoscan SEM help identify structure changes with time of processing.



Figure 4 - Higher-magnification view of Fig. 3 shows pore branching and inclination of divergent pores.

The full circle

Finally, I'd like to return to a subject which I hope you will agree is of the highest importance in our field of surface finishing - research and development.

No society has taken this more seriously than AESF and I would be remiss if I did not pay tribute to the immense amount of work it has sponsored over many years, thus benefitting the world with the numerous publications this has produced. The IMF in its *Transactions of the Institute of Metal Finishing* has also made notable contributions to the advancement of our science and technology. And this is not to denigrate the results of work elsewhere in the world.

However, there has never been any effort to correlate the R&D in one country with another. It reminds me of a sage remark by an Italian researcher, Dr. F. Sacchi, who said that research in anodizing resembled the production of bricks to build a wall. Dozens, hundreds, were being produced, but somehow the wall didn't seem to be getting any higher!

This brings me full circle back to an occasion when Dr. Blum and I were literally in the same platform arguing the case for international cooperation in research, all those years ago - 1954, in fact - at a London conference. Two of the papers dealt with this theme - one by Walter Pinner¹⁷ entitled "Unresolved Problems in the Metal Finishing Industry" and the other by yours truly¹⁸ on "Universal Metal Finishing Problems - A Plea for International Cooperation."

At the conclusion of the session, I put forward the following motion to the assembly: "that the International Council for Electrodeposition be asked to explore the possibility of universal coordination in research projects on metal finishing." It was seconded by none other than Dr. Blum and carried, I believe, unanimously.

May I, in all humility, put this same proposal to you today in the hope that it will produce more practical results than it did some 34 years ago?

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About the author:

This piece was written at the time Dr. Wernick was announced as the recipient of the 1986 Scientific Achievement Award.



Dr. Simon Wernick, recently retired honorary editor of the United Kingdom's Transactions of the Institute of Metal Finishing, has been tapped as the 1986 recipient of the AESF Scientific Achievement Award. The announcement was made by Harry Litsch, CEF, a member of the awards committee, on June 26 during the AESF annual conference in Philadelphia.

The Scientific Achievement Award is the most prestigious of those conferred by the society. It is presented annually to recognize an individual who has made outstanding scientific contributions advancing the theory and practice of electroplating and allied sciences, raised the quality of products or processes, or enhanced the dignity of the profession.

Dr. Wernick studied at London University, graduating with honors and a B.S. degree in chemistry. He later earned M.S. and Ph.D. degrees, specializing in research on electrodeposition. He commenced his career at Siemens Bros. & Co. Ltd. as chemist in charge of the metal finishing department. Simultaneously, he carried out research during the evenings at Sir John Cass Technical Institute, London. He left Siemens upon his appointment as engineer of materials and finishes at Standard Telephones, and later became technical director of Electrometallurgical Research Co. and Aluminium Protection Co. Ltd.

Eventually, he set up as an independent consultant, in which capacity he worked with many well-known industrial concerns and some of the largest metal finishing plants in Europe - notably, those of Wilmot Breedon, Westinghouse, Austin Motors, Wolverhampton Die-Casting, W&T Avery, and Carrier Engineering. His work centered on plant development and modernization, process optimization, and research directed toward finish quality and economy of operation.

He is perhaps best known for his research in these areas:

1. The effect of addition agents on the crystal structure of deposits.
2. Anodizing of aluminum and its alloys. (It is believed that, during the course of his work, separation of the oxide from substrate was effected for the first time.)
3. The identification of process-related defects in nickel deposits on zinc-based die castings.

He is the author of many published works, ranging from the purely scientific to critical reviews, commentaries and notes. They have appeared mainly in publications of the Institute of Metal Finishing (IMF) but also in other European and overseas journals. His contributions to the literature span more than half a century. In 1926, he prepared a paper on addition agents and in 1928 on the effects of colloids in silver plating. Dr. Wernick reported on anodizing processes as early as 1927 and addressed electropolishing, tin, cadmium, zinc, specifications, troubleshooting and many other topics.



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He is also the author of two books - *Electrolytic Polishing and Bright Plating of Metals* (1948) and *Surface Treatment and Finishing of Aluminum and its Alloys* (with Walter Pinner and currently in its fifth printing). Patents were issued in his name for anodizing processes used by manufacturers of fighter aircraft during World War II.

Dr. Wernick served selflessly as honorary secretary general of the IMF from 1929-81 and as honorary editor of its journal until 1985. His service was voluntary and was instrumental in establishing IMF as the largest scientific and technical society for surface finishers in Europe. He was IMF president in 1945-47.

Dr. Wernick also was a founder of the International Union for Surface Finishing (IUSF) and has been honorary secretary general since its inception in 1937. That organization now comprises 16 member societies, of which AESF is one, worldwide. In recognition of his contributions, the IUSF in 1977 established the Simon Wernick International Award for Achievement in Surface Finishing, bestowed biennially on someone whose industrial leadership is exemplary. He has also received IMF's Gold and Hothersall Medals. He is an honorary member of a Dutch metal finishing society (VOM) and was even recognized by Her Majesty the Queen, who proclaimed him an "Officer of the Most Excellent Order of the British Empire for Services to Surface Finishing."

On the invitation of various departments of the United Nations, including UNESCO, Dr. Wernick has provided assistance to at least three developing nations by modernizing finishing plants and combating corrosion problems.