What is Under the Plate?

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In past months, this space has included articles from the AESF Update series, begun in Plating by Dr. Donald Swalheim in the late 1970s. Reaching further into the past, this month's Shop Talk article features one of the true pioneers of our field, George B. Hogaboom, who, in league with William Blum, wrote the definitive text, Principles of Electroplating & Electroforming, first in 1924. It became the "electroplating Bible" as it were. This article goes back before the days of printed circuits, plated on plastics; even before dual nickel and microcracked chromium. What it points out is the critical importance of surface preparation, as critical now as it was in 1934.

This paper is taken directly from the printed proceedings of the 22nd AES Annual Convention, held in Detroit, Michigan during June 11-14, 1923. In those days the proceedings of "SUR/FIN 23" contained the transcripts of the introductory remarks, as well as the Q&A following the paper. Unfortunately, not all references were cited the way we do it today; indeed, some are missing. In his presentation, Mr. Hogaboom refers to research being done by Dr. Blum at the National Bureau of Standards (now NIST). Part of that work was the nascent AESF Research Program, under the Series "A" projects conducted there from 1927 to 1945. It is nearly all here, to capture the flavor of those times.

Thus began the Fourth Education Session, at 9:00 AM on June 13, 1934. The meeting was presided over by Session Chair Walter S. Barrows ...

CHAIRMAN BARROWS: We have six papers on the program this morning, all of them with very good titles and no doubt all very interesting. If there is any discussion, kindly limit your discussion to questions on matters about which you actually want to know.

The first speaker on the program this morning will be a man who has appeared before the supreme body at probably every convention, who has appeared throughout the United States and Canada in, I believe, every branch, and each and every time that he meets with us it is an event--an event to be enjoyed and an event to be remembered. I would like to have the honor of introducing this man, but I am going to call upon a member of the team of Blum and Hogaboom to do that. I am going to call upon Dr. Blum to introduce the speaker.

DR. WILLIAM BLUM (National Bureau of Standards, Washington, DC): Mr. Chairman, I am especially gratified at having this privilege this morning, which I looked forward to last evening, but which I could not have because of the many interesting events of the evening. I looked forward especially to the privilege of introducing one whom we have all honored and who now is an Honorary Member of this Society, although we could not possibly honor him more than we always have for his regard for the interest of the platers, for his devotion to the work, and for his keen analysis.

It is quite characteristic of Mr. Hogaboom that he is never satisfied with things on the surface. He always tries to get down to the bottom of things, so this time he is going down below the plate to find out "What is Under the Plate?" Mr. Hogaboom. (Applause)

GEORGE B. HOGABOOM (Research Engineer, Hanson-Van Winkle-Munning Co., Matawan, NJ): For several years the subject of analytical control of electroplating solutions was discussed at all the meetings of the American Electroplaters' Society. The fact that solution control is essential is evidenced by the familiarity with technical terms and methods by platers who, though denied a training in chemistry, conversed fluently in terms which a few years ago were often as confusing as Egyptian hieroglyphics. With the knowledge gained through chemical control, better solutions were developed, and the technique of the preparation and of the handling of work was improved.

When the successful control of solutions became common knowledge, it was natural that the thoughts of platers and chemists turned to the value of electrodeposited coatings.

There are two reasons for the electroplating of metals to be considered ... ornamentation and protection against corrosion. These two often became one, as both beauty of finish and increase in service duration were demanded for the same object. Stainless steel became a menace, as it possessed both of these requirements. The challenge was accepted, and a research was instituted to investigate the protection electroplated coatings gave to steel. On steel or

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iron the value of ornamental electroplated coatings is measured by its protective life against corrosion. A heavily gold plated radiator shell has less value in service than one that is cadmium coated, even though the cadmium be tissue-paper thick.

For about three years a comprehensive investigation has been made of the protective value of electroplated coatings. Yesterday you listened to the results [*This is in reference to a paper given by Dr. Blum on June 12, 1934, entitled "Summary of Research on Plating at the National Bureau of Standards." This included the first projects of the then-AES Research Program. -JHL*]. You must have declared that the research was comprehensive and worthwhile, and that this contribution to the electroplating industry is of inestimable value. You have seen the weakness of some coatings, and from the data assembled from others you are beginning to realize the importance of definite specifications for the electroplating of steel. It is needless to predict what the results of this research will be. Further work will be done, and you will support a similar investigation of the value of electroplated coatings on non-ferrous metals. You cannot, and I know will not, stop with the protective coatings, but will finish the job so that in the very near future coatings, both for ornament and for protection, will be so processed that electroplated finishes will be more firmly established than ever. Tomorrow you will be as familiar with plating under definite specifications as you are today with the analytical control of solutions.

The work of improving and strengthening the structure of electroplated metals is highly commendable. But upon what are we building? We are increasing our knowledge of electrodeposits, but what do we know about the basis metal? We electroplate on iron, steel, zinc, copper, brass and several other metals and alloys, and know very little about the effect of the foundation (the basis metal) upon the strength and durability of the structure (the deposited metal). We apparently say with the junk man, "Iron is iron, steel is steel, brass is brass." But is that wholly true?

We have overlooked the fact that the metals are composed of crystals that seem under some conditions to be alive. Strains are set up in metals when cold worked. These strains often assert themselves. U. R. Evans said, "Cold worked articles, if not annealed, retain internal stresses which may cause unexpected failure when the articles have been in use some time."[1]

In the tin plate industry the sheet steel, after the final cold rolling, is annealed at not the regular annealing temperature of 760°C (1400°F), nor the normalizing temperature of about 954°C (1750°F), but at 538°C (1000°F) to remove the cold work strains, so that after hot tinning, the sheet metal can be worked without increasing the tendency of the surface of the sheet to pull coarse as by the creation of a large-grained and therefore weak structure.[2]

Cold rolled steel that is to be formed into articles and electroplated comes from the mill cold worked. It is put through forming operations that distort the crystal structure, set up internal strains, and often "pulls coarse." Some forming operations are more severe than others, so that the internal and the external structure is deformed; yet this steel is sent to the plating room to be given a protective coating or an ornamental finish that must be perfect. No attention has been given to the internal structure of the external condition, yet when there is the "unexpected failure." The plating process is invariably considered at fault. If the fabricated steel article is annealed often it is heated in an open flame with no attempt to use the same methods of heat treating as would be given to an ordinary machine tool. The electroplating is expected to correct and cover any and all treatments given the steel in the fabrication processes.

In the manufacture of low carbon cold rolled steel, too little attention is now being given to that which is to be electroplated. If the steel is not clean and the annealing conditions not controlled, the surface of the steel will have a. higher carbon content than the body of the stock. A thin film of steel, with as high as .80 carbon, may be had on the surface of an .04 carbon cold rolled stock. This film cannot be seen with a microscope, but can be detected by the well-known "spark test." This film or "skin" must have an effect upon the character of the deposited metal, especially if the steel is used as a cathode in an electrolytic acid pickle. The effect of hydrogen on high carbon steel under stress is well known. Is it not reasonable to assume that if such a steel were plated with nickel and given an exposure test that the deposit would fail more rapidly than correctly treated steel? If blisters appear and the underside of them is examined, is it not more correct to state that this "skin" has separated from the basis metal and adhered to the deposit, rather than to assume that it is an oxide on the under surface of the blister? Hardened worked surfaces, oxides and such films as noted are often more adherent to an electrodeposit than to the basis metal. This will be referred to again later.

Suppose a piece of steel that has been cold worked is given an electrodeposit of metal. Will the deposit have the same outdoor exposure or salt spray life as a steel that is not in a strained condition? It is well known that steel under a strain will corrode more rapidly. Take the old story of two eight-day clock springs. Wind one, and it has the energy to run a clock for at least 200 hours. Place both in acid. Where does the energy in the wound spring go? It goes into the acceleration of corrosion. Will not the same be true of sheet or fabricated metal that has not been annealed to remove the cold worked strains?

What effect has cold working of steel upon its magnetic properties, upon the distribution of current which has a bearing on a uniform thickness of deposit? If an armature of a motor is annealed after assemb1y to remove cold worked strains the magnetic properties are increased 15%. Do we know what will be the result if fabricated cold rolled steel or any other metal was annealed to remove cold work strains?

What has been said about steel is undoubtedly true in some degree about all other metals that are fabricated and given to the plater to increase their life or add to their appearance. High brass, when cold worked, is subject to internal strain. You well know the effect of mercury or ammonia in developing season cracks. Time often acts in the same manner, and season cracks develop almost any time after the article has been plated and is in use. Polishing and buffing of brass flows the surface of the metal, and that has an effect upon the adhesion of an electrodeposit. The excellent experiment on the adhesion of electrodeposited nickel to brass made by A. W. Hothersall[3] deserves to be told in his own words.

"The influence of the properties of the surface layers of brass on the degree of apparent adhesion of electrodeposited nickel was further illustrated by the following experiment: A piece of sheet brass was carefully buffed to a high finish; the polished layer on one-half the specimen was then removed by rubbing with a medium grade of emery cloth, the other half being protected from accidental scratches by means of gummed paper. The specimen was cleaned by Treatment A, and nickel deposited to a thickness of about 0.76 mm (0.030 in.). After sawing off the edges of the coated specimen, and turning up one corner of the deposit, the nickel could be pulled off the emeried portion with the fingers, but it adhered fairly strongly to the buffed area, and had to be twisted off with pliers. The underside of the deposit was coated with a brass colored film, both in the area which had been in contact with the emeried half, and also that which had covered the buffed half. The adhesion of the nickel deposit was thus greater than the sheer strength of the surface layers of both the buffed portion and the emeried portion. Examination under a microscope of the brass surface from which the nickel deposit had been torn showed that the surface layers had been removed in such a way as to expose the rolled structure of the metal, both in the emeried and the buffed parts of the specimen."

In view of that research, any test made will be incomplete unless the condition under the electroplate is known. This will include surfaces that have been polished, buffed or worked in any similar manner.

If we go into a polishing or buffing room today, we see a line of lathes operated from a common shaft, or if the lathes are motor driven, the speed of each lathe is about the same. Wheels or buffs are used of an indiscriminate size. How much attention is given to the peripheral travel? This is arrived at more by the shape of the article to be finished than by a study of what may occur to the surface of the metal, and later to the electroplated coating. Today the aim seems to be to have as large a wheel or buff as the lathe will carry; to make the buff as hard as possible by all manner of sewing; and to operate at a speed that creates a frictional heat just below the burning point. In fact, if a fire-proof buff is ever available, still higher speeds will be used.

How does such a set-up affect the surface of the metal? Listen to what U. R. Evans says about this: “At one time polishing was regarded as a kind of minute abrasion; the projecting portions of the rough surface, it was thought, worn away by the action of the polishing material. It has, however, been shown that polishing generally consists in making the material flow down from the minute projections on the surface, and fill up, or cover up, the depressions. Thus, when the polishing is complete, the whole surface is covered over with a smooth vitreous layer of more or less ‘amorphous’ metal, produced by the action of cold work. An interesting experiment concerns the polishing of a specimen of copper, the surface of which contains numerous pits, due to gas included in the metal at the time of casting. When the surface is polished the pits disappear, the amorphous film having flowed over and hidden them. When the film was removed, the pits reopened, with the same appearance as at the start.”

Speaking about other mechanical workings of metals, Evans says, “Many authorities have long believed that the added strength of the cold drawn (copper) wire is due to a hard, glassy skin of amorphous copper on the surface. Doubt has, however, been thrown on this view by recent investigations; the hard skin, where it exists at all, appears to be due to oxide scale rolled into the wire. In the case of a brass tube, on the other hand, the existence of an apparently amorphous surface layer appears to be established. It has, in fact, been found possible to strip the layer from the granular material below by the action of dilute ammonium chloride.”[4]

We know something of the effect of this “amorphous” layer on the structure of an electrodeposit metal. This was clearly shown by Blum & Rawdon, and photographs of a deposit of copper on copper, before and after this layer was removed, are found in the text on electroplating, by William Blum and the author of this paper.[5] [*Shown in Figure 1, when copper is deposited from a sulfate bath on copper which has been cleaned with nitric acid, the deposit consists of crystals which are extensions (epitaxial growth) of the crystals present in the basis material, as in “B.” - JHL*]

In a buffing room recently visited, spun copper percolators [coffee pots] having a soft metal spout were buffed with a 16-inch wheel on a lathe run at 2400 r.p.m. The percolators were cleaned and nickel-plated in the regular way, color buffed and chromium plated. The nickel deposit adhered well, but the soft metal spout was covered with “hairline” cracks, typical of chromium deposits. The cause of these “hair line” cracks was the condition of the surface of the soft metal, due to the buffing operations. The plastic deformation of the surface of metal by buffing created a strained condition which asserted itself after the electroplating. This may lead the way to learning the cause of “hairline” cracks on some metals, especially high brass. It has been pointed out that brass flows under the buffing operation, and if this flowed surface is not removed before electroplating, may it not be the cause of “hairline” cracks in the chromium deposits? This surely makes the question of “What is under the plate?” pertinent. Reference was made to the oxide coating on copper. What about the oxide coatings that may be invisible on any metal that is to be electroplated? They are formed easily in the fabricating or the polishing operations. Hedges tells us, “In fact, solutions of alkali render iron definitely passive, which, as will be shown later, is due to the formation of a highly protective film of ferric oxide or hydroxide.”[6]

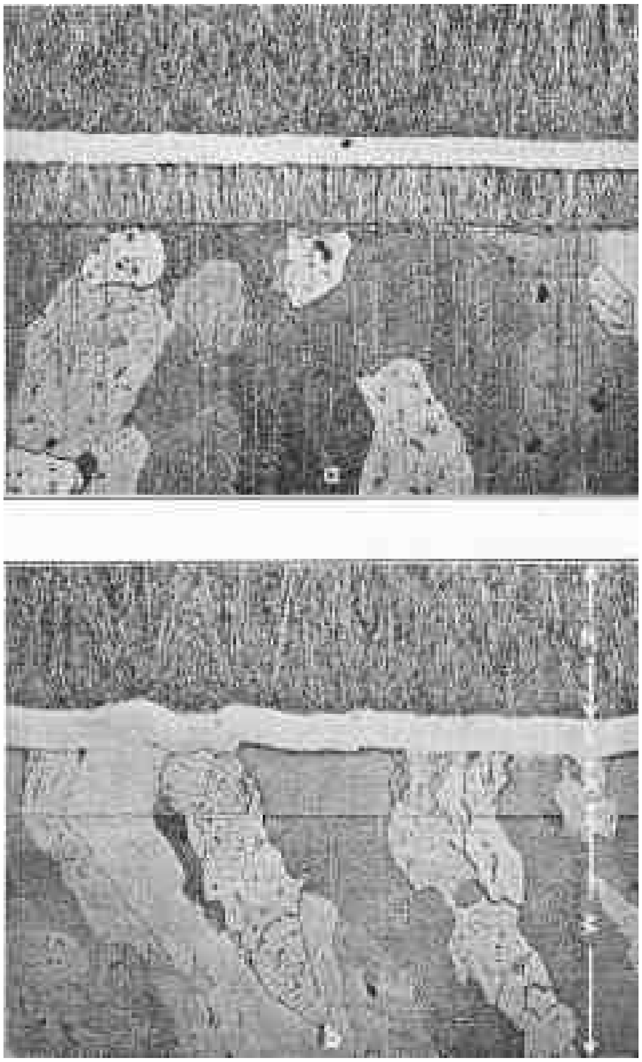

Figure 1—Section of the chilled side of a “pig” of cast copper, upon which copper was electrolytically deposited (100X). (A) The surface was cleaned but not pickled, prior to the electrodeposition (B) The surface was pickled after cleaning. The various zones indicated in (B) are the same throughout both micrographs: w, base metal; x, electrodeposited copper (first layer); y, electrodeposited nickel; z, electrodeposited copper (second layer).

Recently an investigator stated that metal cleaned in an alkaline electrocleaner became passive due to the formation of an oxide film. Are these oxide films that render the surface of a metal passive entirely removed previous to the electrodeposition of a metal? Not only will the passivity of the surface of the metal affect the adhesion of an electroplated coating, but the oxide film, not being adherent to the basis metal, will be the cause of blistering, peeling, and the “unexpected failure” in service. It will be shown that the oxide films, even though invisible to the eye, can be removed as films from a metal. These invisible oxide films also affect the conductivity of metals. Soderberg told of his experience with cadmium plated copper electrical contacts. The cadmium was deposited over an invisible oxide film, and increased the electrical resistivity of the copper 225 times. Aluminum is given an oxide film for that very purpose. These oxide films are often under the plate.

There may be a condition on the surface of metal that will stand or entirely prevent the deposition of metal on some parts of an article. This is generally due to the cold working at a certain place. A picture will be shown of a curtain rod [*not available in the Proceedings - JHL*] made of 3/8 inch steel wire. This wire is purchased in coils and run through a straightener in which the dies rotate around the wire forming a narrow spiral band of worked metal. The rod is rolled to obtain a bright finish, cleaned and pickled. The spiral worked spot will not cover in a brass solution for fully five minutes after the other area has a good brass color. When it is plated, it will be found that the spiral band has a very light plate and if a piece of the rod is immersed in a cyanide solution the deposit on this worked surface will soon be removed. In service this weak band of brass, being porous, will oxidize or rather discolor more rapidly than the other part of the rod, and a distinct bare line will develop where the dies of the straightener have worked the surface of the steel. In the electroplating of sheet steel that has been run through a machine to flatten, in which there is a narrow roller guide, the same bare space is had where the surface is cold worked. The reason for this is that the worked area has a higher potential than the surrounding areas. The difference in potential not only affects the plating, but in any corrosion test or in service the rate of corrosion is increased for both the plated coating and the basis metal. This, again, is a condition under the plate.

In the beginning of this paper it was stated that metal seemed to be alive. In his novel and conclusive work on electrodeposited coatings, Castell found that a copper electroplate did not remain all copper when deposited upon zinc ... *e.g.*, a zinc base die casting. It has been almost universally assumed that a copper deposit on a zinc die casting was absorbed by the zinc. Castell found that the opposite was the case ... the copper absorbed the zinc. Next to the zinc basis metal an alloy forms that is high in zinc and low in copper, and the percentage of copper increases for some distance, forming a yellow brass, a zinc bronze ... the top layer is pure copper.

The phenomenon occurs slowly while the article is in service. The rate depends upon the temperature to which the die casting is exposed. Heating to 260°C (500°F) accelerates the rate of absorption. The alloy next to the basis metal is very brittle and under conditions over which in service there is no control, blisters and peeling of the copper and nickel deposits will occur. The nickel does not separate from the copper, but the copper deposit with the absorbed zinc separates from the basis metal. It need not be stated how often this b1istering and peeling has been attributed to poor cleaning, or to an unbalanced plating solution ... the fault of the plater.

If the die casting itself is investigated an interesting phenomenon occurs that affects the electrodeposit, whether it be nickel alone or nickel with a flash or a heavy deposit of copper under it. The impurities or metals added purposely in the zinc alloys may bring about an internal condition in the fabricated die casting that will cause the electrodeposit to blister or peel. The presence of tin in small quantities, even as low as .01%, has a detrimental effect on the internal structure of the die casting, which in time will assert itself. At one time tin was purposely added to zinc in making die cast alloy to make it “more fluid.” It is now known that even traces of tin must be kept out, and by doing this the plater has been proven not guilty of neglect in his operations. It is essential that the best alloy obtainable is the only safe one to use for zinc base die castings that are to be electroplated. Such an alloy has been developed through research, and the electroplater is indebted to the metallurgist for telling him what is under the plate.

Zinc alloys are not the only alloys in which internal changes occur. Antimonial-lead is another troublesome alloy. At 247°C (477°F), 2.45% of antimony will be dissolved in lead. This is the eutectic. When the temperature of this alloy is decreased to what is commonly called “room temperature,” the amount of antimony held in solution is practically one-tenth of that in the alloy at the higher temperature, or 0.25%. This free antimony is dispersed throughout the alloy, but as heat is applied, or as the alloy “ages” with time, this segregated antimony begins to get together in larger amounts, and soon there will be definite areas of pure antimony and pure lead. This goes on under the plate regardless of whether the antimonial-lead has been made to appear like a noble metal by being given a mantle of pure gold.

Aluminum will dissolve about 6% of copper, and when this mixture is alloyed with other metals the very useful duralumin is made. If the surface of duralumin is burnished, buffed or worked in some similar manner, the surface no longer contains 6% of copper. Some of the copper has been precipitated and a different percentage alloy has been formed.

Previous to electroplating many alloys are cold worked, polished, buffed or burnished. Is there a change on the surface of the alloy, and if so, what effect has that upon the adherence and the protective value of an electrodeposited coating?

This story is but an assembly of known metallurgical facts, but one that has not been given the thought and consideration it should have received. The application of these phenomena ... these known facts ... to electroplating will construct a foundation upon which the real structure of electroplating can be erected. All assembled data on the physical characteristics of electrodeposits and the protection against corrosion of electroplated coatings will lose part of their value, unless more is known about what is under the plate. (Applause)

Q&A

E. A. ANDERSON (New Jersey Zinc Co., Palmerton, PA.): I think that Mr. Hogaboom is to be congratulated for bringing to the American Electroplaters’ Society a discussion of the type that he has just made. We certainly cannot disregard the material that is under the plate.

One could discuss a paper of this sort indefinitely long from a metallurgical viewpoint, but there are just one or two points that I would like to comment on. In the first place, it is pretty well established that the chemical activity of a surface is increased by cold working. You can carry out a number of simple experiments. Take practically any metal and take a piece that is cold worked and a piece that is soft annealed, and free from strains, and expose them to some corrosive influence and you will find the strained material will corrode materially more rapidly than the unstrained, and that is not true only of normal weather corrosion. Hot galvanizers have that trouble with the corners of their galvanizing pots, where they are work-hardened in bending them up. The corners will fail early.

On the question of the failure of zinc die castings, I would like to make one statement, and that is that while tin will do all the things shown, contamination of that type is almost negligible today. The American Society for Testing Materials, the Automotive Engineers’ Society, the American Foundrymen’s Association, all have specifications under which zinc die castings can be purchased which limit the amount of contaminating elements that can be present, and it is perfectly feasible today to buy zinc die castings which will not grow under the plate, although it is a good warning to you to make sure that the die castings you do buy are bought under specification and checked.

W. R. MEYER (General Electric Co., Bridgeport, CT): There are just two problems that I would like to bring up. One is that the question of adhesion of oxide films is dependent, to a great extent, on the thickness of the oxide film, and the thin oxide films adhere much more readily.

Passive films are very adherent to the base metal, and I do not believe Mr. Hogaboom intended to give the impression that these passive films are easily removed. In the removal of these films chemical means have to be used. They pass dry chlorine gas over the metal containing the oxide and volatilize the metal, leaving the remaining oxide film. In practically every case, though, these oxide films still contained traces of the base metal.

There is one other factor, too, and that is on the question of the cracking of nickel deposits on percolator spouts. We certainly have had plenty of experience along that line in producing percolators, and I think Mr. Hogaboom has the cart before the horse. I think that in a great many cases the question of the base metal enters into the question of cracking. I believe one trouble enters into the buffing of the nickel, because you cold work the metal and you can induce peeling and cracking in that respect; but I think, when you consider the tensile relationships between the base metal and nickel, it does not seem possible that cold working would induce these cracks that are quite visible to the eye. The slip band cracks are not visible to the eye, and I cannot correlate the slip band cracks with those visible cracks.

I believe that the cracks, in the main, are due to the same condition that Mr. Romanoff mentioned in his paper yesterday [*entitled "Ductility and Adhesion of Nickel Deposits" - JHL*], the fact that the nickel is embrittled by the hydrogen and chromium deposit, and that induces the cracks in the base metal.

HOGABOOM: If that were entirely correct, then you would have cracking on the copper surface, and you have no hair-like cracks on the copper surface. They are entirely upon the lead.

MEYER: Well, I think it is a question of the relative tensile strength of the base metals. I believe nickel in this case would have a tensile strength from five to ten times greater than that of the lead alloy, and how in heaven a lead alloy having one-tenth the strength of nickel could make those cracks in the nickel I can hardly see.

GUSTAF SODERBERG (Udylite Process Co., Detroit, MI): I should like to say one word about degreasing. It came up yesterday and it came up today. Yesterday the speaker said that in cadmium plating you can very well go directly, at least in many cases, from the degreasing machine to the cadmium plating bath. Today Mr. Hogaboom warns us against films formed in the degreasing operation.

I would just like to make a statement that we have put in degreasing in several places. We have used it a great deal in the laboratory, but I would never go from the degreasing machine into the plating bath, even such an easy bath as cadmium, without any intermediate pickling operation.

One part of the paper dealt at some length with films of oxides. I do not think it is quite right to say that the buffer should not put on so much preasure. That is an economic problem. What we have to do, instead, is to study our pickling a little better than we have, to see how we can change our pickling with the structure of these oxide films and the exact chemical composition of them.

CHAIRMAN BARROWS: This certainly has been a magnificent paper, and it has been presented in a very interesting way. I know we all feel very much indebted to Mr. Hogaboom, and, if there are no further questions, I will call the paper to a close. (Applause)

Thank you very much, Mr. Hogaboom..................

References

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