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July 20, 1955

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GENERAL ELECTRIC

HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

SECONDARY CORROSION BARRIERS - APPLICATION

EA Evans

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A. INTRODUCTION

A program to develop a new fuel element was initiated at Hanford in 1951. A survey of the possible methods of making such a fuel element was completed and a document listing all possible lines of research was written by Schier and Eschbaugh. The problem was outlined as it appeared at that time; various developments which have occurred subsequently have changed this problem to a greater or lesser extent. Essentially the problem concerned the development of a fuel element which would not fail or would fail in a slow and predictable manner and would not cause damage to the pile. A large portion of the research and development was concerned with the application of these layers. This paper will review the research that was done on the development of these corrosion-resistant layers and will evaluate the problem as it appears now after approximately four years have elapsed.

B. PROBLEM

The fuel element considered in 1951 was one which could be charged into the present piles or into similar piles. In other words, it would be a cylindrical fuel element with an outer layer capable of withstanding contact with hot water at high flow rates for a considerable period of time. It would be one which would withstand pile exposure of at pile operating levels up to and heat generation within the fuel element at the rate of about . It would be designed in such a manner that the number of ruptures would be minimized and in case of ruptures, no damage to the pile would occur. The maximum outlet water temperature considered at that time was in the vicinity of 100C. Since that time, temperatures up to 150C have been considered and development of fuel elements capable of operating in this range was initiated. In addition, research was started to develop fuel elements which could withstand much higher temperatures (1300C) in deionized purified water.

The general slug design as considered in 1951 and modified in the intervening period consisted essentially of:

1. A core of uranium, uranium alloy, or some heterogeneous mixture of uranium and one or more other materials.
2. A series of protective layers either bonded to the core or unbonded.

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The protective layers would ensure uniform and adequate heat transfer. In the case of the insulated fuel element, discussed in more detail later, the heat transfer would be such that the desired elevated uranium surface temperature would be obtained.

One concept of a fuel element consisted of at least three components:

1. The core
2. The outer jacket
3. The inner jacket, a thin layer of some suitable material.

Originally, three characteristics of this inner jacket were considered important:

1. A ductile bond would be formed; this bond would not deteriorate under irradiation or break up as a result of thermal or mechanical shock.
2. The layer would prevent excessive interdiffusion of uranium and aluminum either during the fabrication of the fuel element or during exposure in the pile.
3. The layer would afford a certain degree of secondary corrosion-resistance in case the outer jacket was penetrated.

The definition of "satisfactory" secondary corrosion resistance was rather vague. It was decided that a satisfactory corrosion-resistant layer would (1) permit the slug to go to full exposure even after the outer jacket fails, or (2) corrode or dissolve in a slow controlled manner, thus giving sufficient warning and permitting the pile to be shut down without damage to the tubes.

Obviously, there are many materials and methods which could be used for each part of the fuel element. It would be impossible to try every combination and permutation of all these possibilities. A preliminary attempt was made by S&W to eliminate all but the most promising. However, even this resulted in a formidable list, as shown in Table I taken from their document.

Many of the procedures and materials had been considered previously and in some cases extensive research and development work had been done. Electroplating was one of the first methods considered for applying corrosion-resistant layers on uranium. Nickel, copper, tin, molybdenum, lead, chromium, brass, silver, gold, and palladium, and combinations of these materials were electroplated on uranium.

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In fact, "adherent deposits of practically all the ploteable elements have been made on uranium...." (Coating & Corrosion, p. 126)

The standard method of preparing fuel elements consisted of an Al Si froze. Fund brazing had been investigated.

Galvanic deposits of zinc, nickel, lead, aluminum, iron and chromium had been applied. Vacuum die casting and pressure die casting were tried, but were dropped after they appeared to be of little value.

The deposition of a coating by chemical decomposition was attempted. Molybdenum and nickel were deposited by decomposition of the carbonyls.

An attempt to coat uranium with nickel and/or molybdenum by cementation methods showed little promise.

Other methods included vapor plating using MoCl_5 , metal spraying, and immersion in molten oxides or chlorides.

In 1951, when this program was started it was decided to^{do}/the following:

1. Review the previous work cited above in light of knowledge gained recently. Some of these methods had been examined perfunctorily and then dropped because it was necessary to freeze on to one process. It was thought that some of these processes showed considerable promise and with proper study might develop into valuable methods of coating fuel elements. Moreover, new methods of canning fuel elements had been developed and one or more of these processes might be valuable for applying the layer.
2. Consider processes which are new or novel or had not been considered previously.
3. Do such development work as may be necessary to evaluate the processes.

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The research was only part of a large program started at that time to develop a new and improved fuel element. The laboratory facilities and manpower were both inadequate for a satisfactory attack on the problem. Therefore, the problem was outlined to several outside laboratories and their advice was solicited. Research programs to assist Hanford in development of a satisfactory fuel element were started at Ames, Battelle, KAPL, Sylvania, Argonne, and other laboratories.

Several different lines of attack were started but those which appeared the most promising redeived the greatest emphasis. Probably the most attractive method of coating a cylindrical fuel element was electroplating, not only because of the extensive work done previously, but also because this is such a well established process and has a large amount of background information readily available.

Programs on electroplating were started simutaneously at HAPO, BMI, and at KAPL. Battelle and KAPL directed their research along different ~~lines~~ lines. These will be described in detail later.

The number of materials to be considered was limited by the requirements for a satisfactory coat. A satisfactory coat should have the following:

1. Corrosion-resistance
2. Diffusion resistance
3. Availability
4. Economical
5. Low cross section
- 6.
- 7.
- 8.
- 9.
- 10.

A preliminary survey ~~it~~ listed the following materials as satisfactory:

Ni, Fe, Cu, Be, Al, Pb, Zn, Cr, Mo, Fr, Nb, Bi, ~~Ceramics~~. Electroplating is a suitable method for applying Fe, M, Cu, Cr and one or two of the other metals listed

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above, but it is of doubtful value for Zr, Nb, Be, Al, ceramics and others. ~~Therefore~~
Therefore, concurrent research on other methods of application was started. The
initial program was quite comprehensive, and included spraying, sputtering, vapor
plating, gas decomposition, evaporation, electrophoretic deposition.

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III Methods

Types of materials

A. Electroplating

Andelin
Post
BMI
Pitzer
KAPH₁
SEP
DuP

Originally two basis:

1. Improves coat
2. Alloy layer (h.t.)

Investigated 1. Different Baths

Ni { 1. Modified Thompson
2. Watts
3. BMI
4. KAPL
Cu { Prophosphate
Cyanide

Al

Bronze

~~REXN~~
FE Fe(NH₄) SO₄
BMI

Mo

Sn

2 Brass

2. Rock Design

BMI
Udylite
HAPO

3. Heat treatment

Original (C & C: final rpt.)
BMI
HAPO
others

3. a. Heat treatment for diffusion of layers

4. Anodizing etch

a. HCl. H₃PO₄
b. CCl₃C₃OOH
c.
d.

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~~Types of Materials~~

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5. Recovery of solutions
6. Equipment
7. Subsequent treatment (oxidation, etc.,)
- 8.

b. Electroless

Types of material
Original (A. Brenner)
C. Groot
Kanizen
KAPL₁
HAPO¹- trials
conclusion
~~conclusion~~

c. Sputtering
(types of materials)

Original
HAPO (W. E. Roy)
others
Conclusion

d. Evaporation

Types of materials
Original
KAPL₁
HAPO
BMI ~~BMI~~

e. Gas Plating

Types of material
Original (Mo, Fe)
DID-1 (KSPL)
HAPO (200 W)
Commonwealth
General Conclusions

f. Mechanical

1. Roll Clodding	}	{	Types
2. Uniskanning			Locations
3. Winding			Adv.
4. Others			Gen. Limitations
			Conclusions

g. Vapor Plating

Types of material
Original
Ames
KAPL
BMI ¹
ADV.
Gen. Limitation
Conclusions

h. Metal Spraying

i. Die casting

J. Brazes

1. Standard
2. Vacuum
3. Alloy baths (Ames)

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K. Ceramics

1. Spray
2. Fising
3. Choice of Materials
4. Uses
5. Adv.
6. Gen. Limitations
7. Conclusions

IV Conclusions

1. Procedures and materials ruled out definitely
2. P & M of use possibly later on
3. Picture as of present
 - a. Modified table

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Evaluation of Sweater Coats by Undercutting Tests - C. Groot, E. A. Evans

Undercutting tests are run by drilling holes through the jacket of a canned slug to the uranium and exposing the slug to water at 170 C.

The tests measure the rate and type of failure of a slug once the jacket and bonding layer have been penetrated. Good undercutting resistance predicts long warning of slug failure (and "quicke" shutdown); poor resistance predicts stuck slugs and wet piles.

Slugs hot pressed prior to those discussed below have always shown poor undercutting resistance, blistering at points remove from the holes, and splitting the jacket in about four hours. Standard Al-Si canned slugs did much better; they blistered much more slowly and only at the holes drilled through the jacket.

The behavior of previous nickel-plated, hot-pressed slugs might indicate a porous bonding layer as compared to an impervious layer in the Al-Si slug. Supporting this view are the results of recent undercutting tests of nickel-plated slugs which were heat treated before hot pressing. Metallographic examination showed that the uranium-nickel diffusion layers formed during heat treatment of these slugs at 575 C had been broken up during subsequent sizing and hot pressing, and possibly because of the undercutting was consistently somewhat less than that of non-heat-treated pieces. However, the difference between the behavior of heat-treated and non-heat-treated pieces was small compared to that between nickel plated and Al-Si-coated slugs.

Battelle investigators recently reported that the undercutting resistance of plated uranium may be a function of the amount of uranium hydride under the nickel plate. That the hydride occasionally does exist they have shown metallographically and by x-ray. Its formation might occur either electrolytically or by reaction of

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the uranium with solution entrapped under the plate.

To investigate the existence and possible effects of hydride formation, undercutting tests were performed with the following types of slugs: (1) Standard nickel-plated, hot-pressed; (2) Standard but vacuum heat treated for one-half hour at 300 C after plating to remove entrapped solution or decompose UH_3 ; (3) Pure uranium, pickled in nitric acid then wrapped in 0.001 inch nickel foil prior to hot pressing; (4) Bare uranium given a heavy anodizing etch prior to wrapping in foil and hot pressing. ~~#####~~

A fifth type - vacuum hot pressed, nickel plated slugs - were not cameed in time for testing.

The four outgassed slugs were slightly but not significantly better than the four slugs used as standards. However, both slugs were much better than any previously tested. They lasted an average of 11 hours, with one still intact after 23 hours.

~~#####~~ ^{two} The/foil covered pieces lightly etched in nitric acid lasted 24 hours and even then did not fail by undercutting. One failed by bursting of the blister at the hole in the jacket and testing of the other was discontinued only because of a lack of time. The latter had blisters of ca 3/8" diameter around the holes; actual splitting of the jacket might well take another 4-8u hours.

The two foil-covered pieces which had been heavily etched electrolytically failed in only three hours.

The two nickel plated, hot pressed/^{slugs}used a standard lasted 21 hours.

All the slugs discussed in the last three paragraphs above had four holes drilled through the jacket; twelve holes were used in all other tests. The reason for only four holes was that it was desired to keep them away from ~~the~~ overlapping seams in the nickel foil.

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These results are extremely encouraging. They show that nickel-bonded, hot-pressed slugs can be made as good as Al-Si slugs in what was previously their weakest point, the lack of undercutting resistance. This improvement may be the result of any one of a large number of variables in uranium pre-treatment, electroplating, and hot pressing steps. A vigorous concerted effort is being made to determine these variables.

Any test that depended on corroding through the aluminum jacket to the secondary corrosion barrier is more likely to measure the ~~variation~~ variation in the aluminum than the corrosion resistance of the secondary barrier. Mechanical methods of removing the aluminum have the same difficulty. The problem is being attacked by use of the window slug. A half-inch hole is drilled in the base of the can, and an anodized plug inserted. A one-mil aluminum foil disc is placed in the bottom of the can. After the usual hot pressing the plug is removed, and we have a "window" where the aluminum theoretically is only one mil thick. Flowing process water at 120° removes about one mil of aluminum in 15 days so a one-month test of these slugs should show the corrosion resistance, if any, of the sweater coat of nickel or other bonding layer. The principal difficulty is expected to be encountered with variations in the surface roughness of the plated uranium. If the surface is too rough, portions of the aluminum foil may be thinned out or even penetrated.

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Monthly Report - E. A. Evans

Evaluation of KAPL Slugs

The following preliminary conclusions result from studies of # 22 four-inch slugs nickel plated and hot pressed at KAPL:

1. Many of the slugs (6 out of 9 tested) have unbonded areas, particularly near the ends, according to ultrasonic and chisel tests.
2. Most of the slugs show good resistance to corrosion by undercutting according to autoclave tests at 170 C of slugs with 1/16 inch holes drilled through the aluminum and nickel coatings.
3. The resistance of the 0.002-inch nickel coat to corrosion is being studied by removing about four square millimeters of the aluminum can with caustic in order to expose the nickel layer, and then autoclaving the slug in 170 C water. One piece tested in this manner shows no corrosion of the nickel after 63 hours.*
4. The cap to can closure was unsatisfactory on one of three slugs checked by removing about 0.015 inch of the slug jackets with caustic. The cap-can interface was uniformly and deeply attacked by the caustic.

Undercutting Resistance of Nickel-Plated, Hot-Pressed Slugs

It has been reported in previous TAR's that the rate at which a hot-pressed slug undercuts, or fails after water reaches the uranium core through a 1/16" hole in the jacket and electroplate is affected by the uranium metal quality. An even more important variable appears to be the temperature at which hot pressing is performed. Typical preliminary data are shown in Table I below:

* As-plated KAPL slugs have also been tested at 170 C; they failed after 50 days. (Private communication), C. Groot.

[REDACTED] DECLASSIFIED [REDACTED]

TABLE I

HOT PRESS TEMPERATURE AND UNDERCUTTING

<u>Slug No.</u>	<u>Hot Press Temp.</u>	<u>Hours in 170 C Water</u>	<u>Remarks</u>
1	575 C	6	Failed by undercutting
2	"	6	Failed by undercutting
3	"	7 1/2	"
4	"	7 1/2	"
5	"	11	"
6	620	14	"
7	620	30	"
8	"	30	No undercutting
9	"	30	"
10	"	30	"
11	"	30	"

Nickel as a Secondary Corrosion Barrier

The corrosion protection afforded slugs by coating them with various thicknesses of nickel by electroplating and by wrapping with foil is being determined. The slugs are canned by hot pressing. A small area of the aluminum jacket is then removed by cold caustic and the exposed nickel coat is corrosion tested in water at 170 C. Slugs electroplated with 0.001 inch of nickel fail within a few hours, those with 0.002 inch on smooth uranium have not failed in 63 hours. One slug wrapped in foil prior to canning is being tested and has not failed in 40 hours.

Corrosion Tests of KAPL Zirconium Plated Slugs

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Six four-inch slugs coated by the vapor decomposition process were received from KAPL. Two of them were boiled in water to check porosity. They failed by pinholing and blistering of the coat- the first one in three hours, the second one in 72 hours. Two slugs were hot pressed at 600 C, 12 tsi for ten minutes. They were then tested for undercutting resistance by drilling 1/16" holes into the uranium and exposing them to 170 C water. Both slugs failed in less than 3 hours, showing virtually no undercutting resistance.

Combined Point Closure Plus Hot Pressing - E. A. Evans, H. C. Bowen

Twelve four-inch slugs are being nickel plated and canned by the point closure process for shipment to the Wilmington Laboratories of the du Pont Company to determine whether they are amenable to hot pressing by the du Pont fluid bonding method.

Rupture Behavior of Unbonded Slugs - E. A. Evans

A discussion of certain aspects of the corrosion behavior of perforated bonded and unbonded slugs has been written. It is proposed that the pile behavior of such slugs be studied before irradiating large numbers of unbonded slugs.⁽¹⁾

Evaluation of Sweater Coats by Undercutting Tests - H. C. Bowen, V. H. Troutner, E. A. E

Undercutting tests have continued throughout the month. Slugs from SEP, BML, and KAPL have been run as well as pieces canned at HAPC using varying surface treatments, storing environments, and pressing conditions. The variations which have shown evidence of markedly affecting undercutting are uranium quality, depth of uranium etch, and amount of bonding.

Pieces received from SEP and KAPL have shown on the whole more resistance to undercutting than slugs from BML and HAPC. This is probably due to better uranium quality and to the uranium surface treatment. Both SEP and KAPL use an electropolish on the uranium before nickel plating.

(1) J. A. Ayres, E. A. Evans, "Proposed Production Test to Determine Rupture Behavior of Unbonded Slugs", HW-34149, 12-15-54.

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The following variables were studied by drilling four 1/16" holes in hot pressed slugs and exposing them to 170 C water in an autoclave.

1. Solid vs three-piece hot pressing die. ~~fffff~~
2. Comparison of heavy etch, light etch, and electropolish pretreatment of the uranium prior to plating.
3. Heat treating plated slugs in a vacuum prior to hot pressing.
4. Evacuation at 2×10^{-5} for 24 hours at room temperature to remove any adsorbed or occluded liquids prior to hot pressing.
5. Hot pressing in a vacuum.
6. 0.5 mil vs 1.0 mil thick layers of nickel.
7. Hot pressing time of 30 minutes instead of 10 minutes.
8. Slow cooling vs quenching of slugs after hot pressing.
9. Effect of slugs standing in water-saturated air and in dry air for one week at room temperature.

Some slugs in each group showed no undercutting of the jacket after twenty hours or more in the autoclave but others in the same group were extensively undercut after three to eight hours. Metallographic studies of the compound layers are being made.

Eight four-inch slugs electroplated at BMI and hot pressed at Hanford were also tested for resistance to undercutting, with the following results:

TABLE I
UNDERCUTTING TESTS OF BMI SLUGS

<u>Slug No.</u>	<u>Electroplate</u>	<u>Heat Treatment</u> <u>Prior to Hot Pressing</u>	<u>Hours to</u> <u>Failure</u>
1			
2			
3			
4			
5			
6			
7			
8			

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[REDACTED]

The above results lead to a preliminary conclusion that the undercutting resistance of this type of slug may be greatly affected by slight, apparently unimportant variations in either the electroplating steps or in hot pressing. As an example, if all the oxide is not removed from the surface of a slug after it has been electrolytically etched prior to hot pressing it would contaminate the uranium-nickel compound layer after hot pressing; it could make this layer sufficiently porous to allow hydrogen or water to diffuse through it and thus cause undercutting. The amount of this oxide might be expected to vary from slug to slug since it is difficult to remove it completely and it is almost impossible to tell from visual inspection whether or not it has been removed.

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Graphite Coats as Diffusion Barriers in Unbonded Slugs - H. C. Bowen, E. A. Evans

Since uranium-aluminum diffusion can occur at temperatures as low as 200-250 C, it is probably necessary to coat unbonded uranium slugs with some material which will act as a diffusion barrier. A thin layer of ^{Carbon} graphite or uranium oxide is one possibility that has frequently been suggested.

^{In investigating such coatings,}
Six sets of slugs were coated in the following ways, after which they were cold-sized, welded, and tested for diffusion resistance at an arbitrary temperature of 500-515 C in a hot press at 12 tsi for 15 minutes: (1) Spray coat of "Krylon"; (2) Layer of "Kleenex"; (3) Painted coat of dilute "Aquadag"; (4) Uniform uranium oxide coat formed by slowly admitting oxygen to a slug which had been heated to 600 C in a vacuum; (5) Clean uranium except for the oxide film formed during standing in air for about one hour.

The results of the accelerated diffusion test are reported by the Fuel Assembly Unit. The only promising coating was the colloidal graphite. The only precaution that appears to be necessary with this material is to carry out ^{slug assembly and} the sintering in such a way that the graphite is not carried into the interface between the cap and can, where it causes some interference with fusion welding. ^{One way of avoiding this is to weld the cap through a removable paper sleeve which extends about two inches down into the can, and by the same time the annular connection of the can is made.} No diffusion occurred in the case of the Kleenex-wrapped slug but gases given off during welding caused a porous weld. The coating might be suitable for cold-canned slugs having the G. A. last cold-closure.

Some of the advantages of a colloidal graphite coat which should be kept in mind in looking for an aluminum-uranium diffusion barrier include the following:

1. A very thin coating can be applied uniformly and very inexpensively at room temperature to pieces of almost any desired shape by dipping, spraying, or painting.
2. The coating is not broken up by holes and other discontinuities which are almost invariably present when ^{a material as highly reactive as} reactive uranium is coated by spraying or dipping at high temperatures.

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3. Unlike most ceramic coats, a film of graphite is not easily broken up and displaced when subjected to heating, abrasion, or mechanical damage which can usually be expected during slug canning, charging, and pile operation. One way of emphasizing this important advantage is to picture dipping one's finger in graphite and then trying to rub it off.

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~~show that~~ the temperature difference might be appreciably greater than this.

Two more slugs have been vacuum canned using 0.063 inch thick uranium wafers of 1.362 inch diameter. It was found¹ that the wafers were bonded satisfactorily to the can, but for some unknown reason the molten Al-Si did not penetrate the interstices between the wafers. While this might not be an undesirable situation from a stress standpoint⁽²⁾ it is not what is wanted with respect to heat transfer and corrosion. More wafers, both of aluminum and of uranium, have been fabricated and are to be canned and tested.

Heat Treatment of Nickel Plated Slugs - E. A. Evans, H. C. Bowman

Autoclave tests at 170 C of 21 nickel-plated, hot-pressed slugs show that, as many earlier investigators have reported, this type of fuel element is not as resistant to undercutting as is a hot-dipped slug. In addition to this, the data reported on page____ (C. Groot's TAR material) indicate² that the undercutting resistance is even less if the nickel-plated uranium is heat treated prior to hot pressing. Although the heat treatment results in a nickel uranium compound layer which, according to tests of such pieces in boiling water, helps seal any pinholes in the nickel coating, the improvement is more than offset by the destruction of the brittle Ni-U layer during hot pressing. What all this means is simply that heat treatment prior to hot pressing is not desirable from a corrosion standpoint.

In evaluating nickel-plated, hot-pressed fuel elements, it would probably be more valuable to learn how long the slug will last if water penetrates a defective aluminum can and comes into contact with the Ni-Al compound layers, rather than what and how fast something happens after the water has gone clear through the can, the Ni-Al layers, and the pure nickel layer. The major obstacle to such tests is the difficulty of uniformly¹⁴ removing the aluminum without harming the underlying Ni-Al or Ni layers.

(2) E. A. Eschbach, Secret Rough Draft, Uranium Distortion Revisal, 1951.

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Sweater Coatings on Unbonded Fuel Elements - E. A. Evans, H. C. Bowen

At one time consideration was given to sweater coats of Al-Si applied to slugs by hot dipping the slugs prior to hot pressing them, and it was considered possible that such coats might be suitable in cold charring. Eight four-inch slugs were etched, hot dipped in a duplex lead Al-Si bath for periods varying between 50 seconds and four minutes, centrifuged and inspected. In no case was the coating continuous or smooth enough to be suitable for subsequent cold charring. There were small unwet spots and rough, jagged areas caused by aluminum oxide and other dross which was not removed by centrifuging.

Zinc coatings formed by hot dipping and centrifuging have been investigated at Ames. They are being used in hot pressing experiments, but consideration possibly should be given to using them as sweater coats for unbonded slugs, ~~if~~ provided the coats are complete and uniform.

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pressing. ~~to~~

To compare "standard", heavy-etch, 0.001 inch thick coatings with light etch 0.0005 inch thick coatings, the data summarized in Table 1 was obtained in cooperation with the Fuel Assembly unit.

Spec. no.	Etch	Table 1		
		Plate Thickness	(Chisel Test) Bond strength not tested	Bond appearance (visual exam).
1	Heavy Etcholytic	0.001	Excellent	Excellent complete
2	Heavy "	0.001	"	"
3	Light "	0.0005	Good	1 sq. inch spotting, unbonded
4	Light "	"	"	"
5	"	"	"	"
6	HNO ₃ pickle	"	Poor	Occasional, very small (< 1/8 in) unbonded spots over much of surface.
7	"	"	"	"
8	"	"	"	"

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February 7, 1955

TO: J. A. Ayres

FROM: E. A. Evans, H. C. Bowen

INTRODUCTION

~~We have frequently agreed in the past that~~ The secondary corrosion protection offered by an electroplated nickel coating after exposure to hot pressing conditions has never been ^{ACCUATELY} determined. This situation has existed simply because no satisfactory procedure has been available for removing part of the aluminum jacket without at the same time damaging the ^{NICKEL} sweater coating beneath it. The following discussion describes very briefly a procedure which shows considerable promise in evaluating ^{THE CORROSION BEHAVIOR OF ELECTROPLATED, HOT PRESSED} nickel sweater coats.

SUMMARY

~~It has been shown for the first time that~~ As a result of changes occurring during hot pressing, a layer of electroplated nickel less than 0.001-inch thick on lightly etched or electropolished uranium provides a substantial amount of secondary corrosion resistance, as well as resistance to undercutting.

DETAILS

A protective coating on a slug can affect the corrosion behavior of the slug in two ways: (1) It can prevent water from reaching the uranium; (2) it can decrease the rate at which the slug is attacked after water reaches the core.

We have previously reported elsewhere ⁽¹⁾ that by using a relatively high hot pressing temperature a nickel-plated, hot-pressed slug can be made ~~completely~~ resistant to undercutting. The rate at which a perforated slug fails is thereby minimized.

However, an electroplated nickel coating 0.001 inch or less in thickness in the as-plated condition does little to prevent water from reaching the uranium. Even in water at 100 C for example, the as-plated slugs usually showed signs of

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failure after fifty hours and few if any ever lasted as much as 200 hours. In 170 C autoclave water the slugs fail in less than three hours. Of course, only one pinhole can cause the failure of an as-plated slug; whereas the chances of this defect lining up with a jacket defect may be extremely slight.

and its corrosion resistance may be of an entirely different order. During hot pressing, the nickel plate is modified. In the first place, the nickel itself is heat treated and this may decrease its porosity. Secondly, the nickel reacts with the uranium and with the aluminum to form at least six distinct compound layers, part or all of which may be free of the porosity associated with the original electroplate. In order to test the corrosion resistance of the nickel sweater coating after hot pressing, it is essential that part of the aluminum jacket be removed in such a way that none of the underlying layers are appreciably affected. There is little reason to ^{hope} ~~hope~~ that this can be done mechanically. Preliminary experiments using hot concentrated sodium hydroxide solution also showed no promise; ~~For example,~~ a slug with a jacket partially stripped in this manner failed in one hour in 170 C water.

It now appears that part of an aluminum jacket can be stripped from a hot-pressed slug without excessive damage to the underlying coatings of nickel and associated compound layers by using the following procedure:

An area of about one square inch of the aluminum jacket is filed or milled down to within about .005 inch of the nickel coating. The slug is then exposed to cold, dilute (approximately 4%) sodium hydroxide solution until an area of nickel coat of about $1/8$ in.² becomes visible. Visual detection is possible because the exposed nickel is black.

The following table shows results of experiments to date:

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TABLE I

SECONDARY CORROSION RESISTANCE OF NICKEL-PLATED, HOT-PRESSED SLUGS

<u>Slug No.</u>	<u>Description</u>	<u>Treatment</u>	<u>Remarks</u>
S-1	KAPL piece #260	Autoclaved at 170 C	No apparent corrosion after 282 1/2 hours
S-2	KAPL piece #265	Autoclaved at 170 C	No apparent corrosion after 303 1/2 hours
S-3	KAPL piece #100	Autoclaved 170 C 40 hrs. Put in 100 D Flow tube.	Put in flow tube Fri. 2-4-55
S-4	.00085" Foil-HNO ₃ Etched U	Autoclaved 170 C 40 hrs. Put in 100 D flow tube	"
S-5	.00085" Foil - HNO ₃ Etched U	Autoclaved 170 C 40 hrs. Put in 100 D flow tube	"
S-6	.00085" Foil - HNO ₃ Etched U	Autoclaved at 170 C	No corrosion after 305 hrs
S-7	<.001" Ni electroplate Lt. anodized U	Autoclaved at 170 C	No corrosion after 120 hrs
S-8	<.001" Ni Electroplate Electropolished U	Autoclaved at 170 C	No corrosion after 120 hrs

CONCLUSIONS

Preliminary data show that the secondary corrosion protection obtainable from electroplated nickel in hot-pressed slugs is much greater than has previously been assumed at HAPO and at other sites.

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The following tests are planned with electroplated^{or foil wrapped}, hot-pressed nickel coatings 0.0003 to 0.001 inch thick.

1. Boiling in 100 C water.
2. Autoclaving at 170 C
3. Exposure in 100 D flow tubes at 120 C.
4. Metallographic examination of nickel surface to determine how the Ni-Al layers are affected by the caustic.

EAE:HCB:jz

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Electroplated nickel sweater coats satisfactorily prevent uranium-aluminum interaction during hot pressing. They also affect the rate at which a slug fails when ~~water~~ high temperature water reaches the uranium core. This effect has not been dependable in the past, but in recent weeks it has been discovered that by increasing the temperature of hot pressing from 575 C to 600-620 C the extent and consistency of this type of corrosion resistance is improved very markedly.

Finally, the sweater coat provides an undetermined amount of resistance to water attempting to reach the uranium core. The first question involved in considering this matter of secondary corrosion resistance is that of whether the additional nickel required in order to get corrosion resistance can be justified from a reactivity standpoint. Calculations being made by Groot and others indicate that if 30% of our present or future ruptures were caused by corrosion, as contrasted to uranium cleavage, the reactivity loss resulting from a coat of nickel 0.5 mil thick would be justified if the coat protected the core from failure for a period of 35 days*, at present power ~~low~~ levels. If 50% of the ruptures were of the corrosion type, ~~and~~ ^{coating of this thickness} ~~and~~ could be justified if it lasted only 16 days. These figures do not ~~taken into account such factors as the value of fewer ruptures on the basis of pile safety.~~ ^{take into account such} ~~such factors as the value of fewer ruptures on the~~ basis of pile safety.

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Comments regarding nickel electroplating and its alternatives

The primary, long-standing reasons for applying electroplated nickel "sweater coats" to slugs prior to hot pressing are:

- (1) To prevent U-Al reaction during hot pressing or pile irradiation;
- (2) To permit a slug to attain goal exposure even though the aluminum jacket is penetrated by water;
- (3) To slow down the rate at which a slug fails after pile water reaches the uranium core.

There is no argument about the fact that the nickel plate fulfills the first requirement above, i.e. that it is an adequate diffusion barrier.
~~NO INFORMATION~~

At the present time the secondary corrosion resistance of electroplated nickel of 1 mil or less thickness is ~~many~~ unsatisfactory because of porosity. ~~It may be possible to decrease the porosity by:~~

- (1) Using a thicker coat and paying for it in additional reactivity loss;
- (2) Using a flash coat of some metal such as tin over the nickel and making it fuse and fill up pores in the nickel during or prior to hot pressing;
- (3) Mechanically closing the pores by mechanical working, such as shot peening or ball milling. Preliminary investigations of these methods are not promising. ~~One encouraging factor that is frequently~~

lost sight of is that holes in the jacket might not line up with a hole in the electroplate. The effect of the electroplate on the rate at which a perforated slug fails has varied greatly. There seem to be several variables, particularly uranium metal quality, that affect the amount of protection offered by the nickel plate. The chances are good that these variables can be established and adequately controlled.

There are several alternatives to electroplated nickel that have now progressed to the point where we should ^{experimentally} compare the coatings with the electroplated ones from ~~unconformity~~ the various corrosion standpoints. The most promising ones for any application in ~~the near~~ coming months are those prepared by uniskanning and by using nickel foil wrapped around the slug. Uniform, 3 mil zirconium sweaters have been prepared by uniskanning and in the next five or six months it is anticipated that one mil coatings will be available to ~~replace~~ ^{eliminate the necessity of} nickel ~~manufacturing~~ plating prior to hot pressing. Since such coatings are not subject to the porosity and so on that plague electroplating we should arrange to have slugs coated in this manner hot pressed and corrosion tested as soon as possible by the various techniques available. Since the process also ~~has been applied to~~ ^{is applicable} to other metals, such as nickel, we should include both nickel and zirconium jackets.

Two brands of nickel foil

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[REDACTED]

4.47
0.325 ± .010

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(3) Secondary Corrosion Resistance Poor

Solns: dual plates or mechanical densification

b. Undercutting

- (1) At best, as good as A-I, - i.e. no ~~U.C.~~ U.C.
- (2) At worst, large variation in U.C. resistance - ~~sometimes~~ ^{sometimes} little better than unbonded pieces.

Two choices: 1. Is present plate satisfactory
2. Improve electroplate
3. Choose alternative sweater coat

3. Efforts to eliminate "inadequacies"

- a. mech. Treatment for classifying
b. Dual plates
c. Odds on each

d. Determining most important variables affecting u.c.

4. Alternative Sweater coats applied by alternative methods

- a. Uniska III ? closure first end
 present status - hole in slug etc
 Ni not yet tried
 Zn not readily hot pressed - special etching etc

b. Ni foil - ^{High quality} commercially available in any desired thickness
slugs have been coated in this manner; when smooth
U used, has excellent d.c. resisting. Similar
results BNI, ~~some~~ Savannah, etc.

more slugs will be canned next week. By using different $\frac{1}{16}$ thicknesses ~~slugs~~ and exposing it to ^{in flow tubes} a corrosion testing ~~after removal of the~~ we should be able to determine whether the thicknesses which Dr. J. finds economically justified on a resistance basis can ~~provide adequate~~ provide the required amount of secondary corrosion protection.

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<u>Criteria</u>	<u>Properties</u>	<u>Program</u>	<u>Testing</u>
Lowest inhour	Uniformity	A. Electroplating 1. Type of bath - a. Thompson b. Watts c. Dual plate d. Others	A. Lowest inhour 1. 305-pile 2. Microscopic a. Uniformity b. Thickness
Secondary corrosion resistance	Thickness		B. Sec. Corr. Barrier
Undercutting	Porosity	2. Uranium surface - a. Etching b. Polishing c. Pickling d. Metal quality e. Hot cathode f. High C.D. flash	C. Undercutting
Diffusion barrier	Adherence		D. Diffusion Barrier 1. Microscope 2. Baking
Bonding		3. Densification - a. Shot peening b. Triscanning c. Uniskanning d. Vapor buff e. Ball milling Rack design a. Shielding b. Engineering Development c. Pickling d. Etching e. Other (coatings), etc 1. High foil 2. Carbonyl or gaseous coatings 3. Triscanning	E. Bonding

1. BMS - same - 170°C
2. KAPL - 12 - H.P. as per KAPL }
3. Foil - 120-170 flow lab.
4. Water - K
5. SiCg - urea?
6. Undercutting
7. High C.D. hot cathode

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ABSTRACT

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As-plated, nickel sweater coatings 0.001 inch thick offer little or no corrosion protection to uranium; ~~changes which occur in the coating~~ ~~which occur during hot press canning~~ a newly developed procedure shows, however, that these same coatings provide ^{an} excellent ^{secondary} ~~corrosion~~ ^{barrier} ~~protection~~ after changes ^{assembly of the fuel element by} ~~which occur during~~ hot press canning. This conclusion is the result of studies based on a procedure which has been developed for evaluating and comparing the secondary corrosion behavior of wrought, electroplated, and gas deposited coatings.

~~SECRET~~
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INTRODUCTION

A sweater coating is essential in hot press canning to prevent the extensive uranium-aluminum interaction which otherwise occurs during pressing. ~~The~~ The work reported here was initiated to determine whether sweater coatings also enhance the corrosion resistance of the fuel element.

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A. BACKGROUND

1.1 The Purpose of Sweater Coatings

Extensive formation of a very brittle U-Al compound layer occurs during hot press canning unless a sweater coating is used, ~~over the uranium core.~~
This brittle layer cannot be depended upon to provide uniform heat transfer from ~~between~~ the core ~~to~~ the jacket during pile irradiation.

~~Possible~~ Advantages of sweater coatings which have been ^{suggested} ~~proposed~~ but never completely evaluated include: (1) secondary corrosion resistance, and (2) resistance to undercutting.

1.2 Secondary Corrosion Resistance

For the purposes of this discussion, secondary corrosion resistance is defined as the protection which the sweater coating offers a slug after water has penetrated ^{only} the outer aluminum jacket, ~~but not the inner, sweater coating.~~
After water has penetrated ^{the jacket and the sweater coating,} ~~both coatings,~~ the corrosion problem becomes one of ~~the~~ undercutting behavior, involving uranium as well as ^{the} nickel and aluminum. This problem is considered in a separate report ⁽¹⁾.

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1.3 Factors Affecting Secondary Corrosion Behavior

Porosity is the most important factor determining the corrosion protection afforded uranium by ^{the new} coatings ~~now~~ being considered ^{for Hanford piles.} ~~at HAPC.~~ As-plated coatings 0.001 inch ^{thick,} or less ~~thick~~ ordinarily contain large numbers of very small pinholes, ~~FOR REASONS SUCH AS THOSE~~ ~~some possible causes of which are~~ discussed in Reference 2. This porosity can be readily detected by the deposits of oxide which build up at pinholes when as-plated slugs are heated in air or in high temperature water. It can be decreased by methods such as: (1) using a thicker layer, (2) using a very smooth uranium surface, (3) heat treating ^{prior to or during hot pressing}, (4) mechanical densification such as Buffing or ball peening, and (4) application of dual, or composite, plates.

Electrogalvanic action would be expected between an aluminum jacket and any exposed portion of the underlying coating of dissimilar metal. In the case of a nickel sweater coating, ~~one would expect~~ ^{theoretically should} the aluminum ~~to~~ corrode sacrificially and thus protect the exposed nickel layer, although this picture may, of course, be drastically changed by factors such as temperature, composition of the electrolyte, and gas concentrations.

- (2) U. R. Evans and S. C. Shome, Studies in the Discontinuities in Electrodeposited Metallic Coatings. J. Electrodepositor's Tech. Soc., 26, 137-160 (1950)

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1. First of two reports -- flow tubes not available for a while
2. Trying to sell:
 - a. Have corrosion protec. as well as diff. resist.
 - b. Electropl. coats, after h.p. may offer corr. prot. comparable to that from wrought coatings, which normally have much greater corr. resist.
 - c. We now have a way of realist. eval. and comp. electrop. and wrought (foil) coatings.
3. How we did it
4. The data
5. Conclusions and recommendations.

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FOR ELECTROPLATING REPORT:

METAL FINISHING JAN 1955 p. 60 Vol. 53 no. 1

(1) A.A. Wesley & Knapp confirmed that porosity test reagents can produce pores during the test, so that properly produced nickel deposits may be far less porous than previously assumed.

(1) TRANS. INST. MET. FIN. 31, adv. Copy 18.

An important research was reported upon by Ogburn & Benderly⁽²⁾ in the nature, cause & effect of porosity in electrodeposits, in which they pointed out that meas. of initial porosity of a detailed foil has serious limitations.

Plating 41/61, 169

M.F. 964 PRODUCTION OF BRIGHT, CORR. RESIST. DEPOSITS BY NICKEL PLATING AT LEAST 0.000,05 "Ni, FOLLOWED BY AT LEAST 0.000,005 Zn, THEN BUFFING TO CAUSE THE Zn TO PENETRATE THE PORES. FINALLY, Cr PLATED. INVENTORS: HAMMOND & BOWMAN. U.S. PAT 2,676,917 APR. 27, 1954.

Rev-56351 RD
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1.4 Previous Secondary Corrosion Studies

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As-coated samples. The simplest, and most common method of testing ~~secondary corrosion barriers~~ has been to ~~imm~~ expose as-plated samples to boiling water, or to 170 C autoclave water, until failure occurs. ~~on as-plated material~~

There are two principal weaknesses to such tests/for final evaluation of secondary barriers: (1) A coat which is relatively very satisfactory may fail extremely rapidly because of a single, minute pinholes which might never line up exactly with a perforation; (2) The porosity usually associated with thin, ~~and~~ electroplated coatings may be corrected by the heat treatment and/or ~~heat~~ and ~~alloy~~ formation which occurs during hot pressing.

NW-56351 RD

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HCB - Do we have a copy?

RGP

S.C. STATUS

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1-20-55

Written to
V.R. CooperA. IntroductionSTATUS OF SECONDARY CORROSION BARRIERS

This discussion is concerned only with secondary corrosion resistance and will not consider undercutting resistance. This distinction may be clarified by the following descriptive paragraphs:

1. Secondary corrosion resistance is the resistance of the secondary barrier layer to corrosion after the outer jacket is penetrated. This is expressed as the number of days after penetration of the jacket before failure of the slug occurs, ~~and indicates the possibility of a slug with a perforated jacket attaining goal exposure.~~

2. Undercutting resistance is ~~the degree of resistance offered to undercutting~~ ^{and a measure of the difficulty with which water or corrosion products such as hydrogen can penetrate between the uranium core and the sweater coat or between the sweater coat and the uranium jacket.} A fuel element with good undercutting resistance will fail by swelling only at the point of failure. A slug with poor undercutting resistance will show general swelling, the swelling often being more pronounced at areas some distance from the actual point of failure. This latter type of failure is very undesirable as it results in stuck slugs and perhaps ruptured tubes. ~~A measure of the undercutting resistance helps to describe the type of failure expected after water penetrates to the uranium. A measure of the secondary corrosion protection the uranium jacket indicates the possibility of attaining goal exposure after water penetrates the outer jacket.~~

DISCUSSION B. Discussion1. Does as-plated nickel have any corrosion resistance?

Nickel plated on uranium is in practically all cases porous. Only relatively thick coats on smooth slugs have shown any real corrosion resistance. Specifically, the nickel which has been plated on anodically etched uranium has shown little or no corrosion resistance. Thicker plates (1.5-2.0 mils) on electropolished uranium which have been prepared by KAPL have been satisfactory in this respect. All attempts up to the present time to plate a relatively thin (~ 1.0 mils) layer of nickel

Two as-plated pieces prepared by KAPL were exposed to water at 170°C for approximately 50 days before failure.

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on uranium have resulted either in plates which were not corrosion resistant or which blistered or did not bond on hot-press canning. Two possibilities for developing a satisfactory corrosion-resistant layer are being tried.

a. Multiple plates. The simplest method would be a flash coat of nickel (or other metal) followed by a heavier coat of nickel (or other metal). This multiple plate would consist of layers (2 or more) of the same or different materials. The materials could be applied by electroplating, gas plating, uniskanning or by other means. One dual plate being tried at present is a flash coat of nickel from the Thompson bath followed by a thicker coating of nickel from a Watts bath.

b. Densification. The plate could be applied to the uranium by electroplating or by other means and could be subsequently treated to close up the pores. Some appropriate treatments could be shot peening, ball peening, etc.

2. Does heat-treated nickel have any corrosion resistance?

Studies have shown that uranium-nickel alloys corrode at a much slower rate than does uranium. It was suggested that a thin layer of nickel could be placed on a uranium slug and then heat treated to form the corrosion-resistant uranium nickel alloy. By this means a relatively thick corrosion-resistant layer of this alloy might be formed. Battelle Memorial Institute has prepared some slugs in this manner. They have lasted 100-200 hours in boiling water, but still seem to be of little value for pile use.

3. Does a hot-pressed nickel-plated slug have any ^{secondary} corrosion resistance?

During hot pressing, the nickel is changed considerably. Alloys of nickel with aluminum and with uranium are formed. Both of these are corrosion resistant and may aid in protecting the slug in case of failure of the outer jackets. No suitable method for testing the value of this secondary barrier has been devised. If the aluminum jacket is dissolved off, the aluminum-nickel layer is damaged or

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destroyed. It is almost impossible to abrade off or drill through the aluminum and not damage the alloy layers. Some attempts to fabricate slugs with extremely thin layers of aluminum over the nickel met with little success. A pile test has been suggested; in this test the slugs would be canned in defective cans and irradiated in the pile. A comparison of the corrosion protection afforded by nickel layers of different thicknesses could then be made, providing the results were not overshadowed by other factors.

It should also be noted that an imperfection in a sweater coat may not line up with a hole in the can, and thereby cause secondary corrosion. Thus, there may be secondary corrosion.

4. Does any hot-pressed nickel-coated slug have any secondary corrosion resistance?

Electroplated layers may be unsatisfactory because they are porous, non-uniform, or contain hydrogen or other impurities. Perhaps nickel plated by some other method may be much more satisfactory. The following methods appear promising.

a. ^{plating} ~~Gas plating~~ Nickel may be plated by decomposition of nickel carbonyl.

The plate is non-porous even in thin layers and is uniform. Some pieces have been plated and are being tested.

b. ^{Uniskanning} ~~Uniskanned layers~~ It is possible that a very thin layer of some materials

could be placed on uranium by uniskanning. In this manner, the application and densification could be effected simultaneously. Some uniskanned nickel ^{and zirconium} cans have

been requested from the ~~FEU~~ unit.

c. ^{wrapping} ~~Foil~~ A suitable ^{coating} layer of nickel or other materials ^{can} ~~could~~ be applied by wrapping a thin layer ^{of relatively non-porous foil} on the uranium slug. This procedure is being investigated.

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protection even though the sweater coat had an imperfection which would have caused it to fail in the as-plated condition.

An approximate delivery date of March 1, 1955 was specified. If we obtain the cans at this time we can make the comparative evaluations without delay.

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[REDACTED]

3 1/2 Cooper
6 R B Post
5 E A Evans
1 J A Cooper
2 R W Bunker
7 B. F. Snodgrass
4 E A Eastbrook
8 300
7 1/2

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[REDACTED]

[REDACTED]

electroplated on to a uranium slug

SUMMARY

1. ~~Anodically etched uranium slugs which have been electroplated with~~ A thin (≤ 1.0 mil) layer of nickel occasionally containing imperfections, ~~These in which~~ ^{which} ~~imperfections~~ cause noticeable corrosion of the uranium after exposure to boiling water for periods varying from 2 to 200 hours.

2. Thicker ($1.5 > 2.0$ mils) electroplated coats on electropolished uranium are ^{relatively} ~~usually~~ impervious, and ~~resist corrosion for very long periods.~~

3. [The electroplated nickel layer is changed drastically by hot pressing.]

→ The results of corrosion tests of the as-plated nickel cannot be used for evaluation of the secondary corrosion resistance of the nickel layer in hot-pressed slugs.

↙ No extrapolations or comparisons are valid.

4. No satisfactory test for the degree of secondary corrosion protection afforded by the nickel layer in hot-pressed slugs has been designed yet. No valid measurement has been made.

5. The porosity and other imperfections of the as-plated nickel may be corrected or improved by subsequent treatment. ~~Some such treatment may result in a thin, impervious layer of nickel.~~

6. Other methods of depositing nickel are being investigated and tested. ^{or wrapping with foil} Some method such as ~~wrapping or~~ unskanning may give thin impervious nickel plates.

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END