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NONAQUEOUS ELECTROPOLISHING BATH
FOR URANIUM

E. L. Childs

F. E. Evans

THE DOW CHEMICAL COMPANY
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401
U.S. ATOMIC ENERGY COMMISSION
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ABSTRACT

This report describes a nonaqueous bath for electropolishing uranium consisting of sodium hypophosphite in 1,2-ethanediol. Studies were made of the effects of water content, pH, temperature, and salt concentration on this electropolishing procedure. Surface roughness using this method is reduced to about 60 percent of the original value.

CONTENTS

Abstract	ii
Introduction	1
Summary	1
Experimental	1
Results	3
Discussion	4
Acknowledgment	4

INTRODUCTION

Uranium reacts with water to form hydrogen, oxides and hydride; therefore, a nonaqueous system seems desirable to pretreat this metal for plating. A preliminary literature search revealed the work of Couch in which he investigated nonaqueous cleaning systems for use on uranium.¹ Couch developed only one system that resulted in a clean uranium surface. Gore's work investigated surface treatments for uranium prior to aqueous electroplating.² The cleaning methods revealed by this literature search were inadequate for nonaqueous surface treatment of uranium. Some tests were made with sodium hypophosphite dissolved in 1,2-ethanediol. In the course of the investigation this bath was found to have an electropolishing effect.

To find the optimum conditions for the use of this bath for electropolishing, the following variables were checked: concentration of hypophosphite, effect of pH, water content, and temperature. The polishing range was checked with the above conditions by recording current as voltage was increased. Electropolishing is considered to occur at the voltage where the ratio of voltage to current is greatest.³

SUMMARY

Uranium is polished anodically at 13 volts in a 1,2-ethanediol bath saturated with sodium hypophosphite. The bath must be heated to 90°C to remove water. The operating range is 90 to 110°C. A sample of metal can be degreased and polished without any prior treatment. The surface roughness can be decreased about 60 percent by the removal of approximately 0.0018 inch of surface in 45 minutes.

EXPERIMENTAL

The uranium metal for this experiment contained about 100 ppm carbon and 300 ppm iron plus other impurities to approximately 1000 ppm total. The metal had been cast and machined to cylinders 1/2-inch in diameter and 2-inches long. These cylinders were drilled and tapped on one end to accept a threaded stainless steel support rod.

Reagent grade 1,2-ethanediol containing about 0.2 v/o water was used. This was combined with chemically pure sodium hypophosphite monohydrate. The drying was aided by purging with 99.995 percent pure argon.

The surface finish of the uranium cylinders was measured with a Profilometer. The stylus on this device has a tracing speed of 30 inches per second with a 0.0005 inch radius diamond.

A magnetic stirrer hot plate sufficed for the heating and agitation of the bath. The samples were supported on the end of a stainless steel rod chucked into a variable speed stirrer. The lower end of this rod has been wrapped with tape made of Teflon TFE to keep it from drawing current in the bath. A stainless steel beaker served both as a container and cathode for electropolishing experiments. This beaker was insulated from the hot plate by placing it in a glass beaker. A 1/8-inch thick disk of Teflon insulated the inside bottom of the container. A stainless steel loop of 1/8-inch wire held this disk in place. The wire for the loop was cut long enough to allow a handle to be bent vertically up one side of the beaker. Details of the assembly are found in Figure 1. The glass beaker is not shown.

The electropolishing bath contained 600 grams per liter of monohydrated sodium hypophosphite in 1,2-ethanediol. The average water content at make-up was

Figure 1. EXPERIMENTAL APPARATUS FOR ELECTROPOLISHING.

¹Couch, D. E., and Brown, A. M., *Coatings for Uranium*, December 1961, SCR-307.

²Gore, J. K., et al., *Chemical Surface Treatments for Uranium and Their Application to Uranium Technology*, May 13, 1958, No. LA 2190.

³Jacquet, P. A., "Electrolytic Polishing of Metallic Surfaces," *Metal Finishing*, June 1949.

about 3 v/o. The sodium hypophosphite monohydrate actually contained more water than was indicated by its formula. Dehydration was achieved by heating at 90°C for about 12 hours; while bubbling with a continuous stream of dry argon. After 12 hours, the bath usually contained less than 0.1 v/o water as determined by infrared analysis (Table I). This 12 hour drying time was convenient for overnight drying, however when working time was short, 4 hours drying at 120°C would be sufficient.

TABLE I

DRYING TIME OF ELECTROPOLISHING BATH*

Hours	Temperature (°C)	Lab Analysis v/o water
0		2.30
1	90	2.60
2	94	1.65
3	112	1.60
4	105	0.55
5	80	0.32
6	95	0.15
7	94	0.10
23	83	0.03

*Electropolishing bath contains 600 grams of sodium hypophosphite per liter of 1,2-ethanediol at 90°C.

Uranium was electropolished at 13 volts with agitation reduced to a minimum. The temperature range adopted was 90 to 110°C with the process starting near 90°C because of heat generated by the flow of current. The current started initially at about 120 amperes per square foot (asf) and fell to a minimum of about 40 asf as polishing progressed.

Measurements longitudinally on the curved surface of the cylinders served to evaluate the surface finish. Each part had been measured for one inch near the middle of its length in four places 90 degrees apart around the circumference. These uranium parts were marked at the first measurement point and measurements were taken in the same direction each time, therefore, each successive set of measurements was taken in the same area on the part. For example, a reading from part No. 72, position 2 would be from the same area as previous readings from No. 72, position 2. Each set of four measurements, taken as indicated above, was then averaged to enter as data for this experiment.

TABLE II
ELECTROPOLISHING DATA*

Sample No.	Electro-polish Min.	μ in.		Roughness Reduction μ in.	(%) Reduction	Wt Loss (g)
		Before	After			
74	10	46	25	21	46	0.40
76	10	48	25	23	48	0.41
72	10	49	29	20	41	0.35
75	10	53	30	23	43	0.40
73	10	64	31	33	52	0.40
47	10	86	75	11	13	0.42
50	10	86	40	46	53	0.37
37	10	100	68	32	32	0.39
5	10	105	80	25	24	0.41
4	10	109	80	29	27	0.44
3	10	110	83	27	25	0.37
1	10	121	92	29	24	0.44
2	10	128	90	38	30	0.36
21	10	400	306	94	23	0.39
59	20	13	9	4	31	0.55
62	20	18	14	4	22	0.84
16	20	35	24	11	31	0.75
78	20	38	26	12	32	0.65
80	20	44	17	27	61	0.89
79	20	51	20	31	61	0.85
77	20	56	22	34	61	0.87
15	20	85	44	41	48	0.76
9	20	85	50	35	41	0.88
36	20	90	54	36	40	0.87
20	20	103	35	68	66	0.84
13	20	105	51	54	51	0.55
7	20	118	54	64	54	0.74
6	20	120	54	66	55	0.81
8	20	124	86	38	31	0.79
11	20	143	93	50	35	1.23
28	20	203	170	33	16	0.91
14	20	205	54	151	74	0.53
29	20	208	170	38	18	0.93
111	20	400	325	75	19	0.74
49	30	15	10	5	33	1.41
69	30	18	13	5	28	1.31
57	30	23	11	12	52	1.55
82	30	31	14	17	55	1.23
84	30	44	15	29	66	1.33
81	30	46	12	34	74	1.41
83	30	52	16	36	69	1.49
137	30	100	38	62	62	1.20
141	30	100	63	37	37	1.44
11	30	108	59	49	45	1.03
10	30	113	56	57	50	1.09
12	30	114	50	64	56	1.32
13	30	115	44	71	62	1.33
32	30	190	144	46	24	1.30
31	30	218	158	60	28	1.19
33	30	210	125	85	40	1.41
30	30	228	148	80	35	1.04
103	30	400	338	62	15	1.12
37	46	195	73	122	63	2.36
35	46	215	110	105	49	1.62
36	46	217	78	139	64	2.03
34	46	238	95	143	60	1.85
39	60	215	73	142	66	2.01
38	60	220	43	177	80	2.83
40	60	223	75	148	66	3.34
1	60	338	275	63	19	2.11
12	60	388	313	75	19	2.93
9	60	413	356	57	14	1.88
10	60	450	250	200	44	2.51
4	60	525	263	262	50	2.09
8	60	550	488	62	11	1.81
6	60	575	450	125	22	1.88
5	60	600	413	187	31	2.17

*Electropolishing performed in a bath of 1,2-ethanediol saturated with sodium hypophosphite with less than 0.10 v/o water and heated to 90°C.

RMS was measured along one inch of the middle of the sample's length in four places before and after polishing.

RESULTS

The collected raw data is represented in Table II. These data represent runs made after conditions were optimized from results presented later on in this section. These samples are arranged in time-of-electropolish groups in order of increasing initial roughness expressed in micro-inches. These groups were then averaged as shown in Table III and percent reduction of roughness versus time-of-electropolish is plotted in Figure 2.

TABLE III
TABULATION OF AVERAGES*

Electro-polish Min.	Average % Roughness Reduction μ in.	Sample No.	Average Grams Lost per Sample
10	34	14	0.40
20	42	20	0.80
30	46	18	1.29
46	59	4	1.96
60	38	11	2.32

*From data of Table II.

Figure 2. SMOOTHING (REDUCTION IN RMS OF U SURFACE IN BATH)

The effect of water on electropolishing was studied by adding water in known increments to a dry bath and noting polishing current range and visual electropolishing effect between additions. The water content of the electropolishing bath was determined by infrared analysis. Increased water content allowed greater current to flow, but pitting also occurred, especially more so as greater amounts of surface were removed. The effect of water could not be observed below approximately 0.4 v/o. The data shown in Table II was run at less than 0.1 v/o water.

As noted in reference 3, electropolishing is considered to occur at the voltage where the ratio of voltage to current is greatest. This voltage is approximately 18 volts with the hypophosphite-glycol bath but some pitting occurred at this high a voltage. Anodic treatment at 13 volts was still in the electropolishing range and no pitting occurs at this voltage.

To check pH effect, one bath was made up at 600 grams sodium hypophosphite per liter and dried as mentioned previously.

Six uranium samples were electropolished in this bath at 100°C with variable pH. The pH was varied by adding increments of anhydrous ammonia between each run. No difference in polishing effect was observed for six samples run in the pH range of 5.5 to 8.0.

The electropolishing bath operated at room temperature would draw only a small amount of current, 7 asf at 13 volts. As the voltage was continuously applied, the current rapidly dropped off to near zero. A coating of white material formed on the uranium surface. This material was thought to be an organic polymer. It was not soluble in either water or 1,2-ethanediol. By infrared analysis, 1,2-ethanediol could be detected. No further work was done to identify this material. As the temperature of the bath was increased, successive samples tended to be more free of this white substance until at about 80°C no coating formation was detected. As the temperature of the bath was increased further to approximately 130°C, pitting occurred, and bath evaporation and decomposition was evident. The bath darkened at higher temperatures. Samples were polished at temperatures ranging from 50 to 140°C. Runs were made in increments of 10°C between these temperatures.

One bath was made up to saturation (i.e., 600 grams of sodium hypophosphite per liter), and successive samples were run as increments of 1,2-ethanediol were added. The more dilute solutions had a tendency to form the "organic polymer" coating mentioned previously. In these runs, the current was lower, thereby increasing the time needed to treat samples.

DISCUSSION

This report has demonstrated the feasibility of smoothing the finish of an uranium surface by a nonaqueous electropolish. This procedure may have use as pretreatment for uranium metal prior to subsequent treatments in anhydrous environment. This electropolished surface has been examined by x-ray diffraction, mass spectrometry, infrared spectrometry, electron diffraction and the ellipsometer. The x-ray diffraction pattern was no different from that exhibited by uranium stored in air. Two uranium mass spectrograph electrodes were made and polished by this procedure. This polished surface was analyzed for elements by spark impurity analysis with P, Al, Si and Na being found. No organics were detected. The surface of an electropolished sample was washed with high purity acetone and the washings were analyzed using the infrared

spectrophotometer; only trace amounts of hypophosphite could be found in these washings. No ethylene glycol was detected. Electron diffraction gave only an amorphous pattern. An ellipsometer was used to attempt to measure the thickness of the oxide layer. This analysis gave inconclusive results.

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