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Hohman et al.

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[54] **SURFACE TREATMENT OF TITANIUM AND TITANIUM ALLOYS**

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[21] Appl. No.: **407,380**

[52] **U.S. Cl.** **134/3**; 134/7; 134/41; 156/6; 156/18

[51] **Int. Cl.** **B08b 3/02**

[58] **Field of Search** 134/3, 7, 41; 156/6, 18; 252/79.3, 145

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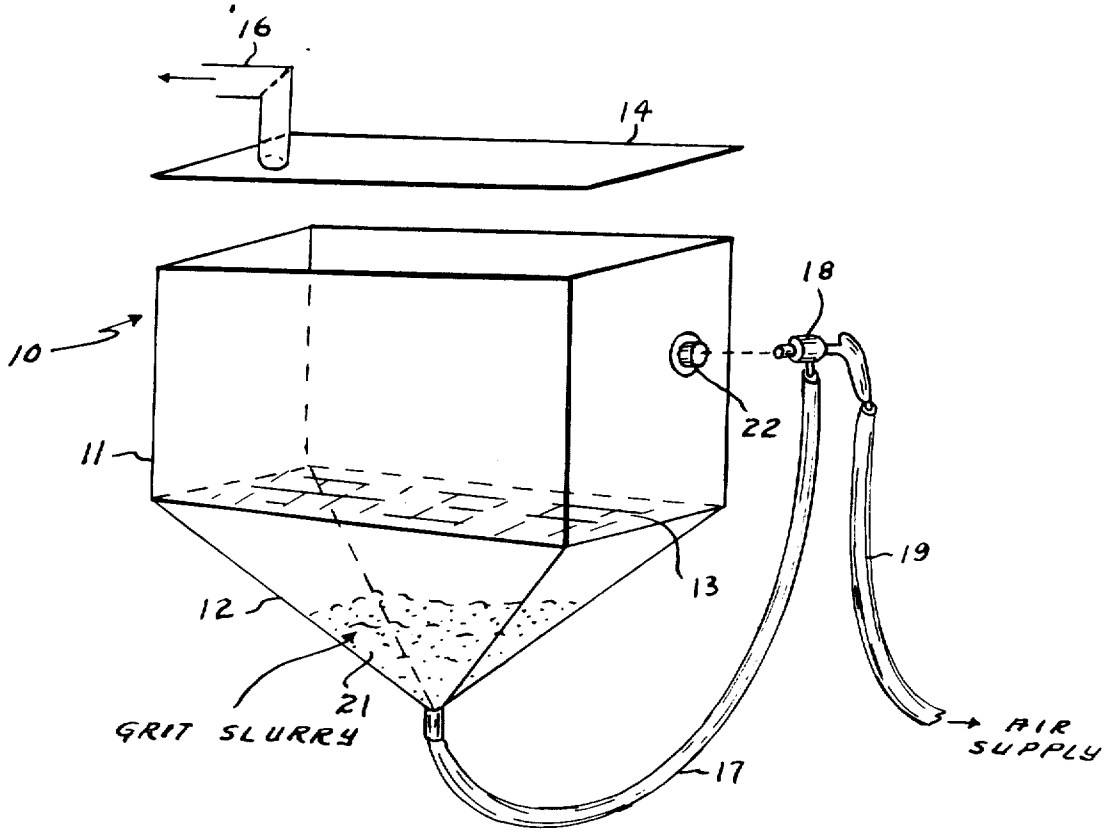
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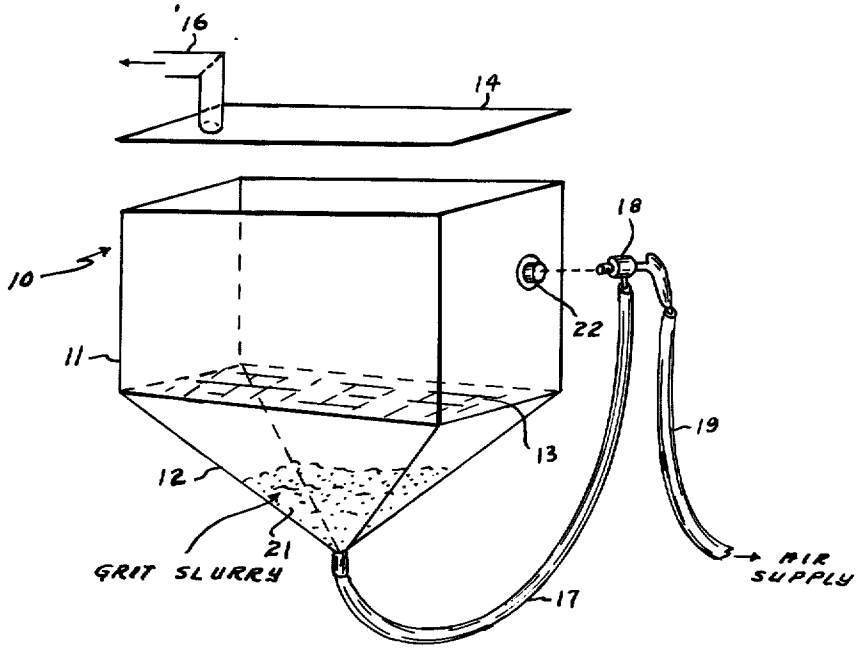
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[57] **ABSTRACT**

A process for treating a titanium or titanium alloy surface to improve its bonding characteristics is provided that comprises directing a stream of a slurry of aluminum oxide grit in a hydrofluosilicic acid solution onto the surface for a period of time sufficient to obtain a uniform, oxide-free surface, washing the treated surface to remove grit and terminate acid reaction, and drying the treated surface. The treatment provides a chemically stable surface that is receptive to adhesives and coatings.

6 Claims, 1 Drawing Figure




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GRIT SLURRY
17
AIR SUPPLY

SURFACE TREATMENT OF TITANIUM AND TITANIUM ALLOYS

RIGHTS OF THE GOVERNMENT

The invention described herein may be manufactured and used by or for the Government of the United States for all governmental purpose without the payment of any royalty.

FIELD OF THE INVENTION

The present invention relates to a process for treating the surfaces of articles fabricated from titanium and titanium alloys so as to improve their bonding characteristics.

BACKGROUND OF THE INVENTION

It has been over 15 years since the first announcement of production bonding of titanium. The bonded assembly was a firewall sandwhich structure of aluminum honeycomb with titanium and fiberglass skins. The purpose of this design was to take advantage of titanium's heat resistance for a relatively short period of time. However, supersonic aircraft require resistance to elevated temperatures for prolonged periods. The need for bonded assemblies, which will remain structurally sound with high strength-to-weight ratios, has prompted adhesive manufacturers to develop organic adhesives which retain good bond strength at high temperatures. In practice, a great deal of difficulty has been experienced in obtaining consistently durable titanium bonded structures.

While many of the inconsistencies were originally attributed to adhesive problems, a recent study suggests that bonding differences with variously treated titanium alloys were caused by variations in the interfacial structure of the treated adherend. Titanium and its alloys are so reactive that even at room temperature metal oxides are formed. The problem is not just one of providing a clean titanium surface but rather of providing a chemically stable surface receptive to bonding and resistant to degradation. The surface obtained must also promote adhesion without forming a weak surface layer or altering the metallurgical characteristics of the alloy.

A process widely used in industry to treat surfaces of titanium articles involves a multi-step procedure. Briefly, the process includes the steps of (1) vapor degreasing, (2) alkaline cleaning, (3) rinsing with water, (4) scale conditioning by contacting with saturated sodium hydroxide at 250°F, (5) rinsing with water, (6) removing oxide by contacting with a mixture of nitric and hydrofluoric acids, (7) rinsing with water, (8) conversion coating, (9) rinsing with water, and (10) drying. An obvious disadvantage of this conventional process is the many steps that are involved in the treatment. A less obvious but greater disadvantage from a quality control standpoint lies in the fact that there is a break in the processing between steps (6) and (8), i.e., between oxide removal and conversion coating by application of a reactive solution. As a result, the freshly cleaned metal rapidly becomes reoxidized before the reactive solution can be applied. When titanium surfaces so treated are bonded to one another, inconsistencies in adhesive reliability are experienced.

It is an object of this invention, therefore, to provide an improved and simplified process for treating the surfaces of titanium and titanium alloy articles.

Another object of the invention is to provide a process for treating titanium and titanium alloy surfaces in which cleaned surfaces are not subject to reoxidation prior to application of the conversion coating.

A further object of the invention is to provide a process for treating titanium and titanium alloy parts so as to provide chemically stable surfaces which are receptive to bonding and resistant to degradation.

Still another object of the invention is to provide a surface treatment process for titanium alloy adherends that makes it possible to fabricate adhesive-bonded titanium structures having high reliability, high ambient and elevated temperature strengths, and high resistance to corrosive environments and weathering.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the accompanying disclosure and the drawing in which the sole FIGURE shows a schematic representation of apparatus, partly in perspective, that can be used in carrying out the process of this invention.

SUMMARY OF THE INVENTION

The present invention resides in a process for treating parts or articles fabricated from titanium or titanium alloy so as to provide surfaces that are receptive to adhesive bonding. Broadly speaking, the process comprises the step of directing a stream of a slurry of aluminum oxide grit in a hydrofluosilicic acid solution onto a surface of a titanium or titanium alloy part for a period of time sufficient to obtain a uniform, oxide-free surface. Thereafter, the treated surface is washed to remove grit and terminate the acid reaction and then dried.

Prior to contacting the surface with the slurry, the surface is generally cleaned with a solvent to remove oil, grease and other foreign material. This can be conveniently accomplished by wiping the surface with cheese cloth saturated with methyl ethyl ketone or other suitable solvent. In cases where the parts are heavily soiled, they are immersed for a minimum of 5 minutes in an alkaline cleaning solution. The actual time of immersion will depend upon the condition of the parts. Any of the commerically available alkaline cleaners can be utilized in forming the solution. An alkaline cleaner sold under the trade mark Ridoline No. 53 by Amchem Products, Inc., Ambler, Pa., has been found to be effective. The solution is formed by adding the cleaner to a tank of hot water (180°F ± 5°F) while agitating the contents to dissolve the solids. After removal from the alkaline cleaning solution, the parts are rinsed with hot water, e.g., by suspending the parts in a hot spray rinse (130° to 140°F) for about 2 minutes.

After completion of the cleaning operation, the bond surface of the titanium or titanium alloy part is vapor blasted with the slurry of aluminum oxide in the aqueous hydrofluosilicic acid solution. The concentration of acid in the solution generally ranges from about 1 to 10 weight percent. However, it has been found that a solution concentration of about 2 percent gives optimum results, being sufficiently strong to etch the titanium yet dilute enough to be easily controlled at minimal material cost. During impingment of the slurry, the treated surface is continuously flooded with the reactive solu-

tion under pressure. As a result it is unnecessary to include a wetting agent in the solution.

The amount of aluminum oxide grit contained in the solution generally ranges from about 15 to 25 volume percent, based upon the volume of solution. A ratio of one volume of grit to four volumes of solution has been found to be particularly effective. However, it should be understood that the optimum ratio of grit to solution will depend to a large extent on the equipment used, e.g., its to propel the slurry against the surface. The aluminum oxide used is preferably a purified Al_2O_3which is sold commerically as white aluminum oxide abrasive. While it is often preferred to employ 240 grit aluminum oxide, from 180 to **300** grit can be used.

A sand blast gun having a line connected to source of slurry and a line connected to an air supply can be advantageously used in conducting the process. The air pressure is of a magnitude that is sufficient to aspirate the slurry and usually falls in the range of about 70 to 100 psi. However, it is to be understood that the actual air pressure used will depend to a large extent upon the equipment employed and may be higher or lower than the specific pressures indicated. The sand blast gun is provided with a tungsten carbide nozzle having a bore diameter of a size that allows sufficient air to flow to aspirate the slurry into the nozzle.

In vapor blasting the surface, the nozzle is kept in constant motion to prevent excess metal removal. The angle of impingment of the slurry stream, i.e., the angle between the stream and the treated surface, is less than 90° and is usually from 15° to 45°. The period during which the slurry stream is in contact with any one spot on the surface usually falls in the range of about 10 to 60 seconds. To define the contact time in another manner, the slurry stream is in contact with the bond surface until a uniform, matte surface free from gloss is obtained. In general, the average metal removal rate is about 0.001 inch per treated surface. After completion of the vapor blasting, the part is allowed to remain in contact with the reactive solution for a period that is not in excess of 15 minutes. The contact time generally ranges from about 3 to 15 minutes. At the end of this period, the part is spray rinsed in cold water to remove aluminum oxide grit and stop the acid reaction. Following the water rinse, the part is dried with filtered dry air. The maximum temperature of the air is about 150°F.

With some titanium alloys, a smut may be produced on the alloy as a result of the treatment. This smut can be readily removed by submerging the part at room temperature in a nitric acid rinse after the above-mentioned water rinse. An immersion of about one minute in 5 percent nitric acid readily removes the smut. Thereafter, the part is spray rinsed in cold water for about 2 minutes. The presence of the smut and the acid treatment for its removal does not have any adverse effect upon the ability of surfaces to be adhesively bonded.

A better understanding of the invention can be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

EXAMPLE I

A series of runs was conducted in which titanium alloy specimens were surface treated in accordance with the process of this invention. The apparatus employed in the process was substantially the same as that illustrated in the drawing. As shown, container **10** comprises an upper portion **11** which can be of any appropriate shape, e.g., a cube, a parallelpiped or a cylinder. Attached to the lower end of upper portion **11** is a lower portion **12** which, as appropriate, is in the form of an inverted pyramid or cone. Resting on the edge where the upper and lower portions intersect is a grate **13.** A closure member **14** provided with a vent pipe **16** is adapted to cover the opening in the top of the container.

Attached to the vertex of lower portion **12** and communicating with the interior of the container is one end of a flexible tube **17.** The other end of the flexible tube is connected to sand blast gun **18.** Tube **19,** also connected to the gun and to a source of air, provides means for supplying air to the gun so as to aspirate a slurry **21** of Al_2O_3 in hydrofluosilicic acid solution into the nozzle of the gun. The gun has a tungsten carbide nozzle with a bore diameter of one-quarter inch. An opening in the side of container **10** having a rubber seal **22** in the shape of an O-ring positioned therein provides means for inserting the nozzle of gun **18** into the container. Because of the flexibility of the rubber seal, the nozzle can be moved therein so as to direct the slurry at a desired angle onto the titanium or titanium alloy part resting on grate **13.**

The apparatus is constructed of polymeric materials because of the possibility of corrosive attack by the reactive solution. Thus, container **10** is formed of polyester fiberglass while grate **13** and closure member **14** are fabricated from acrylic. Flexible tube **17** is formed form polyvinyl chloride.

The specimens that were treated were formed from titanium alloys, namely, Ti–6Al–4V and Ti–6Al–6-V–2Sn. In general, the dimensions of the specimens were 1 × 6 × 0.04 in the case of Ti–6Al–4V and 1 × 6 × 0.045 in the case of Ti–6Al–6V–2Sn.

Initially, the specimens were solvent cleaned to remove oil, grease and other foreign material. This was accomplished by wiping the surfaces with cheese cloth saturated with methyl ethyl ketone. The specimens were then immersed for a minimum of 5 minutes in an alkaline cleaning solution. (The alkaline cleaning step was not necessary for all specimens, but was used so that the specimens might all be similarly treated.) The alkaline cleaning solution was prepared by filling a thoroughly cleaned tank two-thirds full of tap water and heating to 175°F ± 10°F. There was then added 3 to 6 ounces of Ridoline No. 53 per gallon of water at operating level. The tank was next filled to operating level with tap water and heated to 180°F ± 5°F while agitating the contents to dissolve the solids. The 3–6 oz/gal concentration was maintained by periodic addition of the alkaline cleaner as indicated by chemical analysis. Immediately following immersion in the alkaline bath, the specimens were suspended in a hot spray rinse (130°–140°F) for 2 minutes.

The lower portion of the container shown in the drawing was filled with 2 percent hydrofluosilicic acid solution. There was then added an amount of 240 grit aluminum oxide sufficient to provide a ratio of one volume of grit to 4 volumes of the acid solution.

Surfaces of the specimens disposed on the grate were vapor blasted (about 90 psi air pressure) for a minimum of 15 seconds in any one spot. The nozzle was kept in constant motion to prevent excess metal re-

moval. The total time that the specimens remained in contact with the reactive solution did not exceed 15 minutes. The treated surfaces had a uniform matte surface free from gloss. At the end of this period the specimens were spray rinsed with cold tap water to remove abrasive and stop the acid reaction. The Ti–6Al–6-V–2Sn specimens were submerged in 5 percent nitric acid for one minute to remove smut after which they were spray rinsed in tap water for 2 minutes. (This step was unnecessary for the Ti–6Al–4V specimens.) After the water rinse, the specimens were dried with filtered dry air with a maximum temperature of 150°F.

EXAMPLE II

Utilizing Ti–6Al–4v specimens, treated as described in Example I, six lap shear specimens were prepared. A primer (EC–2333 primer sold by 3M Co.) was applied, air dried for 30 minutes, and then force dried at 160°F for 45 minutes. Using 0.09 lb/ft² of epoxy-novolac adhesive (AF–130 adhesive sold by 3M Co.), one-half inch laps were bonded. The cure cycle was 350°F for one hour with a heat rise to 350°F of 10°F per minute. A pressure of 50 psi was maintained throughout the cure. The individual bonded specimens were tested with a grip separation of 0.05 inch/minute.

The results of the shear strength tests conducted at room temperature are shown below in Table I.

TABLE I

Specimen No.	Failure Mode	Strength, psi
1	Cohesive	3257
2	"	3393
3	"	3393
4	"	3411
5	"	3418
6	"	3321

Bonded specimens were also prepared that were tested at a temperature of 350°F. The specimens were prepared as described above except for a post cure or aging for 2 hours at 350°F prior to testing. The results of the shear strength tests are shown below in Table II.

TABLE II

Specimen No.	Failure Mode	Strength, psi
7	Cohesive	2261
8	"	2359
9	"	2268
10	"	2241
11	"	2245
12	"	2124

EXAMPLE III

Lap-shear specimens (0.5 inch lap) were prepared with a polyimide adhesive (FM–34 adhesive sold by American Cyanamide Co.), utilizing Ti–6Al–4V adherends treated as described in Example I. The treated specimens were primed with BR–34 primer (a product of American Cyanamid Co.), dried 30 minutes and then oven dried for 45 minutes at 240°F. The specimens were assembled with 0.135 lb/ft² of FM–34 adhesive and then cured for 2 hours at 350°F under 50 psi. The specimens were then post cured for 2 hours at 550°F followed by 2 hours at 600°F. The bonded specimens were tested at 600°F. The results of the shear strength tests at 600°F are shown below in Table III.

TABLE III

Specimen No.	Failure Mode	Strength, psi
13	Cohesive	1715
14	"	1718
15	"	1694
16	"	1633
17	"	1722
18	"	1648

EXAMPLE IV

The susceptibility of titanium to reoxidation after surface treatment has always hampered production processes for bonding titanium because of the short period available between cleaning and bonding. A series of runs was conducted to determine an allowable "open time" (time between treatment and bonding) for specimens treated according to the procedure described in Example I. The treated specimens were aged in such a way that air could circulate around the specimens but airborne particulates could not settle on the specimens. Both Ti–6Al–4V and Ti–6Al–6V–2Sn alloys were included in the runs. After one hour and at daily intervals, six specimens from each alloy were primed with EC–2333 primer, dried, and then bonded with Af–130 adhesive. The specimens were cured for 90 minutes at 350°F. under 50 psi.

The bonded specimens were tested at ambient temperature, and the results of the test are shown below in Table IV.

TABLE IV

Lapse Time Days	Shear Stength, psi T1-6Al-4V	Ti-6Al-6V-2Sn
1/24	3207	3338
1	3144	3208
2	3363	3200
3	3150	3411
4	3239	3228
6	2930	3368
7	3070	3143
8	2991	3226
9	2982	—
10	2936	—
11	2787	—
13	2763	3357
20	—	3196

The data in the table show a decline in strength for the Ti–6Al–4V alloy with practically no decline in strength for the Ti–6Al–6V–2Sn alloy. Good bond strengths were obtained with both alloys after an "open time" of 9 days.

EXAMPLE V

A series of runs was conducted to test the retention of bond strength of lap-shear specimens after exposure to hostile environments. The bonded specimens were prepared with 0.5 inch lap, utilizing Ti–6Al–4V and Ti–6Al–6V–2Sn adherends which has been treated as described in Example I. The adherends were bonded with both AF–130 and FM–34 adhesives with their respective primers. The bonded specimens were subjected to salt spray and high humidity environments.

For the salt spray exposure, the 0.5 inch lap specimens were individually positioned in such a way that

salt spray had equal access to all sides of the exposure section. the procedure and equipment were in accordance with Federal Test Method No. 151A, Method No. 811.1 "Salt Spray Test". Specimen sets with the AF–130 adhesive were subjected to 30 days of salt spray and tested at 75°F and 350°F. One specimen set was subjected to 24 hours at 350°F, then 7 days of salt spray, and then tested at 350°F. Duplicate specimens were fabricated with F–34 adhesive and tested as the AF–130 bonded specimens except that the elevated temperature was 600°F.

To determine the effect of high humidity on bond strength, bonded 0.5 inch lap specimens as described above were subjected to the high humidity condition in paragraph 4.3.5 of Federal Specification MMM–A–132. Each exposure section was individually positioned in such a way that condensing humidity had equal access to all sides of the exposure section. Specimen sets with AF–130 adhesive were subjected to 30 days high humidity and tested at 75°F and 350°F. One specimen set was subjected to 24 hours at 350°F, then 7 days of high humidity, and then tested at 350°F. Duplicate specimens were fabricated with FM–34 adhesive and tested as the AF–130 bonded specimens except that the elevated temperature was 600°F.

The result of the above-described runs are set forth below in Tables V and VI. The tables also identify the alloys and adhesives used as well as the cure conditions.

TABLE V

Adherends:	.040" Titanium 6Al-4V .45" Titanium 6Al-6V-2Sn (machined)
Adhesive:	AF130/EC2333 Primer
Cure:	90 minutes 350°F autoclave
Test Temperature:	Specified below
Type:	.5" lap

Adherend	Exposure Condition	Test Temp. °F	Ave. Shear Strength (psi)
Ti 6–4	Control	75	3158
	200 hrs. at 350°F	350	2581
	24 hrs. at 350°F; 7 days 95% R.H., 100°F	350	2153
	7 days weatherometer	75	2948
	30 days salt spray	75	3290
	30 days salt spray	350	1737
	30 days 95% R.H., 100°F	75	3071
	30 days 95% R.H., 100°F	350	1885
	24 hrs. at 350°F, 7 days salt spray	350	2093
Ti 6–6–2	Control	75	3156
	30 days salt spray	75	3150
	30 days salt spray	350	1806*
	30 days 95% R.H., 100°F	75	3069
	30 days 95% R.H., 100°F	350	1901*

*Some evidence of adhesive failure between primer and metal adherend.

TABLE VI

Adherends:	.040" Titanium 6Al-4V .045" Titanium 6Al-6V-2Sn (machined)
Adhesive:	FM-34/BR-34 Primer
Cure:	Two hours 350°F autoclave, two hours 550°F postcure
Test Temperature:	Specified below
Type:	.5" lap

Adherend	Exposure Condition	Test Temp. °F	Ave. Shear Strength (psi)
Ti 6–4	Control	75	3302
	150 hrs. at 600°F	600	2138
	480 hrs. at 600°F	600	2054
	1000 hrs. at 600°F	600	1848
	24 hrs. at 600°F, 7 days 95% R.H. at 100°F	600	1888
	7 days weatherometer	75	3342
	30 days salt spray	75	2065*
	30 days salt spray	600	1367
	30 days 95% R.H. at 100°F	75	2284*
	30 days 95% R.H. at 100°F	600	1458
	24 hrs. at 600°F, 7 days salt spray	600	1905
Ti 6–6–2	Control	75	3145
	30 days salt spray	75	1883*
	30 days salt spray	600	1483
	30 days 95% R.H. at 100°F	75	1676*
	30 days 95% R.H. at 100°F	600	1459

*Some evidence of adhesive failure between primer and metal adherend.

The data in the table for the salt spray and high humidity tests show that there is no difference in results due to substrate alloy. The specimens subjected to 30

days of salt spray and then tested at elevated temperatures experienced the greatest loss in shear strength. In the high humidity tests, there was no loss of strength with the AF-130 adhesive, but the specimen bonded with FM-34 did appear to be degraded with prolonged exposure to moisture.

EXAMPLE VI

Runs were conducted to determine the effect of ultraviolet radiation on bond strength. Specimens prepared with both AF-130 and FM-340 adhesives, as described in the preceding examples, were cycled for 7 days in an Atlas Weatherometer. This test exposes specimens to 45 minutes of water spray followed by 15 minutes with the spray off. There is continuous ultraviolet radiation from carbon arc lamps. This exposure had no apparent effect on bond strength of either adhesive.

From the foregoing examples, it is seen that the process of this invention provides a simplified, improved procedure for treating the surfaces of titanium alloy parts. The treated surfaces are receptive to adhesive bonding, making possible the fabrication of titanium structures having high ambient and elevated temperature strengths and high resistance to hostile environments. Furthermore, the process eliminates the problem of reoxidation that occurs in conventional processes between cleaning of the surfaces and application of a conversion coating.

As will be evident to those skilled in the art, various modifications of the invention can be made in view of the foregoing disclosure without departing from the spirit or scope of the invention

We claim:

1. A process for treating an oxidized surface of a titanium or titanium alloy part which comprises directing a stream consisting essentially of a slurry of aluminum oxide grit in an aqueous hydrofluosilicic acid solution onto the surface for a period of time sufficient to obtain about 3 to 15 minutes; washing the surface with water to remove grit and terminate acid reaction; and drying the part. an oxide-free, uniform, matte surface free from gloss, provided that the total period of time the surface is allowed to remain in contact with the slurry is.

2. The process according to claim **1** in which the surface is cleaned with a solvent prior to directing the stream thereon.

3. The process according to claim **1** in which the stream is in contact with the surface for about 10 to 60 seconds.

4. The process according to claim **3** in which the part is dried with filtered dry air.

5. The process according to claim **1** in which the concentration of acid in the solution ranges from about 1 to 10 weight percent and the amount of aluminum oxide grit in the solution range from about 15 to 25 volume percent, based upon the volume of solution.

6. The process according to claim **1** in which the part is immersed in a nitric acid bath after the water washing step; the part is rinsed with cold tap water after removal from the bath; and the washed part is dried with filtered dry air.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,891,456

DATED : June 24, 1975

INVENTOR(S) : Alvin E. Hohman and Gerald W. Lively

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 10, after "its", insert -- capacity --. Col. 5, line 15, change "v" to -- V --. Col. 6, line 37, change "Tl" to -- Ti --. Col. 9, line 11, change "340" to -- 34 --. Col. 10, correct Claim 1 to read as follows: 1. A process for treating an oxidized surface of a titanium or titanium alloy part which comprises directing a stream consisting essentially of a slurry of aluminum oxide grit in an aqueous hydrofluosilicic acid solution onto the surface for a period of time sufficient to obtain an oxide-free, uniform, matte surface free from gloss, provided that the total period of time the surface is allowed to remain in contact with the slurry is about 3 to 15 minutes; washing the surface with water to remove grit and terminate acid reaction; and drying the part.

Signed and Sealed this

ninth Day of *December 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks