WADC TECHNICAL REPORT 55-87
PART II
ASTIA DOCUMENT No. 150989

TREATMENT OF METAL SURFACES FOR ADHESIVE BONDING

BY SAMUEL N. MUCHNICK

THE FRANKLIN INSTITUTE LABORATORIES
FOR RESEARCH AND DEVELOPMENT

FEBRUARY 1958

MATERIALS LABORATORY
CONTRACT NO. AF 33(616)-2347
SUPPLEMENTAL AGREEMENT NO. S3(55-1331)
PROJECT NO. 7340

WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT- PATTERSON AIR FORCE BASE, OHIO

Carpenter Litho & Prtg. Co., Springfield, O.
400 — April 1958

FOREWORD

This report was prepared by Samuel Muchnick at The Franklin Institute Laboratories for Research and Development, Philadelphia, Pennsylvania, under Supplemental Agreement No. S3(55-1331) to USAF Contract No. AF 33(616)-2347. The contract was initiated under Project No. 7340, "Rubber, Plastic and Composite Materials", Task No. 73401, "Structural Adhesives" and was administered under the direction of the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, with Mr. Floyd H. Bair acting as project engineer.

We should like to point out that progress made on this project during the last eight months would not have been possible without the productive cooperation of the sponsors. In particular, we want to express our gratitude to Mr. R.T. Schwartz, Mr. T.J. Martin, and Mr. F.H. Bair.

ABSTRACT

A preliminary investigation of the effectiveness of mild acidic or basic solutions of wetting agents for treating metal surfaces prior to adhesive bonding shows that the strong acid solutions presently in use may possibly be replaced by these milder solutions. Joint strengths approximating the values obtained with strong acid solutions have been obtained with aluminum, stainless steel, and titanium. The pH, concentration of components, and ionic type of wetting agent are specific for each type of metal.

Additional correlative tests were developed for evaluating surface treatments. The interfacial contact angle between oil and water on the treated surface shows a greater sensitivity than the contact angle in air, and makes it possible to differentiate between two treatments that give zero contact angles against water. Contact resistance and hydrogen overvoltage measurements can be definitely correlated with the contact angle measurements. The contact resistance measurement which also evaluates the effect of oxide thickness appears to be a useful instrument for industrial application.

A study of the role of the adsorbed film on adhesive behavior indicates that the more reactive metals, aluminum and magnesium, are more sensitive to differences in the chemical structure of the film. There is also an indication that these films may affect the adhesional characteristics of some type of bonding agent.

The temperature of the rinse water following treatment of aluminum is shown to be important in the adhesional characteristics of the metal. Reproducibility and specificity of attractive forces between adhesive and metal were investigated, and it was apparent that the material and procedural parameters must be studied along with specific affinities in an adhesive system.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

R. T. Schwartz
R.T. SCHWARTZ
Chief, Organic Materials Branch
Materials Laboratory

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SUMMARY OF RESULTS

(1) It has been shown that it is possible to attain adequate conditioning of metal surfaces for adhesive bonding by means of modified solutions of surface active materials. This method of treatment offers promise of a safe, practical relatively non-corrosive method for preparing metal surfaces prior to adhesive bonding. Joint strengths have been obtained with aluminum treated with these solutions which were equal to joint strengths obtained with strong acid treated aluminum. With stainless steel, when the surface had been treated with an alkaline solution of an anionic surfactant, joint strengths exceeding 7000 psi were obtained with Bloomingdale FM-47 adhesive. With titanium, joint strengths up to 6500 psi were found with the same adhesive. Uniformity along the joint area was found to be surprisingly high in many cases.

(2) Four different tests have been found to correlate with the changes in surface properties following an effective treatment. These tests are (a) contact angle of a water drop in air, (b) the interfacial contact angle made by the displacement of a drop of pure mineral oil by water on the treated surface, (c) the hydrogen overvoltage on treated surfaces, and (d) puncture voltage.

In the case of (a), it was seen that the highest and most consistent joint strength results when zero or very low contact angles are made on treated metal surfaces.

The interfacial contact angle between water and mineral oil on the metal surface is at a maximum when the most effective surface treatments were used on aluminum and stainless steel. This work is still in the exploratory stage.

Significant differences were observed between the hydrogen overvoltages on treated and untreated titanium, aluminum, and stainless steel.

The voltage required to break through the adsorbed film on treated and untreated metal showed characteristic values for the several conditions of the surfaces for all the test metals. This method of test is sensitive to adsorbed film and oxide thickness, and may be the most valuable for evaluating the surface for the most reproducible and best conditioning for adhesive bonding.

(3) It was established experimentally that, when treated aluminum surface is exposed to rinse water temperatures exceeding 155°F, changes occur on the surface that reduce bond strength to unacceptable portions of what is found when lower temperatures are used. Joint strengths of 1971 to 2453 psi are found with the high temperature rinse. These values compare unfavorably with the 5400 to 5500 psi resulting with lower temperature rinses. The adhesive used in these experiments was Bloomingdale FM-47.

(4) The results of our preliminary study of the role of the adsorbed film in adhesion indicates that the thickness is more significant than the composition of the adsorbed film. No general conclusions can be drawn yet because most of the results have been obtained with one adhesive.

(5) An examination of the data indicates that the affinity between specific metals and an adhesive must be considered in the selection of an adhesive system. For example, we have repeatedly found that with Metlbond 4021 the joint strength of bonded aluminum is 20-25% higher than that of stainless steel. This occurs despite the greater over-all strength of stainless steel.

SUMMARY OF RESULTS (Continued)

(6) Experiments to evaluate reproducibility of the effect of surface treatments on surface properties and joint strength have shown that procedural and material parameters are of vital importance, and that the need for tests for these parameters is urgent.

(7) Salt spray tests with the Epon 422 adhesive show that the surface treatments used are effective in increasing resistance to salt fog exposure. The character of surface treatment apparently affects the salt spray resistance, but the somewhat erratic results with the different adhesives make it imperative that more tests be run, if correlations are to be made.

(8) A statistical evaluation of the four most promising treatments for stainless steel, aluminum, magnesium, and titanium was carried out. The treatments do not give uniformly good results with all four recommended adhesives.

INTRODUCTION

Purpose

The objectives of this work are:

(a) To find surface treatments for stainless steel, titanium, and magnesium alloys which will adequately condition these surfaces so that maximum joint strengths are obtained when the treated surfaces are bonded with all specified adhesives.

(b) To develop a test to determine when the surface has been adequately treated.

(c) To evaluate the material and procedural factors which may influence strength, durability, and uniformity of the adhesive bonded joints.

(d) To determine the role of the adsorbed film on the metal surface so far as it affects adhesion.

Scope

The research effort during this period was devoted to evaluating the effectiveness of adequate surface treatments developed during the past eight months. Because of the corrosive nature of these strong treatments, other methods for treating metals were sought, in order to supplement or replace these strong acid treatments. It was felt that, theoretically, wetting agents offered promise. A thorough program was developed and correlations were found between type of wetting agent, medium in which it is dissolved, and effectiveness of the treatment.

Test methods for evaluating the effectiveness of the surface treatment were developed that show a greater sensitivity to surface changes than the contact angle in air. Correlations were found among these tests. One test device in particular was found that may develop into a practical instrument. It evaluates both the inorganic and organic films on a metal surface.

Experiments were conducted to determine whether specific affinities exist between the different metals and the adhesive, and whether the ultimate bonding strength of the joint is influenced by the chemical nature of the effective treatments. The influence of the adsorbed film on bonding characteristics was investigated.

Salt spray tests were conducted to determine, among other things, whether the type of surface treatments affects resistance to salt spray.

History

This report, which is both an extensive and elaboration of the work described in WADC Technical Report 55-87, includes the results obtained during the period February 1 to September 30, 1955. In the earlier report it was shown that an understanding of the surface energy relationship in an adhesive system is a prerequisite to surface preparation of metal before adhesive bonding. With at least one adhesive, joint strengths that approached the strength of the adhesive were obtained with four metals. Moreover, the joints showed a uniformity and reproducibility that were well within experimental error.

However, many facets of this rather ramified problem remain obscure. More feasible, sensitive tests for evaluating the surface treatments were desirable. It was definitely a requirement that a program be started for evaluating the specific affinity of adhesive for specific metals. New approaches to surface conditioning that are based on mild non-corrosive attack were necessary. These and other important aspects of the problem of adhesive bonding had to be investigated.

SECTION I

SURFACE ACTIVE AGENTS IN METAL TREATMENTS

Surface treatments based on strong acid attack have been developed for four metals*. These treatments condition the surface so that low or zero contact angles are made against water, and when these treated surfaces are bonded with Bloomingdale FM-47 adhesive, a maximum, relatively uniform, joint strength results. The final selection of the specific treatment was predicated on the assumption that a chemically clean metal surface, as indicated by the low contact angle, will have the highest free surface energy under normal operating conditions of bonding. This condition should result in maximum bonding strength. The results to date substantially support this assumption. Other factors, particularly chemical affinity between metal and adhesive, are significant, but it has been ascertained with some degree of certainty that a prime requisite for an adequate, reproducible bonding strength is a high-energy metal surface.

1.1 Basis for Approach

Under certain conditions it may be possible to produce a prepared metal surface with modified solutions of surface active agents. In the interest of brevity these agents will be termed "surfactants". If the first absorbed layers of the heterogeneous adsorbed film on the metal surface are water, complete displacement of the oleophilic contaminants present on the water layers can be achieved by sufficiently lowering the interfacial tension between the oleophilic layers and the treating liquid. There are numerous surfactants that will reduce interfacial tension between oleophilic liquids and water. Interfacial tensions of 0.1 ergs/cm^2 have been reported.

If the adsorbed layers directly bonded to metal are oleophilic, displacement is more difficult. Several mechanisms can be envisaged, but one appears to be most likely. If the interfacial tension between the solution of surfactant and the oleophilic contamination layers is reduced sufficiently, these adsorbed layers may be displaced from the metal substrate by emulsification or solubilization. By an appropriate adjustment of pH, and by the proper solution of components of the treating mixture, this displacement may be carried to completion.

1.2 Results with Stainless Steel

Stainless steel surfaces degreased with trichloroethylene were treated with dilute solutions of surfactants of the three main classes: anionic, cationic, and non-ionic. Additional experiments were conducted with these solutions of surfactants modified with acids, alkalis, and/or salts. The changes in surface characteristics as a result of these exposures were determined by measuring the contact angle which the treated surfaces made with a drop of distilled water. The procedures are described in Appendix II, and the results are shown in Table 1.

It is seen from the table that none of the surfactants alone altered the surface enough to warrant optimism. In Experiment 1-8, the reduction of the contact angle from 73.5° to 32.5° indicated that the surfactant produced a change, but the resulting 32.5° contact angle indicates that removal of the adsorbed oleophilic layers was not complete. The cationic surfactants in each case raised the contact angle Experiments 1-3 and 1-5. The anionic and non-ionic agents generally

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* See Appendix I for a description of materials used in the experiments.

NOTE: Manuscript released by author 1 December 1955 for publication as a WADC Technical Report

Table 1

CONTACT ANGLES OF WATER AGAINST STAINLESS STEEL TREATED WITH SOLUTIONS OF SURFACTANTS

				Contact Angle of Water on Sample Tested		
Exp. No.	Surface Active Agent*	Modifying Acid, Base, or Salt	Time and Temp. of Bath	After Trichloroethylene Degreasing	After Surfactant Treatment	Remarks
1-1	N-1	-	10 min.140°F	64.5°	62.5°	Solution clouds at about 130°F.
1-2	A-1	-	"	78	71	Solution is clear at 140°F.
1-3	C-1	-	"	65.5	71	Turbid solution.
1-4	A-3	-	"	62.5	73	Hazy solution.
1-5	C-2	-	10 min. 140-170°F	66	101	Turbid solution at all temperatures.
1-6	A-2	-	10 min.140°F	71	68	Clear solution.
1-7	A-4	-	"	78	80	"
1-8	A-5	-	"	73.5	32.5	"
1-9	A-6	-	"	73	94	Almost clear solution.
1-10	A-7	-	10 min. 140-160°F	61.5	53.5	Clear solution.
1-11	A-8	-	10 min.140°F	61.5	53	"
2-1	N-1	HCl:2%	"	66	15.5	Solution clouding at about 140°F; steel slightly mottled and dulled.
2-2	N-1	KOH:2%	"	67.5	19	Solution clouding at about 130°F; steel bright
2-3	A-1	HCl:2%	"	60	19	Solution cloudy; steel mottled and dulled.
2-4	A-1	KOH:2%	"	66.5	27	Solution cloudy; steel bright.
2-5	C-1	HCl:2%	"	70.5	52	Solution cloudy; steel dulled.
2-6	A-3	KOH:2%	"	58	26.5	Solution cloudy; steel bright.
2-7	C-2	HCl:2%	"	63	67	"
2-8	A-2	KOH:2%	"	65	34.5	"
2-10	A-5	"	"	61.5	10.5	Solution clear at 140°F; steel bright.
2-11	A-6	"	"	64	76.5	Solution very thick; partly gelled at room temperature; steel bright.
2-12	A-7	"	"	67.5	18	Solution clear: steel bright.
3-1	A-9	-	"	63	49	Clear solution at 140°F; steel bright.
3-2	A-9	KOH:1%	"	61.5	38	Separation of phases in solution; steel bright.
3-3	-	KOH:2%	"	69	56	Clear solution; steel bright.
3-4	N-1	KOH:1%	"	54.5	24.5	Solution clouds at about 140°F: steel bright.
3-5	A-1	"	"	59.5	25.5	Solution slightly cloudy; steel bright.
3-6	A-3	"	"	65.5	30.5	"
3-7	A-5	"	"	64	18	Solution clear at 140°F; steel bright.
3-8	A-7	"	"	60	37.5	Solution clear: steel bright.
3-9	A-8	"	10 min. 140-160°F	56.5	27.5	Clear solution.
3-10	A-10	HCl:2%	10 min.140°F	58	47.5	Cloudy solution; metal discolored.
3-11	A-10	HCl:1%	"	62	51.5	"
3-12	A-11	-	"	67.5	62.5	Clear solution at 140°F; steel bright.
4-1	A-11	KOH:1%	"	69.5	22	Cloudy solution; steel bright.
4-2	A-11	KOH:2%	"	61.5	29	"
4-3	A-7	KOH:3%	"	64	19.5	Clear solution; steel bright.
4-4	A-7	Trisodium Phosphate:2%	"	67	49.5	"
4-5	N-1	"	"	60.5	17.5	
4-6	A-1	"	10 min. 140-160°F	57.5	13.5	
4-7	A-11	"	10 min. 140-150°F	64.5	16	Clear solution; steel bright.
4-8	A-5	"	"	53.5	18	Clear solution; steel bright.
4-9	A-3	"	10 min.140°F	62.5	13.5	Slightly cloudy solution; steel bright.
4-10	-	HCl:2%	"	64	39	Clear solution. Some gas evolution; steel spotted and dulled.
4-11	-	H_2SO_4:2%	"	54.5	27.5	Clear solution. Slight gas evolution; steel spotted, dulled badly.
4-12	-	HNO_3:2%	"	64.5	59.5	Clear solution. No gas evolution; steel bright.
5-1	A-5	KOH:4%	"	67	26.5	Clear solution with undissolved material; steel bright.
5-2	A-1	Trisodium Phosphate:4%	10 min. 140-150°F	56.5	9.5	Clear solution; steel bright.
5-3	A-3	"	"	68	25.5	Cloudy solution; two liquid phases; steel bright.
5-4	A-1	Trisodium Phosphate:2%	20 min. 140-150°F	69	17	Clear solution: steel bright.
5-5	A-1	"	10 min.194°F	62.0	8.5	"
5-6	A-1	Trisodium Phosphate:4%	15 min.150°F	65	0	"
5-7	A-1	Trisodium Phosphate:6%	"	65	0	"

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* Where Surface Active Agents are used, they are at 1% concentration; see Code Explanation in Appendix IV

produced no drastic changes. The anionics are denoted by an "A" proceeding the number, the cationics by a "C", and the non-ionics by an "N".

When the solutions of surfactants are modified by acids or alkalis, notably larger changes in surface properties are observed, except when cationic agents are used. For example, in Experiment 2-1 where 2% HCl was added to the 1% non-ionic surfactant solution, the contact angle changed from 66° to 15.5°. In Experiment 2-10, the addition of 2% KOH to the anionic solution reduced the angle to 10.5°. These values are comparable to the contact angles resulting from adequate, strong acid treatments. In Experiment 3-1, the surfactant alone reduced the contact angle to 49°, whereas the addition of 1% KOH to the solution of surfactant in Experiment 3-2 reduced the angle to 38°. When 2% KOH solution was used alone, the change in contact angle was substantially the same as when 1% KOH was used (Exp. 5-3), indicating a non-sensitivity in this range of concentrations. The largest changes were observed when the A-1 surfactant was used with 2% trisodium phosphate at 194°F. The contact angles changed from 62.0° to 8.5° with no visible impairment of the stainless steel surface. When the concentration of trisodium phosphate was increased to 4%, the resulting contact angle was zero (Exp. 5-6). A further increase in the amount of the alkaline salt (6%) also produced surfaces with zero contact angle.

Correlations were then sought between the contact angles resulting from these treatments and joint strengths. Degreased surfaces of stainless steel treated with WS-29 and WS-30 were bonded with Bloomingdale FM-47 adhesive. The WS-29 treatment is the preparation used in Experiment 5-6, Table 1; WS-30 is the treatment used in Experiment 5-7, Table 1. When the WS-29 treatment was used, average joint strength ranged from a low of 6189 psi when the contact angle was 15° (Exp. 5, Table 2) to a high of 6937 psi when the contact angle was too low to measure (Exp. 2). These joints were pressed in the same jig with panel joints that had only been degreased, and in each case they had a joint strength that was measurably higher.

When the WS-30 treatment was applied to the surfaces, the average joint strength ranged from a high of 7296 psi (Exp. 10, Table 2) to a low of 6802 psi (Exp. 14). These joints were also pressed in the same jig with joints prepared only by degreasing for comparison. In addition, two panel joints treated with WS-29 were bonded with Metlbond 4021 adhesive. The average joint strengths of the latter were 3935 psi (Exp. 16) and 4113 (Exp. 17). These values are comparable to the strengths found when the surface treatments are strong acids. The degree of scatter of the data is also normal.

1.3 Results with Aluminum

Solvent-degreased aluminum surfaces were treated with anionic, cationic, and non-ionic surfactant solutions, and with surfactant solutions modified with acids, alkalis, and salts. Contact angles with water were measured against these treated surfaces in order to evaluate the changes in surface properties that resulted from the treatment.

From Table 3, it can be seen that it is possible to produce large changes in contact angles with dilute solutions of non-ionic and anionic surfactants. In Experiment 5-9, the contact angle was reduced to less than 10° as compared to contact angles found when the surfaces were treated with A-5 and A-6 which are anionic reagents (Exp. 6-1 & 6-2). We found that we get low angles when the anionic or non-ionic surfactant solutions are modified with dilute acid or alkaline materials (Exps. 5-7, 6-4, 6-5, 6-10, 6-11, and others). The number of experiments are too numerous to evaluate individually, but it is apparent that we can produce very low contact angles of water against aluminum with many of the anionic and non-ionic surfactant solutions, alone or modified.

Table 2

AVERAGE STRENGTHS OF STAINLESS STEEL JOINTS TREATED WITH SURFACTANTS

Stainless steel: Type 302, 1/2-hard, 0.064 inch thick
Adhesive: FM-47, except in Exp.16 & 17 (Metlbond 4021)

Exp.(4) No.	Treatment No.	Avg θ	Shear Strength(psi) Avg	Max	Min	Control Avg(3)	% Control
1	WS-29	<10	6579	6904	6145	2453(1)	268.2
2	WS-29	<10	6937	7242	6757	2453(1)	282.7
3	WS-29	<10	6850	7205	6330	5146	133.1
4	WS-29	<10	6696	7090	6255	5146	130.1
5	WS-29	15	6189	6561	5878	4689	131.9
6	WS-29	<10	6424	6732	5919	5058	127.0
7	WS-8(2)	60-65	6261	6565	6070	5058	123.7
8	WS-29	<10	6472	6643	6188	5255	123.1
9	WS-8(2)	60-65	6223	6762	6010	5255	118.4
10	WS-30	<10	7296	7404	7108	5270	138.4
11	WS-8(2)	60-65	7127	7445	6897	5270	135.2
12(5)	WS-30	<10	6952	7464	6561	5089	136.6
13	WS-8(2)	60-65	6730	7045	6495	5089	132.2
14(6)	WS-30	<10	6802	7070	6510	5306	128.1
15	WS-8(2)	60-65	6336	6747	5910	5306	119.4
16	WS-29	<10	3935	4260	3696	4086	96.3
17	WS-29	<10	4113	4393	3627	4086	100.6

NOTE: 1. Treated aluminum control surfaces showed interference colors.
2. Degreased panels (WS-8) used to compare efficiency of treatment.
3. Controls are clad aluminum 2024-T3 treated in WAC-1 and bonded with same adhesive as test specimens.
4. Six specimens were used in all experiments except No. 10, in which three were used.
5. Bath temperature of stainless steel 150°F.
6. Bath temperature of stainless steel 190°F.

However, it was observed that where low angles were found, evidence of interfacial reaction was present in the form of discoloration. In view of the copious references in the literature to adsorption of surface active materials on aluminum and other metal surfaces, it was tentatively assumed that adsorption of the surfactant in varying degrees took place on the treated surfaces. In order to evaluate the effect on adhesion of these adsorbed films, adhesive bonded joints were prepared with surfaces that had been treated with WAC-7, WAC-9, WAC-10, WAC-11, WAC-12, and WAC-13. These treatments are based on formulations that give low contact angles. In Experiments 1 to 9, Table 4, joint strengths were surprisingly low, ranging from 838 psi with the WAC-7 treatment to 4338 psi when the WAC-11 treatment was used. The percentage scatter of data was also unusually high when compared with the normal range of values for test specimens after the recommended sulfuric acid-sodium dichromate treatment.

The strength of aluminum joints treated with WAC-11 (Exp. 7) began to approach the values found with the standard treatments.

Two additional formulations were prepared for treating aluminum surfaces. They were WAC-14 and WAC-15. The aluminum surfaces treated with WAC-14 developed an average strength of 4809 psi in one panel joint, and 4538 psi in

Table 3

CONTACT ANGLES OF WATER AGAINST ALUMINUM TREATED WITH SOLUTIONS OF SURFACTANTS

Exp. No.	Surface Active Agent*	Concentration of Surface Active Agent	Modifying Acid, Base, or Salt	Time and Temp. of Bath	Contact Angle of Water on Sample Tested: After Trichloroethylene Degreasing	Contact Angle of Water on Sample Tested: After Surfactant Treatment	Remarks
5-7	A-1	1%	Trisodium Phosphate:2%	90 sec.180°F	58.5	9	Clear solution: vigorous hydrogen evolution. Light dulling of surface: edges darkened.
5-8	A-1	1%	Trisodium Phosphate:0.5%	120 sec.149°F	57	31	"
5-9	N-1	1%	-	15 min.140°F	54	<10	Clear solution; clouding at 140°F. Very slow hydrogen evolution. Bronzing: aluminum bright.
5-10	A-1	1%	-	15 min.194°F	56	53.5	Clear solution; no hydrogen evolution. Aluminum bright.
5-11	A-3	1%	-	15 min.185°F	58	79.5	Very slight hazy solution; very slow hydrogen evolution. Surface dulled.
5-12	A-11	1%	-	15 min.190°F	54.5	25	Clear solution; no noticeable hydrogen evolution. Aluminum bright.
6-1	A-5	1%	-	5 min.150°F	52	12	Clear solution; moderately vigorous hydrogen evolution. Light dulling of surface.
6-2	A-7	1%	-	3 min.160°F	61.5	10.5	Clear solution; vigorous hydrogen evolution. Discoloration of surface and edges.
6-4	N-1	1%	HCl:1%	15 min.130°F	49.5	<10	Solution clear up to 145°F: vigorous hydrogen evolution. Surface dulled and etched.
6-5	N-1	1%	Trisodium Phosphate:0.5%	5 min.140°F	45	<10	Solution clear up to 140°F: vigorous hydrogen evolution. Surface dulled.
6-6	A-11	1%	HCl:0.1%	15 min. 140-150°F	48	68	Clear solution: no appreciable hydrogen evolution. Aluminum bright.
6-7	N-1	1%	Isopropyl Alcohol:4%	15 min. 145-155°F	51.5	<10	Clear solution: clouding at about 160°F. Very slow hydrogen evolution. Bronzing; aluminum bright.
6-8	N-1	0.1%	Isopropyl Alcohol:2%	15 min. 155-160°F	57.5	<10	"
6-9	A-12	1%	-	15 min. 185±10°F	54	56	Clear solution; no appreciable hydrogen evolution. Aluminum bright.
6-10	A-12	1%	HCl:0.1%	15 min. 190±10°F	54	<10	Clear solution at 190°F; very slight hydrogen evolution. Bronzing.
6-11	N-1	1%	Trisodium Phosphate:0.2%	5 min. 140±10°F	54	<10	Clear solution at 140°F; hydrogen evolution. Dulled surface.
6-12	A-11	1%	"	5 min. 150±10°F	63	74	Clear solution; moderate hydrogen evolution. Surface dulled.
7-1	N-1	0.1%	Trisodium Phosphate:0.5%	5 min. 140±10°F	56.5	<10	Clear solution; clouds at about 145°F. Fairly vigorous hydrogen evolution. Surface dulled; edges darkened.
7-2	-	-	"	5 min.140°F	43.5	<10	Clear solution; fairly vigorous hydrogen evolution. Surface dulled; edges darkened.
7-3	-	-	HCl:0.5%	5 min.140°F	49.5	11	Clear solution; fairly slow hydrogen evolution. Surface dulled.
7-4	A-12	1%	Trisodium Phosphate:0.1%	10 min.167°F	59	20	Clear solution; slow hydrogen evolution. Surface dulled.
7-5	-	-	H_2SO_4:2.4% Sodium Dichromate:24%	10 min.155°F	-	Approx. 2	WAC-1 clear solution; no appreciable hydrogen evolution. Light dulling of surface.
7-6	N-1	0.5%	H_2SO_4:2% Sodium Dichromate:2%	15 min. 140±10°F	40.5	Approx. 4	Solution becomes cloudy at 140°F; no appreciable hydrogen evolution. Light dulling of surface.
7-7	A-1	0.5%	H_2SO_4:2% Sodium Dichromate:1%	5 min. 195±5°F	62	68.5	Cloudy solution at all temperatures; hydrogen evolution. Surface dulled; edges darkened.
7-8	N-1	0.5%	Sodium Metasilicate:1%	15 min. 120-130°F	42	Approx. 6	Clear solution; cloudy above 140°F. No hydrogen evolution. Slight bronzing.
7-9	N-1	0.5%	Sodium Metasilicate:1% Trisodium Phosphate:1%	15 min. 120-130°F	49	9.5	Solution clouds above 130°F; no hydrogen evolution. Slight bronzing.
7-10	N-1	0.5%	Sodium Metasilicate:1% Trisodium Phosphate:1% Methyl "Cellosolve":4%	15 min. 130-145°F	44	Approx. 5	Solution clouds above 140°F; no hydrogen evolution. Slight bronzing.

* Code Explanation in Appendix IV

Table 3 (Continued)
CONTACT ANGLES OF WATER AGAINST ALUMINUM TREATED WITH SOLUTIONS OF SURFACTANTS

Exp. No.	Surface Active Agent*	Concentration of Surface Active Agent	Modifying Acid, Base, or Salt	Time and Temp. of Bath	Contact Angle of Water on Sample Tested		Remarks
					After Trichloroethylene Degreasing	After Surfactant Treatment	
7-11	A-1	1%	Sodium Metasilicate:0.5% Trisodium Phosphate:2%	10 min. 190-200°F	55	Approx. 7	Solution clear at 194°F: cloudy at room temp. Hydrogen evolution slow after first min. Surface slightly dulled.
7-12	N-2	1%	-	15 min. 160±10°F	44	24	Clear solution; no hydrogen evolution. Bronzing slight; surface bright.
8-1	N-3	1%	-	15 min. 160±10°F	37	24.5	Opaque mixture at all temp. No hydrogen evolution. Metal surface unchanged. Oily film.
8-3	N-5	1%	-	15 min. 130±10°F	46.5	Approx. 2	Clouding occurs above 138°F; no hydrogen evolution. Slight bronzing.
8-4	N-2	1%	HCl:0.2%	10 min. 160±10°F	55	9	Clear solution; slow hydrogen evolution. Surface unchanged.
8-5	N-2	1%	Trisodium Phosphate:0.2%	5 min. 160±10°F	48.5	Approx. 2	Clear solution; vigorous hydrogen evolution. Surface slightly dulled; edges darkened.
8-6	N-2	1%	Trisodium Phosphate:2% Sodium Metasilicate:0.5%	15 min. 170-180°F	49	Approx. 6	Clear solution; clouds at about 190°F; no hydrogen evolution after 60 sec. Slight bronzing.
8-7	N-2	1%	Trisodium Phosphate:1% Sodium Metasilicate:0.1%	5 min. 185±10°F	47	Approx. 1	Clear solution; vigorous hydrogen evolution. Surface dulled & etched; edges darkened.
8-8	N-2	1%	Trisodium Phosphate:1% Sodium Metasilicate:0.3%	15 min. 180±10°F	53.5	Approx. 4	Clear solution; no appreciable hydrogen evolution after 30 sec. Slight bronzing.
8-9	N-2	0.5%	H_2SO_4:2% Sodium Dichromate:2%	15 min. 190±10°F	45	Approx. 4	Clear solution at all temp. No hydrogen evolution; surface lightly dulled.
8-10	N-1 A-11	0.5% 0.5%	-	15 min. 180±10°F	49.5	11.5	Clear solution at 190°F: no appreciable hydrogen evolution. Slight bronzing.
8-11	N-1 A-11	0.5% 0.5%	H_2SO_4:2% Sodium Dichromate:2%	-	-	-	Separation into two phases.
8-12	-	-	"	15 min. 190±10°F	55.5	33	Clear solution at all temp. No hydrogen evolution: surface lightly dulled.
9-1	N-1	0.1%	"	15 min. 140±10°F	56	Approx. 6	Solution becomes cloudy above 140°F; no hydrogen evolution; slightly dulled.
9-2	N-2	0.1%	"	15 min. 190±10°F	59.5	Approx. 6	Clear solution; no hydrogen evolution. Aluminum lightly dulled.
9-3	N-2	0.5%	Trisodium Phosphate:2% Sodium Dichromate:2%	15 min. 170±10°F	63	23.5	Clear solution; no hydrogen evolution after 15 sec. Slight bronzing.
9-4	N-2	0.5%	Trisodium Phosphate:2% Sodium Dichromate:1%	"	56.5	18.5	Clear solution; no hydrogen evolution; slight bronzing.
9-5	N-2	0.5%	Trisodium Phosphate:2% Sodium Dichromate:0.5%	"	62.5	20	Clear solution; hydrogen evolution. Surface dulled; edges darkened.
9-6	N-2	0.5%	KOH:2% Sodium Dichromate:2%	5 min. 170±10°F	61.5	Approx. 8	Clear solution to 180°F; vigorous hydrogen evolution. Aluminum surface & edges darkened.
9-7	N-2	0.5%	H_2SO_4:4% Sodium Dichromate:2%	15 min. 170±10°F	59	Approx. 2.5	Clear solution; no appreciable hydrogen evolution. Aluminum slightly dulled.
9-8	N-2	0.5%	H_2SO_4:4% Sodium Dichromate:1%	"	60	Approx. 3	Clear solution; no hydrogen evolution. Surface slightly dulled & edges slightly darkened.
9-9	N-2	0.5%	H_2SO_4:2% Sodium Dichromate:1%	"	57.5	Approx. 5	Clear solution; no hydrogen evolution. Aluminum slightly dulled.
9-10	N-2	0.5%	H_2SO_4:2% Sodium Dichromate:0.5%	"	55.5	Approx. 4	Clear solution: no appreciable hydrogen evolution. Aluminum slightly dulled.
9-11	N-2	0.5%	H_2SO_4:1% Sodium Dichromate 0.5%	"	56.5	Approx. 4.5	"
10-3	C-1	0.5%	-	"	68	59.5	Cloudy solution at all temp. No hydrogen evolution. Surface coloration (orange & purple).

* Code Explanation in Appendix IV

Table 4

TEST RESULTS FOR ALUMINUM TREATED WITH SURFACTANTS

Aluminum: 2024-T3 Alclad, 0.064 inch thick
Controls: Aluminum bonded with same adhesive used in test joints

Exp. No.	Treatment No.	No. Specimen	Avg θ	Adhesive	Shear Strength(psi) Avg	Max	Min	Control Avg	% Control
1	WAC-7	12	<10	FM-47	838	1091	503	5169	6.24
2	WAC-7	6	<10	"	1158	1816	841	5475	21.1
3	WAC-7	6	<10	"	1625	1893	1363	5475	29.6
4	WAC-8	12	<10	"	3655	3923	3421	5422	67.4
5	WAC-9	12	<10	"	1268	1846	972	5363	23.6
6	WAC-10	12	<10	"	1244	1486	1123	1971	See Note
7	WAC-11	12	<10	"	4338	4525	4110	5010	86.6
8	WAC-12	6	<10	"	3831	4059	3529	5496	69.7
9	WAC-13	6	<10	"	4273	4843	3834	5496	77.7
10	WAC-14	12	<10	"	4696	4918	4490	5347	87.8
11	WAC-15	12	<10	"	4644	4950	4332	5090	91.2
12	WAC-14	12	<10	4021	3537	3711	3424	4003	88.3
13	WAC-16	12	<10	FM-47	4468	4603	4330	5369	83.2
14	WAC-17	6	0	"	4782	4989	4717	5094	93.8
15	WAC-17	6	0	"	5073	5171	5010	5094	99.6
16	WAC-18	12	0	"	4455	4925	3955	4998	89.1
17	WAC-19	12	0	"	4880	5160	4586	5140	95.0
18	WAC-17	6	0	422	2521	2900	2289	2120	118.9
19	WAC-17	6	0	"	2103	2210	2000	2120	99.1
20	WAC-17	6	<10	AF-6	3479	3800	3060	3418	101.7
21	WAC-17	6	<10	"	3515	3820	3193	3418	102.8
22	WAC-17	6	<10	FM-47	4673	4800	4561	5378	86.8
23	WAC-17	6	<10	"	4924	4979	4875	5378	91.5
24	WAC-17	12	<10	4021	3631	3770	3459	4485	81.0
25	WAC-17	12	<10	"	3543	3703	3235	4499	78.7
26	WAC-17	6	<10	"	3641	3816	3547	4808	75.7

NOTE: In Exp. 6 iridescence visible on treated control surfaces.

another for an average of 4696 psi (Exp. 10). When the WAC-15 treatment was used (Exp. 11), the average joint strengths were 4492 psi and 4796 psi for an average of 4644 psi. The adhesive used in these four experiments was Bloomingdale FM-47. These values range from 87.8 to 91.2% of the control specimens. The controls are aluminum joints treated with WAC-1, which is the treatment recommended by WADC.

Another set of experiments were conducted in which the surfaces were treated with WAC-14 and bonded with Metlbond 4021 adhesive (Exp. 12). The percent of the control was of the same order of magnitude as that with Bloomingdale FM-47. We drew the tentative conclusion therefrom that these treatments, composed of 1% surfactants in relatively dilute acid solutions, are just short of being as effective as the strong acid treatment that has been found to be most effective. The mean range of joint strengths within a panel joint is equal to the best obtained with the strong acid treatment. Further work with treatments in which the proportions of components were varied showed that WAC-17 was most effective. This selection was supported by later work in the under-facial contour angle investigation discussed in Section 3. Joints prepared with WAC-17 treated surfaces had strength of 4782 and 5073 psi. These were 93.8 and 99.5% of the control strength.

The treatment was further evaluated with Epon 422 and Scotchweld AF-6 adhesives. When Epon 422 was used with this treatment, the average joint strength was 2521 psi with one panel joint (Exp. 18), and 2103 psi with another (Exp. 19). These strengths are 118.9% and 99.1% of the control strength. The control is the joint strength obtained when the aluminum joints are treated with WAC-1 and bonded with the same adhesive used in the test specimens. The experiments were repeated using AF-6 adhesive (Exp. 20 and 21). The joint strengths were 101.7 and 102.8 percent of the control strength.

This treatment has now been used with the four recommended adhesives on aluminum, and the indications are that it is approximately as effective as the strong acid treatment recommended by WADC. It has the decided advantage that it is mild and probably less costly, and lends itself to use in the field. Also, with some modification it may be effective at lower temperatures. We will explore this possibility.

1.4 Results with Titanium

Anionics and non-ionics in acid and alkaline media were used as treatments for titanium. In addition, the effect on surface properties of the metal with WAC-1 and WT-4 treatments were observed. In this preliminary stage, it was noted that surfactants in alkaline media produced favorable changes. In Experiments 1 and 3, Table 5, it is seen that the contact angles decreased to 7°. When the surfactant was used alone, no changes took place. The WAC-1 treatment that is so effective on aluminum was ineffective on titanium. Surfactant in acid medium resulted in no significant difference in contact angle (Exp. 5).

Table 5

CONTACT ANGLE OF WATER DROP ON TREATED TITANIUM ALLOY

			Contact Angle of Water on Sample Tested			
Exp. No.	Concentration of Surfactant (Active Ingredient)	Modifying Acid, Base, or Salt	After TCE Degreasing	After Surfactant Treatment	Time and Temp.	Remarks*
1	Anionic:1% (Triton X-200)	Trisodium Phosphate:4%	62.5°	7°	15 min. 180±10°F	Solution clear at 180°F.
2	Anionic:1%	-	48	50.5	15 min. 155±5°F	Solution clear.
3	Anionic:1%	Trisodium Phosphate:4%	51	7	"	Solution hazy at 155°F.
4	WAC-1	H_2SO_4:24.4% Sodium Dichromate:2.4%	58.5	44	"	Solution clear.
5	Anionic:0.5%	H_2SO_4:8% Sodium Dichromate:2%	56.5	53.5	"	Solution cloudy at all temps. (R.T. + 155°F).
6	WT-4 Solution		44.5	14	15 min. 120±10°F	Solution clear.
7	Anionic:1%	Potassium Hydroxide:4%	-	11	15 min. 190±5°F	Solution cloudy at all temps. (R.T. + 190°F).
8	Anionic:1%	Trisodium Phosphate:3%	60	14	15 min. 170±5°F	Solution clear.
9	Non-ionic:1%	Trisodium Phosphate:3%	58	9.5	"	"
10	Non-ionic:1%	H2SO4:8% Sod.Dich.:1%	52	25.5	"	"

* In all experiments the titanium surface appearance was unchanged.

The WT-4 treatment which is a highly concentrated acid that was found to be highly effective on stainless steel produced a relatively large change (Exp. 6). This treatment was found to give joint strengths close to 7000 psi with Bloomingdale FM-47. The results of the other experiments indicate that satisfactory treatments for cleaning titanium are possible with dilute modified solutions of suitable surfactants.

Joints were prepared with titanium alloy that had been treated with mild alkaline solutions of an anionic surfactant. In one experiment, joints were prepared from 1 x 4 in. strips, 0.069 in. thick, which had been treated in WT-5. The overall joint strength was 5500 psi (Exp. 1, Table 6). It had been observed that the strips were somewhat deformed, and some question remains as to the validity of these values. In addition, the control specimens which are aluminum were several thousandths of an inch thinner than the titanium, and since they were in the same jig with the titanium specimens, they probably were not subjected to the normal pressing load. As evidence, the joint strength of the control specimens is 3940 psi.

Table 6

SHEAR STRENGTHS OF SURFACTANT TREATED TITANIUM ALLOY JOINTS

Titanium: Rem-Cru 110 M, in strips 1 x 4 in., all 0.05 in. thick except Exp. 1 (0.069 in. thick).

Controls: 2024-T3, 0.064 in. thick, 1 x 4 in., clad aluminum treated in WAC-1 and bonded with same adhesive and in same pressing as the test specimens.

Adhesive: All FM-47 except Exp. 8 (AF-6).

Exp. No.	Treatment No.	No. Specimen	Avg θ	Shear Strength(psi) Avg	Max	Min	Control Avg	% Control
1	WT-5	3	<10	5500	5979	5000	3940*	139.5
2	WT-5	4	<10	5052	5530	4540	4312	117.1
3	WT-6	4	<10	5650	6360	4730	5667	99.7
4	WT-5	6	0	5523	6000	5131	5700	96.9
5	WT-6	3	0	5876	6340	5360	5584	105.2
6	WT-5	6	<10	5216	5990	4635	5497	94.8
7	WT-5	6	<10	5199	5767	4673	5238	99.2
8	WT-5	5	<10	1908	2222	1581	2490	76.6

* Control was 0.005 less in thickness than the titanium and did not receive full pressure.

The experiments were repeated with full size 4 x 8" panels of titanium alloy 0.050 in. thick (Exp. 2). The average joint strength was 5052 psi which is equivalent to 117.1% of the control. Another treatment (WT-6) with the same thickness titanium gave a joint strength of 5650 psi (Exp. 3). We have shown in the earlier report that the nominal joint strength is related to the metal thickness, and therefore we estimate that if the metal were 0.064 in. thick, the nominal joint strength would be in the region of 6500 psi*. Four panel joints were prepared on another occasion and the results were reasonably consistent (Exps. 4, 5, 6, 7).

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* WADC Technical Report 55-87, April 1956.

1.5 Results with Magnesium

A beginning was made in investigating the utilization of surface active materials for treating magnesium alloys. In WM-14 a 1.0% solution of an anionic surfactant is dissolved in a mild alkaline solution. When magnesium alloy was treated with this solution, the resulting contact angles were satisfactorily low but the joint strength was 1510 and 1605 psi (Exps. 1 & 2, Table 7). The treated surfaces had the iridescence that we observed on aluminum after exposure to alkaline solutions of anionics. As with aluminum, joint strength was low.

Table 7

SHEAR STRENGTHS OF SURFACTANT TREATED MAGNESIUM ALLOY JOINTS

Magnesium Alloy: FS1-H24, 0.064 in. thick.

Controls: 2024-T3, 0.064 in. thick clad aluminum treated in WAC-1 and bonded with same adhesive and in same pressing as the test specimens.

Adhesive: All FM-47 except Exp. 5 & 6 (Scotchweld AF-6).

Six specimens were used in all experiments.

Exp. No.	Treatment No.	Avg θ	Shear Strength(psi) Avg	Max	Min	Control Avg	% Control
1	WM-14	<10	1510	1710	1330	5229	28.8
2	WM-14	<10	1605	1710	1490	5229	30.6
3	WM-15	15	3184	3340	2900	4950	64.3
4	WM-15	15	3490	3775	3230	4950	70.5
5	WM-15	14	1632	2240	1000	3787	43.0
6	WM-15	14	1778	2500	1500	3787	46.9

When these same treated surfaces were subsequently immersed in chromic acid solution, the iridescence disappeared. Joints made with these surfaces had joint strengths of 3184 and 3490 psi with Bloomingdale FM-47 (Exps. 3 & 4). With Scotchweld AF-6 this two-stage treatment (WM-15) gave joint strengths of 1632 psi and 1778 psi.

We are investigating the use of non-ionics in treating magnesium. Considerable improvement in joint strength was obtained with aluminum when non-ionics were used in an acid medium, and since the reaction of the two metals to anionics was similar, it is possible that this type of surface treatment may give improved joint strength.

A number of experiments were conducted with WM-15 treated magnesium in which the chromic acid bath was replaced by dilute solutions of hydrofluoric acid. (Above concentrations of 2% HF does not attack magnesium). Concentrations from 2.5 to 10% were used, Table 8. The highest joint strength was found with the 5% HF solutions (Exp. 5). However this joint strength, 2726 psi, was substantially lower than is usually obtained with the WM-15 treatment (Exp. 1).

Table 8

SHEAR STRENGTHS OF SURFACTANT/HYDROFLUORIC ACID TREATED MAGNESIUM JOINTS

Hydrofluoric acid content of rinse is actual HF content by weight.

Magnesium Alloy: FS1-H24, 0.064 in. thick.

Controls: except as noted, 2024-T3 clad aluminum, 0.064 in. thick treated in WAC-1 and bonded with the same adhesive and in the same pressing as the test specimens.

Six specimens used in all experiments; adhesive used is FM-47.

			Shear Strength(psi)				
Exp. No.	Treatment No.	Avg θ	Avg	Max	Min	Control Avg	% Control
1	WM-15	15°	3499	3777	3300	*	
2	WM-14 2.5% HF	<10	1508	1740	1360	*	
3	WM-15 2.5% HF	<10	1622	1673	1500	*	
4	WM-14 5% HF	<10	2195	2480	1820	4996	43.9
5	WM-15 5% HF	<10	2726	2800	2640	4996	54.5
6	WM-15 10% HF	12	2475	2780	2310	5263	47.0
7	"	12	2135	2350	1770	5263	40.5

* Magnesium treated in WM-15 in Exp. 1 was the control for Exp. 2 and 3.

SECTION II

THE INTERFACIAL CONTACT ANGLE

The contact angle that a liquid drop makes with a solid surface is a measure of the affinity of the liquid for the solid surface. If the surface tension of the liquid is known, and a contact angle is made with a solid surface, the attraction (adhesive tension) can be measured. The numerical evaluation is equal to the product of the surface tension (dyne/cm) and the cosine of the angle. This measurement is made with a static drop under conditions of equilibrium. If the liquid drop spreads, we no longer have an equilibrium condition, and an evaluation of adhesion or affinity cannot be made by the method of contact angles in air.

However, it can be shown that when two spreading liquids are competing for a solid surface, the liquid with the greater affinity for the surface will increase its interfacial area with the solid at the expense of the other. We have demonstrated this relationship by depositing a drop of highly-purified paraffin oil (Nujol) on an aluminum surface that had been treated with WAC-1. The drop spread rapidly. We then introduced bulk water into this system and the film of oil drew up to a symmetrical drop that made a contact angle of 155°. If this 155° contact angle measures the condition of the aluminum surface which is most favorable for adhesive bonding when these liquids are used, this test may be an even more sensitive method of evaluating surface treatment than the contact angle in air. The contact angle in air tells us only that both paraffin oil and water will spread. This stripping test tells us that, for the most favorable surface condition of aluminum, the affinity of water for the surface must be greater than the affinity of mineral oil by an energy difference that produces the interfacial contact angle of 155°.

2.1 Surface Condition and Interfacial Contact Angle

The WAC-14 treatment gives a joint strength of approximately 90% of the strength obtained with the WAC-1 treatment. This treatment (WAC-14) consists of 4% sulfuric acid and 2% sodium dichromate in a 1% solution of non-ionic surfactant. Experiments were conducted in which the three components of WAC-14 were varied, and the changes in interfacial angle were noted. The results are shown in Table 9. When the results are placed in order of decreasing interfacial contact angle (column 2), it is seen that three of the four highest interfacial angles are found when the concentration of surfactant is 1.0%.

Table 9

EFFECT OF CONCENTRATION ON INTERFACIAL CONTACT ANGLE

Exp. No.	Interfacial Contact Angle	% Surfactant	% H_2SO_4	% $Na_2Cr_2O_7$	pH of Bath at Room Temp.	Contact Angle of Water Drop in Air
0.0	155.0°	WAC-1 Treatment				0
1	150.0	1.0	4.0	2.0	0.37	4.5
2	149.5	0.1	1.0	3.0	0.96	4.0
3	143.5	1.0	1.0	1.0	0.95	4.2
4	142.5	1.0	8.0	3.0	0.05	2.0
5	141.5	0.0	1.0	2.0	0.95	8.5
6	138.0	0.1	13.0	2.0	<0.0	15.5
7	136.0	0.5	8.0	2.0	0.05	4.0
8	134.5	0.5	4.0	1.0	0.35	7.0
9	133.0	0.5	1.0	0.0	0.88	5.0
10	132.5	0.5	13.0	3.0	<0.0	3.0
11	130.5	0.1	8.0	1.0	0.03	3.5
12	128.5	0.0	13.0	1.0	<0.0	7.0
13	125.0	0.0	4.0	3.0	0.37	9.0
14	123.5	1.0	13.0	0.0	<0.0	10.0
15	105.5	0.1	4.0	0.0	0.35	13.0
16	101.0	0.0	8.0	0.0	0.05	22.0

We also find that the highest interfacial angle of the series results when 1% surfactant is used with 4% acid and 2% sodium dichromate. This is the WAC-14 formulation that gives us the highest joint strength in the series, and it is approximately 90% of the control strength.

At the lower end of the table, it is seen that when the concentration of surfactant is 0.1% or less, with one exception, the interfacial contact angles are lowest. In Experiment 14, where 1.0% surfactant was used and a low interfacial angle resulted, no dichromate was included in the formula.

When 0.5% surfactant concentrations were used, the interfacial contact angles fell midway between the values found with 1% and 0.1% concentrations. The relatively high angles found in Experiments 5 and 6 are being investigated. We find, also, that the higher interfacial angles are associated with the higher concentrations of sodium dichromate; again, there is one exception, Experiment 3, where the concentration of dichromate is 1.0. The lowest interfacial contact angles are found when the dichromate is absent from the formulation (Exps. 14,15,16).

Work is continuing on the relationship between concentration of surfactant and acid and dichromate. We feel that there is an optimum relationship among these components that will adequately condition metal surfaces for adhesive bonding, and that uniformly high joint strengths can be achieved that are equal to the highest attained with strong acid or alkaline treatments.

Specific experiments from Table 9 were repeated for reproducibility. The results are shown in Table 10. In Experiment 0.0, the recommended WAC-1 treatment showed good reproducibility. The interfacial angle was 153.2° as compared with 155.0° reported in Table 9. Experiments 2, 5 and 14 also showed good reproducibility. In the other four experiments, the interfacial angles were substantially higher than those shown in Table 9. These higher values are more in line with values predicted on the basis of composition.

Table 10

INTERFACIAL CONTACT ANGLES ON ALUMINUM

Aluminum: 2024-T3, 0.064 inch thick

		Concentration in Bath (%)			
Exp. No.	Avg Interfacial* Contact Angle	Non-ionic Surfactant	H_2SO_4	$Na_2Cr_2O_7 \cdot 2H_2O$	Avg Contact Angle with H_2O
0.0	153.2°	WAC-1 Treatment			3.5°
2	149.7	0.1	1	3	7
4	153	1	8	3	4
5	140.2	0	1	2	13.5
6	153.0	0.1	13	2	3.5
10	157	0.5	13	3	3.5
11	155	0.1	8	1	4.5
14	118.3	1	13	0	10

* Interfacial contact angle is between Nujol and water.

2.2 Joint Strength and Interfacial Contact Angle

Aluminum joints were prepared with surfaces treated with four different mixtures of sulfuric acid, sodium dichromate, and surfactant. These solutions were WAC-16, -17, -18 and -19. The adhesive was Bloomingdale FM-47. The average joint strengths were 4438 and 4497 psi for the surfaces treated with WAC-16 (Exps. 1 and 2, Table 11). These values are 82.6 and 83.7% of the control strength. The interfacial contact angle on these surfaces was 105.5°. Joints prepared with WAC-17 had strengths of 4782 and 5073 psi and are 93.8 and 99.5% of the control (Exps. 3 and 4). The interfacial contact angle obtained with this treatment was 155°. This value is strikingly close to the interfacial contact angle found with the WAC-1 treatment on the surfaces of the control specimens. The average joint strengths obtained with WAC-18 and -19 ranged from 4446 to 4975 psi which were 89.0 to 96.8% of the control strength. The interfacial contact angles when either of the treatments was used were approximately 150°. This value is about 5% less than the best values after the WAC-1 treatment. The joint strengths are correlatively lower.

Since all these treatments result in very low contact angles in air, an evaluation of a surface treatment by means of the interfacial contact angle is apparently much more qualifying.

Table 11

SURFACTANTS ON ALUMINUM

Aluminum: clad, 2024-T3, 1/16 in. thick.

Controls: 2024-T3 aluminum prepared in WAC-1 and bonded using the same adhesive and in the same press load as the test panels.

Six specimens used in all experiments; adhesive used is FM-47.

			Shear Strength(psi)					
Exp. No.	Treatment No.	Avg θ	Avg	Max	Min	Control Avg	% Control	Remarks
1	WAC-16	<10	4438	4565	4343	5369	82.6	Much H_2 evolved.
2	WAC-16	<10	4497	4640	4316	5369	83.7	"
3	WAC-17	Spread	4782	4989	4717	5094	93.8	Little H_2 evolved.
4	WAC-17	"	5073	5171	5010	5094	99.5	"
5	WAC-18	"	4446	4750	3940	4998	89.0	"
6	WAC-18	"	4465	5100	3970	4998	89.3	"
7	WAC-19	"	4785	5000	4578	5140	93.1	"
8	WAC-19	"	4975	5320	4595	5140	96.8	"

2.3 Interfacial Contact Angles on Stainless Steel

Interfacial contact angles of water/Nujol were measured on treated stainless steel (Table 12). The treatments were WS-1, WS-4, WS-22 and WS-8. The first three treatments have been found to give the highest joint strengths. The last named, WS-8, is merely the degreased surface that gives somewhat erratic results.

Table 12

INTERFACIAL CONTACT ANGLES ON STAINLESS STEEL

Treatment No.	Average Interfacial Contact Angle*	Average Contact Angle of Water Drop
WS-4	135°	5°
WS-1	131	9
	129	12
WS-22	111	9
	141	3
WS-8	67	77

* Interfacial contact angle is between Nujol and water.

WS-1 which is an alkaline treatment had an average interfacial contact angle of 130°. The average contact angle in air was 10.5°. WS-4 with an average contact angle of 5° in air had an interfacial angle of 135°. WS-22 which is strongly acidic and somewhat corrosive had an average contact angle in air of approximately 5.0°; the interfacial contact angles were 111° when the contact angles in air were near 10°, and 141° when the contact angles in air were 2 to 3°. The degreased samples (WS-8) had contact angles in air of 77° and interfacial angles of 67°.

It is more than coincidental that stainless steel treated with WS-4 results in somewhat higher joint strengths than steel treated with WS-1. The lower contact angles in air and the higher interfacial contact angles support this correlation. The wide range of interfacial contact angles with WS-22 indicates a measure of uncertainty regarding the reproducibility of results with this treatment. The low interfacial angle with WS-8 confirms the hydrophobic character of degreased surfaces.

SECTION III

EVALUATION OF SURFACE TREATMENTS BY ELECTRICAL MEASUREMENTS

The sensitivity of certain electrical properties of metals to surface contamination suggested its utilization in measuring changes on the surface resulting from surface treatments. Changes in <u>contact potential</u> and <u>hydrogen overvoltage</u> have been found to be significantly dependent on surface impurities, and probably can be related to contact and interfacial contact angle measurements. Should reproducible correlation be found, we envision the use of the contact resistance apparatus as a rapid, feasible device for evaluating surface treatments in actual service.

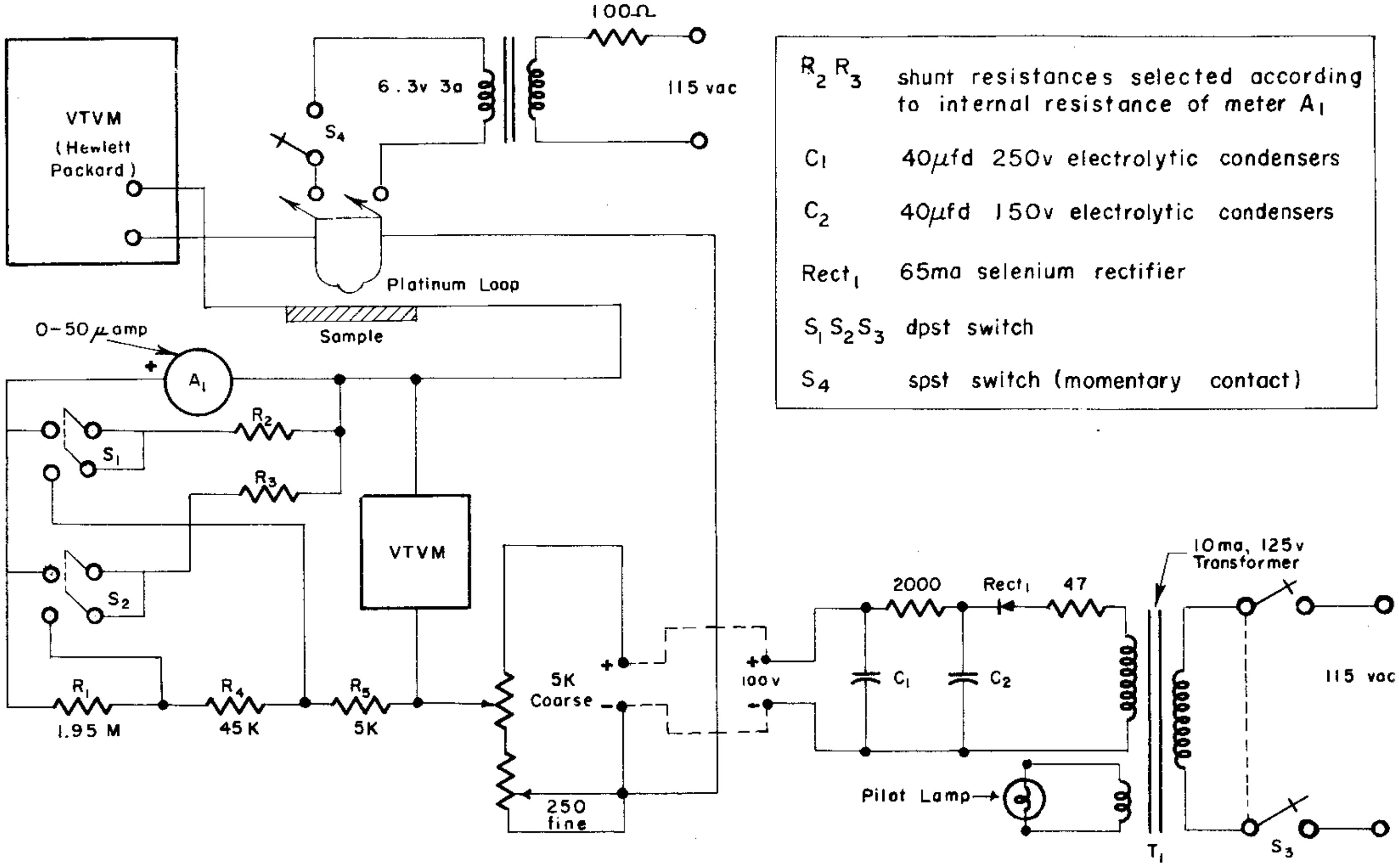
3.1 Contact Resistance Measurements

An apparatus was assembled for measuring the contact resistance of aluminum, stainless steel, magnesium and titanium. The circuit is shown in Figure 1. The experiments were run with degreased and chemically cleaned surfaces that made low contact angles with water drops.

The results of our preliminary experiments showed that we need greater sensitivity in the lower ranges of current and voltage. However, we were able, even with the present apparatus, to determine the breakdown voltage of the films. These values differ significantly with the condition of the metal surface. We find that degreased clad aluminum requires a potential of 75 to 100 volts before a measurable current will flow through the adsorbed film (Exp. 1, Table 13); whereas on aluminum treated with WAC-1 that results in zero contact angle with water, the breakdown potential varies from 4 to 39 volts (Exp. 2). The current flow through the circuit at 100 volts is 0.75 microampere.

Untreated titanium alloy gave such erratic results that we found it difficult even to establish an average value. The titanium specimens that had been treated with WT-4, which gives a low contact angle and high joint strength, had breakdown potentials of 10 volts, 10 volts, and one volt (Exp. 3).

The behavior of stainless steel was opposite to that of aluminum. The degreased specimens (Exp. 4) had breakdown potentials of 22, 10 and 10 volts; the treated specimens (WS-4) were quite uniform and had breakdown potentials between 50 and 55 volts. We are not particularly disturbed by this apparent paradox. We are pleased that the treated surfaces are relatively uniform electrically. A standard breakdown potential may be established. The film on degreased magnesium alloy did not break down at 100 volts (Exp. 6 and 7). Magnesium surfaces treated with a rather mediocre agent showed a breakdown potential of 64 to 100 volts (Exp. 8).



R_2 R_3	shunt resistances selected according to internal resistance of meter A_1
C_1	40μfd 250v electrolytic condensers
C_2	40μfd 150v electrolytic condensers
$Rect_1$	65ma selenium rectifier
S_1 S_2 S_3	dpst switch
S_4	spst switch (momentary contact)

Figure 1. CONTACT RESISTANCE APPARATUS (Schematic Diagram)

Table 13

PRELIMINARY MEASUREMENTS OF CONTACT RESISTANCE

Exp. No.	Metal	Treatment	Breakdown Potential (volts)
1	2024-T3 clad Aluminum	Degreased in trichloroethylene	75 100
2	2024-T3 clad Aluminum	Cleaned in WAC-1	13 4 39
3	Titanium Rem-Cru 110M	Cleaned in WT-4	10 10 1
4	Stainless steel type 302,1/2-hard	Degreased in trichloroethylene	22 10 10
5	Stainless steel type 302,1/2-hard	Cleaned in WS-4	50 50-55 50-55
6	Magnesium Alloy FS 1-H24	Degreased in trichloroethylene	Did not break through under 100 volt potential.
7	Magnesium Alloy FS 1-H24	Degreased in trichloroethylene	"
8	Magnesium Alloy FS 1-H24	Cleaned in 2% trisodium phosphate solution	90-100 64 100

A more detailed study was then made of the puncture voltages of microscopic areas of treated metal surfaces. In Table 14, it is seen that under a 10-mg load, degreased aluminum generally has a much higher contact resistance than aluminum treated in WAC-1. At three or four widely separated points on the degreased surfaces applied voltages of 54, 91 and 95 were required to puncture the film, whereas on the WAC-1 treated surfaces three of the points required 7, 8 and 11.5 volts. One point requiring 46 volts suggests a "hot" point where considerable oxidation probably had taken place. At one point a break-through occurred when 8 volts were applied. The film then quickly recovered, and remained insulating until 73 volts were applied. At this voltage the break-through was permanent. R. Holm(1) suggests that this initial breakdown of the film may be due to a small bridge that was formed by overheating at the point of contact. The continued heating then melts the bridge, and an insulating film reforms.

The puncture voltages on degreased and chemically prepared stainless steel indicate a real difference. The data on the surfactant treated steel suggest a surface on which the surfactant is adsorbed. Until we collect more data and relate it to other measurements, we feel that any conclusions are premature.

On titanium, the surface that was treated with surfactant solution appeared to be relatively uniform when compared with the degreased or chemically treated surfaces. All three metals, regardless of surface treatment, have had

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1. R. Holm, Electrical Contacts, 1st Ed., Gebers, Stockholm, Sweden, 1946.

Table 14

CONTACT RESISTANCE CHARACTERISTICS OF TREATED METALS

	Condition	Puncture Voltage
	(10-mg load)	
Aluminum	Degreased in TCE*	95
	"	54
	"	91
	"	27
	Cleaned WAC-1	7
	"	8
	"	46
	"	11.5
	"	8-73
	Cleaned WAC-17	30
	"	No Puncture
	"	"
	"	"
	"	65
	"	48
Stainless Steel	Degreased in TCE	18
	"	No Puncture
	"	60
	"	70
	"	61
	"	No Puncture
	Cleaned WS-4	42
	"	41
	"	No Puncture
	"	31
	"	48
	"	27
	"	No Puncture
	"	39
	Cleaned WS-30	74
	"	79
	"	No Puncture
	"	19
	"	50
Titanium	Degreased in TCE	81
	"	50
	"	No Puncture
	Cleaned WT-4	"
	"	100
	"	No Puncture
	"	59
	"	No Puncture
	"	52
	Cleaned WT-5	69
	"	69
	"	59
	"	99
	"	60
	"	61
Magnesium	Degreased in TCE	No Puncture
	"	65 break and recover
	"	No Puncture
	"	"
	"	"
	"	98 break and recover
	Cleaned WM-15	No puncture or unsteadiness on any test under 10 mg load
	(200-mg load)	
	Cleaned WM-15	No Puncture
	"	100
	Cleaned WM-13	No Puncture
	"	78
	"	No Puncture

* trichloroethylene

points that resisted break-through up to 100 volts except the surfactant treated titanium. It is apparent that heavy oxide deposits are built up at certain points on aluminum, stainless steel, and probably on titanium, which form strongly insulating points that reform very rapidly after removal by ordinary chemical means.

This effect of rapid heavy oxide formation was quite apparent in our work with the magnesium alloy. Under a 10-mg load there was no permanent puncture up to the maximum voltage of the instrument. This was observed with degreased and cleaned surfaces. When the load was increased to 200 mg a break-through occurred at one point at exactly 100 volts. On the chemically treated surface (WM-13), one break-through occurred at 78 volts.

These preliminary results offer promise of a practical method for evaluating surface treatments in industry. It is simple, rapid and very sensitive to inhomogeneities on the surface.

3.2 Hydrogen Overvoltage Measurements

Hydrogen overvoltage at a given current density of i (amp/cm^2) is defined as the difference between the potential of an electrode at which hydrogen is being evolved and the potential of the reversible hydrogen electrode in the same solution(2). Hydrogen overvoltage varies with the nature of the electrodes, and among other things the condition of the surface, since this phenomenon is essentially a surface property. Overvoltage measurements were made on several metals, both treated and untreated, in order to relate differences in overvoltage with other methods of evaluating surface treatments. The circuit diagram is shown in Figure 2. Significant differences were observed in the preliminary experiments.

Figure 3 indicates that aluminum, as received, showed a rapidly increasing overpotential with an increase in current density from 0.5 to 12.5 μamp/cm^2; whereas the aluminum treated with the recommended sulfuric acid-dichromate solution, showing zero contact angle with water, indicated a relatively slight dependence on current density.

The behavior of stainless steel treated with WS-4 that gives low contact angles also is significantly different from that of the untreated specimen, Figure 4. Again the treated metal shows a small dependence on current density when compared with the rather eccentric behavior of unclean stainless steel. The sharp change in slope of the unclean stainless steel at a current density of 7.5 μamp/cm^2 cannot be explained with our present knowledge. Its counterpart on a smaller scale in the curve for the treated stainless steel at approximately the same current density indicates a possibility that it is related to the electrode characteristics of an alloy.

The overvoltages on treated and untreated titanium are related in the same way as those on treated and untreated aluminum and stainless steel, Figure 5. The extrapolated values for overvoltage are significantly higher for uncleaned metals. An additional experiment with pure copper, Figure 6, that was run for comparison with another pure surface (aluminum), showed almost identical characteristics with the aluminum. The plot of the treated metal is linear with an increase in current density, and the slope is gradual. The overvoltage on untreated copper and aluminum is higher and the slope of the curve varies sharply with current density from approximately 4 μamp/cm^2 to approximately 15 μamp/cm^2.

We are not sufficiently advanced with this work to draw conclusions regarding the correlation of overvoltage values with joint strength. We feel, however, that this method of evaluating surface treatments will be very sensitive to organic and inorganic impurities on the surface, and in conjunction with our other methods, it will contribute substantially to our knowledge of the surfaces.

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(2) Brockris, J. O'M., "Recent Developments in the Study of Hydrogen Overpotential", Chem. Revs, 43, 525 (1948).

R_1	shunt selected according to internal resistance of meter A_1
R_2	100,000 ohm 7w potentiometer
S_1	spdt switch
$S_2 S_3$	spst switch
A_1	0–100 microamperes microammeter

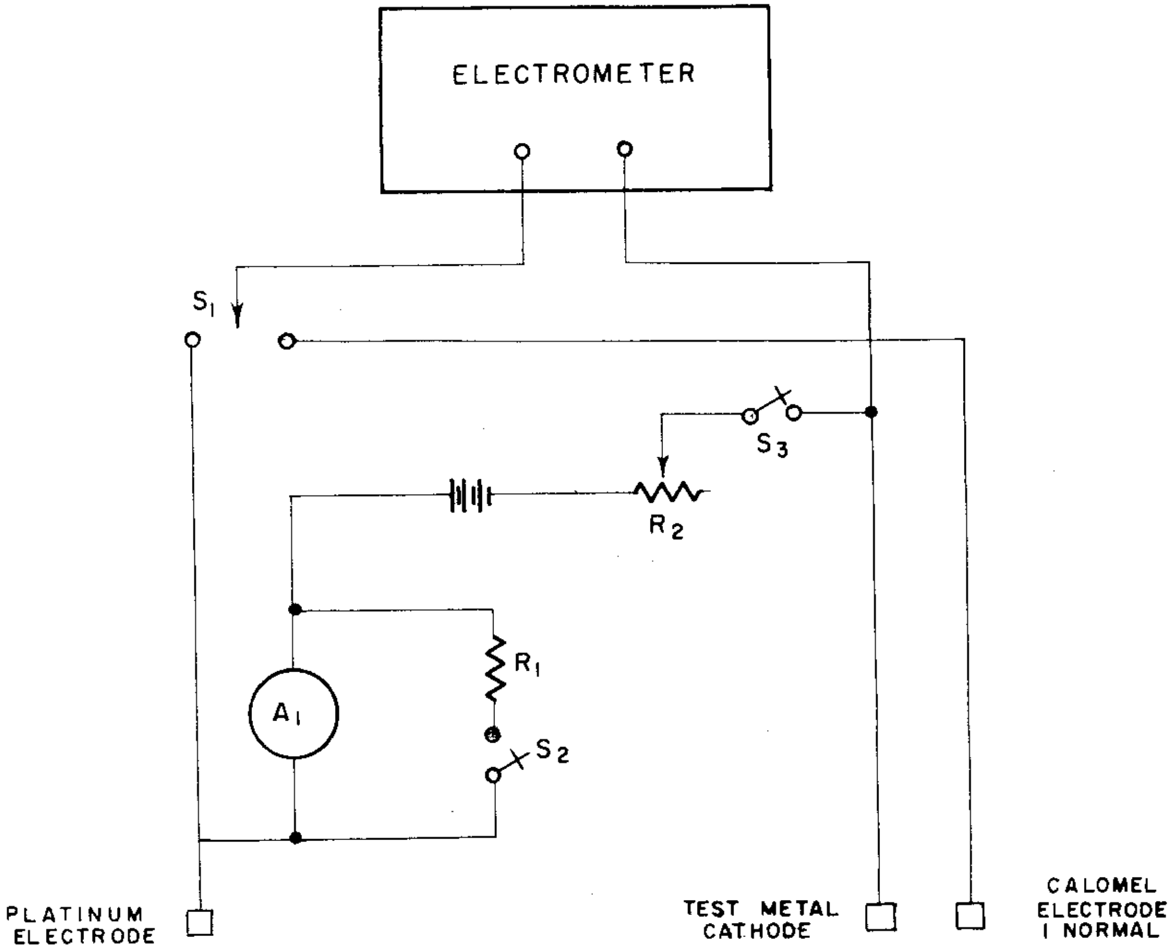

Figure 2. OVERPOTENTIAL APPARATUS

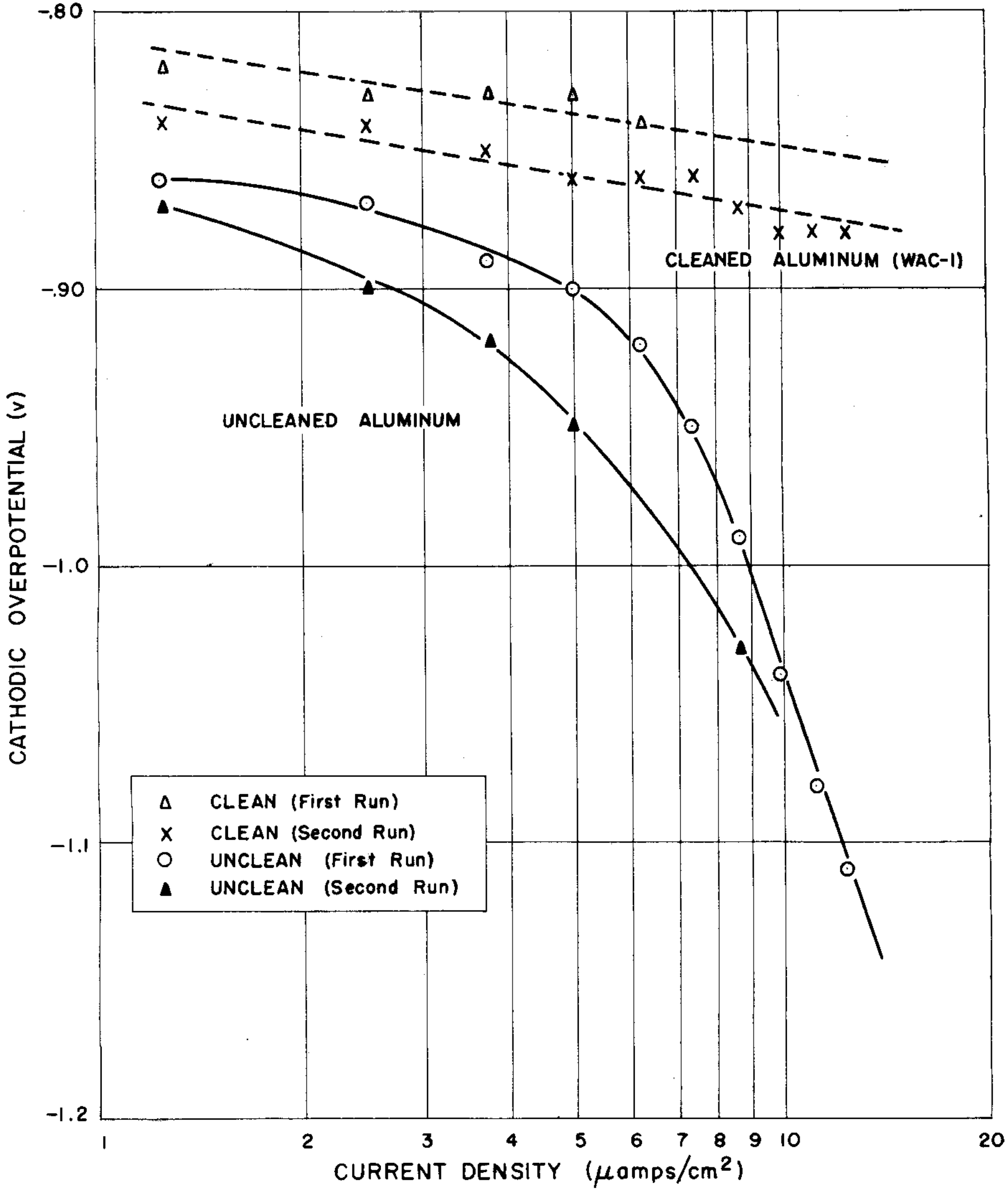

Figure 3. OVERVOLTAGE ON TREATED AND UNTREATED ALUMINUM

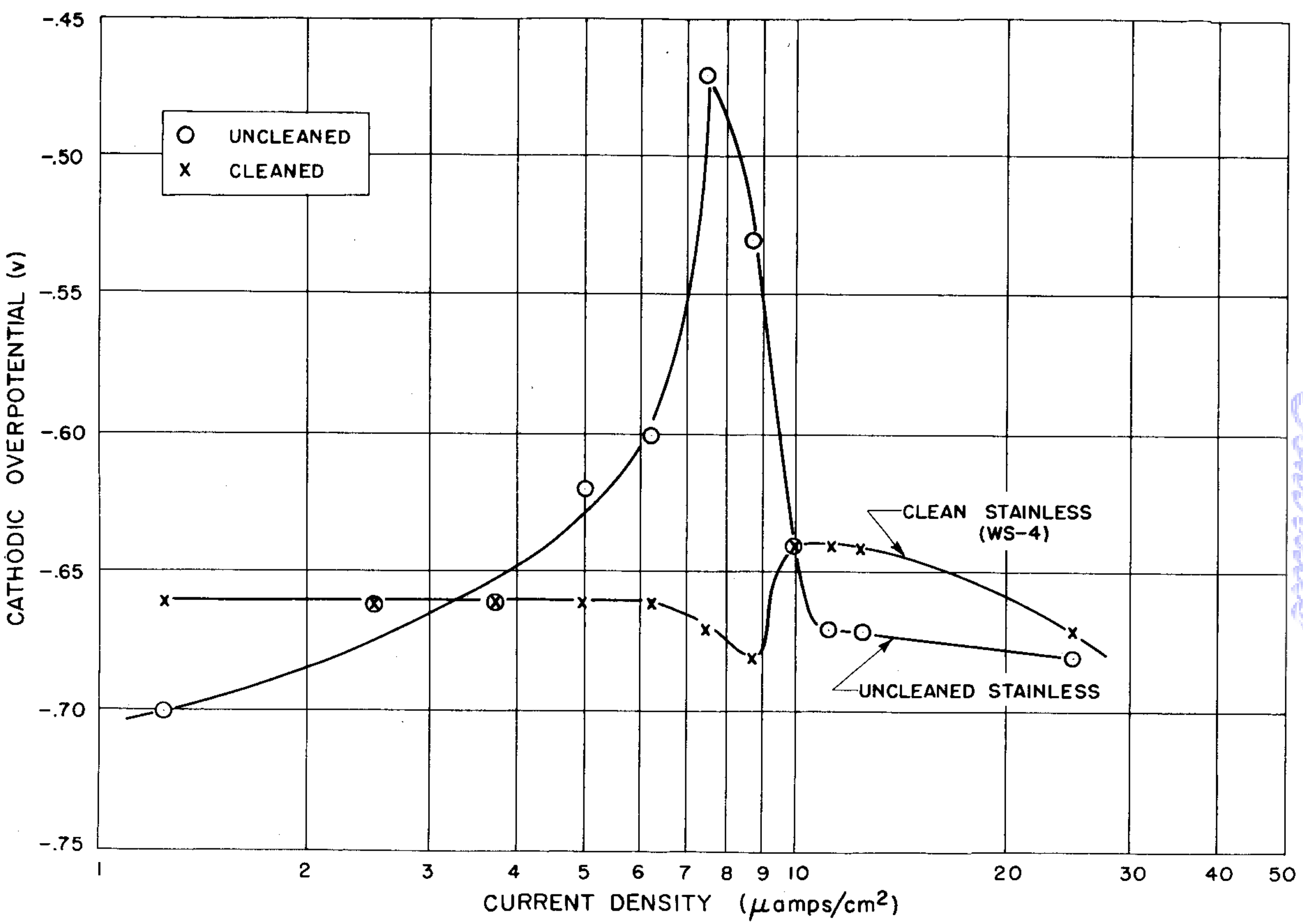

Figure 4. OVERVOLTAGE ON TREATED AND UNTREATED STAINLESS STEEL

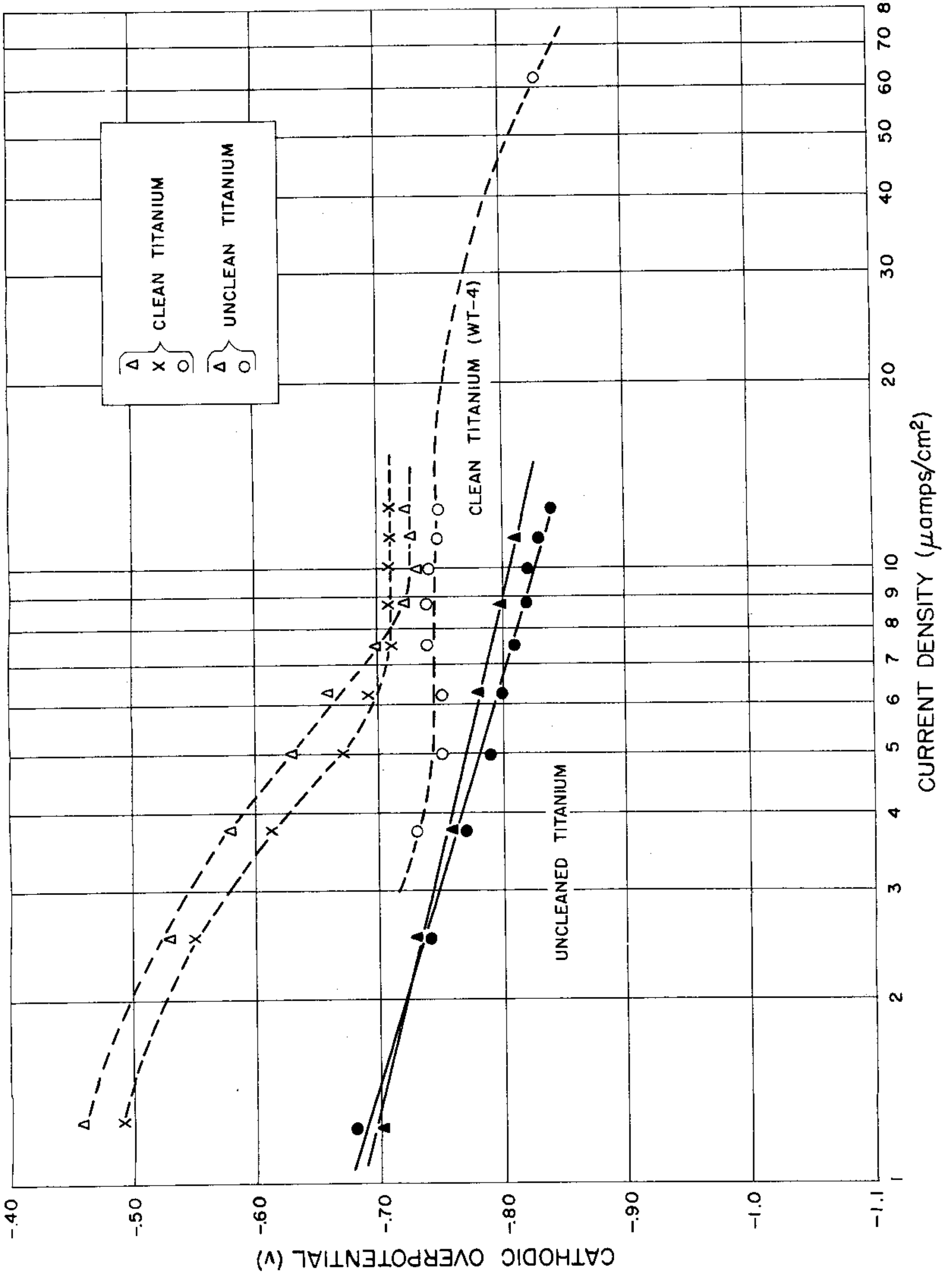

Figure 5. OVERVOLTAGE ON TREATED AND UNTREATED TITANIUM

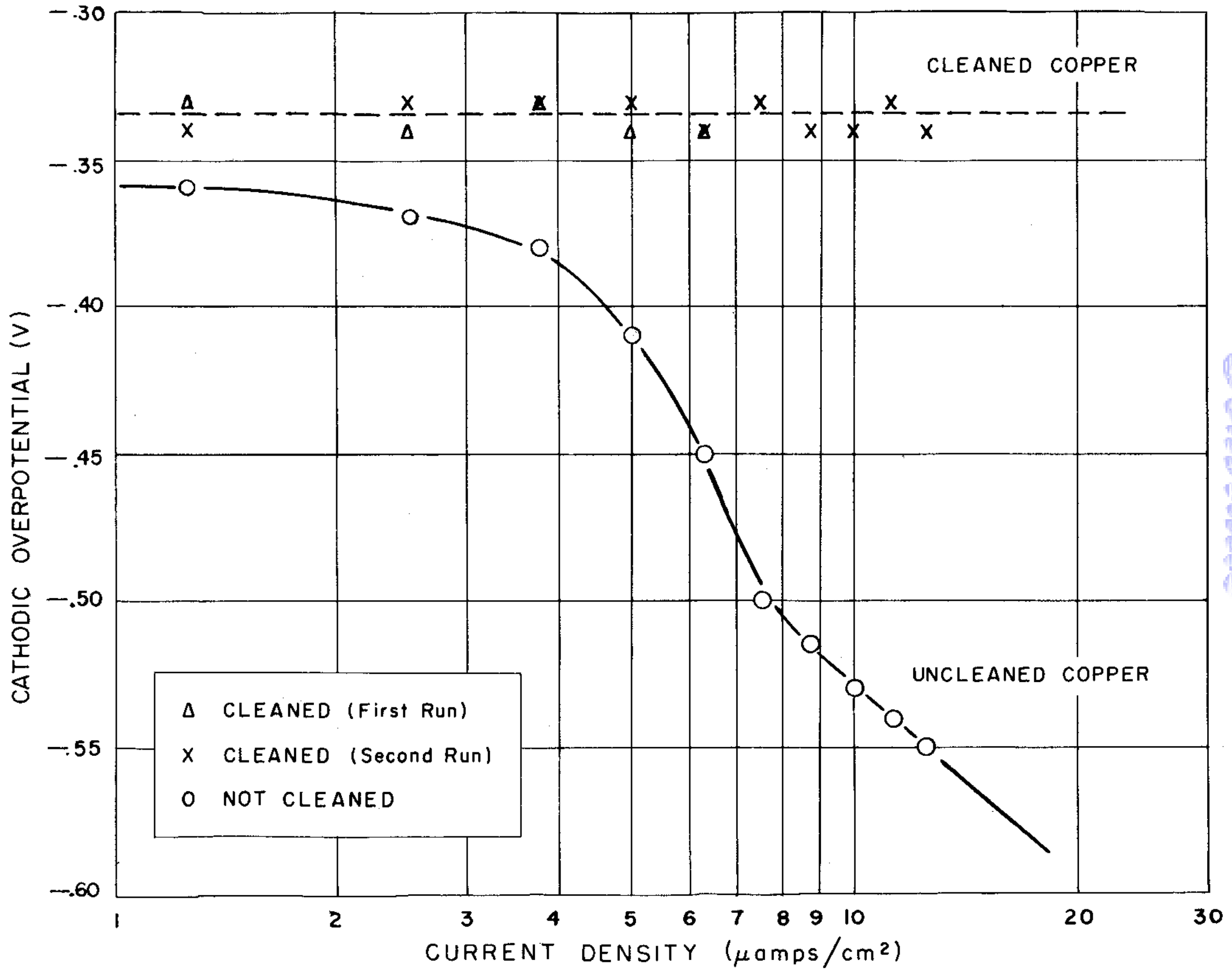

Figure 6. OVERVOLTAGE ON TREATED AND UNTREATED COPPER

SECTION IV

TESTS TO EVALUATE REPRODUCIBILITY AND EFFECTIVENESS OF ADEQUATE TREATMENTS

4.1 Tests on Stainless Steel

Tests were run with stainless steel joints to evaluate and compare the several treatments that give low contact angles. In addition, we explored the possibility that some of the adhesives bond more effectively after a specific type of treatment. We have observed that joint strength with Scotchweld AF-6 and Metlbond 4021 adhesives was generally higher with aluminum joints than with stainless steel. This is contrary to the predicted relationship since stainless steel has a much higher modulus than aluminum.

Table 15 lists the results of experiments with degreased surfaces and treatments that function essentially by inorganic acid attack, or by displacement of the contaminating film by means of wetting agents in a suitable medium. An examination of the data indicates that the WS-4 treatment results in the most consistent and highest joint strength when used in conjunction with Bloomingdale FM-47 adhesive. We have noted this relative superiority in earlier work. However, with stainless steel, differences between degreased and treated surfaces have not been as striking as with the other metals. The results with WS-29 and WS-30, although not as consistent as with WS-4, show promise. Their use invites further exploration because they are essentially mild alkaline solutions of wetting agents.

When Scotchweld AF-6 was the bonding agent, the highest strength was obtained with stainless steel treated with WS-4 or WS-30. However, this superiority was not consistent. More information will have to be obtained concerning the influence of critical heating temperature and pressures plus the information from the more sensitive tests described earlier before we can more fully understand the wide range in joint strengths obtained with one treatment.

Metlbond 4021 adhesive showed up best with WS-1 treatment, and rather poorly after treatment with wetting agent solutions. Again we observed that joint strength with aluminum is generally higher than with stainless steel. We conclude tentatively that there exists a specificity of an adhesive for a particular metal surface which may be further influenced by the nature of the surface treatment.

4.2 Test Results with Magnesium Joints

Tests conducted with adhesive bonded magnesium, treated with WM-13, were relatively consistent with the values obtained in earlier experiments. In Table 16, the average strength for four panel joints show minor variation. Joint strength ranged from 2836 to 3140 psi when Bloomingdale FM-47 was the adhesive. The controls (aluminum joints treated with WAC-1) were as high as any found under the best conditions.

When Scotchweld AF-6 was used, reproducibility was not as good. Joint strength ranged from 1156 psi to 2145 psi, 40.6% to 85.6% of the control strength. The panels in Experiments 1 and 6 were treated in the same bath, and the joint strengths were very close. The panels of Experiments 7 and 8 were also treated together, and the joint strengths are again very similar. The dissimilarity in strength between the two sets of joints indicate a sensitivity to procedural influences. The controls in each case are similar in value.

Table 15

TEST RESULTS FOR STAINLESS STEEL WITH DIFFERENT TREATMENTS

Metal: 302 1/2-hard Stainless Steel, 0.064 in. thick.

Control: 2024-T3 Alclad Aluminum treated with WAC-1 and bonded
with same adhesive used in test joint.

Treatment No.	No. Specimen	Avg θ	Adhesive	Shear Strength(psi)				
				Avg	Max	Min	Control Avg	% Control
WS-4	6	<10	FM-47	6842	7737	6386	4912	139.2
WS-4	5	<10	FM-47	6881	7178	6386	4912	140.0
WS-8	6	<83	FM-47	6812	7138	6387	5534	123.0
WS-8	6	<83	FM-47	6266	6862	5454	5488	114.0
WS-30	6	<10	FM-47	6150	6632	5727	5349	114.9
WS-30	6	<10	FM-47	6725	7200	6280	5349	125.7
WS-30	6	10.5	FM-47	6374	6831	5623	5488	116.1
WS-29	6	<10	FM-47	5992	6500	5620	5310	112.8
WS-29	6	<10	FM-47	6585	7070	6270	5310	124.0
WS-29	5	<10	FM-47	6721	7360	6181	5534	121.4
WS-1	6	<10	AF-6	2503	3166	2093	2368	105.7
WS-4	6	<10	AF-6	4014	4588	3740	3776	106.3
WS-4	6	<10	AF-6	1958	2406	1386	2495	78.4
WS-4	6	<10	AF-6	2160	2585	1922	3289	65.6
WS-4	6	<10	AF-6	2052	2333	1826	3289	62.3
WS-8	6	-	AF-6	2406	3111	2108	2910	82.7
WS-8	6	78	AF-6	1798	2210	1544	3085	58.2
WS-8	6	80	AF-6	1589	2098	1089	2329	68.2
WS-22	6	<10	AF-6	2377	2519	2116	3407	69.7
WS-29	6	<10	AF-6	3399	3920	2920	3465	98.0
WS-29	6	<10	AF-6	2573	2760	2460	2537	101.4
WS-29	6	<10	AF-6	2696	3000	2430	2537	106.2
WS-29	6	<10	AF-6	1828	2363	1603	3085	59.2
WS-30	6	<10	AF-6	2204	2460	1887	2329	94.6
WS-30	6	<10	AF-6	3490	3683	3207	3590	102.6
WS-30	6	<10	AF-6	4051	4416	3860	4547	89.0
WS-30	6	<10	AF-6	3325	3469	3140	3776	88.0
WS-30	6	<10	AF-6	4124	4479	3700	4547	90.6
WS-1	6	<10	4021	2938	3083	2775	3747	78.4
WS-4	6	<10	4021	4846	5376	4514	4213	115.0
WS-4	6	<10	4021	4343	4660	3980	4213	103.0
WS-8	6	83	4021	2921	3274	2680	4620	63.2
WS-8	5	83	4021	3837	3990	3673	4820	79.6
WS-22	6	<10	4021	3445	3831	3110	3576	96.3
WS-29	6	<10	4021	2339	2420	2151	4035	57.9
WS-29	6	<10	4021	2417	2820	1890	4895	49.3
WS-29	6	<10	4021	3267	3830	2686	4895	66.7
WS-29	5	<10	4021	3257	3740	2564	4620	70.4
WS-30	6	<10	4021	3184	3530	2436	3785	84.1
WS-30	6	<10	4021	1689	1910	1460	4583	36.8
WS-30	6	<10	4021	1844	2134	1610	4583	40.2
WS-30	6	10.5	4021	3701	3940	3445	4820	76.7

Table 16

ADHESIVE BONDED MAGNESIUM JOINTS

Metal: FS1-H24 Magnesium, 0.064 in. thick.

Control: 2024-T3 Aluminum treated with WAC-1 and bonded with the same adhesive used on test joint.

					Shear Strength(psi)				
Exp. No.	Treatment No.	No. Specimen	Avg θ	Adhesive	Avg	Max	Min	Control Avg	% Control
1	WM-13	6	15	FM-47	3140	3440	2870	5678	55.3
2	WM-13	6	15	FM-47	2836	3000	2500	5678	49.9
3	WM-13	6	-	FM-47	3055	3310	2880	5439	56.1
4	WM-13	6	-	FM-47	3111	3280	2820	5439	57.1
5	WM-13	6	17	AF-6	2145	2220	2010	2509	85.6
6	WM-13	6	17	AF-6	2210	2210	1700	2509	80.7
7	WM-13	6	15	AF-6	1200	1560	880	2846	42.1
8	WM-13	6	15	AF-6	1156	1560	900	2846	40.6

SECTION V

JOINT STRENGTHS WITH METALS HAVING KNOWN ADSORBED FILMS

5.1 Stainless Steel Joints

The investigation to evaluate the role of the adsorbed film in surface treatments was continued. Aluminum, stainless steel, and magnesium were studied. Films of toluene or mineral oil were adsorbed on the metal surface by treating the degreased surfaces with solutions that resulted in low or zero contact angles with water. It can be presumed that under these conditions only an adsorbed water film is present on the metal. The presence of even patches of hydrophobic material would give sizeable contact angles. While immersed in toluene or mineral oil, a thickness of 0.005 in. was removed in the milling machine. The jig holding the panel and the end mill have been previously treated to zero contact angle so that the freshly exposed surface was not contaminated.

After removal from the jig, the surfaces were given treatments in the normal fashion and bonded with one of three adhesives, Table 17. In the experiments with stainless steel that had adsorbed toluene, the joint strength was low with both untreated and treated surfaces (Exps. 1 and 2). Despite the low contact angle resulting from treatment with WS-4, the joint strength was 101.7% of the aluminum control strength, which is actually lower than that for the untreated metal. When Epon 422 adhesive was used, however, the joint strength was approximately that which was found with unmilled specimens.

The results with stainless steel having adsorbed mineral oil are more in line with reported results. When normally effective treatments were used and Bloomingdale FM-47 was the bonding agent, the joint strength ranged from 129.2 to 139.5% of the control strength. One striking contrast is found. Panel joints 17 and 18 were bonded in the same load. The joint with degreased surfaces (WS-8) has an average joint strength of 6698 psi. The joint of surfaces treated with WS-4 had a strength of 7711 psi.

Table 17

TEST RESULTS WITH METAL WITH KNOWN ADSORBED FILMS

Metal: pretreated panels, Stainless Steel in WS 4 and Magnesium in WM-13.

Controls: 2024-T3 Clad Aluminum, 1/16 in. thick bonded with the same adhesive and in the same press load as test panels, control treatment is WAC-1.

Four specimens are used in all experiments except 11, 12 & 13, which used five.

Exp. No.	Treatment No.	Avg θ	Adhesive	Shear Strength(psi) Avg	Max	Min	Control Avg	% Control	Remarks*
1	None		FM-47	4778	4939	4632	4181	114.2	Pretreated stainless steel has adsorbed film of toluene.
2	WS-4	<10	FM-47	4256	4383	4040	4181	101.7	"
3	None		Epon 422	3068	3235	2767	2939	104.3	"
4	WS-4	<10	Epon 422	2720	2909	2514	2939	92.5	"
5	WS-8		FM-47	6077	7341	4971	4453	136.4	Pretreated stainless steel has adsorbed film of mineral oil.
6	WS-1	<10	FM-47	6037	6838	4451	4453	135.6	"
7	None		FM-47	2788	2901	2696	5462	51.0	Pretreated magnesium has an adsorbed film of toluene.
8	WM-13	<10	FM-47	3553	3862	3107	5462	65.0	"
9	None		Epon 422	1026	1078	980	2650	38.7	"
10	WM-13	<10	Epon 422	1700	1875	1500	2650	64.2	"
11	WAC-1M	>70	FM-47	5074	5500	4420	-		Pretreated aluminum has an adsorbed film of mineral oil.
12	WAC-3M	0	FM-47	4038	4305	3839	-		"
13	WAC-17M	0	FM-47	5045	5163	4901	5354	94.2	"
14	WAC-1M	0	4021	3891	4000	3823	4813	80.8	"
15	WAC-17M	0	4021	4388	4470	4280	4813	91.1	"
16	WS-4M	<10	FM-47	7711	7969	7428	5527	139.5	Pretreated stainless steel has adsorbed film of mineral oil.
17	WS-8M	>70	FM-47	6698	6979	6474	5527	121.1	"
18	WS-29M	<10	FM-47	6698	7083	6198	5184	129.2	"
19	WS-4M	<10	4021	2328	2604	2133	4854	47.9	"
20	WAC-1M	0	4021	4351	4411	4274	4854	89.6	Pretreated aluminum has adsorbed film of toluene.
21	WAC-1M	0	FM-47	5393	5515	5291	5184	104.0	"
22	WAC-17M	0	FM-47	4820	5120	4260	5617	85.8	"

* Stainless steel: Type 302, 1/2-hard, 1/16 in. thick;
Magnesium alloy: FS-1 H24, 1/16 in. thick.

5.2 Magnesium Joints

Magnesium panels were cleaned in the alkaline bath of the WM-13 treatment, dried, and milled under toluene. Two panel joints were prepared with the milled surfaces, whereas two others were prepared with milled surfaces that were treated with WM-13. When Bloomingdale FM-47 was the bonding agent, the joints prepared with the untreated surfaces had an average joint strength of 2788 psi which was 51.0% of the control strength (Exp. 4). The treated surfaces gave an average joint strength of 3553 psi, 65% of the control. When Epon 422 was used the untreated surfaces had an average joint strength of 1026 psi, 38.7% of the control strength. The treated surfaces gave a joint strength of 1700 psi which was 64.2% of the control (Exp. 5).

5.3 Aluminum Joints

Experiments were conducted with aluminum surfaces that had adsorbed mineral oil or toluene films. Comparisons were made between the effectiveness of strong acid treatments and solutions composed principally of wetting agents. In Table 17 (Exps. 2 & 3) it is seen that when the adsorbed film is mineral oil, the wetting agent solution is as effective as the WAC-1 treatment (strong acid-dichromate solution). The strength of the degreased surfaces (Exp. 1) was substantially lower. When the adsorbed film was toluene, the strong acid treatment was more effective, 5393 psi as compared with 4820 psi. The adhesive used in these experiments was Bloomingdale FM-47. When Metlbond 4021 adhesive was used with aluminum surfaces that had adsorbed toluene films, the WAC-1 treatment produced a zero contact angle, but joint strength was 4351 psi. This value compares unfavorably with 4854 psi obtained when the same treatment was used on the unmilled surfaces.

When the mineral oil was the adsorbed film, the joint strength was even lower than when the WAC-1 treatment was used. More effective conditioning was obtained with the WAC-17 treatment. Apparently, the presence of a wetting agent results in a more effective removal of mineral oil.

SECTION VI

RESULTS WITH 30-DAY SALT SPRAY TEST OF STAINLESS STEEL JOINTS

Stainless steel joints were prepared for testing in the salt spray cabinet. This work is designed to compare the salt spray resistance of joints conditioned with the several treatments that have resulted in the highest joint strengths with the adhesives recommended by WADC. From the results of these tests, we hope to learn whether the chemical properties of the surface treatment influence resistance of the joint to salt spray.

Stainless steel panels treated with WS-1, WS-4, WS-8 and WS-22 were bonded with the four adhesives. These treatments differ chemically, and on stainless steel they produce the highest joint strength. Two other types of treatments were evaluated, WS-29 and WS-30. These are dilute solutions of anionic surfactants in alkaline media for which the joint strengths at room temperature were as high or higher than those found with the strong acid or alkaline treatments.

We are submitting the data in Table 18 without further comment. We feel at this point that there are not enough experiments to attempt a correlation between surface treatment and salt spray resistance.

Table 18

RESULTS OF 30-DAY SALT SPRAY TEST FOR STAINLESS STEEL PANELS

Stainless steel: Type 302, 1/2-hard.

Original strengths are the average strengths of panels prepared in the same bath and bonded with the same adhesive and in the same press load as the panels placed in the spray cabinet.

Six specimens used in all experiments.

Exp. No.	Treatment No.	Avg θ	Adhesive	Shear Strength(psi) Avg	Max	Min	Original Avg	% Original
1	WS-1	<10	FM-47	4060	4660	3584	6486	62.5
2	WS-4	<10	FM-47	5091	5564	4415	6683	76.1
3	WS-8	<10	FM-47	5937	6475	5373	6425	92.4
4	WS-22	<10	FM-47	6238	6666	5731	6769	92.1
5	WS-29	<10	FM-47	4499	5220	3079	6189	72.6
6	WS-1	<10	4021	1945	2364	564	2938	66.2
7	WS-4	<10	4021	903	1428	693	3162	28.5
8	WS-8	<10	4021	1668	2019	1626	3373	49.4
9	WS-22	<10	4021	998	1346	600	3445	28.9
10	WS-4	<10	AF-6	2439	2591	2352	1958	124.5
11	WS-22	<10	AF-6	2883	3099	2480	2377	121.2
12	WS-1	<10	AF-6	3603	3896	3465	2503	143.9
13	WS-8	65	AF-6	2277	2555	1750	2406	94.6
14	WS-29	<10	AF-6	2322	2460	2123	3399	68.3
15	WS-30	<10	AF-6	3363	3800	2783	3490	96.3
16	WS-8	<10	422	2334	2515	2173	2830	82.7
17	WS-22	<10	422	2762	2895	2524	3153	87.6
18	WS-1	<10	422	2404	2514	2213	3265	73.6
19	WS-4	<10	422	2868	3366	2174	3320	86.3
20	WS-29	<10	422	2546	2680	2388	2984	85.3
21	WS-30	<10	422	2384	2620	2138	2519	94.6
22	WS-30	<10	FM-47	2538	2833	1980	6224	40.7
23	WS-29	<10	4021	1355	2079	792	2339	57.9
24	WS-30	<10	4021	1034	1366	504	3184	32.4

SECTION VII

SURFACE TREATMENTS FOR BONDED TITANIUM JOINTS

Experiments were conducted with titanium. Three different adhesives were used in these experiments. Six test specimens which had been treated with WT-4 were bonded with Bloomingdale FM-47. These test specimens were prepared from 1 in. x 4 in. strips bonded in a 1/2-in. overlap and bonded in a jig for curing individual specimens. Three specimens (Nos. 1, 3 & 5) were tested and had an average joint strength of 6626 psi (Exp. 1, Table 19). The remaining three specimens from this press load were tested at Wright Air Development Center and their average joint strength was 6930 psi (Exp. 2).

Three joints treated with WT-4 and bonded with Bloomingdale FM-47 were pressed simultaneously with three test specimens treated with WT-2 which was also bonded with FM-47. The average strength of the joints treated with WT-4 was 6743 psi (Exp. 3), the specimens treated with WT-2 had an average joint strength of 5556

Table 19

TEST RESULTS WITH ADHESIVE BONDED TITANIUM JOINTS

Titanium: Rem-Cru 130-A sheet, 0.064 in. thick.

Tests are run at room temperature.

Standard 1/2 in. overlap joints are used as test specimens.

Exp. No.	Treatment No.	No. Specimen	Avg θ	Adhesive	Shear Strength(psi)		
					Avg	Max	Min
1	WT-4	3	0	FM-47	6626	6810	6500
2*	WT-4	3	0	FM-47	6930	7010	6890
3	WT-4	3	0	FM-47	6743	7000	6400
4	WT-2	3	0	FM-47	5556	5890	5120
5	WT-2	2	0	FM-47	6758	6816	6700
6	WT-22	6	0	AF-6	1487	2210	660
7	WT-22	6	0	4021	2796	3100	2140

*Tested at WADC

psi (Exp. 4). Two additional joints bonded with Bloomingdale FM-47 and treated with WT-2 had an average strength of 6758 psi (Exp. 5). These two test specimens were bonded separately from the joints similarly treated above. Since all the surfaces in Experiments 4 and 5 had zero contact angles, the substantial difference in joint strengths is probably due to a procedural misstep in the application of the adhesive in Experiment 4. We have found that this step in the bonding process is a sensitive one.

A series of experiments was begun to evaluate joint strengths of treated titanium surfaces by using different approved adhesives. Treatment WT-22 which gave high joint strengths with Bloomingdale FM-47 at room temperature was used with Scotchweld AF-6 and Metlbond 4021 adhesives. Despite zero contact angles, the average joint strength with AF-6 was 1487 psi with considerable scatter in the data (Exp. 6). When 4021 adhesive was used, the values were better. The average joint strength was 2796 psi (Exp. 7).

SECTION VIII

BONDED MAGNESIUM JOINTS

It has been observed that magnesium joints prepared from surfaces treated with WM-13 did not show unquestionable superiority over joints bonded after the WM-12 treatment. A number of experiments were conducted for both treatments (with Bloomingdale FM-47 as the adhesive) to arrive at a predictable average joint strength for surfaces treated with WM-13; these values were compared. Test results are shown in Table 20. The average strength of all the WM-13 joints was 3404 psi. This value is only 81 psi greater than the average with WM-12 treatment. We feel then that neither treatment can be rated superior to the other.

Table 20

TEST RESULTS WITH ADHESIVE BONDED MAGNESIUM JOINTS

Metal: Dow FS-1-H-24, 0.064 in. magnesium.
Tests are run at room temperature.
Standard 1/2 in. overlap joints are used as test specimens.

					Shear Strength (psi)				
Exp. No.	Treatment No.	No. Specimen	Avg θ	Adhesive	Avg	Max	Min	Control Avg	% Control
1	WM-13	6	<10	FM-47	3291	3390	3219	5328	61.7
2	WM-13	6	<10	FM-47	3433	3617	3250	5328	64.4
3	WM-13	6	<10	FM-47	3428	3588	3262	5716	59.9
4	WM-13	6	<10	FM-47	3551	3730	3423	5716	62.1
5	WM-12	6	<10	FM-47	3116	3284	2923	5456	67.1
6	WM-12	6	<10	FM-47	3278	3390	3180	5456	60.1
7	WM-12	6	<10	FM-47	3551	3540	3340	5292	65.0
8	WM-12	6	<10	FM-47	3460	3580	3290	5292	65.4
9	WM-13	6	15	FM-47	3595	3833	3401	5572	64.5
10	WM-13	6	15	FM-47	3350	3686	3039	5572	60.1
11	WM-13	6	<10	FM-47	3628	3848	3420	5460	66.4
12	WM-13	6	<10	FM-47	3507	3676	3310	5460	64.2
13	WM-13	3	<10	FM-47	3710	3919	3585	5468	67.8
14	WM-13	3	<10	FM-47	3204	3292	3060	5468	58.5
15	WM-13	6	<10	FM-47	3085	3280	2580	5415	56.9
16	WM-13	6	<10	FM-47	3066	3163	2970	5415	56.6

SECTION IX

EFFECT OF TEMPERATURE OF RINSE WATER ON JOINT STRENGTH OF BONDED ALUMINUM JOINTS

It has been observed here that when adequately treated aluminum panels are exposed to boiling rinse water for more than a few minutes, interference colors developed. Joints prepared with these surfaces had substantially lower strength than is normally obtained with aluminum surfaces not exposed to such high temperatures. Typically low values for joints prepared with surfaces showing iridescence are 1971 and 2453 psi as compared with 5270 psi for surfaces showing no iridescence.

A series of experiments were run that covered every method of rinsing that might have been used in these laboratories. In method 1, the treated panels were immersed for ten minutes in boiling distilled water after a preliminary rinse for 10 minutes in hot running tap water at 135°F. The average strength of joints bonded with these surfaces was 1808 psi (Exp. 1, Table 21). In method 2, the treated panels were rinsed in cold distilled water followed by a ten-minute immersion in boiling distilled water. The joint strength was 2217 psi (Exp. 2). In method 3, the treated panels were rinsed in hot running tap water for ten minutes at 135-145°F, and then immersed for 10 minutes in boiling distilled water from an outside source. The joint strength was 2217 psi (Exp. 3). In methods 4, 5, 6 and 7, exposure to boiling water was limited to 2 minutes or less, and the joint strength rose from 4740 psi after the two-minute exposure to 5106 psi when the exposure was momentary (Exps. 4 to 7). The results of this series of experiments indicate that the **physio-chemical** changes on a zero-contact-angle aluminum surface that result from an exposure to a temperature above 155°F adversely affect joint strength. An understanding of this phenomenon is being sought.

Table 21

EFFECT OF TEMPERATURE OF RINSE WATER ON STRENGTH OF ALUMINUM JOINTS

Clad aluminum 2024-T3, 0.064 in. thick.
Six specimens used in all experiments; adhesive used is FM-47.

Exp. No.	Treatment No.	Avg θ	Shear Strength (psi) Avg	Max	Min	Type of Rinse
1	WAC-1	<10	1808	1960	1653	Method 1
2	WAC-1	<10	2217	2306	1930	Method 2
3	WAC-1	<10	2217	2373	2010	Method 3
4	WAC-1	<10	4740	5353	4480	Method 4
5	WAC-1	<10	4999	5245	4892	Method 5
6	WAC-1	<10	5106	5235	4950	Method 6
7	WAC-1	<10	5001	5240	4801	Method 7

Method 1: After treatment the panels were immersed in hot running tap water. They were then immersed for 10 minutes in boiling distilled water.

Method 2: After treatment the panels were given three successive rinses in cold distilled water followed by 10 minutes in boiling distilled water.

Method 3: After treatment the panels were immersed in hot running tap water followed by 10 minutes in boiling distilled water from another source.

Method 4: After treatment the panels were given two successive rinses in hot tap water followed by a boiling tap water immersion rinse for 2 minutes.

Method 5: After treatment the panels were rinsed by allowing hot running tap water to flow over the panels.

Method 6: After treatment, the panels were rinsed by allowing hot tap water to flow over them. Boiling distilled water was then allowed to flow over them.

Method 7: After treatment the panels were given two successive rinses in cold distilled water. Followed by allowing hot tap water to flow over them.

SECTION X

STATISTICAL EVALUATION OF STRONG TREATMENTS

In an effort to evaluate the most promising of the strong treatments developed on this contract, an analysis was carried out on a statistical basis. The four main treatments, WS-4 for stainless steel, WT-4 for titanium, WM-13 for magnesium, and WAC-1 for aluminum, were used with the four adhesives recommended by WADC. The results shown in Table 22 give the value of the mean ($\overline{X}$), the value of one standard deviation (σ), and the 95% confidence interval of the mean. The tests used were:

(1) Room temperature shear.
(2) 30-day salt spray.
(3) Elevated temperature shear.
(4) Shear at elevated temperature after heat aging.

Table 22

SUMMARY OF DATA: STATISTICAL EVALUATION OF STRONG TREATMENTS

Adhesive	Room Temp. Shear			30 Day Salt Spray				Elevated Temp. Shear			Heat Aged		
	$\bar{X}$	σ	95% Conf. $\bar{X}$	$\bar{X}$	σ	95% Conf. $\bar{X}$	Control $\bar{X}$	$\bar{X}$	σ	95% Conf. $\bar{X}$	$\bar{X}$	σ	95% Conf. $\bar{X}$
TREATMENT: WAC-1 - METAL: Aluminum 2024-ST3													
FM-47	5158	163	5094-5222	5034	130	4919-5149	5044	2017	480	1537-2497	2662	684	1978-3346
4021	3926	175	3857-3995	2274	255	3275-3727	4150	2483	296	2187-2779	2916	199	2717-3115
422	2484	132	2432-2536	2274	103	2182-2366	2455	*2414	304	1855-2973	*2019	243	1279-2759
422								**1810	69	1686-1934	** 262	81	16-508
AF-6	2808	487	2575-3041	3385	184	3221-3549	3363	535	68	440-630	1268	202	987-1549
TREATMENT: WS-4 - METAL: Stainless Steel, Type 302, 1/2 Hard													
FM-47	6532	459	6351-6713	5769	410	5403-6135	6575	1277	155	1122-1432	2101	287	1814-2388
4021	2630	427	2462-2798	1551	238	1339-1763	2711	1396	325	1071-1721	1716	226	1490-1942
422	3380	181	3309-3451	2804	81	2732-2876	3358	*2746	604	1637-3855	3156	66	2956-3356
422								**2122	177	1798-2446	0	-	-
AF-6	1984	450	1807-2161	1380	203	1199-1561	2519	667	114	553-781	663	289	374-952
TREATMENT: WM-13 - METAL: Magnesium, FS 1-H4													
FM-47	3537	277	3428-3646	2136	332	1526-2746	3688	1762	280	1482-2042	3567	900	2667-4467
4021	2063	720	1779-2347	581	566	76-1086	1218	1263	659	604-1922	1099	482	617-1581
422	1594	86	1560-1628	1451	708	637-2265	1524	*1458	58	1352-1564	*1340	140	915-1765
422								**1090	47	1003-1177	0	-	-
AF-6	2441	595	2206-2676	1119	492	627-1611	2101	595	345	250-940	1132	275	857-1407
TREATMENT: WT-4 - METAL: Titanium, Rem Cru 110-M													
FM-47	7004	411	6818-7190	4275	262	4041-4509	5068	1898	337	1561-2235	4172	475	3697-4647
4021	2916	605	2677-3155	1446	268	1207-1685	2413	1965	296	1669-2261	1912	256	1656-2168
422	2000	138	1946-2054	821	512	364-1278	1671	*1901	88	1740-2062	*1362	95	1073-1651
422								**1714	152	1435-1993	** 607	93	324-890
AF-6	1569	240	1474-1664	1493	205	1310-1676	1440	742	624	118-1366	732	232	500-964

* at 300°F

** at 500°F

The shear tests at elevated temperature were carried out at 180 ± 2°F except in the case of Shell Epon 422 where the temperatures used were 300°F and 500°F. The elevated temperature shear tests after aging were carried out at 180 ± 2°F after 200 hours at 180 ± 2°F except in the case of Epon 422 where the test was carried out at 300 ± 2°F after 192 hours at 300 ± 2°F and at 500 ± 2°F after 192 hours at 500 ± 2°F.

The results with AF-6 are erratic and seem to indicate an aged adhesive. No conclusions may be drawn from the AF-6 data but the treatments seem to be satisfactory with FM-47 except for WM-13. In this case salt spray results on the unprotected metal are low as a result of corrosion under the bond line. WM-13 generally does not show the necessary corrosion protection and, if used, would require a protective paint or other coating.

SECTION XI

CONCLUSIONS AND RECOMMENDATIONS

11.1 Conclusions

(1) The effectiveness of treatments for stainless steel, magnesium, and titanium has been confirmed to a large degree with Bloomingdale FM-47 and to a lesser degree for the other adhesives. They are WS-4 treatment for stainless steel; WT-4 treatment for titanium; and WM-13 treatment for magnesium. These treatments are based on strong acid attack on the metal surface to remove organic and inorganic impurities.

(2) Surface treatments for stainless steel, aluminum, and titanium have been developed which consist essentially of dilute solutions of wetting agents in relatively mild acidic and basic media, and show promise of replacing the strong acid solutions. The problem of selecting the most effective treatment depends apparently on the proper selection of concentration, pH, and temperature. Joint strengths equal to the strength obtained with the strong acid treatment have been found with these mild solutions. They offer a feasible, relatively harmless, inexpensive solution to the problem of surface treatment.

(3) Test methods have been developed that are more sensitive to surface energy changes than contact angles in air. They are:

(a) Interfacial contact angle.
(b) Contact resistance.
(c) Hydrogen overvoltage.

The use of these tests to supplement the contact angle in air will probably make it possible to select the treatment and surface condition that is best prepared for maximum, uniform joint strength.

(4) The degree of scatter in data with the adhesives other than Bloomingdale FM-47 indicates a high degree of sensitivity of the adhesive to procedural and material variables, and points to the probability that specific affinity between metal and adhesives is an important parameter in the selection of an adhesive system. In addition, this parameter may be further compounded by a dependence of this affinity on the chemistry of the surface treatments.

(5) The results of the investigation into the role of the adsorbed film in adhesion indicate that the presence of an adsorbed film may influence bonding characteristics of one metal more than another. In addition, one type of adequate treatment may not effectively remove a particular type of film. Actually, we do not have enough data to warrant drawing firm conclusions. Additional work this coming year should give us enough information to enable us to relate the nature and thickness of the adsorbed film to effectiveness of the surface treatment and bonding characteristic in general.

11.2 Recommendations

We recommend that these areas be explored further:

(1) Continue the investigation of the change in surface properties of the test metals when modified solutions of wetting agents are used. Determine the effect of pH, concentration of acids and/or alkalis and their salts, and effect of type of wetting agent on cleaning performance.

(2) Investigate further the effect on surface properties and subsequent adhesional behavior of inorganic and organic preparations. These treatments are not to attack the metal to a point where dimensional changes take place.

(3) Continue the investigation of test methods for evaluating surface treatments. These are to include:

(a) Contact angles in air.
(b) Interfacial contact angles.
(c) Contact resistance measurements.
(d) Hydrogen overvoltage.
(e) Color indicators.

(4) Investigate the relationship of the chemical nature of the adhesives to type of surface treatment as shown by variations in joint strength.

(5) Continue the investigation of the role of the adsorbed film in adhesive bonding. Included in this study will be the relationship between the chemical structure of the film and adhesive strength for a variety of adhesives whether one effective treatment can remove all types of films, organic and inorganic.

(6) Tracer studies should be made of the wetting agents and inorganic radicals to ascertain whether adsorption occurs on the metal surface and to what extent these adsorbed materials affect adhesion and resistance to salt spray and heat.

(7) Effect on joint strength of the degree of humidity at the time of bonding.

(8) Continue salt spray tests.

APPENDIX I

MATERIALS USED IN THE EXPERIMENTS

METALS

(1) Aluminum alloy, Type 2024-ST3 clad, conforming to Federal Specification QQ-A368.

(2) Stainless steel, Type 302, conforming to military specification MIL-S-5059. Condition, 1/2 hard, No. 2 bright finish.

(3) Magnesium alloy, Dow FS-1-H24, .064 inch thickness.

(4) Titanium, Type RC-130-A, .064 inch thickness.

(5) Titanium, Type RC-110-M, .050 inch thickness.

ADHESIVES

(1) FM-47 (vinyl-phenolic type) Bloomingdale Rubber Co., Chester, Pennsylvania.

(2) Scotchweld AF-6 tape (nitrile rubber-phenolic type) Minnesota Mining and Manufacturing Co., Bristol, Pennsylvania.

(3) Metlbond 4021 tape (nitrile rubber-phenolic type) Narmco Resin & Coating Co., Costa Mesa, California.

(4) Epon 422 (epoxide-phenolic type) Shell Development Co., Emoryville, California.

APPENDIX II

EXPERIMENTAL PROCEDURE IN CONTACT ANGLE MEASUREMENTS

(1) 3/4" test squares of the metal are hand-wiped to remove superfluous grease and dirt.

(2) The squares are degreased by immersion for 10 minutes in trichloroethylene, with agitation.

(3) The squares are shaken air-dried.

(4) A square is placed in the teflon cell and a water drop of 3-4mm in diameter is placed on the sample.

(5) A profile photograph is taken after the drop has come to equilibrium for two minutes in the covered cell. The contact angle on the degreased surface is measured from this photograph.

(6) The metal sample is treated as described in the specifications with agitation.

(7) The sample is rinsed in warm (or 130°F) tap water (running 5 minutes very briefly in warm distilled water) and then air-dried.

(8) A drop is measured on the surface as above.

APPENDIX III

SURFACE TREATMENTS

All specimens are degreased in trichloroethylene for 10 minutes at room temperature before treatment.

ALUMINUM

WAC-1	Treat for 10 min at 150-160°F in:	
	30 parts water	
	10 parts sulphuric acid (sp. gr. 1.84)	
	1 part sodium dichromate	
WAC-7	Treat for 15 min at 140 ± 10°F in:	
	Triton X-100	1% by weight
	Water	99% by weight
WAC-9	a. Treat for 15 min at 150 ± 10°F in:	
	Triton X-100	1% by weight
	Isopropyl alcohol	4% by weight
	Water	95% by weight
	b. Treat in 1% trisodium phosphate solution for 10 min at room temperature until the discoloration is gone	
WAC-10	Treat for 15 min at 140 ± 10°F in:	
	Triton X-100	0.5% by weight
	Sulphuric acid (sp. gr. 1.84)	2.0% by weight
	Sodium dichromate	2.0% by weight
	Water	95.5% by weight
WAC-11	Treat for 15 min at 190 ± 10°F in:	
	Pluronic F-68	0.5% by weight
	Sodium dichromate	2.0% by weight
	Sulphuric acid (sp. gr. 1.84)	2.1% by weight
	Water	95.4% by weight
WAC-12	Treat for 5 min at 150 ± 10°F in:	
	Trisodium phosphate	0.5% by weight
	Water	99.5% by weight
WAC-13	a. Treat as in WAC-12	
	b. Rinse and treat in 0.5% HCL solution at 150 ± 10°F for 5 min	
WAC-14	Treat for 15 min at 170 ± 10°F in:	
	Pluronic F-68	0.5% by weight
	Sodium dichromate	2.0% by weight
	Sulphuric acid (sp. gr. 1.84)	4.2% by weight
	Water	93.3% by weight
WAC-15	Treat for 15 min at 170 ± 10°F in:	
	Pluronic F-68	0.5% by weight
	Sodium dichromate	2.0% by weight
	Sulphuric acid (sp. gr. 1.84)	6.3% by weight
	Water	91.2% by weight

WAC-16	Treat for 15 min at 155 ± 5°F in:	
	Pluronic F-68	0.1% by weight
	Sulphuric acid (sp. gr. 1.84)	4.2% by weight
	Water	95.7% by weight
WAC-17	Treat for 15 min at 155 ± 5°F in:	
	Pluronic F-68	0.1% by weight
	Sodium dichromate	1.0% by weight
	Sulphuric acid (sp. gr. 1.84)	8.4% by weight
	Water	90.5% by weight
WAC-18	Treat for 15 min at 155 ± 5°F in:	
	Pluronic F-68	1.0% by weight
	Sodium dichromate	2.0% by weight
	Sulphuric acid (sp. gr. 1.84)	4.2% by weight
	Water	92.8% by weight
WAC-19	Treat for 15 min at 155 ± 5°F in:	
	Pluronic F-68	0.1% by weight
	Sodium dichromate	3.0% by weight
	Sulphuric acid (sp. gr. 1.84)	1.0% by weight
	Water	95.9% by weight
WM-12	a. Treat for 10 min at 160-190°F in:	
	Sodium metasilicate	3.0 oz
	Sodium pyrophosphate	1.5 oz
	Sodium hydroxide	1.5 oz
	Nacconal NR	0.5 oz
	Water	1.0 gal
	b. Rinse and treat for 15 min at 175°F in 20% chromium trioxide solution	
WM-13	a. Treat for 10 min at 160-190°F in:	
	Sodium metasilicate	3.0 oz
	Tetrasodium pyrophosphate	1.5 oz
	Sodium hydroxide	1.5 oz
	Nacconal NR	0.5 oz
	Water	1.0 gal
	b. Rinse in cold water and treat for 15 min at 150°F in 20% chromium trioxide solution	
	c. Rinse in cold water. Final rinse in boiling water not to exceed 10 sec	
WM-14	a. Treat for 15 min at 150 ± 10°F in:	
	Trisodium phosphate	2.0% by weight
	Triton X-200	3.6% by weight
	Water	94.4% by weight
	b. Rinse in cold water. Final rinse in boiling water not to exceed 10 sec	
WM-15	Treat as in WM-14 followed by treatment in part b of WM-13	

STAINLESS STEEL

WS-1	Treat for 10 min at 160-190°F in:	
	Sodium metasilicate	3.0 oz
	Tetrasodium pyrophosphate	1.5 oz
	Sodium hydorxide	1.5 oz
	Nacconal NR	0.5 oz
	Water	1.0 gal
WS-4	Treat for 15 min at 120°F in:	
	35 ml saturated solution of sodium dichromate	
	1.0 liter sulphuric acid (sp. gr. 1.84)	
WS-8	Degrease by immersion in trichloroethylene for 10 min with intermittent agitation	
WS-22	Treat for 10 min at 150-160°F in:	
	Sulphuric acid (sp. gr. 1.84)	10% by volume
	"Activol 57-X"	0.5% by wt of H_2SO_4
	Water	90% by volume
WS-28	a. Treat for 15 min at 194°F in:	
	Triton X-200	3.6% by weight
	Trisodium phosphate	2.0% by weight
	Water	94.4% by weight
	b. Rinse and immerse for 10 min at room temperature in:	
	Nitric acid	10% by volume
	Hydrofluoric acid	2% by volume
	Water	88% by volume
WS-29	Treat for 15 min at 150°F in:	
	Triton X-200	3.6% by weight
	Trisodium phosphate	4.0% by weight
	Water	92.4% by weight
WS-30	Treat for 15 min at 150 ± 10°F in:	
	Triton X-200	3.6% by weight
	Trisodium phosphate	6.0% by weight
	Water	90.4% by weight

TITANIUM

WT-2	Treat for 15 min at room temperature in:	
	Nitric acid	22.5% by volume
	Hydrofluoric acid	2.5% by volume
	Water	75.0% by volume
WT-3	Same as WS-29	
WT-4	Same as WS-4	
WT-5	Treat for 15 min at 150°F in:	
	Triton X-200	3.6% by weight
	Sodium hydroxide	2.0% by weight
	Water	94.4% by weight
WT-6	Treat for 15 min at 150°F in:	
	Triton X-200	3.6% by weight
	Sodium metasilicate	2.0% by weight
	Water	94.4% by weight
WT-8	Same as WS-8	

APPENDIX IV

CODE FOR SURFACE ACTIVE AGENTS

	Code No.	Chemical Composition
Triton X-200	A-1	Sodium salt of an alkyl aryl polyether sulfonate
Triton 777-conc.	A-2	Sodium salt of an alkyl aryl polyether sulfonate
Tergitol wetting Agent P-28	A-3	Sodium salt of di-2-ethylhexyl phosphate
Alipal co-436	A-4	Sulfate ester of an alkyl phenoxy-polyoxyethylene ethanol
Alconox	A-5	Alkyl naphthalene sulfonate + polyphosphate
Igepon CN-42	A-6	Sodium-N-cyclohexyl-palmitoyl taurate
Nullapon BF-12	A-7	Tetrasodium salt of ethylenediamine tetra-acetic acid
Nullapon FE-12	A-8	Not known
Tergitol 7	A-9	Sodium Heptadecyl sulfonate
Activol 57X	A-10	Not known
Nacconal NR	A-11	Alkyl benzene sulfonate
Aerosol OT 75%	A-12	Sodium dioctyl sulfosuccinate
Triton K-60	C-1	Stearyl dimethyl benzyl ammonium chloride
Armac 12-D	C-2	Doceylamine acetate + laurylamine acetate
Triton X-100	N-1	Alkyl aryl polyether alcohol
Pluronic F-68	N-2	Polyoxypropylene-polyoxyethylene condensate
Pluronic L-61	N-3	Polyoxypropylene-polyoxyethylene condensate
Pluronic L-62	N-4	Polyoxypropylene-polyoxyethylene condensate
Pluronic L-64	N-5	Polyoxypropylene-polyoxyethylene condensate

NOTE: A - Anionic
C - Cationic
N - Non-ionic