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TECHNICAL REPORT 3495

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Technical Report 3495

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by

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OBJECTIVE

To compare the effect of deionized water immersion and tap water immersion on the bondability of 2024 aluminum which has just undergone sulfuric acid-sodium dichromate surface treatment.

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SUMMARY

The effects of immersion in deionized water and in tap water on the bondability of 2024 aluminum which had been surface-treated with sulfuric acid-sodium dichromate solution were compared. Substantial losses in bond strengths were experienced with aluminum that had been immersed in deionized water. Poor bonding surfaces were readily identifiable from the formation of an iridescent coating which further investigation revealed to be related to the thickness of the hydrate layer formed. Addition of certain multivalent compounds to the deionized water was found to affect the formation of the hydrate layer and subsequently to increase the bond strengths.

CONCLUSIONS

Prolonged immersion (15 minutes or more) of sulfuric acid-sodium dichromate pretreated aluminum in deionized rinse water at 60°C results in iridescent appearance of surfaces and subsequent substantial loss in adhesive bondability of the surfaces. Limited tests have shown that the development of the iridescence and loss of bondability are not related to the acid pretreatment but that these phenomena are solely functions of the deionized water immersion.

When the aluminum is immersed in pure deionized water at 60°C, $Al_2O_3 \cdot 3H_2O$ is formed, a phenomenon known as sealing. This hydrated layer is cohesively weak and greater than 1000 A units thick, hence the visible interference colors (iridescence).

Multivalent compounds added to deionized water preferentially absorb into the aluminum oxide and block the entrance of water, thereby preventing further attack. The mechanism for this might

p2

be through the formation of spinels; hence, no buildup in thickness or the oxide layer due to formation of the trihydrate occurs, no interference colors are visible, and good bond strengths are obtained.

If the deionized water is made acidic or alkaline (defined here as having a pH below 5.5 or above 7.5), the hydrated oxide is dissolved and only a thin Al_2O_3 layer remains. Therefore, good bond strengths are obtained.

RECOMMENDATIONS

Since the mineral salt content of potable tap water varies widely throughout the country, it is recommended that, when chemical treatments of aluminum alloys are used prior to adhesive bonding, a modified deionized water be used in rinsing the treated surface. The modification should involve the addition of certain types of compounds to a high purity deionized water. These compounds should preferably be such as to effect a slight acidity (pH below 5). Multivalent compounds such as H_2SO_4, $MgSO_4$, CrO_3, $Na_2Cr_2O_7$, Na_2SO_4, $FeCl_2$, and $FeCl_3$ are effective for modifying deionized water to give good bonding surfaces.

It is further recommended that alkaline compounds such as $NaHCO_3$, Na_2CO_3, and K_2CO_3 be omitted. These allow good bond strengths to be obtained but have been found to attack and discolor the aluminum.

It is further recommended that additional studies be made of the effects of adding the ions mentioned in the first recommendation above on the corrosivity of the aluminum.

Specification MIL-A-9067C, "Adhesive Bonding, Process and Inspection Requirements For" should be revised to caution users of the danger of prolonged rinse times, when deionized water is used after sulfuric acid-sodium dichromate treatment of aluminum surfaces.

INTRODUCTION

In a previous investigation by Wegman (Ref 1) of the effects of an inert atmosphere on the bonding of metals it was found that, when aluminum alloy is immersed in water at temperatures above 60°C prior to adhesive bonding, the resultant bond strength is related to the type of water in which the part is immersed and, to a lesser degree, to the temperature of the water. Immersion of the aluminum in warm distilled or deionized water was reported to be undesirable from the standpoint of adhesion while immersion in potable tap water was found less harmful to adhesion. Most process specifications for the adhesive bonding of aluminum in use today (military and civilian) call for the use of warm deionized water rinses after the chemical treatment of the metal. Further investigation of the effect of using various types of water was therefore considered imperative.

During the initial studies, some preliminary investigations of the use of electron diffraction were made. On the basis of these investigations, a contract was awarded to Stevens Institute of Technology under which they were to attempt to determine the differences in the surfaces which existed after various prebonding treatments. Weil and Everson (Ref 2) concluded that substances found on the surfaces of aluminum treated for bonding were essentially noncrystalline and that the noncrystalline material appears to obscure the pattern obtained by reflection diffraction. They also reported that some samples immersed in deionized water showed extra diffraction rings which were tentatively identified as Cr_2O_3. Reevaluation of these rings (Ref 3) since publication of their report indicates that they might also be $Al_2O_3 \cdot 3H_2O$ (bayerite).

DISCUSSION OF RESULTS

In conjunction with the electron diffraction studies conducted by Weil and Everson at Stevens Institute of Technology, adhesion studies were conducted at Picatinny Arsenal. A summary of the results of these studies is shown in Table 1. The data shows that the relative effect of the deionized water on aluminum is the same with respect to adhesion regardless of the pretreatment. In all cases, a substantial loss in bond strength occurred after deionized water rinse as compared to tap water rinse. The treatment given as acid etch (Ref 4) is a 10-minute immersion in a solution consisting of 1 part by weight (pbw) sodium dichromate, 10 pbw concentrated sulfuric acid, and 30 pbw water. The electropolishing was done by Stevens Institute in a solution consisting of 25 cc methyl alcohol, 25 cc nitric acid, and 1 cc hydrochloric acid at a current density of 10.7 amp/sq in.

During the investigation, a number of possibilities were considered as to why deionized water immersion gives lower bond strengths than tap water immersion. The first was the difference in the pH of the two waters. In the preliminary work the pH of the deionized water was reported as being 6.38 while the pH's of two sources of tap water were reported as being 7.77 and 7.45. The respective adhesive bond strengths were reported as 990, 2960, and 2920 psi. To evaluate the effect of this variation in pH, the aluminum alloy was treated in solutions of varying pH values. The pH values of the solutions were determined at 23°C before and after the aluminum was immersed for the prescribed 30 minutes at 60°C. The aluminum parts were allowed to air dry and were then bonded together to form lap shear specimens having a 1 × 1/2-inch bonded area. The data obtained from tensile testing of these specimens can be seen in Table 2. It can be noted from this data that, in general, there was a rise in pH level after the 30-minute immersion. The bond strengths obtained in this set of experiments indicated that adjusting the pH up to that of the tap water does not eliminate the bonding problem. However, the addition of magnesium sulfate or chromium trioxide did appear to eliminate the problem. The addition of sodium chloride resulted in an initial pH of 5.5, as with the magnesium sulfate. However, the bond strengths were not comparable in these two cases. In all cases in which poor bonds were obtained, the typical failure was adhesive and the faying surface was discolored and iridescent.

For the purposes of this report, an adhesive failure will be considered as a failure which occurs outside of the adhesive. It may be at the adhesive-adherend interface or in the surface layer of the adherend material. Cohesive failure always occurs in the adhesive, leaving a layer of adhesive on both faying surfaces after failure of the bond.

The second possibility considered was that some ion from the acid etch was present on the surface of the samples treated in the tap water but not on those treated in deionized water. It was thought that if the chromium ion, for instance, was absorbed on the surface during the acid etch it might be dissolved off in the deionized water. Possibly, however, the high salt content of the tap water would not allow the dissolving of all of the chromium from the surface. To investigate this possibility, samples of aluminum treated by the various immersions were analyzed by x-ray fluorescence techniques. The results of these analyses are given in Table 3. From the results, it is concluded that nothing significant is added to the surface by the acid etch which is removed by the deionized water and not by the tap water.

A third consideration to be investigated was whether the observed phenomenon was peculiar to the alloy or true of pure aluminum also. It was thought that possibly the alloy constituents had something to do with this phenomenon. A set of experiments was drawn up in which both alclad and bare 2024 alloy specimens were used. The length of time in the acid etch was also changed so as to use both 5- and 10-minute immersions to determine any acid attack on the alloy constituents. The results are shown in Table 4. The data in this table shows that discoloration, iridescence, and poor bond strengths after immersion in deionized water are not peculiar to either the alloy or the pure aluminum and have nothing to do with the immersion time in the acid over the time periods studied in this test series. To further investigate the role of the acid etch, parts made of both alclad and bare 2024 alloy were vapor degreased in perchloroethylene vapors and subjected to 30 minutes immersion at 60°C in either tap or deionized water without an intermediate acid treatment. The results of this investigation can be seen in Table 5. From the data in this table, it is again evident that immersion in deionized water is undesirable from the standpoint of adhesion, and that the discoloration and iridescence which appear on the surface have nothing to do with the acid etch. As expected, the bond strengths were lower than when the surface was acid etched.

To review the findings to this point, it was seen that the difference in pH of the tap water and the deionized water is not the cause of the iridescence and poor bond strengths. Further, the problem has nothing to do with adding anything to or removing anything from the acid etch solution. Also, the problem is not peculiar to either pure or alloy aluminum.

As was pointed out in the original investigation, when aluminum is corroded in water the product is usually beta-trihydrate. When the water temperature is maintained at 70° to 100° C, the alpha-monohydrate tends to form. It was also pointed out that Harrington and Nelson showed in 1940 (Ref 5) that sheet aluminum which is not anodized will acquire a film of alpha-monohydrate when it is heated in water at 80° C or higher but not when it is heated at 60° C.

The next theory to be investigated then was that the iridescent colors and the weak bonds were related to absorbed water or water of hydration. By use of x-ray fluorescence techniques, a comparison of the relative thickness of the surfaces was made. Analyzing for aluminum gave the following counts per 100 seconds:

Bare vapor-degreased 2024T-3 alloy	1008
Acid-etched 2024T-3 alloy	1080
Acid-etched and tap-water-immersed 2024T-3 alloy	1095
Acid-etched and deionized-water-immersed 2024T-3 alloy	867

If the count obtained is related to the thickness of a coating, then the lower the count obtained, the thicker the coating on the surface. What can be deduced from these figures then is that the acid etch removes the oxide from the bare alloy, and atmospheric oxidation reoxidizes the surface in a short time but not to the original thickness. Immersion in tap water does not appear to cause any further buildup in the thickness of the oxide coating. However, immersion in deionized water for 30 minutes at 60°C increases the thickness of the coating. Crude calculations reveal that the increase in thickness over that on the acid-etched alloy is 1000 A units or greater. It was noted during testing that while the specimen is under the vacuum for analysis the iridescence appears to diminish. It is assumed that the vacuum dehydrates the oxide.

To further study hydrated aluminum oxide, panels of 2024T-3 bare alloy were treated with the acid etch and then immersed in deionized water at 60°C for 15 minutes. Again the iridescent colors developed. One-half of the panels were air dried for about 2 hours at room temperature and then bonded while the other half were force-dried in a tube furnace at 260° C for 1 hour in a flow of dry nitrogen. After the force-drying, most of the iridescence had disappeared. The bond strength to the air-dried iridescent surface was about 2000 psi, the failure being adhesive. The bond strength to the force-dried specimen was about 3100 psi, the failure being cohesive.

Thus the data shows that, when the aluminum is immersed in deionized water, a hydrated surface more than 1000 A units thick is formed to which strong bonds cannot be obtained or which is very weak cohesively in its structure. However, this does not explain why tap water acts differently, i.e., why it is more desirable from the standpoint of adhesion.

Wernick and Pinner (Ref 6) in their book on surface treatments of aluminum point out that "when aluminum is immersed in hot water, a more-or-less dense protective oxide film forms. The structure of this film and its chemical composition vary particularly with the temperature of the water. In pure water up to about 75° to 80° C this film appears to consist mainly of bayerite, $Al_2O_3 \cdot 3H_2O$, with some other undefined hydrates." These authors go on to explain the growth of the hydrated oxide film by the following half-cell reactions:

The anodic reaction is

$$Al \rightarrow Al^{+3} + 3e^-$$

while the cathodic reaction is

$$H_2O + e^- \rightarrow OH^- + \tfrac{1}{2} H_2.$$

Hydrogen, which is evolved as a gas, can be seen leaving the surface in the early stages of immersion. The cathodic reaction renders the solution more alkaline than the original (note the final pH readings in Table 2). The hydroxyl ion reacts with the aluminum ions to form the hydrated oxide and similar compounds

$$2Al^{+3} + 6OH^- \rightarrow Al_2O_3 + 3H_2O$$

The authors (Wernick and Pinner) refer to the work of Ginsberg and Wafer (Ref 8), who believe that in hot water, aluminum ions migrate through the oxide film, the free lattice sites being taken up by oxygen ions to form an oriented hydrate. Further reference is made to the work of Domony and Lichtenberg-Bajza (Ref 9), which states that an equilibrium is set up between oxidation and movement of metal ions at an oxide/metal interface. The equilibrium is disturbed when the oxide is soluble in the environment. Since the resistance of the hydrate is less than that of the oxide, the film continues to grow. Under these conditions, therefore, the temperature determines not only the thickness but also the structure.

While discussing the sealing of aluminum surfaces, Wernick and Pinner (Ref 7) also discuss the effect of water characteristics. They point out that not only the temperature and time but also the type of water used for sealing is important: "with nearly neutral tap water the sealing efficiency, even at optimum temperature, does not reach 100%, probably due to precipitation of lime in the pores...with distilled water, however, complete sealing is obtained even at 80° C." Figure 1 is a graph based on information taken from Wernick and Pinner (Ref 7) which shows sealing efficiency as a function of sealing temperature for three types of water. If it is recalled that the water immersion investigations were conducted at 60° C, it will be seen that in deionized water the surfaces will be approximately 80% sealed and, as mentioned earlier in this report, the compound formed will be mainly $Al_2O_3 \cdot 3H_2O$. It has been known for a long time that good bonds cannot be effected to aluminum surfaces that are anodized and hot water sealed.

It has been recognized for some time that potable tap water can vary from one location to the next. That is why the use of deionized water has been called for in process specifications for the fabrication of bonded assemblies. A further reason for the use of deionized water in the production setup has been a matter of economics. It is too costly to be constantly discarding rinse waters, yet quality control requires fresh supplies of rinse waters. Deionization units are therefore used to purify and reclaim the

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water. Because it saves money, deionized water is and will continue to be used to rinse production lots of aluminum parts which are chemically prepared for bonding. Since we now have a better understanding of what happens to parts immersed in deionized water at 60° C, the problem is to prevent the formation of the undesirable hydrated surfaces.

To determine a possible solution to this problem, a different chemical was added to each of several samples of deionized water. Acid-etched alclad aluminum alloy was then immersed in one of the solutions for 30 minutes at 60° C. Table 6 identifies the additive, the bond strength obtained after immersion, the type failure after test, the color of the faying surface after immersion, and the valence of the compound. From the data presented in this table, it can be seen that when multivalent compounds are added, there is no coloration of the metal, and high subsequent bond strengths with cohesive failure are obtained. Addition of monovalent compounds to the deionized water, on the other hand, results in iridescence, adhesive failure, and lowered bond strength. The addition of sulfuric acid and hydrogen peroxide lowers the pH of the solution below the initial 5.5. No coloration develops, since the acid dissolves the oxide coating as it is formed. The addition of basic compounds such as the carbonates and the bicarbonate caused typical alkaline attack, with a gaseous evolution and darkening of the aluminum surface. However, the pH is such that, as fast as the $Al_2O_3 \cdot 3H_2O$ is formed by OH^-, it is also dissolved. The bond strength to the resultant surface is good, with cohesive type failure resulting when the joint is loaded to ultimate strength. However, the addition of chemical compounds to deionized rinse water should not be considered for production application without further investigation as to the effects on the metal and on the durability of the bond.

TABLE 1

Effects of pretreatment before water immersion on the adhesive bond strength to aluminum

Treatment	al Average Shear Strength, psi
al Acid Etch	3240
Acid Etch + 30 min immersion in tap water at 60°C	3030
Acid Etch + 30 min immersion in deionized water at 60°C	1850
al Electropolish + acid etch	2130
Electropolish + acid etch + 30 min immersion in tap water at 60° C	2030
Electropolish + acid etch + 30 min immersion in deionized water	400

TABLE 2

Effect of pH variation on the bondability of water-immersed aluminum alloy

Solution	Deionized Water	NaOH-pH adjusted Deionized H_2O	0.05% NaCl in Deionized H_2O	0.05% $MgSO_4$ in Deionized H_2O	150 ppm CrO_3 in Deionized H_2O
Initial pH (before aluminum immersion)	5.9	7.8	5.5	5.5	3.5
Final pH (after aluminum immersion)	8.8	7.8	6.9	7.5	3.6
Bond Strengths, psi	1580	1570	1500	2700	2660
	1380	700	1560	2800	2640
	820	500	1240	2840	2860
	1580	1350			
	1420	1100			
Average	1360	1040	1430	2780	2720
Type of Failure	Adhesive	Adhesive	Adhesive	Cohesive	Cohesive
Appearance of Faying Surface after Immersion	Discoloration and iridescence	Discoloration and iridescence	Medium discoloration and iridescence	No color or iridescence	No color or iridescence

TABLE 3

X-ray fluorescence analyses of aluminum surfaces

	Elemental Analysis														
Specimen	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Ti	Ca	Sb	Sn	Si	Cl	S	Mg
Vapor-degreased 2024T-3	Tr[a]	Pr[b]	Pr[b]	Possible trace	Pr[b]	Tr[a]	None	Tr[a]	Tr[a]	None	Present	Tr[a]	Tr[a]	Tr[a]	Not tested
Acid-etched 2024T-3	Tr[a]	Pr[b]	Less than original	Possible trace	Pr[b]	Tr[a]	None	Tr[a]	Tr[a]	None	Negative	Tr[a]	Tr[a]	Tr[a]	
Acid-etched 2024T-3, tap water immersed	Tr[a]	Pr[b]	Less than original	Possible trace	Pr[b]	Tr[a]	None	Tr[a]	Tr[a]	None	Negative	Tr[a]	Tr[a]	Tr[a]	
Acid-etched 2024T-3, deionized water immersed	Tr[a]	Pr[b]	Less than original	Possible trace	Pr[b]	Tr[a]	None	Tr[a]	Tr[a]	None	Negative	Tr[a]	Tr[a]	Tr[a]	
2024T-3 alloy composition, %	0.1	0.6	0.5	-	4.5	0.1	-	Tr[a]	-	-	-	0.5	-	-	1.5

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[a] Tr = trace.
[b] Pr = present.

TABLE 4

Effect of water immersion on acid-etched alclad and bare aluminum

	Alclad				Bare Alloy			
		Shear Strength,	Type of Failure			Shear Strength,	Type of Failure	
Treatment	Appearance	psi	% Adhesive	% Cohesive	Appearance	psi	% Adhesive	% Cohesive
10 min. acid etch, 30 min. deionized water immersion	Brownish with some iridescence	1040[a]	100		Iridescent	1640[a]	100	
		460[a]	100			1920[a]	100	
		720[a]	100			960[a]	100	
10 min. acid etch, 30 min. tap water immersion	No iridescence	3160		100	No iridescence	3100		100
		3260		100		3040		100[c]
		3280		100		3320		100
5 min. acid etch, 30 min. deionized water immersion	Iridescent	1180[a]	100		Iridescent	380[a]	100	
		1140[a]	100			660[a]	100	
		1320[a]	100[b]			740[a]	100	
5 min. acid etch, 30 min. tap water immersion	No iridescence	2880		100	No iridescence	3280		100
		2880		100		3100		100
		3360		100		3200		100

---

[a] Scatter in values was noted as a function of the type of failure in the adhesive fillet.

[b] 95% to one adherend, 5% to other adherend.

[c] Cohesive failure very close to interface.

TABLE 5

Effect of water immersion on vapor-degreased alclad and bare aluminum alloy

	Alclad				Bare Alloy			
		Shear Strength	Type of Failure			Shear Strength,	Type of Failure	
Treatment	Appearance	psi	% Adhesive	% Cohesive	Appearance	psi	% Adhesive	% Cohesive
Vapor degreased, 30 min. deionized water immersion	Iridescence	520	100		Iridescence	280	100	
		360	100			400	100	
		380	100			600	100	
Vapor degreased, 30 min. tap water immersion	No iridescence	1460	85	15	No iridescence	1760	75	25
		1940	85	15		2380	75	25
		1380	85	15		1980	75	25

TABLE 6

The effect of additives to deionized water on bond strength to treated aluminum

Group	Additive	Strength, psi	Type Failure	Color After Immersion	Valence	Comments
A	$NaHCO_3$	3240	Cohesive	Tan	Mono	Alkaline attack
		3120				
		2780				
		Avg 3050				
B	$Na_2Cr_2O_7$	3160	Cohesive	No color	Di	
		3120				
		3110				
		Avg 3130				
C	$FeCl_3$	3260	Cohesive	No color	Tri	
		2800				
		3240				
		Avg 3100				
D	$BaCl_2$	2420	Cohesive	No color	Di	
		2940				
		3000				
		Avg 2790				
E	H_2SO_4	3060	Cohesive	No color	Di	Acidic attack
		3180				
		3270				
		Avg 3170				
F	None	1240	Adhesive	Iridescent	--	
		1200				
		1120				
		Avg 1190				
G	None	900	Adhesive	Iridescent	--	
		680				
		1000				
		Avg 860				
H	$MgSO_4$	2700	Cohesive	No color	Di	
		2800				
		2840				
		Avg 2780				
I	CrO_3	2660	Cohesive	No color	Di	
		2640				
		2860				
		Avg 2760				
J	Na_2CO_3	2540	Cohesive	Brown	Di	Alkaline attack
		2360				
		2940				
		Avg 2610				

TABLE 6 (Cont)

Group	Additive	Strength, psi	Type Failure	Color After Immersion	Valence	Comments
K	K_2CO_3	2140 2600 2280 Avg 2340	Cohesive	Brown	Di	Alkaline attack
L	$NaC_2H_3O_2$	1060 Broke in handling 980 Avg 1020	Adhesive	Iridescent	Mono	
M	KCl	420 1220 960 Avg 870	Adhesive	Iridescent	Mono	
N	$NaNO_2$	300 760 360 Avg 470	Adhesive	Iridescent	Mono	
O	K_2SO_4	2700 2960 2880 Avg 2850	Cohesive	No color	Di	
P	$FeCl_2$	2680 3060 2780 Avg 2840	Cohesive	No color	Di	
Q	NaCl	480 420 1440 Avg 780	Adhesive	Iridescent	Mono	
R	H_2O_2	2900 3000 2360 Avg 2750	Cohesive	No color	--	Adjusted to pH 4.5 from initial pH 5.5
S	$NaHCO_3$ repeat of (A)	2540 3040 2800 Avg 2790	Cohesive	Tan	Di[a]	Alkaline attack
T	Tap water used instead of deionized	3030 Avg of many tests	Cohesive	No color	--	

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[a] It is possible that some carbonate is formed.

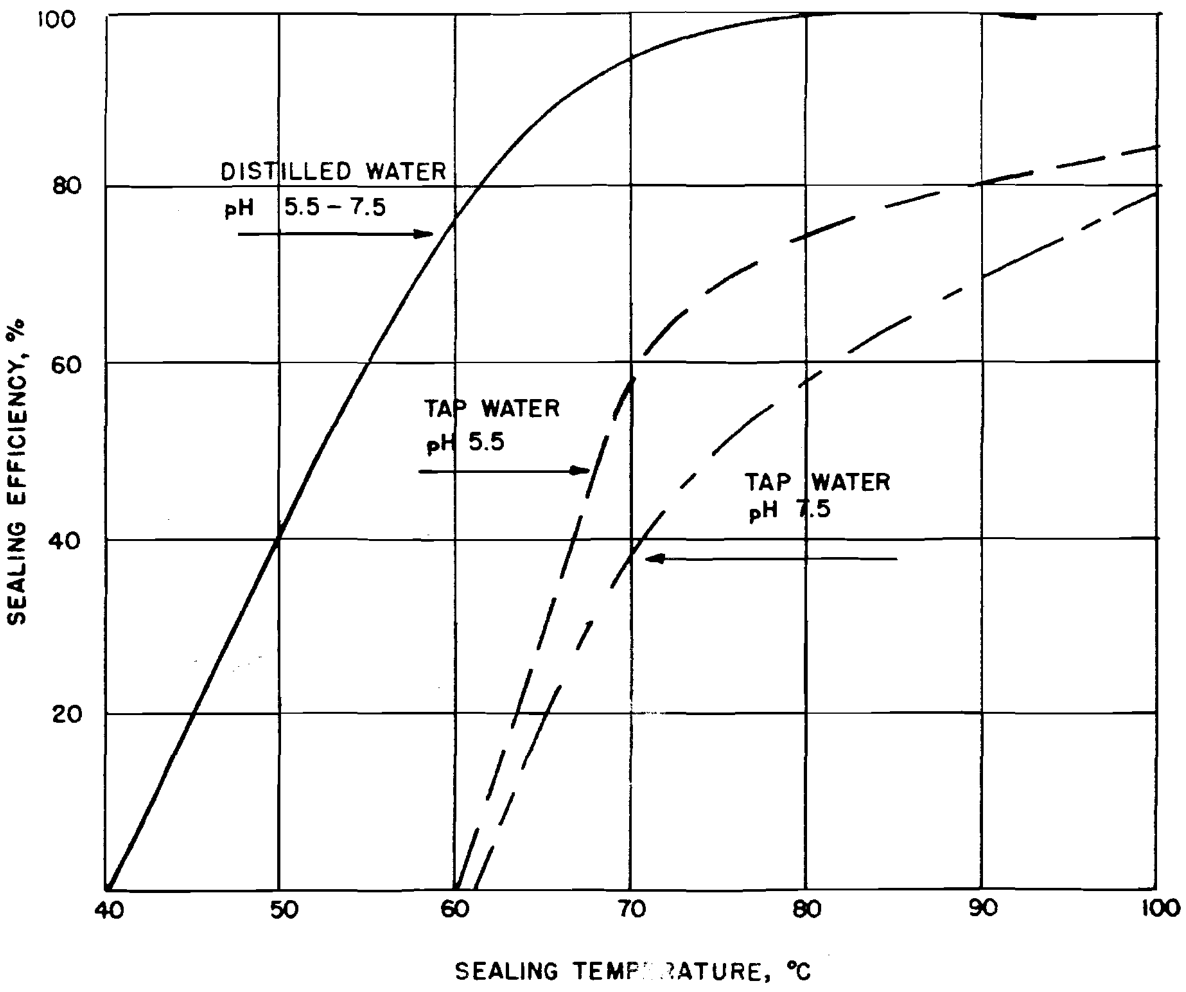

Fig 1 Effect of temperature, type of water and pH on sealing of alumina (Ref 7)

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13. ABSTRACT

The effects of immersion in deionized water and in tap water on the bondability of 2024 aluminum which had been surface-treated with sulfuric acid-sodium dichromate solution were compared. Substantial losses in bond strengths were experienced with aluminum that had been immersed in deionized water. Poor bonding surfaces were readily identifiable from the formation of an iridescent coating which further investigation revealed to be related to the thickness of the hydrate layer formed. Addition of certain multivalent compounds to the deionized water was found to affect the formation of the hydrate layer and subsequently to increase the bond strengths.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Adhesives						
Surface treatment						
2024 aluminum						
Deionized water						
Bond strength						
Bonding of aluminum						
Bonding metals						

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