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Adhesion Promoters for Bonding Titanium

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DAVID W. TAYLOR NAVAL SHIP RESEARCH AND DEVELOPMENT CENTER

Bethesda, Md. 20084

ADHESION PROMOTERS FOR BONDING TITANIUM

by

M. E. Schrader and J. A. Cardamone

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RESEARCH AND DEVELOPMENT REPORT

April 1977

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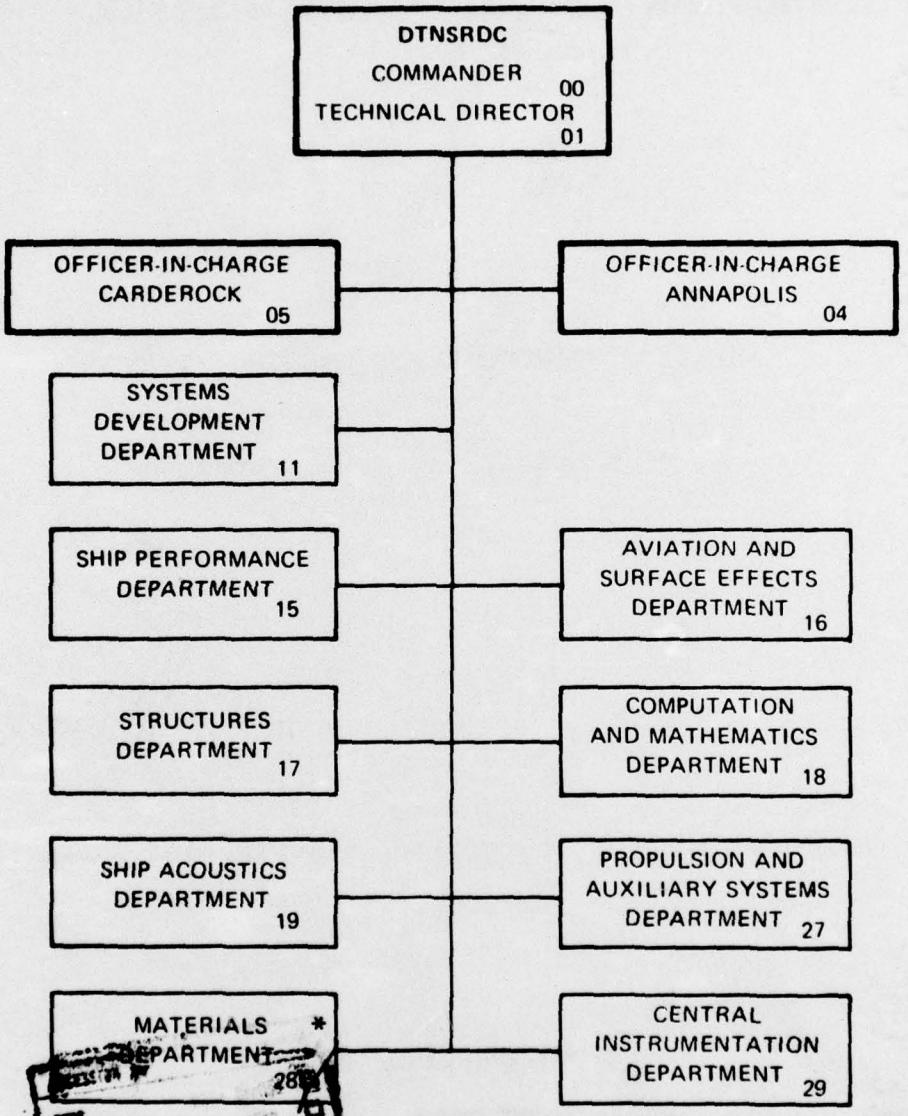

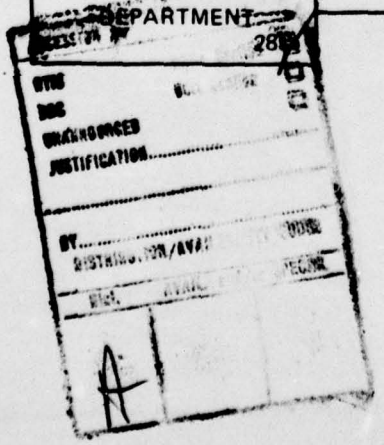

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An investigation was undertaken to determine the feasibility of using adhesion promoters to improve the interfacial bond between titanium and structural adhesives. A compound was sought whose molecules contain one functional group that can chemically bond to the titanium surface and another functional group that can chemically bond to the desired adhesive resin.

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20. Abstract (cont)

Inasmuch as certain titanium compounds chemically bond to a silica surface via an Si_s-O-Ti linkage (the subscript s represents a surface atom), it was deemed possible that compounds of silicon can chemically bond to a titanium surface via a Ti_s-O-Si linkage, where the oxygen originates from the surface oxide layer always present on titanium. To verify this postulate, the dry and wet strengths of titanium/epoxy/titanium lap-shear joints were determined, utilizing gamma-aminopropyltriethoxysilane as the adhesion promoter. The lap-shear joints using gamma-aminopropyltriethoxysilane were found to be approximately 25% stronger dry and more than 50% stronger after water exposure than joints prepared with standard surface treatments. It may be inferred that similar improvements can be expected when suitable organosilane compounds are used as adhesion promoters for bonding titanium with polyester, phenolic, and other thermosetting resins.

(Authors)

ADMINISTRATIVE INFORMATION

This investigation is part of an in-house research program of the David W. Taylor Naval Ship Research and Development Center. It was conducted under Task Area ZR 0220101. Work was performed under Work Unit 2870-108.

LIST OF ABBREVIATIONS

APS - gamma-aminopropyltriethoxysilane

BDMA - benzyldimethylamine

° C - degrees Celsius

cm - centimetres

etc - and so forth

° F - degrees Fahrenheit

NMA - nadic methyl anhydride

phr - parts per hundred of resin

psi - pounds per square inch

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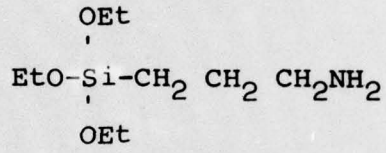
ABSTRACT

An investigation was undertaken to determine the feasibility of using adhesion promoters to improve the interfacial bond between titanium and structural adhesives. A compound was sought whose molecules contain one functional group that can chemically bond to the titanium surface and another functional group that can chemically bond to the desired adhesive resin. Inasmuch as certain titanium compounds chemically bond to a silica surface via an Si_s-O-Ti linkage (the subscript s represents a surface atom), it was deemed possible that compounds of silicon can chemically bond to a titanium surface via a Ti_s-O-Si linkage, where the oxygen originates from the surface oxide layer always present on titanium. To verify this postulate, the dry and wet strengths of titanium/epoxy/titanium lap-shear joints were determined, utilizing gamma-aminopropyl-triethoxysilane as the adhesion promoter. The lap-shear joints using gamma-aminopropyl-triethoxysilane were found to be approximately 25% stronger dry and more than 50% stronger after water exposure than joints prepared with standard surface treatments. It may be inferred that similar improvements can be expected when suitable organosilane compounds are used as adhesion promoters for bonding titanium with polyester, phenolic, and other thermosetting resins.

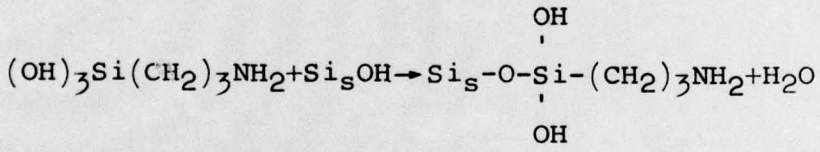
INTRODUCTION

The need for materials with a high strength-to-weight ratio for high performance naval vessels has led to considerable effort in promoting the increased utilization of titanium. Development of a fabrication technology for this metal has been a goal of vital importance in effecting its increased utilization in both aircraft and sea-going vessels. The fabrication of titanium for naval application has been especially difficult because of the thicker sections required as compared to those utilized in aircraft structures. One method of alleviating problems in fabrication has been the use of high strength organic adhesives in place of conventional welding or riveting. Since adhesion at the interface of metal and adhesive is often the weak link in adhesive bonding, treatment of the metal surface is of vital importance in improving the strength, reliability, and environmental resistance of the structural adhesive bond. Of particular importance is the possibility of water penetration at the interface of adhesive and titanium, due to the strongly hydrophilic nature of the titanium surface.

A similar problem has been encountered in the glass-fiber-reinforced plastics industry, where the hydrophilic nature of glass resulted in the entry of liquid water along the fiber-resin interface when subjected to long-term immersion in water at ambient temperature or short periods of immersion in water at elevated temperatures. It was found that this problem could be solved through the use of adhesion promoters called coupling agents which would form a bridge of chemical bonds between the glass surface and the resin matrix, thus preventing the entry of liquid water into the interface with concomitant debonding of resin from fiber.[1] In addition to the prevention of degradation from moisture exposure, it has been found that these adhesion promoters also improve dry-state adhesion at the interface in these composites. Coupling agents for glass/resin systems are usually silane derivatives. An example of a coupling agent for glass-reinforced epoxy resin systems is APS*



where the ethoxy (OEt) groups hydrolyze to form hydroxyls, which in turn condense with silanols on the fiber surface to form siloxane linkages, as follows:



The NH_2 in turn reacts with the epoxy resin to complete the bridge of chemical bonds. The stability of the surface siloxane linkage is, of course, not surprising since glass itself is composed of siloxane linkages. When silane-based coupling agents have been randomly tried on other types of reinforcement, such as carbon fibers however, the treatment was not effective since no bond of comparable stability to the siloxane bond could be formed.

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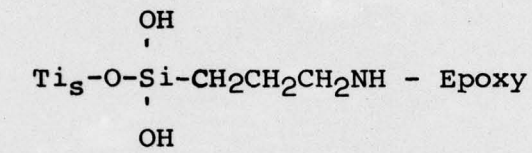
[1]Superscripts refer to similarly numbered entires in the Technical References at the end of the text.
*Definitions of abbreviations used are given on page i.

In a recent study on the kinetics of reaction of various vapors with the surface of silica gel,[2] it was found that $TiCl_4$ is very reactive to Si_sOH groups (where Si_s is surface silicon), apparently yielding the Si_s-O-Ti group. Inasmuch as the Si_s-O-Ti linkage, based on a surface silicon and attached titanium, is so stable, it is quite likely that the Ti_s-O-Si linkage, consisting of a surface titanium and attached silicon, is also stable. Since there is always a layer of chemisorbed oxygen or oxide on an air-exposed Ti surface, the same compounds and methods used to form the Si_s-O-Si linkage on glass might be used to form the Ti_s-O-Si bond on titanium. This means that the coupling agents presently used to chemically link glass to various resins can be used to link titanium to these same resins. For example, APS could couple titanium to epoxy as follows:



Since the efficacy of the -NH- epoxy bond is well established, the performance of this compound should depend solely on whether or not hydrolytically stable Ti_s-O-Si linkages are indeed formed on application of the coupling agent to the titanium surface under suitable conditions. If they are formed, then members of the family of silane derivatives that have been developed for selectively coupling glass fibers to different types of resin (each derivative is specific to a certain type of resin) could now be useful for selectively improving the adhesion of titanium to these resins when used as structural adhesives. To test the validity of the concept (formation of the Ti_s-O-Si linkage), epoxy titanium adhesive joints were prepared with and without APS coupling agent and their strengths compared both in the dry state and after prolonged exposure to water at elevated temperature.

MATERIALS

A 6Al-4V alloy of titanium was used in fabricating the adhesive joints. A liquid adhesive was formulated from a commercial diglycidyl ether of bisphenol epoxy resin catalyzed with 90 phr NMA and 1 phr BDMA and cured at elevated temperatures. Solid adhesives utilized were a nitrile-modified epoxy and a nylon-modified epoxy. The pickling bath was a 15% by volume aqueous solution of 70% HNO_3 and 3% by volume of 50% HF. One percent aqueous solutions of APS were prepared from the pure concentrate.

PROCEDURE

SPECIMEN PREPARATION

Adhesive lap joints 6.45 square centimeters (1 square inch) in area were prepared from 11.4- x 2.5- x 0.16-cm (4 1/2- x 1- x 1/16-inch) titanium bars. The titanium surfaces were prepared for adhesive bonding by degreasing with acetone, sandblasting with alumina, and then rinsing in methanol. The methanol rinse is a cleaning procedure for testing purposes only and should not be applied to a titanium surface that is to be incorporated into a structure.

In one method, procedure I, a set of five joints, designated as "untreated," was prepared by drying at 110° C (230° F) for 20 minutes immediately after the methanol rinse and then bonding with epoxy adhesive. A second set of five joints, designated as "treated," was immersed for 2 minutes in freshly prepared 1% aqueous APS solution immediately after the methanol rinse, dried at 110° C (230° F) for 20 minutes, and then bonded with epoxy adhesive.

In procedure II, the same method as in procedure I was followed except that both "treated" and "untreated" titanium bars were rinsed in distilled water immediately prior to heating at 110° C (230° F) for 20 minutes and then bonded with epoxy adhesive.

In procedure III, five samples were degreased with acetone, sandblasted with alumina, rinsed in methanol, then immersed in pickling solution for 30 seconds.[3] This was followed by rinsing in distilled water and drying at 110° C (230° F) for 20 minutes and then bonding with epoxy adhesive. The other five samples were treated with APS as in procedure II.

In all three procedures, after the epoxy adhesive was applied, the bars were aligned in a jig with provision for controlling the adhesive thickness to approximately 0.01 cm (4 mils). A pressure of 120 psi was maintained during cure.

EVALUATION

Tensile lap-shear tests were performed in both dry and wet conditions on a Universal testing machine.

Tests in the dry condition were performed at room temperature in air. Specimens to be evaluated in the wet condition were immersed in boiling water for 24 hours and then tested at room temperature in air immediately after removal from the water bath.

RESULTS

Table 1 presents the results of lap-shear tests on titanium adhesive joints formed with the liquid epoxy adhesive system after utilizing three different surface treatments (procedures I through III). The test results using the procedure I surface treatment indicate an improvement of 21% in dry strength for the APS-treated titanium epoxy adhesive joints as compared to the adhesive joints formed from untreated titanium surfaces. Wet strength tests yield an improvement of 64% for the APS-treated titanium joints as compared to the untreated set.

TABLE 1
STRENGTH OF TITANIUM/LIQUID/EPOXY ADHESIVE JOINTS
WITH AND WITHOUT APS ADHESION PROMOTER

Procedure	Test Mode	Lap Shear Strength, psi*			Increase in Strength of Treated Over Untreated Specimens, %
		Treated with APS	Untreated	Treated with Pickling Solution	
I	Dry	3080	2550	-	20.8
	Wet	2280	1390	-	64.0
II	Dry	2630	2050	-	28.3
	Wet	2120	1430	-	48.2
III	Dry	2720	-	2160	25.9
	Wet	2300	-	1500	53.3

*Average of five tests.

In the case of procedure II, where APS treatment was followed by a distilled water rinse, the dry strength of the APS-treated joints increased by 28% while their wet strength increased 48%.

In procedure III, where APS treatment was compared to a surface pickling treatment often used commercially, the APS-treated joints yielded an improvement of 26% in dry strength and 54% in wet strength.

While the APS treatment used in this investigation is intended for bonding of titanium by means of liquid epoxy resin-forming systems, lap-shear joints were also prepared with two solid-state film adhesive systems, namely a nylon-modified epoxy and a nitrile-modified epoxy. The results in table 2 indicate that the APS treatment was of benefit even in these cases, yielding 20% wet and 1.5% dry strength improvement for the nitrile-modified epoxy adhesive and 34% improvement in wet and 13% in dry strength for nylon-modified epoxy adhesive.

TABLE 2
STRENGTH OF TITANIUM-MODIFIED SOLID-EPOXY ADHESIVE JOINTS WITH AND WITHOUT APS ADHESION PROMOTER

Test Mode	Adhesive System	Lap Shear Strength, psi*		Increase in Strength of Treated Over Untreated Specimens, %
		Untreated	Treated with APS	
Dry	Nylon-modified epoxy	5670	6430	13.4
Wet	Nylon-modified epoxy	3070	4100	33.5
Dry	Nitrile-modified epoxy	4770	4840	1.5
Wet	Nitrile-modified epoxy	3270	3910	19.6

*Average of five tests.

DISCUSSION

The salient features of the action of APS as an adhesion promoter for the titanium/epoxy interface are a rather dramatic increase in wet strength retention (even under the severe conditions of 24 hours of exposure to boiling water) combined with a more moderate increase in the dry strength. This behavior is typical of the well-established action of organosilane compounds in promoting adhesion at glass/resin interfaces. It may therefore be assumed that hydrolytically stable Ti_s-O-Si linkages (analogous to the Si_s-O-Si linkage formed on glass) have been formed by APS on the titanium surface.

The performance of APS at the interface of titanium/epoxy adhesive joints warrants the inference that other silane-based coupling agents will generally perform for specific titanium/resin systems in the same manner as for glass-fiber-resin systems. That is, a given organosilane which has been useful for a certain glass-fiber-reinforced polyester resin system should also improve the properties of a titanium joint bonded with the same polyester resin, etc. The usefulness of these organosilane adhesion promoters for naval craft would be optimum for bonded structures that are submerged or close to the waterline.

CONCLUSIONS

The chemical linking of titanium compounds to a silica surface via the Si_s-O-Ti linkage can be reversed by linking silicon compounds to a titanium surface via the Ti_s-O-Si linkage. Any organosilane which is used to couple glass fibers with a specific resin will consequently couple titanium with the same resin. The use of APS to promote adhesive bonding of titanium with an epoxy adhesive, for example, results in lap-shear joints 25% stronger dry and more than 50% stronger after water exposure than joints prepared after utilizing a standard surface treatment without APS.

FUTURE WORK

While the surface-chemical principles involved do not predict that organsilane adhesion promoters will necessarily work with metals other than titanium, the possibility will be investigated for the case of APS in aluminum/epoxy and stainless steel/epoxy adhesive joints.

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