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EVALUATION OF ADHESIVE SYSTEMS FOR BONDING 5109S NEOPRENE-TO-STEEL AND ALUMINUM SUBSTRATES

Final Report

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EVALUATION OF ADHESIVE SYSTEMS FOR BONDING 5109S NEOPRENE-TO-STEEL AND ALUMINUM SUBSTRATES

Final Report

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Evaluation of Adhesive Systems for Bonding 5109S Neoprene-to-Steel and Aluminum Substrates

The primary objective of this project was to characterize the commercial adhesive system Chemlok 205/220 based on response and fracture/debonding properties, and to apply this information to an understanding of why it functions as well as it does. Complementary goals were to identify three alternative adhesive systems that perform as well as the Chemlok 205/220 system and to prepare performance test specifications to qualify adhesive systems for use in the production of TR-317R head mass assemblies (HMA).

Three phases or major tasks were defined. In Phase I, ten adhesive systems were screened for suitability for use in the TR-317R HMA application. A large test matrix of 240 model head mass assemblies (MHMAs) was employed to charter the effect of four environments and two levels of flaws on the debonding/ fracture relaxation to be demonstrated and elastic behavior to be evaluated with a replication of three specimens for each combination.(1)

Thirty-two MHMAs were molded for each adhesive system following the manufacturers recommended procedure of application. All systems were exposed to 315°F during the 5109S vulcanizing process. Each set of thirty-two MHMAs were then divided into three groups containing ten samples each, with two remaining as back-ups. All three groups were painted with the Matcote EM-664/FM-6671 coating system. On the first set of samples the coating was allowed to overlap the rubber face slightly and a bead of PRC PR-611 polysulfide sealant was applied to the rubber-metal interface. The second set was similarly prepared except that the Dow Corning 3140 RTV silicone was used in lieu of the polysulfide. The final set was prepared without the protective sealant bead and the Matcote coating did not cover the rubber-metal interface.

The results for the MHMA's investigation showed wide variations in times-to-failure for similar specimens, which is consistent with fleet experience on the TR-155F. There is a strong implication that application of a polysulfide bead (PRC-611) to the bondline results in a more durable bond. Early failures (less than one week) permitted the elimination of four of the ten systems. The survivors were all Chemlok or Thixon products. The polysulfide sealant was shown to be effective in delaying failure.(2)

Further analysis of the durability data for the MHMA's and modified strip blister specimens indicated that the prominent adhesive systems with respect to their resistance to cathodic delamination were Chemlok 205/220 and Thixon P10/GPO. Neat adhesive specimens were fabricated and tested. Water absorption tests were executed that indicated a primer with high resistance to swelling in the presence of OH- and a topcoat with similar volume change behavior in the presence of OH- would perform best as an adhesive system.(3)

Stress analysis of the head mass assembly of a TR-317R sonar transducer was conducted using the finite element code VISTA (Viscoelastic Stress Analysis of Adhesively Bonded Joints). Modeling of bond terminations, debonds, and viscoelastic materials may be accomplished with this computer program developed at the University of Texas. In summary, VISTA finite element analysis of the transducer geometry indicated that the most severe stresses occur in the annular region between the head mass and the shroud. This region is not exposed to seawater. Although lower stresses occur at the rubber/shroud interface, the aggressive marine environment coupled with the stresses may result in an increased incidence of bond failure in this region. The stress analysis of various crack growth scenarios in the production head mass assemblies indicates that cracks could grow along the rubber/shroud bondline, beginning from the seawater environment side and propagating to the interior of the device to provide a leakage path.(4)

In Phase 2 a number of adhesive systems were characterized and their response to accelerating parameters recorded. Accelerating variables included potential, temperature, and environment.(5,6) The failure mode for Chemlok 205/220 system appears to be primer degradation due to the incursion of hydroxide with resultant increased water uptake causing internal stresses between the primer and metal oxide. Chemlok 205 appears to be primarily composed of a phenolic/resole resin with a chlorinated rubber. Fillers present include titanium dioxide, carbon black, aluminum silicate, zinc oxide, and inorganic lead dispersed in a ketone solvent blend. Chemlok 220 appears to be composed of chlorinated rubber, carbon black, and inorganic lead dissolved in an aromatic solvent combination of toluene and xylene.(7) It has been shown that the failure of rubber-to-metal bonds was related to degradation of the phenolic resin in the primer by hydroxyl ions generated by the cathodic reactions on the steel surface.

The mechanisims responsible for the alkaline degradation of Chemlok 205 were determined by using Fourier transform infrared spectroscopy (FTIR). Infrared spectra obtained after immersing the Chemlok 205 primer in alkaline solutions were analysed by analysis of the location and intensities of the bands present before and after exposure.(16)

Due to the complexity of the degradation reaction, the identity of the intermediates was not determined. However, in the final stages of degradation, the bonds between the phenyl groups are probably broken due to oxidation of the carbonyl groups, resulting in the formation of carboxylate groups.

Some indirect evidence for the formation of carboxylate groups was obtained from the infrared spectra. In addition, direct evidence for the formation of carboxylate groups in Chemlok 205 films exposed to basic solutions for long times was obtained from x-ray photoelectron spectroscopy (XPS). The oxidation of the primer in this basic environment followed by dissolution of the low molecular weight fragments would lead to delamination of the rubber-to-metal bonds.(16)

Investigation revealed that delamination is preceeded by the formation of a weakened bond area. The weakened bond consists of ligaments of degraded adhesive with voids. The crack tip may coincide with the weakened bond or it may linger behind it. If the peel stress level is sufficiently high, then the weakened bond breaks and is subsequently reformed through a diffusion process. There is evidence that bond integrity may be partially regained when the specimen is dried. The amount of strength which can be regained seems to be higher when the specimen has been exposed to artificial seawater than those in concentrated NaOH.(8,9)

Bond deterioration may be conditional on some interaction between hydroxide ions and water molecules in the primer. Hydroxide ions evidently increase the velocity of diffusion and saturation in the adhesive, which may be due to degradation of the polymer.

The resistance to cathodically induced delamination can be elevated by a factor of four when optimum concentration of silane is added to the 205 primer. The silane coupling agent providing a prodigious increase in bond durability was the amino-propyltriethoxysilane. The silane coupling agent should be added to the primer slowly with high speed stirring, and the mixture should be immediately used after preparation. The optimum concentration of silane is between 8 and 12% (w/w). The silane coupling agent should be packaged under an inert gas and repackaged under nitrogen after usage. The use of a silane coupling agent reduces the importance of surface preparation quality factors.(10,11,12)

A number of molding variables can affect the service life of adhesive bonds by a factor up to two. The mold, rubber, and substrate must be at molding temperature for the best bond to be produced. Molding time for the rubber must be at least 50 minutes at 315°F for optimum bond durability. Primer must be applied to freshly prepared surfaces and the primed surfaces are stable as long as they are protected from airborne contaminants.(13)

The details of the service environment affect bond durability. Delamination rate is proportional to the cathodic current density which is a function of the dissolved oxygen content. Factors of 10 to 100 in magnitude of current density can be achieved by varying the oxygen concentration in the vicinity of the delamination front. Thus, the rate of delamination varies exponentially with the oxygen concentration. High temperature service environments affect the bond lifetimes. The rate of delamination varies exponentially with temperature. Applied or residual stresses, particularly those resulting in the peel mode, reduce bond durability.(12,13)

The quality of the metal surface preparation affects the durability of the bonds. Contaminated or poor quality vapor degreasing solvent produces poor quality bonds. Using contaminated grit produces inferior quality bonds. Solvent wiping with contaminated solvent produces bonds of inferior quality than if the step were eliminated. Grit blasting at high pressure and a normal angle of incidence result in the best surface for bond formation.(13)

Phase 3, which is being accomplished under another contract (N00024-86-C-5136), involves an inter-institutional testing matrix to determine the effects of wide variations of temperature,environment, and electron current density on bond durability. The first portion of this work plan was a round-robin experiment designed to determine the inter-laboratory variability of the durability test. Each of the institutions involved received six double-sided strip blister specimens for testing. Two of the six samples had an A-1100 amino-silane coupling agent incorporated into the Chemlok 205 primer at a loading of 10% by weight. The other two specimens were prepared with standard Chemlok 205/220. The two environments for the samples were 1 N NaOH at 30°C with an applied potential of -0.9V, and 3.5% artificial seawater at 30°C with an applied potential of -1.0V. Comparison of the results between the institutions involved are in progress.(14)

In addition, the final matrix involves testing of two commercial adhesive systems as received and modified with the amino-silane coupling agent. The two systems are Chemlok 205/220 and Thixon P-10/GPO. The samples will be subjected to five different electron current densities, three temperatures, and two different force levels applied to the bond line. The testing solutions are 3.5% artificial seawater and 1 N NaOH.(14)

The results obtained from the inter-institutional matrix testing will serve to correlate a majority of the factors which affect The lifetime of the adhesive bond in sonar transducers.

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