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Compatibility of Gelled Inhibited Red Fuming Nitric Acid with Aluminum Alloys

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This paper presents data obtained from electrochemical methods, weight loss studies, and surface studies to determine compatibility of gelled inhibited red fuming nitric acid (IRFNA) with aluminum alloys. Comparisons are presented between liquid IRFNA and gelled IRFNA with and without added inhibitor (P_4O_{10}). The 1100 and 2014 aluminum alloys behave in a similar fashion when exposed to gelled IRFNA, based upon the weight loss investigations. The addition of phosphoric oxide is beneficial with the 1100 Al systems according to the electrochemical results. However, the weight loss data suggest that the gels are satisfactory without added P_4O_{10}, especially when compared to a liquid IRFNA system. The x-ray photoelectron spectroscopy shows that the fluorine from the hydrofluoric acid inhibitor in IRFNA is not consumed entirely by the silica gelling agent, and is available to the metal surface as in gel systems without P_4O_{10}. Aluminum, silicon, and phosphorous will compete for the fluorine present in the systems with added inhibitor. In general, all corrosion rates are small and decrease with time. These rates appear acceptable for long-term storage of gelled IRFNA; they are consistent with the storage of IRFNA in the field.

Nomenclature

a = area exposed to oxidizer, cm^2
B = $b_a(-b_c)/2.303(b_a - b_c)$, V
b_a = anodic Tafel constant
b_c = cathodic Tafel constant
E_{corr} = rest potential, mV
i_{corr} = corrosion current density, $A/m^2 \approx$ corrosion rate, mm/year
R_p = polarization resistance, Ω
r^2 = least-squares-fit value

Introduction

Inhibited red fuming nitric acid (IRFNA), which is composed of 14% dinitrogen tetraoxide (N_2O_4) by weight, 0.7% hydrofluoric acid (HF) by weight, and nitric acid (HNO_3), as the remaining balance, is a common rocket propellant oxidizer that has been used for many years. Aluminum alloys have been used successfully to contain liquid IRFNA for over 20 years.

Gelling of storable propellants offers the benefits of safety and handling of rocket systems in the field. Previous work,[1] with gels of different compositions other than those used in this study, concluded that gelled IRFNA is more corrosive than liquid IRFNA. These previous works recommended the addition of P_4O_{10} to reduce corrosion as it forms well-known metal corrosion inhibitors.

The research described here encompasses a new methodology involving the use of glass electrochemical cells. The specific methods used in this research were reported in detail elsewhere,[2,3] as was the validation of these methods.[1,3] The current research resulted in changes to the techniques that improved the accuracy and the reproducibility of results, specifically, centrifuging of the gels. Centrifuging the gels led to significant differences from earlier data. The procedure was applied to alloy/oxidizer systems of current interest in the industry.

This research used two different brands of silica gelling agent for the IRFNA, Aerosil 200® and Cab-O-Sil® (manufactured by De Gussa and Cabot, respectively). The six experimental systems listed in Table 1 provide direct comparisons while eliminating variables that exist between the previous research activities.[1,4]

The experimental analysis involved electrochemistry, weight loss, and x-ray photoelectron spectroscopy (XPS). The dc potentiostatic method of linear polarization resistance[5] yields results in the form of resistance that convert into corrosion current densities. The weight-loss experiments used a simple, common method.

The XPS methods were used to determine concentrations of atomic species left behind from corrosion products on the metal surface. The XPS studies were performed at three different time periods for each of the systems.

Experimental Procedures

The IRFNA used in these experiments was MIL-SPEC MIL-P-7254. Both Aerosil 200 and Cab-O-Sil (M-5 grade) fumed silica were used as gelling agents.

The gelled propellant samples (with and without P_4O_{10}) were prepared in the laboratory using batch processes.[3] Some gases

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appear entrapped in these gels during the mixing and transfer processes. A possible reaction within the gel mixture could also be a source of the gas, since the gas appeared and behaved differently between the two gels. This gas is a reddish brown vapor characteristic of red fuming nitric acid ($N_2O_4 \leftrightarrow 2NO_2$).

The gel was centrifuged after it was loaded into the containers for all of the studies and before any aluminum coupons or electrodes were immersed. Centrifuging the gel at approximately 200 *g* for 10 min eliminated the gas or voids in the gels. Some liquid was seen after centrifuging, but most of the liquid was absorbed into the gel mixture.

Preparation of Aluminum Samples (Coupons)

The thickness of the 1100 Al and 2014 Al coupons was 0.16 and 0.20 cm, respectively. The surface study and electrochemical coupons were 1 × 1 cm, and the weight loss coupons were 2 × 2 cm. The surface preparation and installation procedures were previously reported.[1]

Preparation of Electrochemical Cells

The glass electrochemical cell was designed to give the user optical access to the placement of the electrolyte and the aluminum and platinum electrodes. The placement of the electrodes is crucial to the results.[2] In addition, it is critical that they remain immobile for the duration of the experiment. The platinum wires passing through the Teflon® cap were scarred to immobilize them. The aluminum wire connected to the working electrode was forced through a smaller hole to minimize movement and leakage.

The gel cells were assembled empty and a line marked to show immersion at approximately half of the working electrode. Gel was added to the cell to a point slightly above the line. The cell was centrifuged without the electrodes in place and using a temporary cap. The electrodes were then immersed in the cell and the excess gel removed by pipette to the selected level.

Table 1 Experimental systems

Liquid IRFNA, wt %	Gelling agent, wt %	Added inhibitor, wt %	Alloy
100.0	——	——	2014 Al
95.50	Aerosil 200, 4.5	——	2014 Al
95.50	Cab-O-Sil, 4.5	——	2014 Al
94.927	Cab-O-Sil, 4.5	P_4O_{10}, 0.573	2014 Al
95.50	Cab-O-Sil, 4.5	——	1100 Al
94.927	Cab-O-Sil, 4.5	P_4O_{10}, 0.573	1100 Al

Electrochemical Instrumentation

The wires that protrude through the Teflon screw caps of the electrochemical cells were attached by alligator clips and shielded cables to the Schlumberger 1286 electrochemical interface, a potentiostat. These glass cells were placed in a temperature-controlled, water circulating bath maintained at 24–25°C. The potentiostat was connected to a personal computer and manipulated through a software package, ERIC from CAPCIS (Ref. 6).

Weight-Loss Procedures

Gel was transferred into large Teflon jars, centrifuged and loaded with weight-loss coupons that had been weighed to five decimal places. The coupons were placed in the gel with their faces vertical and spaced so that they did not touch. These jars were placed in plastic bags and then in a 21–22°C water bath. Once a week, coupons were removed and washed three times in distilled water. Each time a coupon was washed it was also scrubbed using a Teflon teat. After washing, the coupon was dried at 110°C for approximately 10 min, cooled in open atmosphere, and weighed to five decimal places.

XPS Procedures

XPS was performed on polished coupons after 8, 12, and 16 weeks of exposure to oxidizer and on control blanks. These coupons were treated similarly to the weight-loss coupons. Gel was transferred into Teflon centrifuge tubes and centrifuged to remove any gas. The coupons were immersed vertically and placed so that they remained separated from each other in the gel.

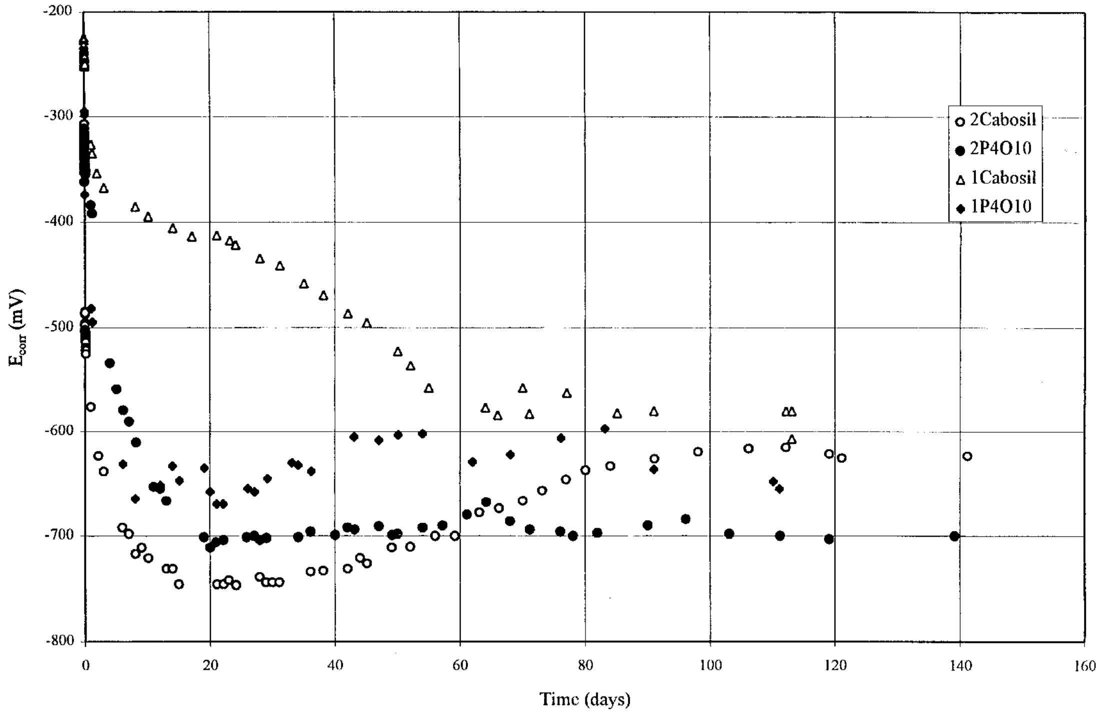

Fig. 1 E_{corr} **vs time for 2014 and 1100 aluminum, Cab-O-Sil, and** P_4O_{10} **systems.**

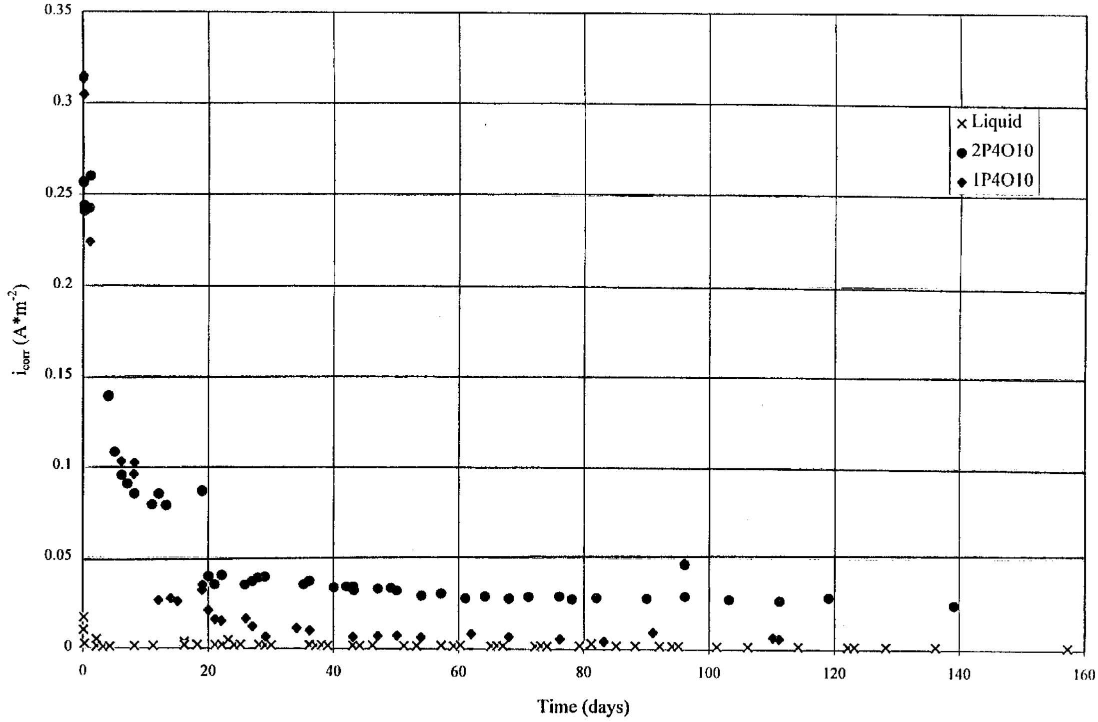

Fig. 2 i_{corr} **vs time for IRFNA and P_4O_{10} gels with B = 0.045.**

Experimental Results and Discussion

Observations

Dinitrogen tetraoxide vaporized from the gel and condensed either onto the gel or collected in the outer annular ring of the electrochemical cell. The liquid in contact with the gel was reabsorbed. The working electrode wire became coated with SiO_2, but the other wires did not.

The R_p values measured in this investigation produced r^2 values of 0.99 for all Cab-O-Sil and P_4O_{10} systems; whereas the r^2 values from the previous investigations were as low as 0.900 (Ref. 1). This improvement is attributed to the centrifuging of the gels.

Electrochemical Results

The behavior of E_{corr} vs time yields information on surface film modification processes.[4] Figure 1 is a typical example of data obtained with the gels. The initial, very fast, decrease is attributed to a very rapid reaction of the acid (hydrofluoric acid) stripping off the Al_2O_3 coating present on all Al. The subsequent decrease and leveling off of E_{corr} with time is a result of the replacement of the coating with a buildup of the passivation layer. Figure 2 is a plot of i_{corr} vs time, which is, again, typical of liquid IRFNA and gels. The curves in Fig. 2 show the very rapid reaction with high i_{corr} values, then a decrease to very low values with the formation of a good passivation layer. The corrosion process is described by the Stern–Geary equation[5]

$$i_{corr} = \frac{1}{2.303(R_p)a} \cdot \frac{b_a(-b_c)}{b_a - b_c} = \frac{B}{(R_p)a}$$

The data reduction program generates the (R_p) value using Ohm's law and the surface area of the working electrode. The $(R_p)a$ values shown in Fig. 3 are consistent with low reaction rates (high resistance to corrosion) and a surface layer of high resistance.

The anodic and cathodic Tafel constants b_a and b_c and, consequently, B, can be determined from a Tafel polarization that involves polarizing around E_{corr} with large polarizing voltages. These voltages damage the working electrode by stripping or increasing the surface film of corrosion products.[2] Because of hysteresis effects in the generated curves from large polarization, calculating b_a and b_c can be made difficult. Richings[7] found a range of experimental B values from 0.0343 to 0.0496 for IRFNA mixes. Dove et al.[1] used a value of B = 0.045. This value was used in this case because the experimental value was considered closer to the realistic value in a practical system.

Table 2 Electrochemically predicted corrosion values

System	i_{corr} mm/year	In 20 years, mm	r^2 for run
Liquid/2014	0.0016	0.033	0.9729
Aerosil/2014	0.10	2.0	0.9966
Cab-O-Sil/2014	00.13	0.26	0.9979
P_4O_{10}/2014	0.026	0.53	0.9881
Cab-O-Sil/1100	0.033	0.66	0.9964
P_4O_{10}/1100	0.0059	0.012	0.9958

The corrosion rate in mm/year is approximately equal to i_{corr} in units of A/m^2. This permits predictions of corrosion rates and comparisons between the systems. With B = 0.045, i_{corr} values listed in Table 2 show the projected corrosion of metal over 20 years. The i_{corr} values in Table 2 are those measured after 112 days. The initial i_{corr} values were larger in all cases. Therefore, the i_{corr} values followed the typical curves shown in Fig. 2. In general, all predictions of corrosion in mm are inversely proportional with time. A prediction using the i_{corr} value at 112 days would be a worst-case scenario because all values were still decreasing with time when the experiments were concluded. The P_4O_{10} gel/1100 Al system is seen as less corrosive than the Cab-O-Sil gel/1100 Al and the P_4O_{10} gel/2014 Al system. The P_4O_{10} gel/1100 Al system achieves the lowest i_{corr} value seen in all of the gel systems after 111 days. The Aerosil/2014 gel has a rate at least 10 times greater than the other systems. The electrode showed movement in the gel. When movement was noted, the rate changed. Therefore, this high rate is attributed to problems in the experimental procedure and should not be compared directly.

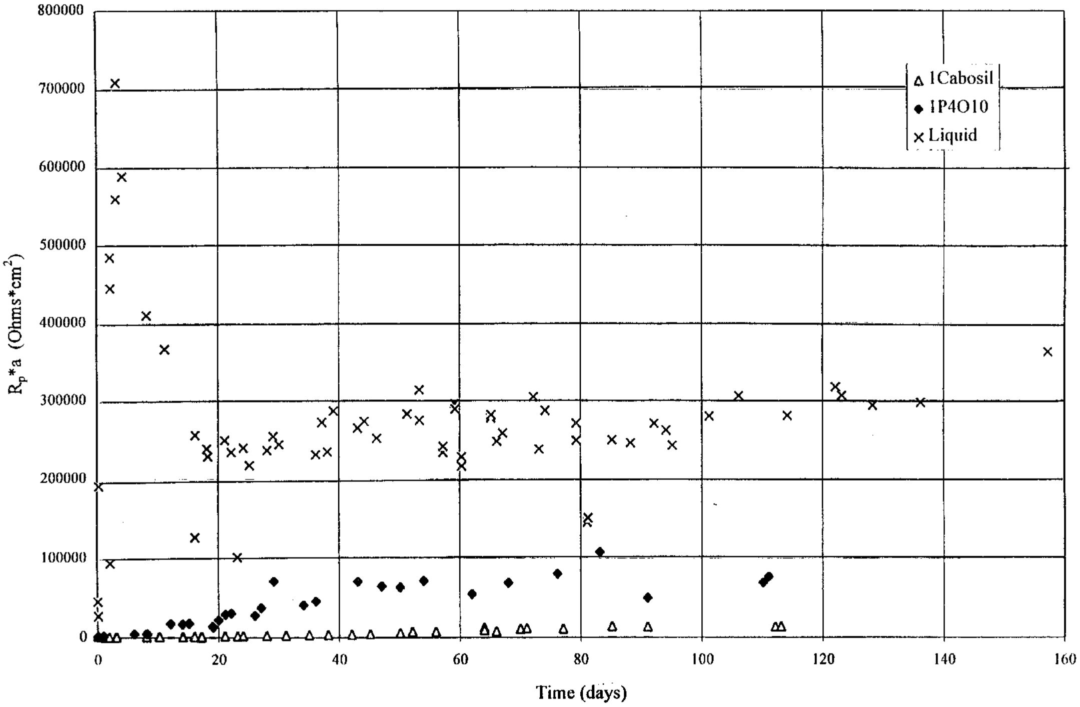

Fig. 3 (R_p)*a* vs time for Cab-O-Sil and P_4O_{10} gel, 1100 Al, and liquid IRFNA, 2014 Al.

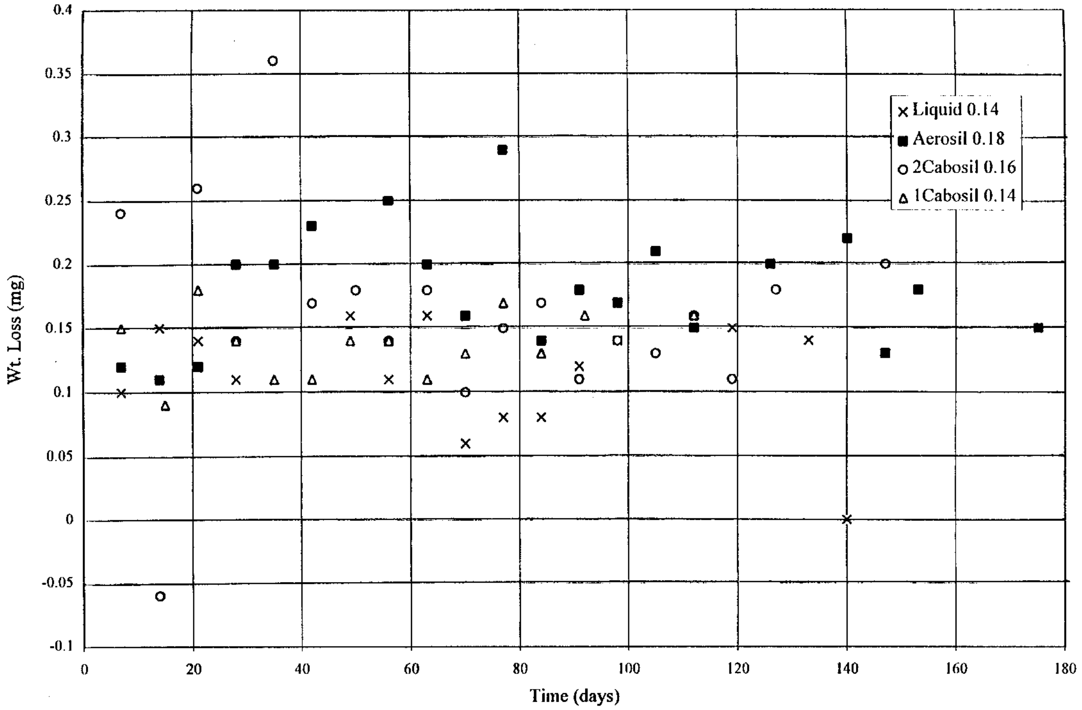

Fig. 4 Weight loss vs time for all normal systems.

For all of the systems, the removal or buildup of the oxide and layering of protective corrosion products is shown in the increase and decrease of i_{corr} values (Fig. 2). All of the systems have the same behavior, with the only differences being the magnitude of the values and the rates at which this process occurs.

Weight-Loss Results

A different aluminum coupon (sample) was removed from each of the gel systems every week during the investigation. The data from the weight-loss studies for each of the systems show interesting trends. In general, the amounts of weight loss for the normal systems (without P_4O_{10}) do not vary significantly with time (Fig. 4). The weight loss after the first week is approximately the same as the last week for these systems. All four of these systems had weight losses in the same range throughout the investigated period. The average weight loss for all of the normal systems are listed in Table 3. In these systems, the fluorine passivation coating (AlF_3) forms rapidly and it is difficult to diffuse through this coating.

The added inhibitor increases the weight loss for both P_4O_{10} systems. Figure 5 shows the weight loss for all systems. The total increase in weight loss with the added P_4O_{10} could be expected as it removes more of the AlF_3 layer forming an oxide passivation layer. The 1100 P_4O_{10} system seems to be stable after about 80 days. The reason for the change of the 2014 P_4O_{10} system at about 100 days is not known, nor do we know where it levels off. Additional data are needed to answer these questions. However, the data in Fig. 4 for the regular gels, the liquid, and the 1100 P_4O_{10} system all show a very low total weight loss for the systems.

Table 3 Average weight loss for all normal systems

System	Average weight loss, mg
Liquid/2014	0.13
Aerosil/2014	0.18
Cab-O-Sil/2014	0.16
Cab-O-Sil/1100	0.14

Electrochemical and Weight-Loss Comparisons

All electrochemical corrosion rate values decrease with time and generally level off. For all normal systems corrosion values determined from weight loss remain relatively constant with time (Fig. 4). All corrosion determinations from weight loss are even smaller than those from electrochemistry. The smallest values from electrochemistry compare well with the larger values from weight loss. Differences in values can be expected since the two experiments used different samples. While care was taken to keep as many variables constant as possible, all parameters were not equivalent. The corrosion rates in both cases are low, and when such small changes are measured, variations are not considered unusual. These low values are consistent with long-term rates obtained in the Lance system and when similar electrochemical tests were performed.[4]

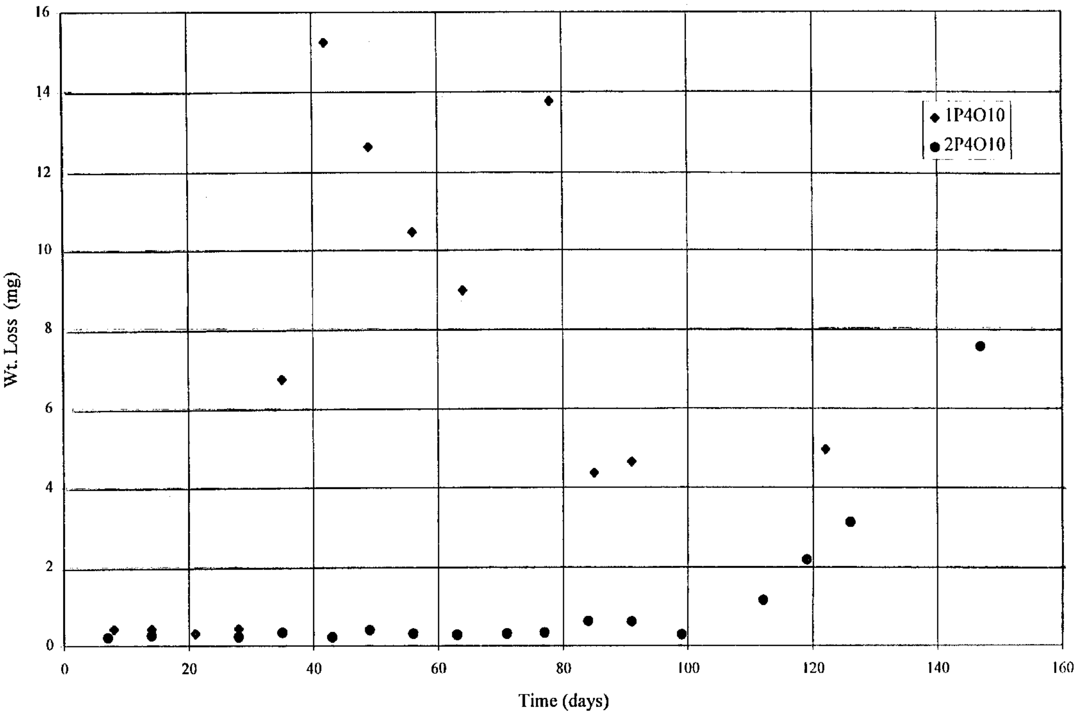

Fig. 5 Weight loss vs time for 1100 and 2014 Al P_4O_{10} gel systems.

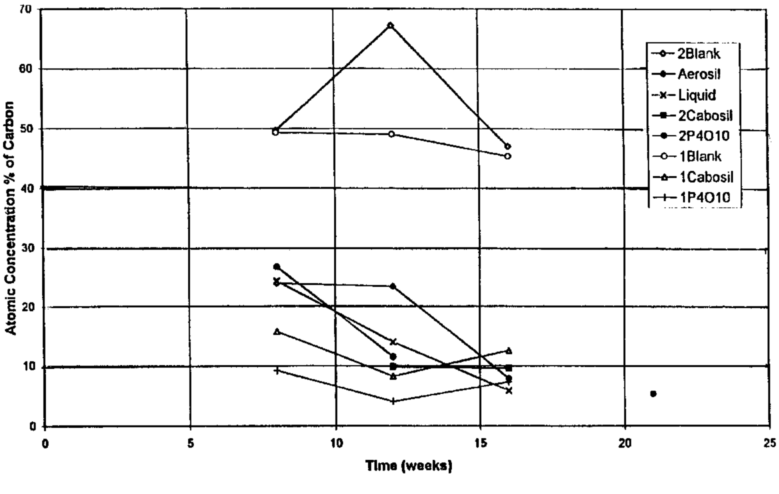

Fig. 6 Carbon concentration from XPS vs time for all systems.

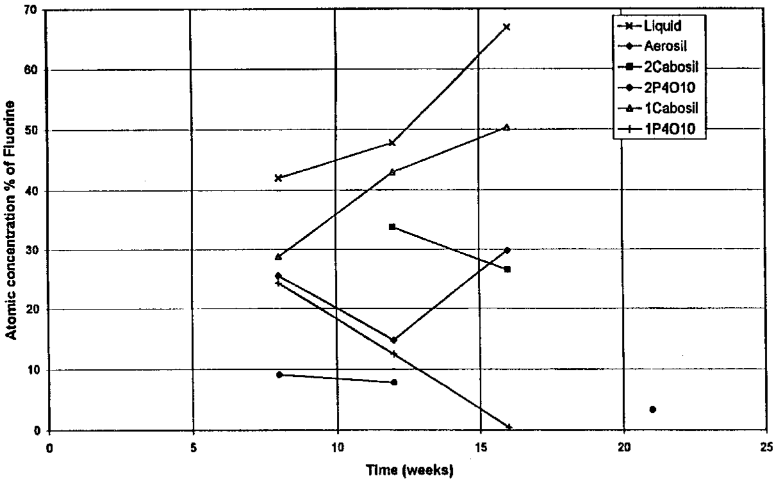

Fig. 7 Fluorine concentration from XPS vs time for all systems.

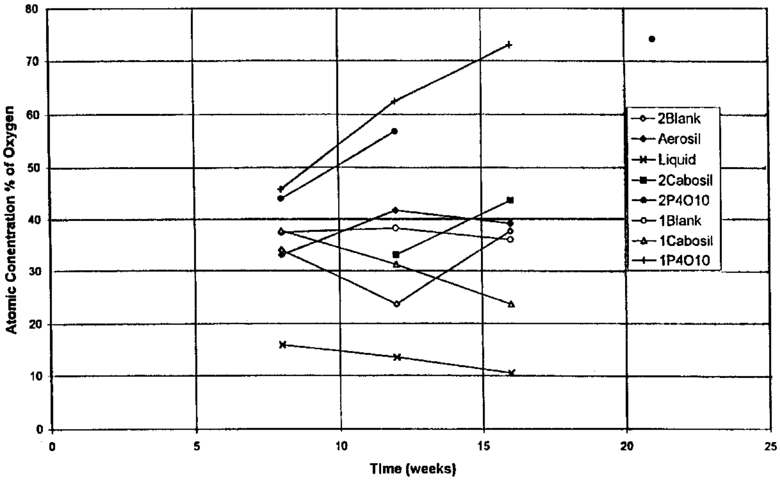

Fig. 8 Oxygen concentration from XPS vs time for all systems.

XPS Results

Samples drawn from the gels and control blanks were analyzed by XPS. The blanks exhibited a high concentration of carbon. As mentioned earlier, the side of the aluminum coupon analyzed by XPS was polished using a fine silicon carbide paper that left a carbon layer embedded in the surface of these coupons. The degreasing of the coupons, using 1,1,1 trichloroethane, is also a possible source of the carbon. All of the coupons exposed to IRFNA had lower levels of carbon on the surface than the control blanks (Fig. 6). The oxidizer reacted with the surface layer of the coupon and either removed the carbon layer or covered it with corrosion products.

Figures 6–8 show values measured after analyzing the surfaces at a glancing angle of 30. Error within these values could be as high as ±5 atomic concentration based upon results using this technique on other systems. The fluorine concentrations are shown in Fig. 7. The liquid IRFNA/2014 Al system displays the highest fluorine concentrations, which increase with time to 67%. For the Cab-O-Sil gel/1100 Al system, the fluorine concentration also increased with time to 50%. Fluorine availability exists for all the normal systems. A longer initial time period is needed for the fluorine to build up on the surface from the gelled IRFNA. Because of the decreased concentration of fluoride ion in the gels as compared to liquid, this is to be expected. In addition, the diffusion of the ions to the metal surface could be expected to be slower in the viscous gels. A decline in fluorine is seen over time for both the P_4O_{10} systems. Oxides increase with time (Fig. 8). Therefore, P–O–Al compounds are competing with Al–F compounds on the surface. All oxide concentrations are within the same range for the normal gels and the control blanks. A decrease in oxygen exists because of the increase in fluorine for the liquid IRFNA/2014 Al system. The oxygen concentration in both P_4O_{10} systems is higher than the fluorine concentration for the liquid system as expected. This indicated that a good P–O–Al protective layer is formed using P_4O_{10}.

Conclusions

The corrosion current density values from electrochemistry increased in comparison to earlier studies. The weight-loss values are much smaller than any previously reported values for the normal systems. A possible explanation of this difference could be that centrifuging the gel, which removed voids, allowed more surface area of the metal to come into contact with the fluorine inhibitor from the IRFNA.

The weight-loss studies suggest that, when added, P_4O_{10} reacts as an inhibitor for the 2014 and 1100 aluminum alloys and that the normal gels are acceptable without an added inhibitor, especially in comparison to the liquid IRFNA/2014 Al system. The P_4O_{10} adds large concentrations of oxide to the metal surface, thereby changing the protective corrosion product layer.

The electrochemical data obtained previously on Lance aluminum alloy tanks are similar to the results obtained in this study. IRFNA was stored in the Lance tank for over 15 years. A prediction based on this similarity would indicate that gels would likewise store for at least 15 years. Storage in aluminum alloy storage containers (in variable thermal cycles) has been demonstrated for over 20 years.

All corrosion rates from electrochemistry are low and decrease with time. The different values of B were used in the Stern–Geary equation to evaluate change in corrosion rates that could be predicted. The value $B = 0.045$ was used because it was considered to provide a worst-case scenario.

All corrosion rates are decreasing with time and leveling off to limiting values.

The XPS studies show that fluorine is available to the metal surface and that the Al–F coating simply takes longer to form on the surface in contact with the gelled IRFNA than when in contact with liquid IRFNA.

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