215

Corrosion Effects Of The Interreaction
Of
6061 Aluminum With Aqueous Mixtures
And
Solutions Of Selected HE's

G. L. Clink

An Interim Report

Sandia Laboratories/Albuquerque

P.O. 93-1830

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CONTENTS

	Page No.
ABSTRACT.....	1
INTRODUCTION.....	2
EXPERIMENTAL	
Section 1. The Silver Perchlorate System.....	7
Section 2. The Sodium Perchlorate System.....	19
Section 3. The O-phthalic Acid System.....	27
Section 4. The Hexaamminecobalt III Perchlorate (HCP) System.....	37
Section 5. The CATCP Dimer System.....	57
Section 6. The TF-AK Modified CATCP System.....	74
Section 7. The TF-AH Modified CATCP System.....	114
Section 8. The PETN, HNAB, HMX, and RDX Systems.....	166

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SOLUTIONS OF SELECTED HE'S

ABSTRACT

The behavior of several selected HE and HE-component materials in aqueous media in contact with 6061 aluminum has been studied via conductance, cathodic tendencies (cell EMF measurements), pH, and visual analysis (photomicrographs) of the 6061 electrodes and media contacted rods. Addition of ortho phthalic acid (OPA) to the media was also made to study potential corrosive effects possibly due to some breakdown of the polyphthalate systems in contact with these materials. Overall assessment of data is not made at this time due to the interrelationship of these data with data which should be obtained from unfinished portions of the study.

INTRODUCTION

The physical systems by which potential corrosion effects resulting from the interreaction of selected materials in aqueous media with 6061 aluminum are being studied consist of the following:

Cell, conductance: a three neck 500 ml flask (\$) to which has been fitted a standard thermometer, a calomel reference electrode, and a machined rod of 6061 aluminum which functions as the working electrode (Fig. 1). Minimal agitation of the electrolyte solution (or mixture) is by means of a magnetic stirrer using a button-shaped Teflon-coated stirring bar. Measurement is made of both the cell resistance (continuous monitoring) and the cell EMF (periodic monitoring) by means of a Keithley Model 600B electrometer and a Keithley Model 370 recorder (Fig. 2).

Cell, pH: a three neck 500 ml flask (\$) to which has been fitted a standard thermometer, and standard pH and calomel reference electrodes (Beckman). A machined rod of 6061 aluminum is placed in the flask and minimal agitation of the electrolyte solution (or mixture) is by means of a magnetic stirrer using a button-shaped Teflon-coated stirring bar. Measurement of pH is by means of a Beckman Expandomatic pH meter with a Hewlett-Packard recorder.

Cell, pH, Static: As a reference check on the monitored pH values, a 500 ml flask containing the corresponding solution (or mixture) and a 6061 aluminum bar is gently stirred for 6 hours with no imposed voltage (current flow) between pH electrodes during run. Only the initial and final pH values are measured and recorded.

The electrolyte solutions (or mixtures) were made up with Fisher conductivity water. Elapsed times of runs varied from the normal 6 hours up to 70. The following systems have been completed at this time:

CONCENTRATION RANGES

	<u>Electrolyte</u>	<u>O-phthalic Acid (N)</u>
AgClO ₄	10 ⁻² N	---
AgClO ₄	10 ⁻² N	2.5 x 10 ⁻³ - 3 x 10 ⁻³
AgClO ₄	3 x 10 ⁻³ N	---
NH ₄ ClO ₄	10 ⁻² N	---
NH ₄ ClO ₄	10 ⁻² N	1.3 x 10 ⁻³
NH ₄ ClO ₄	3 x 10 ⁻³ N	---
NH ₄ ClO ₄	3 x 10 ⁻³ N	5 x 10 ⁻⁶ - 10 ⁻⁵
O-phthalic Acid		5 x 10 ⁻⁵ - 2 x 10 ⁻³
HCP (hexaamminecobalt III perchlorate)	1.5 x 10 ⁻⁴ N	---
HCP (hexaamminecobalt III perchlorate)	1.5 x 10 ⁻⁴ N	5 x 10 ⁻⁵ - 10 ⁻⁴
CATCP, dimer (SL-UN-2)	70-900 mg/l	---
CATCP, dimer (SL-UN-2)	70-900 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP (TF-AH)	70 mg/l	---
Modified CATCP (TF-AH)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP, filtrate (TF-AH)	70 mg/l	---
Modified CATCP, filtrate (TF-AH)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP, Water Insolubles (TF-AH)	70 mg/l	---
Modified CATCP, Water Insolubles (TF-AH)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP (TF-AK)	70 mg/l	---
Modified CATCP (TF-AK)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP, filtrate (TF-AK)	70 mg/l	---
Modified CATCP, filtrate (TF-AK)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴
Modified CATCP, Water Insolubles (TF-AK)	70 mg/l	---
Modified CATCP, Water Insolubles (TF-AK)	70 mg/l	5 x 10 ⁻⁵ - 10 ⁻⁴

Modified CATCP (TF-AK)	133-880 mg/l	---
Modified CATCP (TF-AK)	880 mg/l	$5 \times 10^{-5} - 2.5 \times 10^{-4}$
PETN	200 mg/l	---
PETN	200 mg/l	$5 \times 10^{-5} - 10^{-4}$
HNAB	200 mg/l	---
HNAB	200 mg/l	$5 \times 10^{-5} - 10^{-4}$
RDX	200 mg/l	---
RDX	200 mg/l	$5 \times 10^{-5} - 10^{-4}$
HMX	200 mg/l	---
HMX	200 mg/l	$5 \times 10^{-5} - 10^{-4}$

Length in cm

Fig. 1. Machined 6061 aluminum used as pH reaction interface (left) and as working electrode (right)

Fig. 2. Corrosion Study Cell Measurement Arrangement

EXPERIMENTAL

SECTION 1

SILVER PERCHLORATE, AgClO_4

The decision to investigate 6061 aluminum systems with silver perchlorate was dictated by its common but not exclusive use as an intermediate reactant in the preparation of the inorganic perchlorate species of several HE's. The introduction of o-phthalic acid into these systems (in conjunction with AgClO_4) was dictated by the potential breakdown and/or hydrolysis of the diallylphthalate polymer used in conjunction with various materials.

The conductivities of AgClO_4 solutions (Fig. 3) show divergent patterns as o-phthalic acid becomes part of the electrolyte systems. These acidified systems indicate trends toward increased conductance. The cell EMF values (Fig. 6) show similar divergencies in behavior as found with the conductances. Similar to the conductances and cell EMF values, the pH trends of the two systems are initially divergent in behavior, but indicate that both approach a near-constant value after 4-5 hours (Fig. 7). After ~ 5 hours both systems have gone cathodic relative to the original systems ($t = 0$ hrs), however, the non o-phthalic acid systems initially go through a pattern of anionic behavior. Photomicrographs of the aluminum rods show substantial pitting in both the conductance and pH runs (Figs. 4,5,8,9). The pH of AgClO_4 solutions (10^{-2}N) at various concentrations of o-phthalic acid are presented in Figs. 10, 11 and 12. In Fig. 12, an anomaly as a function of o-phthalic acid concentration seems to occur in that the higher concentration of the acid ($8.4 \times 10^{-4}\text{N}$) affords a trend toward a basic condition whereas at a lower concentration ($2.5 \times 10^{-4}\text{N}$) and in the non-acid system the trend is toward the acidic side.

Comments

The silver perchlorate systems in this study show higher conductance levels when acidified with o-phthalic acid. They tend toward a less cathodic condition when acidified with o-phthalic acid. The pH of AgClO_4 solution decreases while the acidified system increases over the time period studied (6 hrs), they show an approach to a near common constant value.

Fig. 3. Cell resistance of various AgClO_4 solutions (aqueous) using 6061 aluminum working electrode

Fig. 4. Photomicrographs of 6061 aluminum electrode used in conductance cell with 10^{-2} AgClO_4 (aqueous)

$t = 0$

$t = 6$ hrs, AgClO_4 only

$t = 6$ hrs, AgClO_4 ; 3×10^{-4}
N in OPA

$t = 6$ hrs, AgClO_4 ; 10^{-3} N
in OPA

Fig. 5. Photomicrographs of 6061 aluminum electrode used in conductance cell containing OPA and 10^{-2} AgClO_4

Fig. 6. Cell EMF of 6061 Aluminum Electrode with various AgClO_4 Systems (aqueous)

— 10^{-2} N
- - - 10^{-2} N; 3×10^{-3} N in O-phthalic acid

Fig. 7. pH of Various AgClO_4 solutions (aqueous) in contact with 6061 aluminum

t = 0

t = 6 hrs

t = 0

t = 12 hrs

Fig. 8. Corrosion of 6061 aluminum in contact with 10^{-2} N AgClO_4 (pH run)

$t = 0$

$t = 6 \text{ hrs, AgClO}_4; 10^{-2} \text{ N in OPA}$

$t = 6 \text{ hrs, AgClO}_4; 10^{-2} \text{ N};$
 $5 \times 10^{-5} \text{ N in OPA}$

$t = 6 \text{ hrs, AgClO}_4; 10 \times 10^{-5}$
 N in OPA

Fig. 9. Photomicrographs of 6061 aluminum rod in contact with various solutions of AgClO_4 (pH runs)

Fig. 10. pH of various solutions in contact with 6061 aluminum

Fig. 11. pH of various solutions in contact with 6061 aluminum

Fig. 12. pH of AgClO_4 Solutions (10^{-2} N) in contact with 6061 aluminum at various concentrations of O-phthalic acid

SECTION 2

AMMONIUM PERCHLORATE (NH_4ClO_4)

Due to the occasional but usually infrequent presence of ammonium perchlorate in various inorganic HE's (e.g., amine coordination compounds) which presumably result from either material preparative carryover and/or hydrolysis of the final material to generate NH_4ClO_4 , it was deemed advisable to make an abbreviated study of its possible corrosion effects on 6061 aluminum.

Fig. 13 presents cell resistance behavior as an apparent function of electrolyte concentration and component makeup. Higher concentrations of NH_4ClO_4 produce increased cell conductance as expected ($@ 10^{-2}\text{N}$), and presents a near constant value after ~ 1 hour. At a lower concentration of the electrolyte ($3 \times 10^{-3}\text{N}$) the system presents a somewhat dynamic behavioral pattern showing an initial increase in conductance followed by a reversion to decreasing values with no indication of a levelling off over the time period studied (~ 5 hrs). The introduction of o-phthalic acid into the system does not increase the system conductance but rather presents greater cell resistance accompanied by an overall trend towards a condition of lower conductance, relative to the non-acidified NH_4ClO_4 systems.

Photomicrographs of the 6061 rods (electrodes) following conductance runs are presented in Fig. 14. These present visual indication that o-phthalic acid may passify the pitting of the aluminum to some degree.

Cell EMF values however, show an overall increase in the degree of cathodic behavior with the o-phthalic/ NH_4ClO_4 systems as opposed to those containing NH_4ClO_4 alone (Fig. 15).

The pH behavior of the various systems (Fig. 16) show somewhat linear trends following initial variations which occur within the first hour. The $3 \times 10^{-3}N$ NH_4ClO_4 solution undergoes an initial increase in pH while that which is $10^{-5}N$ in o-phthalic acid undergoes a substantial initial decrease. Photomicrographs of the 6061 aluminum rods are presented in Fig. 17. As in the case of the conductance runs, it appears from visual data that the o-phthalic acid affords some degree of passivation to the system. Fig. 18 presents similar data obtained from static pH runs wherein the system was not subjected to imposed voltages across the electrodes during the runs.

Comments

The presence of o-phthalic acid decreases the cell resistance with aqueous NH_4ClO_4 over the concentration range studied.

Photomicrographs indicate that o-phthalic acid affords some degree of passivation of the aluminum electrodes relative to pitting.

Cell EMF shows greater cathodic behavior when o-phthalic acid is present in the system.

The pH behavior of the un-acidified and the acidified NH_4ClO_4 systems show divergent behavioral patterns.

Fig. 13. Cell resistance of various $\text{NH}_4 \text{ClO}_4$ solutions (aqueous) using a 6061 aluminum working electrode

19.3

38.1

20
2
1

$t = 0$

$t = 6 \text{ hrs}, 10^{-2} \text{ N}$
 NH_4ClO_4

$t = 6 \text{ hrs}, 3 \times 10^{-3}$
 NH_4ClO_4

$t = 6 \text{ hrs}, 3 \times 10^{-3} \text{ N}$
 $\text{NH}_4\text{ClO}_4; 10^{-4} \text{ N in OPA}$

$t = 6 \text{ hrs}, 3 \times 10^{-3} \text{ N}$
 $3 \times 10^{-3} \text{ N NH}_4\text{ClO}_4;$
 $5 \times 10^{-5} \text{ N in OPA}$

Fig. 14. Photomicrographs of 6061 aluminum electrode used in conductance cell with 10^{-2} , $3 \times 10^{-3} \text{ N NH}_4\text{ClO}_4$

Fig. 15. EMF of cell using various NH_4ClO_4 solutions (aqueous) with a 6061 aluminum working electrode

- 10^{-2} N
- - - 3×10^{-3} N
- 3×10^{-3} N; 5×10^{-6} N in O-phthalic acid
- 3×10^{-3} N; 10^{-5} N in O-phthalic acid

Fig. 16. pH of various NH_4ClO_4 solutions (aqueous) in contact with 6061 aluminum

$t = 0$

$10^{-2} \text{ N NH}_4\text{ClO}_4$
 $t = 6 \text{ hrs}$

$10^{-2} \text{ N NH}_4\text{ClO}_4$
 $t = 6 \text{ hrs (static)}$

$3 \times 10^{-3} \text{ N NH}_4\text{ClO}_4$
 $t = 6 \text{ hrs}$

$3 \times 10^{-3} \text{ N NH}_4\text{ClO}_4$;
 $10^{-4} \text{ in OPA, } t = 6$
 hrs

$3 \times 10^{-3} \text{ N NH}_4\text{ClO}_4$;
 $5 \times 10^{-5} \text{ in OPA}$
 $t = 6 \text{ hrs}$

Fig. 17. Photomicrographs of 6061 aluminum corrosion in contact with NH_4ClO_4 solutions (pH runs)

6061 aluminum
(t = 0 hrs)

NH_4ClO_4 (10^{-2} N);
 1.3×10^{-3} N in OPA
Initial pH 5.45
Final pH 5.55
Static, t = 6 hrs

NH_4ClO_4 (10^{-2} N);
 3×10^{-3} N in OPA
Initial pH 6.2
Final pH 4.5
Static, t = 6 hrs

Fig. 18. 6061 aluminum following interaction with NH_4ClO_4 solution at various concentration of OPA

SECTION 3

O-PHTHALIC ACID, $C_6H_4(COOH)_2$

Due to the use of phthalate group polymers in some HE systems, and their potential breakdown through hydrolysis, it was decided to investigate the behavior of aqueous systems of phthalates in the form of o-phthalic acid.^a

Fig. 19 presents the conductance patterns of OPA (aqueous) systems using 6061 aluminum as the working electrode. Note the non-sequential trends as a function of concentration which occur. A further visual inspection of these trends (Fig. 20) relates cell resistance as a function of concentration. The greatest conductance values lie at an intermediate concentration range while those on either side of this range are far removed in relative conductance. Fig. 21 presents photomicrographs of the aluminum electrodes before and after the individual system runs.

The results of pH runs (Fig. 22) of these solutions present a near adherence to nominal value changes which are themselves in a sequential order as a function of concentration. Fig. 23 presents photomicrographs of the aluminum rods following these runs. Static runs at which the pH was measured at 1-hour intervals (Fig. 24) show no appreciable difference between the monitored runs and the static, with the exception of an initial decrease during the first one-half hour for the higher concentration ($10^{-4}N$). Extended pH runs (up to 100 hrs) present dynamic

^a o-phthalic acid will be referred to by its chemical acronym, OPA, for the remainder of this report.

systems following the nominal time period of $t = 6$ hours (Fig. 25). When the system vehicle was changed from aqueous to ethanolic/aqueous (Fig. 26) the systems are sequential in pH values as a function of concentration (decrease), but all systems approach a constant value after ~ 10 hours. That of greater concentration (lowest pH) is anomalous in that its pH increases but still approaches the constant value of the other systems.

Comments

The conductance behavior of OPA solutions over the concentration ranges studied presents a system which undergoes an initial near-linear trend to lower conductance values as a function of increasing concentration, then undergoes a radical reversal to lower conductance through an intermediate range of concentration followed by a return to substantially decreased conductance at the high end of the concentration range.

The pH of the several OPA systems do not present anomalous behavior trends but adhere to a somewhat linear sequence relative to concentration.

Extensive pitting of the 6061 seems to occur at intermediate concentrations of OPA.

Fig. 19. Cell resistance of various o-phthalic acid concentrations (aqueous) using a 6061 aluminum working electrode

Fig. 20. Cell resistance of various o-phthalic acid solutions using a 6061 aluminum electrode at $t = 7$ hours

$t = 0$

$6 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

$13 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

$84 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

Fig. 21. Photomicrographs of 6061 aluminum (working electrode) at various concentrations of OPA (topograph).

Fig. 22. pH of various o-phthalic acid solutions (aqueous) in contact with 6061 aluminum

Fig. 23. Photomicrographs of 6061 aluminum rod after contact with various concentrations of aqueous OPA solutions (pH runs)

$26 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

$84 \times 10^{-5} \text{ N}$
 $t = 6 \text{ hrs}$

$210 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

$t = 0$

$5 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

$13 \times 10^{-5} \text{ N}$
 $t = 7 \text{ hrs}$

— $5 \times 10^{-5} \text{ N}$
 - - - $10 \times 10^{-5} \text{ N}$

Fig. 24. pH of various o-phthalic acid solutions (aqueous) in contact with 6061 aluminum (static runs)

Fig. 25. pH of aqueous 0-phthalic acid solutions in contact with 6061 aluminum

Fig. 26. pH of ethanolic (95%) solutions of o-phthalic acid in contact with 6061 aluminum

SECTION 4

HEXAAMMINECOBALT III PERCHLORATE, HCP

Due to the frequent occurrence of HCP as a by-product in the preparation of the majority of amine complexes, the effect of HCP on 6061 aluminum in unicomponent and in OPA acidified aqueous systems was studied. Some data on saturated 95% ethanolic systems was also obtained.

Fig. 27 presents the cell resistance trends of unicomponent HCP and of HCP/OPA systems. Although some individual variations can be seen to occur, the overall general behaviors are quite similar; a somewhat precipitous increase in cell resistance at the onset followed by a nearly similar but reversed behavior to substantially lower resistance values and subsequently a somewhat vacillating behavior at increased conductance. Photomicrographs of the 6061 electrodes (Fig. 28) give visual indications of a greater degree of pitting with the non-OPA systems. The residues (evaporates) from the conductance runs show no appreciable change in the molecular functionality of the systems (IR spectra, Fig. 29) but there are slight variations in the thermal behavior patterns of the systems (DTA thermograms, Fig. 30).

Cell EMF behavior (Fig. 31) presents quite similar patterns for HCP and HCP with the higher concentration of OPA. That system containing the lower concentration of OPA shows an anomalous behavior pattern, while the former systems undergo a substantial increase in cathodic character at the onset followed by a similar but reversed pattern toward anodic characteristics the latter system undergoes a relatively moderate trend in a cathodic direction. All three systems tend toward a general common range of EMF values.

Results of a pH study (Fig. 32) show an expected sequential display as a function of concentration with no indication of radical reaction behavior. All systems increase toward a more basic system at the onset followed by a general drifting in that direction.

The extent of pitting of 6061 aluminum in the previous systems is visually displayed through photomicrographs (Fig. 33). Although pitting seems more substantial in the OPA systems, the unicomponent HCP systems appear more extensive and general.

The molecular functionality of the evaporates as shown by IR spectra (Fig. 34) indicates overall retention but with indication of the presence of an ammonium compound (NH_4 , $\delta_d \sim 7.00\mu$). Inspection of white particles present in the evaporates show this material to be ammonium perchlorate, NH_4ClO_4 . That this reaction has taken place is indicated by the eventual loss of the yellow coloration of the solutions during extended elapsed times (~ 50 hrs). The same occurrence was found in regards to the conductance evaporates (Fig. 35, spectra A & B).

DTA thermograms of pH evaporates show some variations in the thermal behavior of the materials (Fig. 36), with the emergence of an exotherm at ~ 315 C.

At increased concentrations of HCP (~ 900 mg/l) cell resistance behavior of the HCP and HCP/OPA systems are essentially the same (Fig. 37). In an OPA system which is $\sim 2.5 \times 10^{-4}$ N there is a substantial initial increase in conductance followed by an immediate but opposite behavior. When OPA becomes part of the HCP system, there is no indication of this behavior.

Cell EMF for these systems (Fig. 38) show generalized trends toward a more cathodic character for both HCP and HCP/OPA systems.

pH behavior of these systems (Fig. 39) shows a large increase at the onset for the HCP system followed by general minimal change. The HCP/OPA system undergoes a near continual undulating action but always in the direction of a more basic system.

Pitting effects on 6061 aluminum are shown in Fig. 40, and appears, at these increased concentrations, to be far more extensive in the HCP/OPA system.

When a saturated 95% ethanolic solution of HCP is run, quite similar conductance behavior is found for both HCP and for HCP/OPA (Fig. 41). The pH runs of these systems show somewhat divergent behavior patterns at the onset, but overall very little change from the original conditions, $t = 0$ hours (Fig. 42).

Fig. 39 shows the relative cell EMF values for the ethanolic system as compared to that of the aqueous. The ethanolic systems initially assume a more cathodic condition but revert to a gradual increase to anodic behavior.

Comments

Aqueous HCP systems, including those with OPA added, undergo an initial rapid decrease in conductance followed immediately by an increase of approximately the same magnitude. Photomicrographic data indicates a greater degree of pitting of 6061 aluminum with the non-OPA system. Some variation is seen to occur in the thermal characteristics (DTA) as a result of the conductivity environment. Cell EMF data indicates a lesser extent of cathodic drift with the intermediate system, i.e., the lower concentration of OPA.

pH behavior is essentially static. Pitting of 6061 in these systems shows a more general overall corrosion with the non-OPA solution. Ammonium perchlorate is found to occur during the course of the runs in both conductance cell and in the pH cell. Increased concentrations of HCP (900 mg/l) show far more extensive pitting of the 6061 aluminum stock.

HCP saturated ethanolic systems indicate a general trend in conductance to a near common value, with or without OPA in the system. The pH behavior is essentially static.

Fig. 27. Cell resistance of HCP solutions using a 6061 aluminum electrode

$t = 0$

70 mg/l

70 mg/l; 0.5×10^{-4}
N in OPA

70 mg/l; 1×10^{-4} N in OPA

Fig. 28. Photomicrographs of 6061 aluminum rod used as working electrode in HCP systems

Fig. 29. Infrared spectra of HCP residues (evaporated solutions) after conductance runs (6 hrs)

Fig. 30. DTA thermograms of various HCP conductance residues

Fig. 31. Cell EMF of HCP solutions using A6061 aluminum electrode

Fig. 32. pH of HCP solutions in contact with 6061 aluminum

$t = 0$

70 mg/l

70 mg/l; 0.5×10^{-4} N in OPA

70 mg/l; 1.0×10^{-4} N in OPA

Fig. 33. Photomicrographs of 6061 aluminum rod following pH runs with HCP solutions

Fig. 34. Infrared spectra of HCP residues (evaporated solutions) after pH runs (6 hrs)

pH run

Conductance run

Fig. 35. Infrared spectrum of white evaporate from pH and conductance runs of HCP (6 hrs)

Fig. 36. DTA thermograms of various HCP pH study residues

Fig. 37. Cell resistance of various solutions using a 6061 aluminum electrode

Fig. 38. Cell EMF at HCP solutions using a 6061 aluminum electrode

Fig. 39. pH of various systems in contact with 6061 aluminum

$t = 0$

910 mg/l

910 mg/l; 1.5×10^{-4}
N in OPA

910 mg/l; 3×10^{-4}
N in OPA

Fig. 40. Photomicrographs of 6061 aluminum rods following pH runs in HCP solutions of increased concentration

Fig. 41. Cell resistance of ethanolic (95%) solutions of HCP using a 6061 aluminum electrode

Fig. 42. pH of various ethanolic (95%) solutions of HCP in contact with 6061 aluminum

SECTION 5

UNMODIFIED CATCP - SANDIA LOT SL-UN-2

This material is the "dimer" molecule which is the precursor of "modified" CATCP. Its investigation was undertaken due to the probability of minimal amounts occurring in the modified material through less than total "polymerization" of the dimer in the preparative process. Fig. 43 presents the cell resistance behavioral patterns which are quite similar in spite of the variation in the compositional nature of the particular system under study. Overall, the conductance of all systems approach a decrease to the same general values. Infrared spectral results (Fig. 44) obtained from the conductance evaporates show only slight variations occurring at $\sim 7.00\mu$. DTA thermograms (Fig. 45) do show variations in the thermal behavioral patterns of the evaporates, relative to the original material.

Cell EMF behavior (Fig. 46) depicts a general decrease to a more cathodic condition for both OPA/CATCP systems, but an anomolous behavior for the non-OPA system: a sharp increase in the anodic direction initially followed by a reversal to a high degree of cathodic character which eventually approaches a general cell EMF value attained by the other (OPA) systems.

Photomicrographs of 6061 electrodes (Fig. 47) show the greatest extent of corrosion found to occur with the lower OPA concentration, with essentially very little corrosion indicated for the other two systems.

At significantly increased concentrations, i.e.; ~ 900 mg/l, overall cell resistance values are found to be in the same value range as that found to occur for lower concentrations, i.e., 70 mg/l (Figs. 43,49). Photomicrographs of the

6061 electrodes from these higher concentration systems are inconclusive although they appear to show corrosion to be more general.

The pH values of the various systems are sequentially decreasing as a function of the composition and are only involved in a gradual general trend toward slightly more basic systems. Static pH values are somewhat varied from those obtained from the continually monitored systems (Fig. 50). Infrared spectra of the pH evaporates (Fig. 51) indicate only slight variations occurring in the general spectral region of $6.00 - 7.25\mu$, and indicate formation of some ammonium compound ($\text{NH}_4 + \delta_d, 7.25\mu$).

DTA thermograms of the evaporates do show variations in the thermal behavior with the emergence of a significant exotherm at $\sim 325^\circ\text{C}$ (Fig. 52). As seen in the previous cell resistance results (70 mg/l systems) photomicrographs of the 6061 rods show the greatest amount of corrosion found with the lower OPA concentration system (Fig. 53).

The pH behavior of these systems (increased SL-UN concentration) show the greatest variations in the non-OPA systems but essentially minimal change after ~ 10 hours (Fig. 54).

When SL-UN-2 is run as a saturated system in 95% ethanol the pH behavior of the non-OPA system is quite erratic with a continuing substantial increase toward a basic system while the OPA acidified system presents only a somewhat dormant though vacillating system with no significant overall change in the pH (Fig. 55). Photomicrographs of the 6061 rods give visual indications of generally more intense corrosion in the non-OPA system, which would correlate with results of pH behavior (Figs. 55,56) which is somewhat anomalous to the aqueous system.

Comments

Conductance behavior of these systems (70 mg/l) are essentially the same; following an immediate initial increase in conductance a general trend toward a decreased conductance of approximately the same magnitude relative to that at $t = 0$ hours is observed. A 13 fold increase in the concentration of SL-UN-2 (900 mg/l) does not essentially change the overall conductance values of the various systems. Indication of the formation of NH_4 material(s) is found in the evaporates of the various systems. Cell EMF values show an overall increase in cathodic behavior and character. The highest degree of corrosion of the 6061 rods is found with the lower OPA concentration in both conductance and in pH runs. The pH behavior is fairly dormant but with general slight increases toward more basic systems. DTA thermograms show changes in the thermal character of the evaporates.

Ethanollic solutions of SL-UN-2 (saturated) show substantial though somewhat step-wise increases in pH while the SL-UN/OPA system shows little appreciable change. Photomicrographs present anomalous behavior patterns for these systems, relative to those of the aqueous, in that the greatest degree of corrosion is seen to occur in the non-OPA system.

— 70 mg/ℓ
 - - - 70 mg/ℓ; 5×10^{-5} N in OPA
 — 70 mg/ℓ; 10×10^{-5} N in OPA

Fig. 43. Cell resistance of various SL-JN-2 solutions using a 6061 aluminum electrode

Fig. 44. Infrared spectra of SL-UN-2 evaporates from conductance runs

EXO
↑
ΔT
↓
ENDO

Fig. 45. DTA thermograms of SL-UN-2 evaporates from conductance runs

— 70 mg/l
 --- 70 mg/l; 5×10^{-5} N in OPA
 - - - 70 mg/l; 10×10^{-5} N in OPA

Fig. 46. Cell EMF of various SL-UN-2 solutions using a 6061 aluminum electrode

$t = 0$

70 mg/l
($t = 6$ hrs)

70 mg/l; 5×10^{-5} N
in OPA ($t = 6$ hrs)

70 mg/l; 10×10^{-5} N
in OPA ($t = 6$ hrs)

Fig. 47. Photomicrographs of 6061 aluminum electrode after use in SL-UN-2 solutions

$t = 0$

900 mg/l
($t = 45$ hrs)

900 mg/l; 2.5×10^{-4}
N in OPA
($t = 40$ hrs)

Fig. 48. 6061 aluminum electrode after contact with SL-UN-2 solutions

Fig. 49. Cell resistance of CATCP (SL-UN-2) solutions using a 6061 aluminum electrode

Fig. 50. pH of various SL-UN-2 solutions in contact with 6061 aluminum

Fig. 51. Infrared spectra of SL-UN-2 evaporates from pH runs

Fig. 52. DTA thermograms of SL-UN-2 pH evaporate

$t = 0$

70 mg/l
($t = 6$ hrs)

70 mg/l; 5×10^{-5} N
in OPA ($t = 6$ hrs)

70 mg/l; 10×10^{-5} N
in OPA ($t = 6$ hrs)

Fig. 53. Photomicrographs of 6061 aluminum after contact with SL-UN-2 solution (pH runs)

Fig. 54. pH of various solutions in contact with 6061 aluminum

Fig. 55. pH of various ethanolic solutions in contact with 6061 aluminum.

$t = 0$

Ethanol (sat) with
SL-UN-2 ($t = 60$ hrs)

Ethanol (sat) with
SL-UN-2 with 0.05
meq OPA

Fig. 56. Photomicrographs of 6061 aluminum contact with saturated ethanolic (95%) solutions of SL-UN-2 (pH runs)

SECTION 6

MODIFIED CATCP (SANDIA LOT TF-AK)

This system was investigated in a fractional study which included the solubles system, the insolubles system, and the solubles/insolubles system. The first two systems were effected through aqueous extraction of the original material followed by filtration through a sintered frit.

Group A. The TF-AK Solubles/Insolubles System

The cell resistance behavior of this system (Fig. 57) shows similar overall conductance patterns, but with an anomalous initial increase in conductance for the non-OPA system relative to the sharp initial decrease found with those systems containing OPA. Spectral data obtained from the residues (Fig. 58) show appreciable changes occurring in the region of $\sim 6.0 - 7.3\mu$. DTA thermograms of the residues show significant changes occurring in the exothermal patterns, particularly that of highest OPA concentration (Fig. 59, thermogram D), and also indicated by the visual evidence of overall corrosion of the 6061 electrodes (Fig. 60).

Cell EMF results depict the same anomalous trend as found with the non-OPA cell conductance values (Fig. 61). All three systems do tend toward a more cathodic and generally common EMF value.

Photomicrographs (Figs. 62,63) of 6061 aluminum from non-OPA systems with substantial increases in CATCP concentration show extensive corrosion.

The pH trends of these systems (Fig. 64) show small but generally linear increases for the three systems in a sequential manner as a function of concentration of OPA. Spectral results again show a substantial change in the 6.0 - 7.5 μ region (Fig. 65). However, changes which are seen to occur in DTA exothermic patterns for pH run residues are not indicative of those seen for the conductance runs (Figs 59D,66D).

At increased concentrations of CATCP (non-OPA systems), the pH increases are quite appreciable and when monitored for extended periods (up to 70 hrs) are seen to be quite erratic in a somewhat periodic manner at an intermediate concentration (Fig. 67).

The pH behavior of highly concentrated systems (880 mg/l) show a wide range of values which generally increase sequentially as a function of concentration with relatively unique behavior seen for the non-OPA system (Fig. 68). Extended periods (70 hrs) show a gradual, though continuing increase to a more basic system. The relative corrosion effects are shown in photomicrographs of the 6061 rods (Fig. 69).

Group B. The TF-AK Solubles System

Although the actual conductance value is significantly higher at an increased concentration of solubles ($\sim \times 2$), the lower concentration system overall is more dynamic (Fig. 70). At the nominal concentration of solubles (70 mg/l, less insolubles) the acidified systems indicate some degree of passivation in the system at higher OPA concentration. As with the solubles/insolubles systems, spectral data show significant changes occurring in the region of $\sim 6.0 - 7.5\mu$ (Fig. 71). Photomicrographs of the electrodes (Fig. 72) show appreciable general corrosion in the non-OPA solubles system at higher concentration (137 mg/l)

but does not appear as "selective" as that at 70 mg/l. There is visual indication of a degree of passivation of the 6061 rod in the OPA systems.

Cell EMF data shows the greatest change toward cathodic character in the non-OPA system at 137 mg/l (Fig. 73), while the acidified systems show a general overall dormancy.

The pH behavior depicts a somewhat static condition in the 70 mg/l solubles system while that for the 137 mg/l concentration shows a linear but significant increase (Fig. 74). The acidified systems show an abrupt initial decrease followed by a gradual near linear increase in pH for the lesser concentrated OPA system, while the more concentrated system shows only a gradual though linear increase. All four systems show a sequential order of decrease in pH as a function of concentration. Noteworthy is the nearly consistent anomalous behavioral pattern of the lower concentration OPA systems relative to other systems, which has been found to occur so frequently in other systems studied.

Spectral results of the solubles evaporates show changes occurring at $\sim 6.0 - 7.5\mu$ (Fig. 75), which also occurred in this region in the conductance cell systems.

Photomicrographs of the 6061 aluminum rods from these pH studies are presented in Fig. 76.

Fig. 57. Cell resistance comparison of TF-AK systems (solubles/insolubles) using a 60 61 aluminum electrode

Fig. 58. Infrared spectra of TF-AK solubles/insolubles residues (conductance runs)

Fig. 59. DTA thermograms of various TF-AK solubles/insolubles conductance run residues

A. $t = 0$

B. 70 mg/l
($t = 6$ hrs)

C. 70 mg/l
 5×10^{-5} N in OPA
($t = 6$ hrs)

D. 70 mg/l
 10×10^{-5} N in OPA
($t = 6$ hrs)

Fig. 60. Photomicrographs of 6061 aluminum after contact with TF-AK solutions (solubles/insolubles)

100
100
100
100

Fig. 61. Cell EMF of TF-AK solubles/insolubles systems using a 6061 aluminum electrode

$t = 0$

440 mg/l
 $t = 70$ hrs

880 mg/l
 $t = 70$ hrs

Fig. 62. Photomicrographs of 6061 aluminum after contact with TF-AK solutions (solubles/insolubles)

Fig. 63. Photomicrographs of 6061 aluminum electrode after contact with TF-AK solutions (solubles/insolubles)

Fig. 64. pH of TF-AK solubles/insolubles systems in contact with 6061 aluminum

Fig. 65. Infrared spectra of TF-AK liquid/solid phase residues (pH runs)

Fig. 66. DTA thermograms of TF-AK solubles/insolubles pH study residues

Fig. 67. pH of TF-AK solubles/insolubles systems in contact with 6061 aluminum

Fig. 68. pH of TF-AK solubles/insolubles systems in contact with 6061 aluminum

A. $t = 0$

B. 880 mg/l
($t = 70$ hrs)

C. 880 mg/l
 5×10^{-5} N in OPA
($t = 70$ hrs)

D. 880 mg/l
 26×10^{-5} N in OPA
($t = 70$ hrs)

Fig. 69. Photomicrographs of 6061 aluminum after contact with TF-AK solubles/insolubles systems

Fig. 70. Cell resistance of TF-AK solubles using a 6061 aluminum working electrode

Fig. 71. Infrared spectra of TF-AK solubles evaporates (conductance runs)

Fig. 72. Photomicrographs of 6061 aluminum electrodes after contact with TF-AK solubles

Fig. 73. Cell EMF of TF-AK solubles using a 6061 aluminum electrode

— 137 mg/l
 -.- 70 mg/l
 --- 70 mg/l; 0.5×10^{-4} N in OPA
 —○— 70 mg/l; 1.0×10^{-4} N in OPA

Fig. 74. pH of TF-AK solubles in contact with 6061 aluminum

Fig. 75. Infrared spectra of TF-AK solubles evaporates (pH runs)

A. $t = 0$

B. 137 mg/l
($t = 6$ hrs)

C. 70 mg/l
($t = 6$ hrs)

D. 70 mg/l
 5×10^{-4} N in OPA
($t = 6$ hrs)

Fig. 76. Photomicrographs of 6061 aluminum after contact with TF-AK solubles

Group C. The TF-AK Insolubles System*

This system produces highly active behavioral patterns of cell resistance change (Fig. 77). Although overall trends of all three systems are generally similar, an interesting facet is the initial rapid decrease in conductance followed abruptly by a substantially greater increase within the first few minutes. Addition of OPA does not appreciably alter the behavioral patterns. Spectral results (Fig. 78) show changes occurring at $\sim 7.0\mu$, but more noteworthy is the indicated presence in the residuals of terminal cyano groups ($\sim 4.9\mu$) in addition to the bridged cyano at ~ 4.5 . Photomicrographs of the exposed electrodes are presented in Fig. 79, where the most general corrosion pattern is again found in the lower OPA concentration system.

Cell EMF behavior (Fig. 80) shows a general though small increase in cathodic character of the systems, but with an appreciable amount of vacillating behavior in that system of highest OPA concentration.

Investigation of pH behavior of these systems (Fig. 81) show them to be substantially active but anomalous to each other. The non-OPA system undergoes an initial substantial decrease followed by a near static behavior. The lower concentrated OPA system produces an initial decrease followed by a reversion to increased pH and static behavior. The highest concentrated OPA system undergoes an initial substantial increase that precedes a static condition. All three systems approach a generalized common range of pH after ~ 1 hour.

* The amount of insolubles retained after aqueous extraction, considering losses in filtering frit, handling, etc., was $\sim 73\%$.

Spectral results are presented in Fig. 82. Photomicrographs of the 6061 rods are shown in Fig. 83; more appreciable corrosion occurs with the lower concentration OPA system.

Comments - Systems Comparison

Cell resistance behavior of the non-OPA systems (Fig. 84) show generally similar patterns for the solubles and for the solubles/insolubles systems, but a distinctly anomalous behavior for the insolubles system. It is noted that immediately following initiation of the runs a substantial amount of insolubles solids flow to and adhere to the electrode, but this occurrence is seen for both the insolubles and for the solubles/insolubles systems which leaves the sharp initial decrease in conductance of the insolubles system as anomalous in character.

Cell EMF of these systems (Fig. 85) show the insolubles system undergoing the greatest increase in cathodic character, both in relative change and in absolute value. The cell EMF for these same systems containing $0.5 \times 10^{-4}N$ OPA again show the greatest degree of cathodic change in that of the insolubles systems (Fig. 86).

Cell resistance comparison of the solubles/insolubles and the solubles systems, both with and without OPA (Fig. 87) show a general increase in conductance for the insolubles system while that with OPA and the solubles system, both with and without OPA show general decreases in conductance. Cell EMF behavior for these systems show a general moderate increase in cathodic behavior for all systems (Fig. 88). The solubles/insolubles system, with and without OPA, undergo the most erratic patterns.

The pH comparison of the three fractionate systems (Fig. 89) show the solubles system in a near static condition while the insolubles system undergoes the greatest change. Although the insoluble system changes to a more acidic state, the other systems become slightly more basic.

The pH comparison of the solubles/insolubles and of the solubles systems (Fig. 90) show general though slight increases toward a more basic system with only the insolubles/OPA system showing any anomalous behavior; an abrupt decrease at the onset followed by a gradual slight increase.

Fig. 77. Cell resistance of TF-AK insolubles using a 6061 aluminum electrode

Fig. 78. Infrared spectra of TF-AK insolubles solution residues (conductance runs)

t - 0

70 mg/l

70 mg/l; 0.5×10^{-4} N
in OPA

70 mg/l; 1.0×10^{-4} N
in OPA

Fig. 79. Photomicrographs of 6061 electrode after 6 hrs contact with TF-AK insolubles

Fig. 80. Cell EMF of TF-AK insolubles systems using a 6061 aluminum electrode

Fig. 81. pH of TF-AK insolubles systems in contact with 6061 electrode

Fig. 82. Infrared spectra of TF-AK insolubles systems residues (pH runs)

$t = 0$

70 mg/l

70 mg/l; 0.5×10^{-4} N
in OPA

70 mg/l; 1.0×10^{-4} N
in OPA

Fig. 83. Photomicrographs of 6061 aluminum after 6 hrs contact with TF-AK insolubles (pH runs)

Fig. 84. Cell resistance comparison of various TF-AK fractionate systems using a 6061 aluminum electrode

Fig. 85. Cell EMF comparison of various TF-AK fractionate systems using a 6061 aluminum electrode

Fig. 86. Cell EMF comparison of IF-AK fractionate systems using a 6061 aluminum electrode with OPA concentration at 0.5×10^{-4} N

— 70 mg/l
 - - - 70 mg/l 0.5×10^{-4} N in OPA
 —•— 70 mg/l (less insolubles); 0.5×10^{-4} N in OPA
 —○— 70 mg/l (less insolubles)

Fig. 87. Cell resistance comparison of various TF-AK fractionate systems using 6061 aluminum electrodes

Fig. 88. Cell EMF comparison of various TF-AK fractionate systems using 6061 aluminum electrode

Fig. 89. pH comparison of various TF-AK fractionate systems in contact with 6061 aluminum

Fig. 90. pH comparison of TF-AK fractionate systems in contact with 6061 aluminum

SECTION 7

MODIFIED CATCP (SANDIA LOT TF-AH)

This system was investigated in a manner identical to that of TF-AK (Sec. 6) i.e., through fractionate study by aqueous separation of the material.

Group A. The TF-AH Solubles System

Cell resistance behavior (Fig. 91) presents highly similar patterns for the non-OPA and lower content OPA systems; an abrupt initial increase in conductance followed by an equally abrupt decrease which undergoes a slowly drifting increase for the non-OPA and a slight decrease in the acidified system. The higher content OPA system is distinctly anomalous in behavior, undergoing a significant decrease in conductance during the first hour then assuming a slight but general decrease to even lower conductance.

Fig. 92 shows slight variations occurring in the spectral patterns of the acidified systems (residual evaporates) in the region of $\sim 6.4\mu$. DTA results (Fig. 93) do not indicate any appreciable changes in the thermal patterns. Visual appraisal of the electrodes through photomicrographs (Fig. 94) indicate the more general and extensive corrosion occurs in the non-OPA system. Cell EMF measurements tend to support this observance in that the most radical change in cathodic character is found with the non-OPA system (Fig. 95), but the greatest overall change toward a more cathodic condition occurs with the highest content OPA system.

Fig. 91. Cell resistance of the TF-AH solubles system

A. 70 mg/l
(less insolubles)

B. 70 mg/l
(less insolubles)
 0.5×10^{-4} N in
OPA

C. 70 mg/l
(less insolubles)
 1.0×10^{-4} N in
OPA

Fig. 92. Infrared spectra of TF-AH solubles evaporates (conductance runs)

Fig. 93. DTA thermograms of the TF-AH solubles systems evaporates from conductance studies

$t = 0$

70 mg/ μ^2
(less insolubles)

70 mg/ μ^2 ; (less insolubles)
0.5 x 10⁻⁴ N in OPA

70 mg/ μ^2 ; (less insolubles)
1.0 x 10⁻⁴ N in OPA

Fig. 94. Photomicrographs of 6061 aluminum electrodes after contact with TF-AH solubles

Fig. 95. Cell EMF of the TF-AH solubles system

The pH trends (Fig. 96) display near dormant though slightly increasing values for the OPA containing solutions while that of the non-OPA shows a relatively active system increasing to a significantly more basic condition. Similar to the conductance runs the spectral results show some change occurring at $\sim 6.4\mu$ (Fig. 97). DTA results of the evaporates are not indicative of any appreciable changes (Fig. 98). Anomalous behavior is found in the photomicrographs of the 6061 rods following the pH runs in that unlike the conductance run electrodes the heaviest, albeit selective, erosion is found with the non-OPA and the higher concentration of OPA (Fig. 99). Photomicrographs of the rods from the static pH runs show the greatest pitting occurs in the non-OPA system (Fig. 100).

Group B. The TF-AH Insolubles System

The conductance patterns of all three systems are highly similar; those of OPA content are very close in value and pattern while the non-OPA system is significantly greater in terms of magnitude of change (Fig. 101). Significant changes are seen to occur in the spectral patterns of these residues (Fig. 102), particularly in the regions of $4.5 - 5.0\mu$ (CN), $6.8 - 7.0\mu$, and $11 - 12\mu$. Photomicrographs of the electrodes are presented in Fig. 103.

As found with the conductance patterns the cell EMF behavioral trends of the three systems are highly similar; an abrupt increase in cathodic character initially followed by a gradual but undulating drift to a less cathodic condition but maintaining more cathodic character than at $t = 0$ hours (Fig. 104).

The pH behavior is again quite similar among the three systems with the order of trend occurrence in a decreasing sequential manner as of function of concentration of the OPA content (Fig. 105).

Fig. 96. pH of the TF-AH solubles system in contact with 6061 aluminum

Fig. 97. Infrared spectra of TF-AH solubles systems evaporates (pH runs)

Fig. 98. DTA thermograms of various TF-AH solubles system evaporates (pH runs)

A. 70 mg/l
(less insolubles)

B. 70 mg/l
(less insolubles)
 0.5×10^{-4} N in
OPA

C. 70 mg/l
(less insolubles)
 1.0×10^{-4} N in
OPA

Fig. 99. Photomicrographs of 6061 aluminum rod after contact with TF-AH solubles systems (pH runs)

A. 70 mg/l
(less insolubles)

B. 70 mg/l
(less insolubles)
 0.5×10^{-4} N
in OPA

C. 70 mg/l
(less insolubles)
 1.0×10^{-4} N
in OPA

Fig. 100 Photomicrographs of 6061
aluminum rods after contact
with TF-AH solubles systems
(static pH runs)

Fig. 101. Cell resistance of the TF-AH insolubles system using a 6061 aluminum electrode

Fig. 102. Infrared spectra of TF-AH insolubles system residues (conductance runs)

$t = 0$

70 mg/l
(less solubles)

70 mg/l; (less solubles)
 0.5×10^{-4} N in OPA

70 mg/l; (less solubles)
 1.0×10^{-4} N in OPA

Fig. 103. Photomicrographs of 6061 aluminum electrodes after contact with the TF-AII insolubles systems

Fig. 104. Cell EMF of TF-AH insolubles system using a 6061 aluminum electrode

Fig. 105. pH of the TF-AH insolubles system

There is some change occurring spectrally in the evaporates of the systems albeit not as extensive as found in the residuals of the conductance runs (Fig. 102,106).

Photomicrographs of the 6061 rods (Fig. 107) show the more general corrosive action found in the non-OPA system. The static pH runs produce this same result, however, with significant but selective corrosion in the OPA system the extent of which is not apparent in the results from the monitored pH runs (Fig. 108).

Group C. The TF-AH Solubles/Insolubles System

Cell resistance behavior of the non-OPA system is significantly different from those of the OPA systems which are themselves quite similar (Fig. 109). The non-OPA system undergoes an abrupt and substantial decrease in conductance initially, followed by a trend of general dormancy while the OPA systems show a moderate initial increase in conductance followed by a significant decrease to one of near dormancy.

Spectral results show appreciable changes occurring in the functional group patterns (Fig. 110). The results of DTA show an appreciable change in the exothermic character from that of the original material (Fig. 111). The more general corrosion of the 6061 electrodes is found in the lower OPA concentration system (photomicrographs, Fig. 112).

The cell EMF results show the greatest difference and activity in the non-OPA system while those of the OPA systems are generally similar (Fig. 113).

The pH results (Fig. 114) show similar behavior for the OPA containing systems but different from the non-OPA run. Their order is in a sequentially decreasing

pH as a function of concentration of acid.

Spectral results show appreciable changes occurring in all systems (Fig. 115). DTA results also show a significant change occurring relative to the thermal patterns of the original material (Fig. 116). Photomicrographs of the 6061 rods following the pH runs are presented in Fig. 117.

Comments - Systems Comparison

Cell resistance of the non-OPA systems show anomalous behavior patterns for all three (Fig. 118). The greatest changes which occur in overall cell conductance are found in the insolubles system while the solubles system changes only slightly overall, save for a brief pattern of vacillation initially. The solubles/insolubles system pattern does not, at this time, appear to logically relate to the curves of its components.

The cell EMF comparison portrays similar behavior patterns for both the solubles and insolubles systems, but again it does not readily appear how it relates to their composite (Fig. 119).

The pH behavior (Fig. 120) shows a significant though meandering path of increase toward a more basic system for the solubles system, while the insolubles system shows a somewhat reversed path initially although increasing slightly beyond that point. The composite system (solubles/insolubles) produces values somewhat intermediate to those of its components: a very slight increase is seen for this system.

Comparison of pH behavior for the solubles system (Fig. 121) when one considers the initial and final values from both the monitored and static runs ($t = 0$, 6 hrs & $t = 15$ minutes and 6 hrs, respectively) show consistently lower values obtained in the static runs. An anomaly exists in the case of the lower concentration of OPA in that this system produces converging values; one increasing and one decreasing. The insolubles system again produces this anomaly with the lower OPA content system (Fig. 122). The solubles/insolubles system does not show this behavior (Fig. 123).

Fig. 106. Infrared spectra of TF-AH insolubles systems (pH runs)

A. 70 mg/l
(less solubles)

B. 70 mg/l
(less solubles)
 0.5×10^{-4} N
in OPA

C. 70 mg/l
(less solubles)
 1.0×10^{-4} N
in OPA

Fig. 107. Photomicrographs of 6061 aluminum rods after contact with TF-AH insolubles system (pH runs)

A. 70 mg/l
(less solubles)

B. 70 mg/l
(less solubles)
 0.5×10^{-4} N
in OPA

C. 70 mg/l
(less solubles)
 1.0×10^{-4} N
in OPA

Fig. 108. Photomicrographs of 6061 aluminum rods after contact with TF-AH insolubles system (static pH runs)

Fig. 109. Cell resistance of the TF-AH solubles/insolubles system

Fig. 110. Infrared spectra of TF-AH solubles/insolubles systems residues (conductance runs)

Fig. 111. DTA thermograms of the TF-AH solubles/insolubles residues from conductance studies

Fig. 113. Cell EMF of the TF-AH solubles/insolubles system

Fig. 114. pH of the TF-AH solubles/insolubles system in contact with 6061 aluminum

Fig. 115. Infrared spectra of TF-AH solubles/insolubles system residues (pH runs)

Fig. 116. DTA thermograms of the TF-AH solubles/insolubles system (pH runs) residues

$t = 0$

70 mg/l
($t = 6$ hrs)

70 mg/l
 5.0×10^{-5} N
in OPA ($t = 6$ hrs)

Fig. 117. Photomicrographs of 6061 aluminum after contact with TF-AH solubles/insolubles systems

Fig. 118. Cell resistance comparison of the TF-AH fractionation system

Fig. 119. Cell EMF comparison of the TF-AH fractionate system

Fig. 120. pH comparison of the TF-AH fractionate system

Fig. 121. pH comparison of static and monitored values (initial & final only)

Fig. 122. pH comparison of static and monitored values (initial & final only)

- + 70 mg/l
- 70 mg/l; 0.5×10^{-4} N in OPA
- 70 mg/l; 1.0×10^{-4} N in OPA

Fig. 123. pH comparison of static and monitored values (initial & final only)

COMPARISON OF THE MODIFIED CATCP TF-AH AND TF-AK SYSTEMS

Group A. The Solubles Systems

Fig. 124 portrays the conductance behavior of the TF-AH system to be of a considerably more erratic character than that of TF-AK. The TF-AH system indicates an eventual drift to increased conductance values while the TF-AK system undulates to decreasing conductance. Cell EMF of the systems reflects this behavior with the TF-AH system undergoing the greater overall changes in cathodic behavior (Fig. 125), while the TF-AK system undergoes a gradual drift to a somewhat greater cathodic condition. Similar to the cell resistance and cell EMF patterns the pH behavior of the TF-AH system is emphatically more active than that of TF-AK (Fig. 126).

Group B. The Insolubles Systems

The cell resistance behavior of both the TF-AH and the TF-AK systems are highly similar in pattern (with time) except that the corresponding magnitude of change for the TF-AH is considerably greater (Fig. 127). Cell EMF behavior for TF-AH is again significantly greater in the magnitude of change (Fig. 128). The overall increase in cathodic character is significant for both systems. Surprisingly, the pH patterns of the two systems show only a minimal increase for the TF-AH system while the TF-AK system undergoes a relatively large decrease initially followed by a leveled near static value (Fig. 129).

Fig. 124. Cell resistance comparison of TF-AH & TF-AK solubles systems

Fig. 125. Cell EMF comparison of TF-AH & TF-AK solubles systems

Fig. 126. pH comparison of TF-AH & TF-AK solubles systems

Fig. 127. Cell resistance comparison of TF-AH & TF-AK insolubles systems

Fig. 128. Cell EMF comparison of TF-AH & TF-AK insolubles systems

Fig. 129. pH comparison of TF-AH & TF-AK insolubles systems

Group C. The Solubles/Insolubles Systems

The TF-AH system shows the greatest overall change (increase) in conductance ($\sim \times 2$ from $t = 0$ hrs) while the TF-AK system, although undergoing an erratic pattern overall, does not appreciably change its value of conductance at $t = 6$ hrs relative to $t = 0$ (Fig. 130). The cell EMF of these systems (Fig. 131) again show the TF-AH system to be the most dynamic, undergoing a significant increase in cathodic character ($\sim \times 2$). The pH behavioral patterns are quite similar for both (Fig. 132).

Group D. The Relative Behavior of HCP to the TF-AH, TF-AK Solubles System

Because of the presence of HCP in the CATCP systems a comparison of the cell resistance, cell EMF, and pH behavioral patterns is presented. The magnitude of changes seen is to be weighed, however, as the relative concentration of the CATCP system are considerably less than that of HCP.

The cell resistance behavior (Fig. 133) depicts a conductance pattern for HCP which is more dynamic than either of the CATCP patterns. If the systems were normalized (concentration) the TF-AH system would probably be the most active upon visual appraisal. Again, the same generalized appraisal of cell EMF behavior (Fig. 134) for the three systems can be made. The pH behavioral patterns show the TF-AH system to be the most active of the three (Fig. 135).

The overall assessment of these systems would indicate that the TF-AK material undergoes and/or causes the least amount of change to occur in reference to conductance, cathodic character, and pH.

Fig. 130. Cell resistance comparison of TF-AH & TF-AK solubles/insolubles systems

Fig. 131. Cell EMF comparison of TF-AH & TF-AK solubles/insolubles systems

— TF-AH, 70 mg/l
--- TF-AK, 70 mg/l

Fig. 132. pH comparison of TF-AH & TF-AK solubles/insolubles systems

Fig. 133. Cell resistance comparison of TF-AH & TF-AK solubles and HCP

Fig. 134. Cell EMF comparison of TF-AH, TF-AK solubles and HCP

— HCP, 70 mg/2
 - - - TF-AH, 70 mg/2 (less insolubles)
 - · - TF-AK, 70 mg/2 (less insolubles)

Fig. 135. pH comparison of TF-AH, TF-AK solubles and HCP

SECTION 8

THE PETN, HNAB, HMX AND RDX SYSTEMS

To determine whether the corrosive effects of the previously discussed materials (Sec. 1-7) are specifically unique to ionic/inorganic materials, a similar study of presently employed explosives materials was made. Since none of these substances is appreciably soluble in water, the studied systems were limited to mixtures of water and HE (i.e., a liquid/solid phase system) in the OPA and non-OPA system.

Group A. The PETN System

This system produces cell resistance patterns of high similarity for both OPA and non-OPA compositions (Fig. 136). A sequence of increasing conductance and decreasing magnitude of change occurs as a function of OPA concentration.

There is a very substantial change in the conductance during the initial 15-minutes for the non-OPA/PETN system. All three systems approach a generally common range of conductance values after ~ 3 hours.

The cell EMF patterns are also quite similar with a small degree of anomalous behavior found at the lower concentration of OPA (Fig. 137). This particular system shows an overall substantial increase in cathodic character of approximately 35% relative to $t = 0$ hours.

Photomicrographs of the 6061 electrodes (Fig. 138) show a definite degree of corrosion albeit no visual indication of the extent found to occur with the previously discussed inorganic systems (Sec. 1-7).

Fig. 136. Cell resistance of PETN mixtures (aqueous)

Fig. 137. Cell EMF of PETN mixtures (aqueous)

A. $t = 0$ hrs

B. 70 mg/l

C. 70 mg/l
 0.5×10^{-4} N in OPA

D. 70 mg/l
 1.0×10^{-4} N in OPA

Fig. 138. Photomicrographs of 6061 aluminum electrode after contact with various PETN systems

The pH behavioral patterns (Fig. 139) show little dissimilarity occurring among the three systems, the degree of eccentricity of the initial increase (up to $t = 1$ hr) decreasing with increasing OPA content. The system sequentially decreases as a function of the OPA concentration.

Not seen to occur in the conductance studies is the degree of "selective" corrosion (pitting) of the 6061 aluminum found in the "static" pH runs (Fig. 140).

Group B. The HNAB System

This system produces conductance patterns (Fig. 141) which are generally similar but showing only an undulating increase for the non-OPA system while those of OPA content undergo an initially sharp decrease in conductance followed by a substantial increase. All three systems essentially approach relatively dormant values after ~ 2 -3 hours. Their conductances are sequential as a function of OPA concentration.

The behavioral patterns from cell EMF data show a slight but undulatory increase in cathodic character for the non-OPA system (Fig. 142). Those of OPA content undergo reversals following initially sharp increases in cathodicity.

Visual appraisal of the 6061 electrodes (Fig. 143) shows that significant corrosion does occur in the HNAB system; more selective and extensive in the higher content OPA system but less selective and more general in the others.

Fig. 139. pH of PETN mixtures (aqueous)

A. 70 mg/l

B. 70 mg/l
 0.5×10^{-4} N
in OPA

C. 70 mg/l
 1.0×10^{-4} N
in OPA

Fig. 140. Photomicrographs of 6061 aluminum rod after contact with PETN systems (static pH runs)

Fig. 141. Cell resistance of HNAB mixtures (aqueous)

Fig. 142. Cell EMF of HNAB mixtures (aqueous)

A. $t = 0$ hrs

B. 70 mg/l

C. 70 mg/l
 0.5×10^{-4} N in OPA

D. 70 mg/l
 1.0×10^{-4} N in OPA

Fig. 143. Photomicrographs of 6061 aluminum electrode after contact with various HNAB systems

The pH behavior is seen to be quite similar (Fig. 144) for the non and lower concentration of OPA: a slight increase followed by somewhat dormant activity. The higher OPA content system produces an anomalous behavior pattern, undergoing an initially sharp decrease followed by a slight increase to rather dormant behavior. The systems are sequentially decreasing in value as a function of OPA concentration.

As with the PETN system, the corrosive effect in the "static" pH runs are seen to be substantially more extensive than found in the conductance study (Fig. 145).

Group C. The HMX System

The conductance behavior of the non-OPA/HMX system is somewhat uneventful, showing only a slight though undulating increase (Fig. 146). With the addition of OPA to an HMX system the extent and activity increases slightly at the lower concentration but has essentially the same pattern while the higher concentration of OPA ($\sim \times 2$) produces a significant change in its behavior; a considerable decreased conductance undergoing an initially sharp increase then levelling after the first 10-15 minutes to a near dormant though undulating state.

Cell EMF patterns show erratic comparisons but the greatest increase in overall cathodic character is found with the non-OPA system (Fig. 147).

A visual inspection of the 6061 electrodes shows considerable corrosion in all three systems but the greatest degree of selectivity is found to occur in the non-OPA system (Fig. 148).

- 70 mg/l
- - - 70 mg/l; 0.5×10^{-4} N in OPA
- 70 mg/l; 1.0×10^{-4} N in OPA

Fig. 144. pH of HNAB mixtures (aqueous)

A. 70 mg/l

B. 70 mg/l
 0.5×10^{-4} N
 in OPA

C. 70 mg/l
 1.0×10^{-4} N
 in OPA

Fig. 145. Photomicrographs of 6061 aluminum rod after contact with various HNAB systems (static pH runs)

Fig. 146. Cell resistance of HMX mixtures (aqueous)

Fig. 147. Cell EMF of HMX mixtures (aqueous)

A. $t = 0$ hrs

B. 70 mg/l

C. 70 mg/l
 0.5×10^{-4} N in OPA

D. 70 mg/l
 1.0×10^{-4} N in OPA

Fig. 148. Photomicrographs of 6061 aluminum electrodes after contact with various HMX systems

The pH behavior is most active in the non-OPA system (Fig. 149). Those of OPA content essentially undergo slight though gradual increases while the non-OPA system experiences an initial sharp increase followed by a linear moderate increase after approximately one hour. They sequentially decrease as a function of OPA concentration.

Inspection of the aluminum rods following static pH runs again indicate an apparently increased degree of corrosion compared to those used as electrodes in the conductance runs (Fig. 150).

Group D. The RDX System

The non-OPA system is anomalous in its conductance behavior relative to those containing OPA (Fig. 151); a sharp initial decrease abruptly followed by a sharp increase of an approximate equal magnitude, decaying into an undulating and slightly increasing value. Those of the acidified systems are somewhat similar in pattern.

The cell EMF data from the non-OPA system produces a pattern of radical increase in cathodicity but levels off to a slightly increased value after the first one-half hour (Fig. 152). The behavioral patterns of the OPA systems are, again, relatively similar.

Photomicrographs of the electrodes show corrosion to be in evidence for all three systems; the OPA containing systems show the corrosion to be more selective and extensive (Fig. 153).

Fig. 149. pH of HMX mixtures (aqueous)

A. 70 mg/l

B. 70 mg/l
 0.5×10^{-4} N
 in OPA

C. 70 mg/l
 1.0×10^{-4} N
 in OPA

Fig. 150. Photomicrographs of 6061 aluminum rod after contact with various HMX systems (static pH runs)

Fig. 151. Cell resistance of RDX mixtures (aqueous)

Fig. 152. Cell EMF of RDX mixtures (aqueous)

A. $t = 0$ hrs

B. 70 mg/l

C. 70 mg/l
 0.5×10^{-4} N in OPA

D. 70 mg/l
 1.0×10^{-4} N in OPA

Fig. 153. Photomicrographs of 6061 electrodes after contact with various RDX systems

The pH behavior for all three systems is similar and sequentially decreasing as a function of OPA concentration, but with increasing eccentricity of increment in the initial stages as a function of OPA content (Fig. 154).

Photomicrographs of the aluminum rods following static pH runs indicate that more extensive corrosion occurs in these runs than in the conductance runs (Fig. 155).

Fig. 154. pH of RDX mixtures (aqueous) in contact with 6061 aluminum

A. 70 mg/l

B. 70 mg/l
 0.5×10^{-4} N
 in OPA

C. 70 mg/l
 1.0×10^{-4} N
 in OPA

Fig. 155. Photomicrographs of 6061 aluminum rod after contact with various RDX systems (static pH runs)

Systems Comparisons

An inspection of the cell resistance behavior for the non-OPA containing systems of PETN, HNAB, HMX, and RDX (Fig. 156) show the most active systems in conductive behavior to be those of PETN and RDX. More interesting is the high degree of similarity of these two systems in behavioral patterns with time, considering that one is a symmetric aliphatic chain structure (PETN) while the other is a symmetric heterocyclic (RDX). From structure and compositional considerations one would expect that similarities in behavioral patterns of conductance, if they occur, would be found with RDX and HMX; but that is not the case.

However, cell EMF data from the four systems show RDX and HMX to behave in a somewhat similar manner (Fig. 157). The results do indicate that all four systems are capable of altering the cathodic behavior of 6061 aluminum and this alteration is not the total result of possible initial physical occurrence about the electrode, i.e., polarization etc.

Investigation of pH results, specifically photomicrographic data of the aluminum rods from static pH runs, does show that corrosion of these specific HE systems (Sec. 8) is not entirely the result of the imposed voltage across the cell, but rather results (at least in part) from the latent reactive and/or catalytic effects inherent in the aqueous systems (mixtures) themselves.

Fig. 156. Cell resistance comparison of various HE systems (aqueous)

Fig. 157. Cell EMF comparison of various HE systems (aqueous)

PROJECT COMMENTS

Due to the incomplete portions of this study which are undoubtedly interrelated to those portions completed (Sec. 1-8), overall correlative assessment of the results will not be attempted at this time. With the completion of studies involving the similar investigation of such materials as the poly diallylphthalates, a relatively high purity "modified" CATCP, the "silver double complex" of the CATCP system, and selected other materials, an overall analysis of the total accumulated data will be made which should be completed in a few weeks.