A PROCESS FOR PRODUCING HIGHLY WETTABLE ALUMINUM 6061 SURFACES COMPATIBLE WITH HYDRAZINE

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ABSTRACT

NASA's Global Precipitation Measurement (GPM) mission is an ongoing Goddard Space Flight Center (GSFC) project whose basic objective is to improve global precipitation measurements.

The space-based portion of the mission architecture consists of a primary or core spacecraft and a constellation of NASA and contributed spacecrafts. The efforts described in this paper refer to the core spacecraft (hereafter referred to as simply GPM) which is to be fabricated at GSFC. It has been decided that the GPM spacecraft is to be a "design-for-demise-spacecraft." This requirement resulted in the need for a propellant tank that would also demise or ablate to an appropriate degree upon re-entry. Composite overwrapped aluminum lined propellant tanks with aluminum propellant management devices (PMD) were shown by analyses to demise and thus became the baseline configuration for GPM.

As part of the GPM tank development effort, long term compatibility and wettability testing with hydrazine was performed on Al 6061 and 2219 coupons fabricated and cleaned by conventional processes. Long term compatibility was confirmed. However, the wettability of the aluminum as measured by contact angle produced higher than desired angles (> 30^0) with excessive scatter.

The availability of PMD materials exhibiting consistently low contact angles aids in the design of simple PMDs. Two efforts performed by Angeles Crest Engineering and funded by GSFC were undertaken to reduce the risk of using aluminum for the GPM PMD. The goal of the first effort was to develop a cleaning or treatment process to produce consistently low contact angles. The goal of the second effort was to prove via testing that the processed aluminum would retain compatibility with hydrazine and retain low contact angle after long term exposure to hydrazine. Both goals were achieved. This paper describes both efforts and the results achieved.

INTRODUCTION

OVERVIEW

The Global Precipitation Measurement (GPM) core spacecraft will be designed such that it demises ("burns up") below a specified amount of debris at the end of its mission upon entering the atmosphere. Crucial to a successful design for demisable spacecraft is the demise of its propellant tank. A composite overwrapped aluminum lined tank with a surface tension propellant management device (PMD) made of aluminum is the leading design for a demisable tank[1,2]. Such a tank would be the first hydrazine spacecraft tank to use aluminum for all of its wetted surfaces (as reported in open and unclassified sources).

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For a surface tension propellant management device to function satisfactorily, the propellant (hydrazine) must wet the active surfaces of the device and interior tank shell. Wetting depends not only on the metal alloy chosen but also depends on detailed characteristics such as manufacturing methods, cleaning processes, and surface condition of the item.

For some missions, surface tension propellant management devices using classic elements may be designed to accommodate contact angles on some surfaces of up to about 18°. For rare applications, contact angles even greater than 18° have been accommodated; however, wetting is required on all active surfaces and contact angles less than 8° are preferred. In all cases, consistently and reliably achieving less than the target contact angle is as important as the actual target value.

A surface treatment process has been developed for aluminum that produces surfaces that hydrazine will wet with acceptably low contact angles[3]. This surface cleaning and treatment process includes solvent degreasing, an alkaline detergent soak that provides cleaning and deoxidation of the surface, and multiple rinses in hot water (hydrothermal rinse). During the hydrothermal rinses, a highly wettable surface with an amber or light amber color is formed. The amber or light amber color is due to the surface film that is formed during the hydrothermal rinses.

The presence of this surface film raises the following issues:

(1) Is there a surface component produced in the cleaning process that will affect long-term hydrazine compatibility, either producing hydrazine decomposition or generating residue in the hydrazine?

(2) Will the surface retain its high wettability and low contact angles over long-term exposure to hydrazine?

The hydrazine compatibility of aluminum samples subjected to the surface treatment process and their wettability after prolonged hydrazine exposure were evaluated by accelerated ageing carried out at an elevated temperature[4]. The wettability by hydrazine of the surfaces of the specimens was evaluated by contact angle measurement before and after accelerated ageing in hydrazine, and the hydrazine decomposition rate during accelerated ageing was measured.

BACKGROUND

There is a great deal of information available in the technical literature on the preparation of aluminum surfaces. Many of these processes are related to mechanical performance, corrosion protection, and appearance. To a lesser degree, the behavior of aluminum surfaces has been investigated in terms of wettability associated with heat exchange processes and surfaces treatments.

Lyerly and Peper reported the achievement of wettability of aluminum surfaces[5]. However, there are indications that surface cleaning was incomplete and that contaminants were carried forward or reintroduced on the test surfaces. It is likely that the reported wettability is a result of residual silica embedded in the aluminum oxide surface layer.

Dartevelle, et. al., observed the following during their investigations of plasma treatment to improve adhesive bonding by the removal of surface organic contaminants[6]: (1) plasma treatment increased surface wetting; (2) a 63-degree contact angle increased 10 degrees when measured 13 minutes after treatment; (3) an increase to 90 degrees occurred after one-month storage in "ambient laboratory air," which was interpreted as covering of the hydrophilic oxide surface with hydrophobic adsorbed volatile organic compounds.

Min and Webb investigated methods to promote wetting on aluminum fins[7]. Acetone cleaning was ineffective, but surface grinding resulted in somewhat smaller receding contact angles. They concluded smaller contact angles resulted from contaminant removal by grinding rather than an effect of increased surface roughness.

Strohmeier reported that oxygen plasma treatment removes a significant portion of surface contamination and that a portion of the residual contamination remains bound to the aluminum oxide surface and "cannot be removed.[8]" Plasma treatment produced initial contact angles of 5 degrees or less which increased to 30 degrees after exposure to ambient air for 1 day and to 60 degrees after 10 days.

Trevoy and Johnson investigated water wettability of metal surfaces including aluminum[9]. They advance that notion that clean metal surfaces free of organic and inorganic contamination exhibit zero contact angles. They reported water contact angles of less than 5 degrees by a process of chemical cleaning on aluminum surfaces prepared with powerful oxidizing acids followed by electropolishing in a sulfuric acid-phosphoric acid bath. Attempts to prepare clean surfaces using mechanical polishing (abrasion) followed by elaborate solvent rinses proved ineffective. Organic solvents followed by surface oxidation treatment and electropolishing to restore a smooth finish produced wettable surfaces.

Hong, et. al., evaluated the effects of oxidation and surface roughness on contact angles of water and other fluids on aluminum and copper[10]. The surfaces were cleaned using solvents and washing with detergents, then roughened with abrasives. Sessile drop contact angle measurements of water on aluminum gave contact angles of 57 degrees to 94 degrees.

These studies indicate the need to remove contaminants from the aluminum surface and to prevent recontamination. Surface cleaning with organic solvent is not effective in increasing wettability.

DEVELOPMENT OF SURFACE TREATMENT PROCESS

APPROACH

Hydrazine has been observed to not adequately wet specimens of Aluminum 6061 and 2219 in which the aluminum surfaces were treated by a typical aerospace process[2]. Consequently, work was initiated to develop a surface conditioning or cleaning process that can be implemented as a part of a propellant management device (PMD) manufacturing process to enable aluminum surface tension PMDs to be used in GPM missions.

Experimental investigations of the effects of surface treatment processes on surface wetting and liquid contact angle were performed. Coupons of Aluminum 6061 subjected to different surface conditioning processes were tested for wettability. Surface treatment processes were progressively changed as the experimental investigation proceeded to converge on a process that produced wettable surfaces and that can be reasonably implemented in a PMD manufacturing process.

A test cell was designed and fabricated to facilitate observation and photograph of contact angle and surface wetting behavior[3]. Contact angle photographs were processed digitally and contact angles were measured from the photographs. Contact angle observations were made in purified nitrogen atmospheres in the test cell. Contact angle observations were made with water, hydrazine, and 2-propanol.

To achieve high wettability a surface treatment process must include the following elements: (1) removal of surface contamination such as grease or oil films; (2) removal of existing oxide layer; (3) controlled reformation of a new surface layer; (4) maintenance of surface cleanliness.

The final surface treatment process that emerged from the process development work consists of precleaning, solvent degreasing, an alkaline detergent soak to provide cleaning and removal of the existing oxide film, and multiple rinses in hot water (hydrothermal rinses) to provide controlled reformation of a surface layer. During the hydrothermal rinses a new, highly wettable surface layer with an amber tint is formed. The final surface treatment process is shown in Table 1.

CONTACT ANGLE MEASUREMENT PROCEDURE

A contact angle cell was designed and fabricated to accommodate aluminum specimens and provide a controlled environment in which to conduct the wetting tests. The cell consists of an aluminum frame with glass side panels. Three droppers, which dispense drops of test fluid, were arrayed over the specimen test surface. A removable specimen holder provides vertical and longitudinal adjustment to properly position the specimen in relation to the droppers. The cell is equipped with purge ports to permit testing using different gaseous environments.

Table 1. Final Surface Treatment Process

STEP	PROCESS	METHOD
1	Pre-Clean	Remove oil or grease films. Precleaning process shall conclude with: 1) Naphtha wipe, 2) 99% IPA wipe and 3) 70% IPA wipe.
2	Degrease	Immerse part in room temperature Naphtha. Ramp heat circulating solvent to 44 ^{0}C. Circulate solvent over parts surfaces for 1 hour at 44 ^{0}C. Lightly brush part upon immersion and under immersion prior to removing part from solvent.
3	Detergent Brush	Place part in suitable tank or tray to allow complete immersion of part below surface of alkaline detergent. Moderately brush all surfaces, removing naphtha films.
4	Alkaline Clean	Immerse part in cleaning tank of pre-dissolved, room temperature alkaline detergent solution. Ramp heat the circulating solution to 55 ^{0}C and circulate over parts at 55 ^{0}C for 135 minutes. Lightly brush prior to removing part from solution.
5	Flush	Quickly transfer part to room temperature distilled water. Flush part with flowing distilled water. Lightly brush all surfaces while immersed.
6	Rinse 1	Immerse part in rinse tank of room temperature distilled water. Ramp heat the circulating water to 55 ^{0}C and circulate over part surfaces for 20 minutes at 55 ^{0}C.
7	Rinse 1 flush	Quickly transfer part to flush basin filled with room temperature distilled water. Flush with flowing distilled water. Quickly transfer part to rinse tank.
8	Rinse 2	Repeat steps 6 and 7.
9	Rinse 3	Repeat steps 6 and 7.
10	Dry	Dry part with blast of ultrapure Nitrogen.
11	Store	Place parts in clean polyethylene bags and purge with Nitrogen.
Note 1. Aqueous alkaline detergent solution is 1.7% by weight Alconox or equivalent. Note 2. Ramp heating such that final temperature is reached in 10 to 30 minutes.		

Contact angles were measured using the sessile drop method whereby the angle between the baseline of the drop and the tangent at the drop boundary is measured. A dropper was used to place a drop of liquid on the flat, level specimen test surface. The contact angle cell was used to prevent contamination of the test surface and to provide a saturated atmosphere. For all contact angle tests, the contact angle cell was filled with ultrapure nitrogen and saturated with the vapor of the liquid being tested. Contact angle did not increase over time even if the specimen remained in the cell in an ultrapure nitrogen atmosphere for several days between tests[3].

Several individual photo frames were shot during each contact angle test session for each specimen as drops were placed on the specimens from the left, center, or right droppers. Each photo frame is an observation of a drop or drops on the surface of the specimen being tested. Figure 1 shows a contact angle measurement photo of a highly wettable specimen. Contact angle measurements were taken from those frames of a drop or puddle that are free from edge effects and that correctly show the drop contact angles. In these measurements, contact angle did not increase over time between drops. This is consistent with previous results[3].

For screening observations, contact angles were estimated using a protractor or simply estimating angles visually when very high contact angles were observed. This approach allowed a rapid qualitative assessment of surface wettability. Smaller contact angles were measured from photographs to quantitatively define contact angle. The camera lens was aligned to provide distortion-free close-up images of the drops and the test surfaces. The contact angles were measured from enlarged digital images and were accurate to within ± 0.5 degree.

CONTACT ANGLE RESULTS

A total of eighteen specimen surfaces prepared by the process of Table 1 were tested with high purity water, and a total of thirteen specimen surfaces were tested with ultrapure hydrazine. For the surface treatment process of Table 1, a total of thirty hydrazine contact angle measurements were made on eight specimens. The average hydrazine contact angle for the thirty observations is 3.45 degrees with a standard deviation of 1.53 degrees.

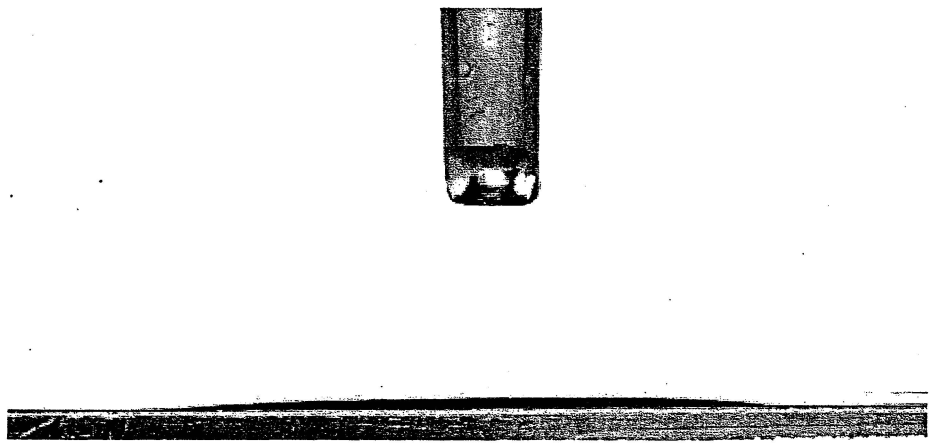

Figure 1. High Wettability Specimen Contact Angle Measurement Photo

LONG TERM COMPATABILITY OF WETTABLE SURFACES

APPROACH

The hydrazine compatibility and wettability before and after accelerated ageing in hydrazine of aluminum specimens subjected to the cleaning process of Table 1 and to variations of the Table 1 process were evaluated[4]. The pre-ageing and post-ageing contact angles were measured for fifteen specimens that were aged in hydrazine. Six of the fifteen specimens were treated by strictly following the Table 1 process, and nine of the fifteen specimens were subjected to variations of the Table 1 process. The process variations carried out one at a time included: changing the ratio of specimen surface area to volume of alkaline detergent solution, replacement of brushing steps with ultrasonic agitation, omitting or reducing intensity of the brushing steps, bagging in HEPA filtered air, and exposure to ambient air after processing. Hydrazine decomposition during ageing due to the treated aluminum surfaces was quantitatively measured for ten specimens and compared to witness samples of hydrazine subjected to the same ageing.

The accelerated ageing tests were carried out at a temperature of 160°F for up to thirteen weeks. The ageing tests were carried out in a temperature controlled, heated aluminum block, as shown in Figure 2, that was designed and built for accelerated ageing testing of propellants. This thermal block is insulated on all six sides when fully assembled and maintains accurate and precise temperature control. The ageing tests were performed by immersing specimens individually in small Pyrex glass vials containing hydrazine that were fitted with an aluminum and Teflon cap and configured such that the volume of gas evolved in the vial over a period of time could be measured. The vials and tubes were purged with ultrapure nitrogen after filling with about 10 milliliters of hydrazine. Up to twenty vials could be aged simultaneously in the temperature-controlled block. Sample vials were removed to simulate 3.3, 4.88, 5.12, 5.16, 10.0 and 10.95 year ageing.

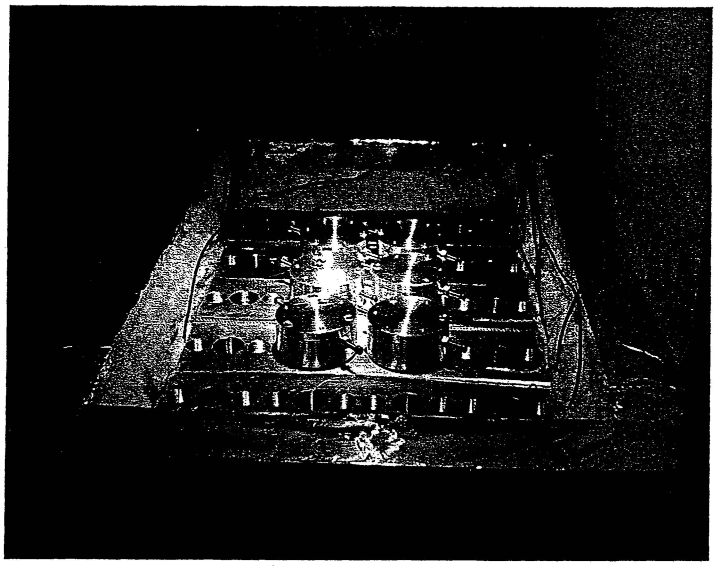

Figure 2. Aluminum Heater Block Used for Accelerated Ageing Test

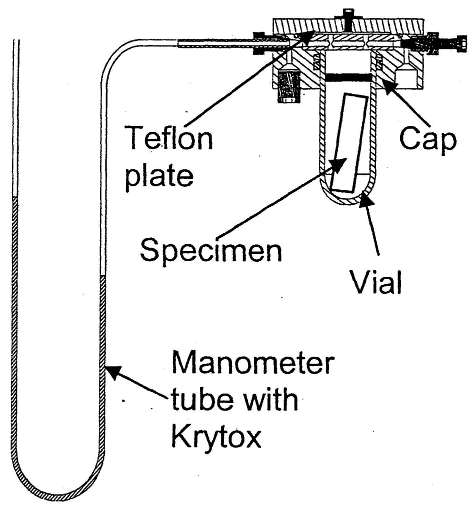

Figure 3. Schematic Diagram of the Manometric system

A manometric system, as shown in Figure 3, was used to measure the volume of gas evolved over a time interval due to decomposition of hydrazine in the specimen container. The system consists of vertical U shaped tubes of 24" height from the bottom of the U to the top of the open tube. The tube is made of fluorinated ethylene propylene (FEP) and is of 1/16" inner diameter by 1/8" outer diameter. Each manometer tube was filled with DuPont Krytox fluid to a height of about 11" from the bottom of the U.

To measure gas evolution, one end of a manometer tube was connected to the output port of a specimen container using an FEP connector tube of the same inner and outer diameters. When not connected to the manometer tubes, the connector tubes were loosely plugged, and coiled inside the heater box assembly to keep them at 160^{0}F over their entire length, thus creating a long diffusion path without a thermal gradient or hydrazine partial pressure gradient to minimize diffusion of hydrazine vapor out of the test container.

After the manometer tubes were connected, the differences in Krytox height between the two vertical sections of the manometer U-tubes were recorded every 20 minutes for 2 to 4 hours. Gas evolution rates were also recorded for two witness samples in every measurement session to account for background hydrazine decomposition.

CONTACT ANGLE RESULTS

Pre-ageing and post-ageing contact angles were measured for fifteen specimens that were subjected to ageing in hydrazine. The pre-ageing and post-ageing contact angles are shown in Table 2.

Table 2. Summary of Contact Angle and Decomposition Rate Measurements

Wettability	Specimen Number	Pre-ageing Contact Angle (Degree)	Post-Ageing Contact Angle (Degree)	Decomposition Rate, R	Cleaning Process
High	13	6	3.5	Not Measured	Strict Table 1
High	23	5.4	4.8	Not Measured	Strict Table 1
High	62	6.8	5	17.680	Strict Table 1
High	57	3.3	5.3	18.772	Strict Table 1
High	58	4.6	5.4	18.601	Strict Table 1
High	61	2.7	2.3	19.103	Strict Table 1
High	56	< 2	Not Measured	18.268	Strict Table 1
Moderate	3	10	3.6	Not Measured	Variation Table 1
Moderate	30	7.9	3.3	Not Measured	Variation Table 1
Moderate	60	12.4	23.3	Not Measured	Variation Table 1
Moderate	54	8.5	5.2	Not Measured	Variation Table 1
Moderate	F	11.5	5.4	18.141	Variation Table 1
Moderate	46	12.2	3.4	16.795	Variation Table 1
Moderate	48	8.6	1.5	17.315	Variation Table 1
Moderate	49	8.8	1.5	18.280	Variation Table 1
Low	37	18.4	10.9	18.894	Variation Table 1

Process variations carried out one at a time included: changing the ratio of specimen surface area to volume of alkaline detergent solution, replacement of brushing steps with ultrasonic agitation, omitting or reducing intensity of the brushing steps, bagging in HEPA filtered air, and exposure to ambient air after processing.

Six specimens processed by strictly following the process of Table 1 had high wettability (contact angle < 7 degrees) before ageing and also had high wettability after ageing. The pre-ageing contact angle measurements of these six highly wettable specimens gave an average pre-ageing contact angle of 4.8 degrees with a standard deviation of 1.58 degrees. The average post-ageing contact angle for these six specimens is 4.4 degrees with a standard deviation of 1.23 degrees.

Eight specimens processed by variations of Table 1 as described above had moderate wettability (contact angle between 7 and 15 degrees) before ageing, and seven of these eight had high wettability after ageing. As shown in Table 2, the pre-ageing contact angles for these eight specimens are between 7.9 and 12.4 degrees. The average pre-ageing contact angle for these eight specimens is 10.0 degrees with a standard deviation of 1.81 degrees. The average post-ageing contact angle for seven of these eight specimens is 3.41 degrees with a standard deviation of 1.56 degrees. The remaining specimen had low wettability (contact angle > 15 degrees) after ageing, likely because the Teflon cover plate for the vial was inadvertently omitted, which resulted in loss of about half the hydrazine initially in the container and infusion of ambient air into the container.

One specimen subjected to ageing had low pre-ageing wettability (contact angle of 18.4 degrees) due to contamination resulting from loss of bag purge and prolonged exposure to ambient air (a few days). The post-ageing contact angle for this specimen improved to 10.9 degrees (moderate wettability).

Post-ageing contact angle measurements of thirteen aged specimens (six with high pre-ageing wettability and seven with moderate pre-aging wettability) gave an average post-ageing contact angle of 3.86 degrees with a standard deviation of 1.45 degrees.

DECOMPOSITION RATE

Decomposition rates were measured for ten specimens over various time intervals during their ageing periods. Manometer tube height difference measurements over time were used to calculate hydrazine decomposition rate using the approach of Williams[11], where R is defined as

$$R = \log (\text{molecules reacting area}^{-1}\ \text{time}^{-1}).$$

The decomposition rate R can be calculated as

$$R = \mathrm{Log}\ [K\ ((p\ \Delta V)\ /\ (R_g T))\ (1/nas)],$$

where K = Avogadro number, p = Pressure, ΔV = Gas volume increase, R_g = Gas constant, T = Temperature, n = Moles gas per mole N_2H_4, a = Surface area, and s = Time.

The observed decomposition rates for the specimens were corrected for the background decomposition rate due to the specimen containers, using the decomposition rates of two witnesses that contain only hydrazine.

The decomposition data for ten specimens are shown in Table 2 and in Figures 4a and 4b. The specimen to specimen decomposition rate R for the ten specimens ranged from 16.795 to 19.103. The decomposition rate data for all ten specimens and the average molar decomposition rate is shown in Figure 5. The average decomposition rate R for the ten specimens is 18.185. For comparison the values for R for hydrazine in Titanium (6AL4V) given by Williams[11] vary from 15.997 at 30^0C to 17.894 at 70^0C. The average hydrazine decomposition rate R for the ten specimens and various materials[11] is shown in Figure 6.

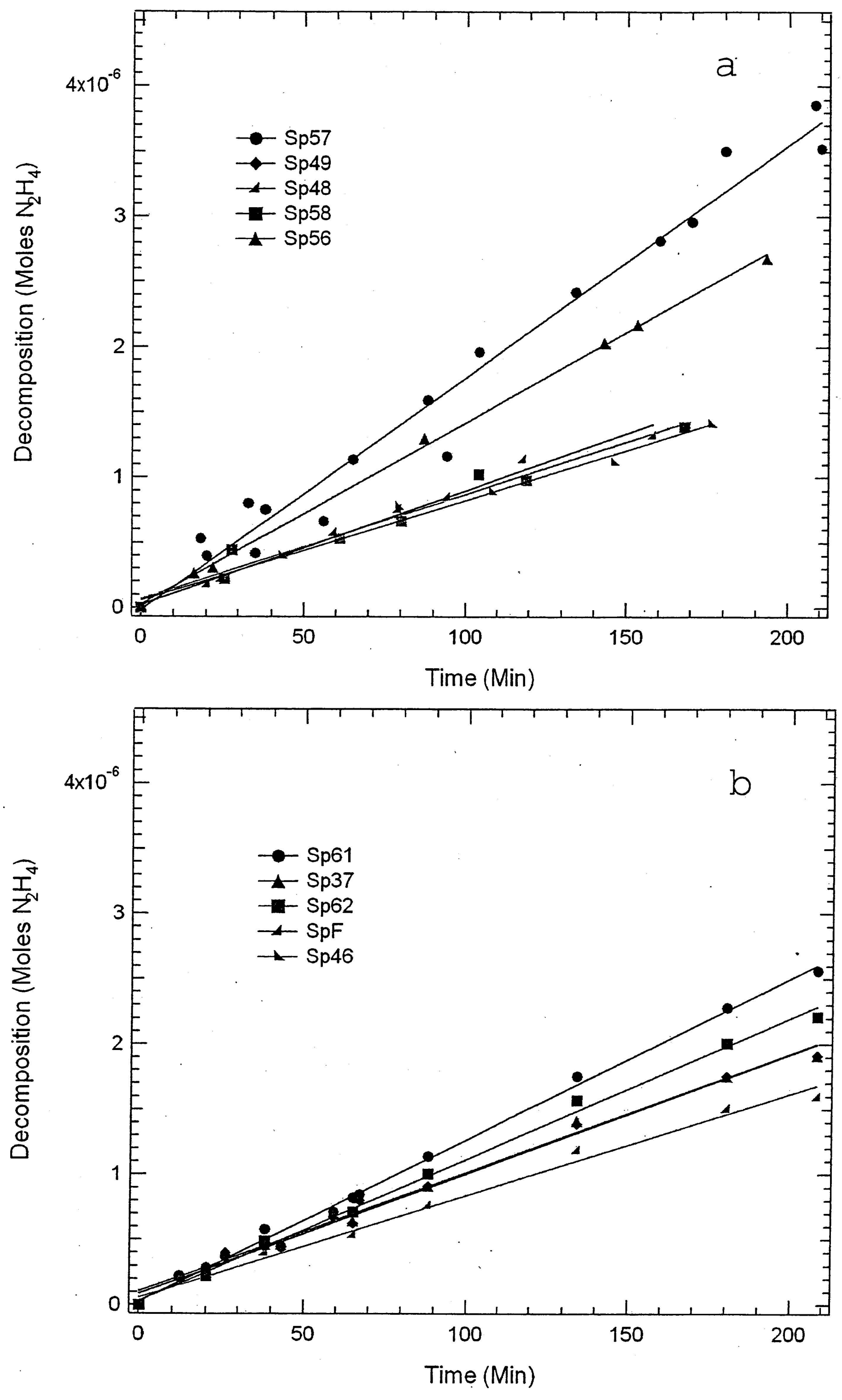

Figure 4. Hydrazine Decomposition Rates. (a) Specimens 57, 49, 48, 58, and 56. (b) Specimens 61, 37, 62, F, and 46.

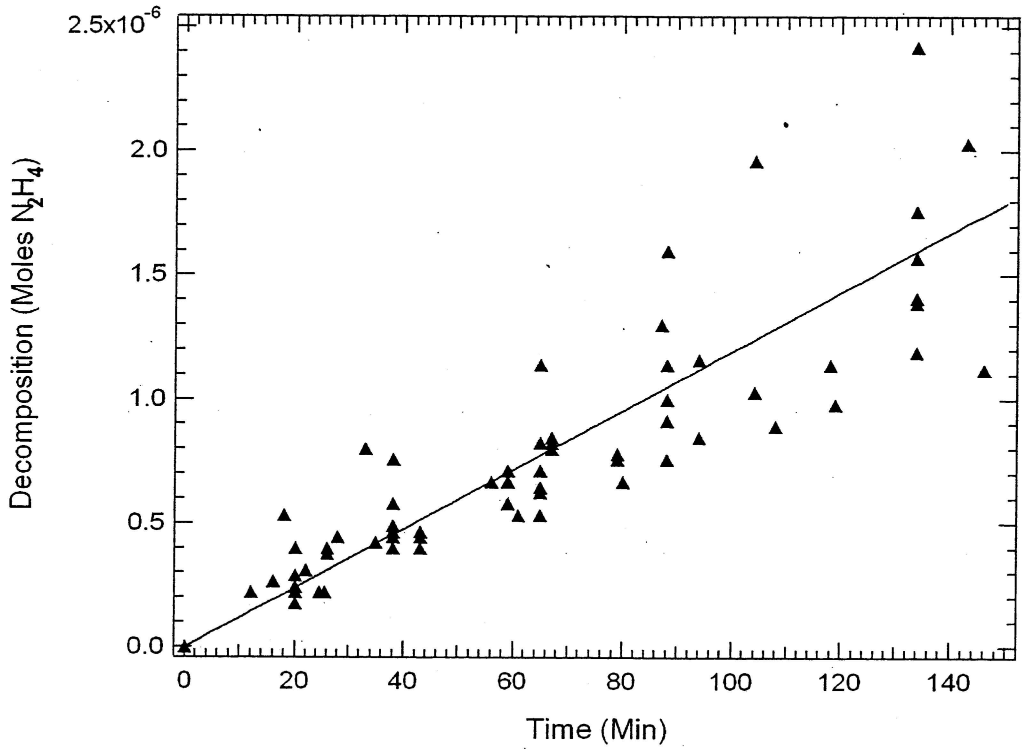

Figure 5. Hydrazine Decomposition Rate of Aluminum Specimens

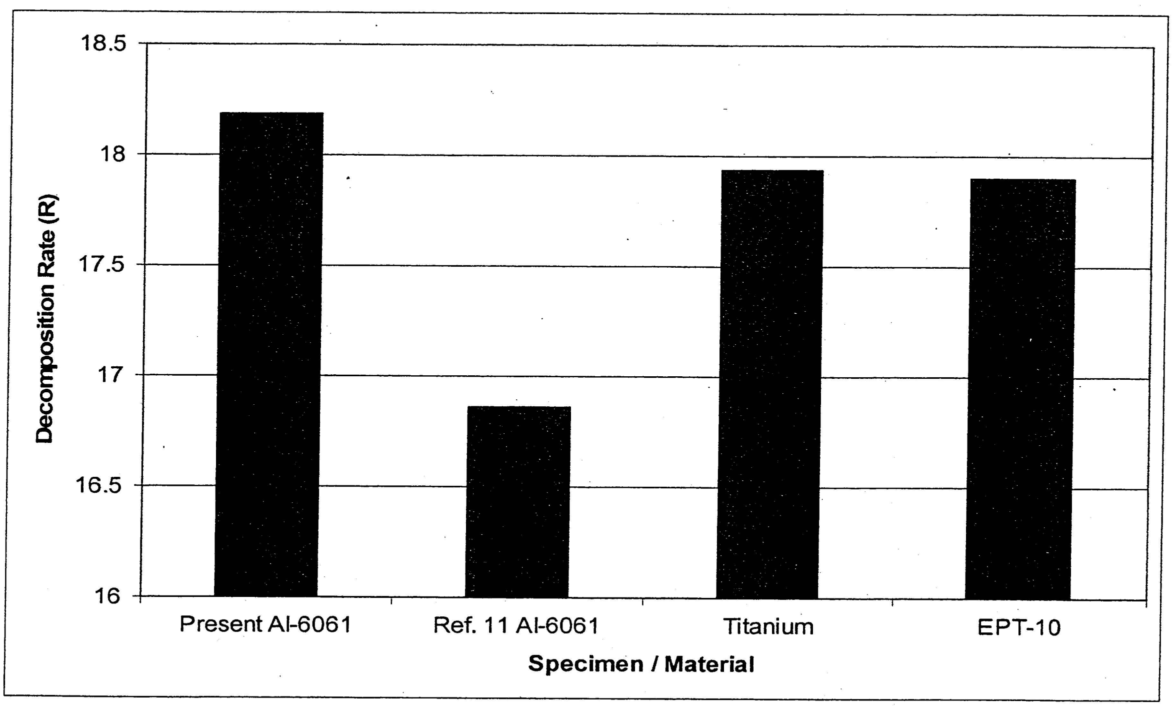

Figure 6. Comparison of Hydrazine Decomposition Rates

CONCLUSIONS

The aluminum surface treatment process given in Table 1 produces highly wettable surfaces that retain their wettability after equivalent ageing in hydrazine of over ten years. These aluminum surfaces produce hydrazine decomposition rates comparable to Titanium 6AL4V.

Ageing in hydrazine improves wettability of surfaces treated by the process of Table 1. The improvement in wettability was observed for 3.33 to 10.95 years equivalent ageing. All specimens with initial high wettability maintained it after ageing, and moderately wettable specimens treated by variations of Table 1 became highly wettable after ageing. Post-ageing chemical assay of hydrazine samples revealed no harmful constituents.

The decomposition rate R of hydrazine in contact with ten treated aluminum specimens during ageing ranged from 16.795 to 19.103 with an average of 18.185. This is comparable to hydrazine decomposition rates of 15.997 to 17.897 in contact with Titanium at 70 ^{0}C[11].

Scratches in or damage to an amber surface that has not been aged in hydrazine will impede the spreading of hydrazine across the surface. However, ageing in hydrazine mitigates the effect of damage and no significant difference between wettability of damaged and non-damaged surfaces was observed after ageing.

For surfaces to maintain high wettability, care must be taken during storage and handling to avoid contamination. Limited exposure to HEPA filtered air can be acceptable, but exposure to particulates and organic molecules borne by ambient air must be avoided.

The surface treatment process of Table 1 is sufficiently robust to be implemented for flight hardware; however, process parameters must be maintained within boundaries given in Table 1 and References 3 and 4 to achieve high wettability.

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