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# TECHNICAL MEMORANDUM

## A REVIEW OF THERMAL CONTROL COATING DEGRADATION BY THE SERVICE MODULE REACTION CONTROL SYSTEM ROCKET EXHAUST AND ESTIMATED EFFECTS ON SKYLAB

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ABSTRACT

The Service Module (SM) Reaction Control System (RCS) is most damaging to Skylab thermal control surfaces 1) when fired for an extended duration and 2) when fired in a series of several hundred pulses at low engine temperatures. Extended firings overheat the surface. Pulse firings deposit contaminants, most likely monomethyl hydrazine nitrate. The properties of monomethyl hydrazine nitrate have not been well established with respect to effects on coating materials, but it persists in vacuum in a pure crystalline form, which is explosive, or, after absorbing water, in a viscous form which is probably non-explosive.

In general, coating degradation by rocket exhausts has not been formulated well enough to predict effects for the general case, and tests simulating mission conditions are often difficult to perform accurately. In this study, available data, especially from related smaller engine tests, is evaluated in light of the Skylab space environment, firing schedule, and geometry. The Skylab surface area most susceptible to degradation by rocket exhaust is the SM RCS sun side door (at Quad A). This door can receive concentrated exhaust plume impingement, and an end-of-mission solar absorptance of 0.5 can be expected even without any post-docking firing events. According to North American calculations, this RCS door requires a solar absorptance below 0.6 to maintain propellant tank temperatures. Since the present Skylab SM RCS firing schedule does not include long continuous firings (except possibly after separation) or a long series of short pulse type firings, the SM RCS likely will not degrade the RCS door area much beyond the 0.5 absorptance value.

In future mission planning, potential degradation problems can be avoided by proper scheduling of RCS firing events or by using different coating materials. It is recommended that full scale testing be avoided.



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## I. INTRODUCTION

The coatings on all Skylab external surfaces are chosen for their particular thermal radiation properties. One of the mechanisms that can degrade, or alter, these properties is interaction with rocket exhaust products. For some Skylab surfaces, the Service Module (SM) Reaction Control System (RCS) rocket engines are the most potentially damaging source for this degradation. The RCS exhaust products can be particularly harmful, and they interact with a significant surface area, especially on the SM.

The immediate question is whether such degradation will be more of a problem for the Skylab missions than for the already completed Apollo missions, which differ in the following pertinent ways:

1) The Skylab missions are much longer than the Apollo missions. The longest Apollo mission lasted a little over 10 days. The Skylab missions will be a year or more, and the Skylab SM's will be in orbit up to 56 days.

2) The Skylab thermal environment is more severe than Apollo. During a lunar mission, the Apollo SM rotates about its long axis to smooth circumferential temperatures. During the Skylab earth orbit missions, the nominal attitude is solar inertial, and one side of the Skylab assembly continuously faces the sun. Therefore, a rotating Apollo SM positioned with the long axis perpendicular to the solar vector receives 141 BTU/HR $FT^2$ average incident solar heating; and a fixed Skylab SM receives 0 to 444 BTU/HR $FT^2$ solar heating on the exposed side.

3) Skylab has more area exposed to rocket exhaust. Figure 1 shows the SM RCS exhaust plume profile from one cluster of 4 RCS engines superimposed on the Skylab assembly. A significant portion of the assembly lies within the 90.7% mass flow boundary.

Comparing the two missions in this way, RCS rocket exhaust degradation of thermal control coatings appears more significant for Skylab. The environmental extremes require new coating patterns that are critical for thermal control, and the longer mission time permits all forms of coating degradation to mature, including that due to RCS rocket exhaust products.

Although all surfaces exposed to RCS rocket exhaust should be examined, the coating on the RCS doors bears particular scrutiny. It is a Dow Corning "white" coating, which has a low solar absorptance ($\alpha$) and high IR emittance ($\varepsilon$). This combination of thermal radiation properties protects door mounted fuel tanks from overheating. But the coating is exposed to a combination of direct rocket exhaust and damaging solar radiation that together could increase $\alpha$ beyond acceptable limits.

Ultimately, the RCS firing duty cycles will determine the significance of exhaust-caused coating degradation for Skylab. The pre-docked and docked phases are most important for the SM, since it is discarded before re-entry. During the pre-docked phase, a few minutes of RCS firings occur for maneuvering and docking. During the docked phase, control moment gyros mounted on the Apollo Telescope Mount (ATM) substantially reduce the number of RCS firings needed for attitude control. By comparison, over 50,000 RCS firings occurred during Apollo 11 - most for attitude control purposes. This is encouraging and might clearly indicate the absence of a problem if the two missions, as compared above, were more similar. In addition, other uses for the SM RCS are being explored, such as spinning the Skylab assembly to create an artificial gravity effect, maneuvering and control for the earth resources experiments, and radial docking for crew overlap. Therefore, a study of RCS exhaust induced coating degradation is especially timely for Skylab.

Part II briefly considers the Skylab surfaces exposed to SM RCS rocket exhaust products and how much they degrade from other mechanisms. With the long Skylab missions, RCS exhaust effects must be considered with the knowledge that other mechanisms will continuously degrade coatings also. Part III describes the SM RCS rocket engine. Part IV examines the various ways rocket exhaust can degrade Skylab coatings. This part relies strongly on past studies and research. Part V presents the conclusions from this study and some recommendations pertaining to current and possible future mission configurations.

## II. GENERAL DEGRADATION CHARACTERISTICS FOR SKYLAB COATINGS SUSCEPTIBLE TO RCS EXHAUST IMPINGEMENT

The white coating on the SM RCS sun-side doors is definitely the most critical, as mentioned above. However, other surfaces also receive some exhaust degradation, and they will be discussed briefly as a group.

### The Dow Corning White Coating on the RCS Sun-Side Door

As listed in the manufacturer's bulletin[1], Dow Corning 92-007 thermal control coating is "a white, elastomeric silicone coating that cures to a tough, rubbery film when exposed to moisture in air." More precisely, it is a rutile titanium dioxide ($TiO_2$) pigment in a polymethylsiloxane vehicle, or binder[2]. The Dow Corning bulletin lists $\alpha$ = 0.14 to 0.20 and $\varepsilon$ = 0.84 to 0.90. In addition, it is considered resistant to weathering, moisture, ultraviolet rays, ozone and chemicals. However, white coatings of this type are well known to degrade.

When white coatings degrade, characteristically $\alpha$ increases, and $\varepsilon$ remains almost constant. With the resulting increase in absorbed solar heating, thermally controlled items, the RCS fuel tanks in this case, heat up.

Coating degradation is caused by many mechanisms: exposure to vacuum, exposure to ultraviolet radiation from the sun, particulate radiation, micrometeroid impact, heating, and contamination.* RCS exhaust products are the major contaminant affecting the Dow Corning 92-007 coating, but there are other contaminants such as vented gases and liquids.

In the Skylab low earth orbit, particulate radiation effects are negligible. The magnetic field of the earth deflects particles streaming from the sun (solar wind), and particles trapped in the Van Allen belt are at high energy levels and penetrate coatings without causing much damage.

Based on OSO-III measurements, Millard concluded that micrometeroids had a negligible effect on polished metal surfaces for an 11-month mission. Rubber-like silicone coatings probably withstand such bombardment even better than metallic surfaces; therefore, micrometeroid effects probably are negligible for the 92-007 coating.

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* For a more detailed discussion see Reference 3.

Ultraviolet radiation from the sun can increase α for coatings in a vacuum. As stated by Swofford, Mangold, and Johnson[4] "The deterioration caused by ultraviolet radiation can be appreciable for nonmetals and for organic-based materials such as acrylic and silicone vehicles containing high purity metallic oxides." The 92-007 titanium dioxide in silicone coating fits this description and should be expected to degrade.

Pinson and Wybelt[5] conducted some tests that indicated only a slight degradation for the 92-007 coating exposed only to ultraviolet radiation in vacuum, but their results are not conclusive. Their main objective was to examine the synergistic effects of ultraviolet radiation, particle radiation, and vacuum, and they exposed the coating to only 190 equivalent sun hours of ultraviolet radiation alone, without particle radiation. In the Skylab mission, the RCS doors receive approximately 500 to 600 equivalent sun hours of full exposure. In addition, Pinson and Wybelt made their measurements after exposing the coatings to the atmosphere, which has a bleaching effect. According to B. Sidenberg, who has done much work in this area at Goddard, α can decrease substantially and quickly after a degraded white coating is removed from vacuum. Pinson and Wybelt attempted to curtail this effect by making the measurements "immediately" after removal, but some unknown amount of atmosphere bleaching still occurred.

One of the thermal control coating samples on the OV1-10 satellite[6], the "78B2" coating sample, was a rutile type titanium dioxide pigment in a silicone binder and is probably close to the 92-007 coating. The OV1-10 satellite followed a 340 x 416 nautical mile orbit. Although particle radiation effects are larger than for the Skylab 235 nautical mile orbit, they are still relatively minor. The initial α value was 0.22; after approximately 500 hours in orbit, α increased to 0.27. These data, plus data for similar zinc oxide coatings[7,8], indicate that an α increase of 0.05 can be expected for the Skylab mission from solar exposure in vacuum.

Apollo 9 Results

Before the Apollo 9 launch, three identical coating samples were attached to the SM on the electrical-power-system radiators[9]. Figure 2 shows the location of these samples. Each sample contained two white coatings*, a "titanium dioxide white paint" (Dow Corning 92-007) and a "zinc oxide-potassium silicate white paint" (Z-93). The astronauts retrieved the coating samples approximately 73 hours after lift-off.

Smith and Luedke list the following sources of contamination on the Apollo 9 spacecraft[9]:

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*Other coating samples were included also, but only the two white coating samples are important to this study.

1. Plume impingement from the tower jettison and Saturn II retromotors and from the Service Module and Lunar Module reaction control system engines,

2. Boost heating effects,

3. Outgassing products of ablative materials,

4. Pyrotechnic discharge products,

5. The natural space environment.

During the first 73 hours of the mission, the coatings received only a relatively few hours of sun exposure, therefore, most of the measured degradation can be attributed to the launch effects.

Table I lists $\alpha$ and $\varepsilon$ preflight and postflight measurements for the Apollo 9 samples. All samples degraded, and the Dow Corning samples consistently suffered the largest $\alpha$ increases. With the various sources of contamination acting to produce the final degradation, it is difficult to discern any singular degradation mechanism. It should be noted, however, that the upper right sample location showed a slightly smaller increase in $\alpha$ for both coating types. This location is farthest from the RCS jets, which were fired for maneuvering and attitude control. In addition, Smith and Luedke observed under oblique lighting a "definite deposition" of plume products for the upper left sample, located nearest the plume centerline.

Inflight values for $\alpha$ were almost certainly higher than the postflight Table I data indicate, although there is no way of determining the difference now. Sample measurements were made after many hours of exposure to spacecraft and earth atmospheres, allowing plenty of time for atmosphere bleaching to partially restore the coatings.

<u>An Estimate of the Total 92-007 Coating Degradation, Excluding Special RCS Effects</u>

The Apollo 9 postflight $\alpha$'s in Table I represent coating conditions early in the mission. Assuming similar Skylab early mission coating degradation, $\alpha$ will be approximately 0.4 after the SM docks to the cluster. Some areas might have higher or lower $\alpha$ values depending on distance from the RCS jets, but 0.4 is probably a reasonable average. Adding 0.05, the increase in $\alpha$ expected from ultraviolet exposure in vacuum for 56 days, a 0.45 end-of-mission value is obtained. This $\alpha$ does not include 1) the difference between inflight and postflight Apollo 9 $\alpha$ values, 2) contamination from Skylab vented gases and liquids, and 3) RCS firing effects while the SM is docked. Therefore, $\alpha = 0.50$, the normally listed fully degraded value for white coatings, must be expected as a minimum. The possibility of RCS firings increasing $\alpha$ beyond 0.50 will be discussed in Section IV.

TABLE I - SUMMARY OF APOLLO 9 THERMAL PROPERTY MEASUREMENTS ON THE SM WHITE COATING SAMPLES

| Material | Sample location | Absorptance ($\alpha$) | | | Emittance ($\varepsilon$) | | $\frac{\alpha}{\varepsilon}$ | |
|---|---|---|---|---|---|---|---|---|
| | | Preflight | Postflight | Change, percent | Preflight | Postflight | Pre | Post |
| Zinc oxide- | Service module | | | | | | | |
| potassium | Upper left | 0.20 | 0.28 | 40 | 0.93 | 0.93 | 0.215 | 0.302 |
| silicate | Upper right | .20 | .25 | 25 | .93 | .93 | .215 | .269 |
| | Lower right | .20 | .27 | 37 | .93 | .93 | .215 | .290 |
| Titanium | Service module | | | | | | | |
| dioxide- | Upper left | 0.25 | 0.37 | 48 | 0.86 | 0.88 | 0.291 | 0.420 |
| silicone | Upper right | .24 | .34 | 42 | .86 | .88 | .280 | .387 |
| | Lower right | .24 | .40 | 67 | .86 | .87 | .280 | .460 |

At the present clocking angle, one of the SM RCS doors is approximately 30° from the subsolar point on the SM hull. For $\alpha$ = 0.60, North American calculations[10] show that barely acceptable RCS tank temperatures occur. Therefore, the question of RCS exhaust degradation of the coating is critical. The maximum acceptable $\alpha$ is 0.60, and the minimum estimate for $\alpha$ is 0.50.

Other Skylab Surfaces Susceptible to RCS Exhaust Impingement

Figure 1 shows almost all of the Skylab assembly lying within the 90.7% mass flow boundary. The 100% mass flow boundary encompasses an even larger portion of the assembly. This only serves to indicate the potential surface areas influenced by SM RCS exhaust products. Not all are affected. Some surfaces are blocked from direct impingement; some surfaces receive only small concentrations due to distance or exposure angle; and some surfaces do not require stable $\alpha$ and $\epsilon$ coating properties.

Almost the entire SM cylindrical surface is exposed in some degree to RCS exhaust products; but, except for the RCS sun-side door, coating degradation does not appear to be a problem. Although the coatings can degrade, they are not needed for adequate thermal control. The fuel cells and the fuel cell radiators shut down early in the mission, and the environmental control system radiators run cold and might even require striping to raise temperatures.

In the remaining portion of the Skylab assembly, four areas requiring controlled surface properties receive direct exhaust product impingement: 1) Mounted components, including the Charger Battery Regulator Module (CBRM) assemblies, located on the +X Skylab axis of the ATM rack, 2) the Airlock Module (AM) radiators, 3) the back side of the ATM solar arrays, and 4) windows on the AM and the Multiple Docking Adapter (MDA). These surface areas can be considered together as a group. They are all relatively far from the RCS jets (probably beyond the continuum portion of the plume), and except for the solar arrays they are affected primarily when the forward axial thrusters are used during docking and separation. RCS contamination of these surfaces should be only a secondary problem and is probably only one of several equally important degradation sources. Therefore, these surfaces are only cited to indicate their susceptibility, to a lesser degree, to some of the same degradation effects described for the 92-007 coating on the RCS doors.

There is a possibility during a second Skylab mission that a Command and Service Module will be radially docked to the MDA +Z axis (opposite the ATM). Although such docking is not examined in this study, it should be noted that the forward axial thrusters used during docking and separation could impinge a significant area with exhaust products. To visualize this, imagine the 90.7% mass flow cone in Figure 1 directed upward from beneath the MDA. The MDA itself is covered with a radiator whose white thermal control coating is important for waste heat rejection. At such distances affected surfaces probably will only receive impingement from the less damaging free molecular flow of the RCS exhaust.

## III. A DESCRIPTION OF THE SM RCS ROCKET ENGINE

Figure 4 shows the Marquardt R-4D rocket engine[12] used in the SM RCS. The construction and operation of this engine is basically simple. The liquid fuel and oxidizer are pressure fed through the two solenoid valves into the combustion chamber with the injector assembly assuring proper mixing. The fuel and oxidizer ignite spontaneously when mixed, and the hot reaction products expand out through the nozzle extension. At steady state, approximately 100 pounds of thrust are developed.

The fuel is monomethyl hydrazine ($CH_3\ NH\ NH_2$), usually abbreviated as MMH. The oxidizer is nitrogen tetroxide ($N_2O_4$). Since these two constituents react spontaneously when mixed, they form a "hypergolic" liquid propellant combination.

A group of four R-4D engines mounted on a common housing form one quad. There are four such quads equally spaced circumferentially on the SM cylindrical hull. To reduce exhaust plume impingement, the engine centerlines are canted 10° outboard from the SM surface.

## IV. COATING DEGRADATION CAUSED BY THE SM RCS EXHAUST

The effect of rocket exhaust products on a surface coating depends on many factors: engine size and design, firing timeline, total exposure time, coating properties, propellant properties, geometry, and the space-thermal environment. Although some studies and tests have been conducted, rocket exhaust degradation effects have not been well formulated, and for a given situation, a test simulating all of the above factors is desirable. Such tests are generally difficult. For the SM RCS, they are especially difficult because the 100-pound engine can fill test chambers with exhaust gases and quickly degrade the all important vacuum. With the complex coupling between flow dynamics and chemical combustion, it is difficult to scale results from more feasible, smaller engine tests.

Before examining the action of the SM RCS rocket exhaust, it is useful to categorize the various processes leading to or directly producing coating degradation. Based on a general survey of the available literature, it appears that rocket exhaust degradation is caused by the following mechanisms:

1. Heating,

2. Erosion by particulate matter,

3. Direct plume deposition and condensation,

4. Secondary condensation from a cloud,

5. Chemical reaction with coating materials.

These mechanisms will be explained separately, and an effort will be made to establish the importance of each.

Heating

Figure 3 shows the plume impingement lines of constant heating plotted on a flat development of the SM surface. These lines were redrawn from North American plots,[14] which represent their best available plume heating data. Because the SM surface curves away from the tangential jets (roll jets), they do not heat the surface as much as the axial jets (pitch jets).

As an indication of the potential areas of heating damage, the North American heating rates in Figure 3 were converted into equilibrium temperatures by assuming an adiabatic SM surface radiating to deep space with a 0.9 emittance value. The 92-007 coating is serviceable to 500°F,[1] and the underlying layer of cork begins to degrade and ablate at approximately 500°F.[15] Therefore, areas with equilibrium temperatures above 500°F are the potential heating degradation areas. Of course, once degradation begins, outgassing cork alters plume flow and heating patterns, and the temperatures in Figure 3 are not actually attained. In addition, even without cork ablation, enough heat flows into the SM hull to lower temperatures 20 or 30°F below the Figure 3 values. Despite these drawbacks, Figure 3 indicates the large area on the RCS doors that can be charred by the axial and the tangential jets.

The actual area damaged by heating depends on the RCS firing duration and the transient temperature changes. In a recent presentation,[16] North American stated that for the tangential jets, the maximum allowable continuous burn is 110 seconds due to the 500°F coating temperature limit. Subsequent allowable firing durations depend on cork cool-down time. Since the North American study considered only the limitations on using tangential jets, no time limit was given for firing of the axial jets.

To estimate the transient plume heating effects, a simple one-dimensional lumped parameter model (nodes and conductors) has been formulated assuming that in the thin, low conductance cork layer heat flow in a direction parallel to the surface is negligible. The plume heating rates were taken from the North American data in Figure 3 and applied to the first node in the cork layer. The lumped parameter representation of the SM hull is described in the Appendix.

Results are presented in Figure 3 as the time required for a surface, initially at 105°F, to exceed the limiting temperature of 500°F when heated by the jet plume. Again, once the cork begins to outgas, or ablate, plume heating patterns will change, and the times shown in Figure 3 will increase. However, Figure 3 still gives a good indication of the time required to damage the SM surface, especially near the plume centers where ablation initiates.

Cork thickness varies on the RCS doors. For this study, a 0.6 inch thickness was used under the axial jet and a 0.155 inch thickness was used under the tangential jet. These are the current design values[14] under the plume centers. The effect of cork thickness can be seen by comparing the time required to exceed 500°F for different thicknesses at the same heating level. For example, in Figure 3, at a 0.6 BTU/FT$^2$ SEC, it takes 271 seconds under the axial plume and only 234 seconds under the tangential plume, where the cork is much thinner.

It should be noted that at the center of the tangential plume, Figure 3 shows 114 seconds to exceed 500°F. It is for this same situation that North American calculated 110 seconds indicating good agreement between the two sets of calculations.

From Figure 3 it can be seen that heating degradation by the tangential jets is no problem. It takes 114 seconds to initiate degradation, and even then only a very small area ablates. With some simple scheduling of the RCS burns, all heating degradation from the tangential jets can be avoided.

By contrast, the axial jets can char a relatively large area in less than 100 seconds of firing. The actual degradation of the SM surface might be even larger than indicated, since ablated cork material can be carried downstream in the plume and deposited over a larger area. However, for the present Skylab missions, axial firings for maneuvering and docking are nominally on the order of 10 seconds or less duration, and, unless a closely spaced series of such firings occurs, heating degradation by the axial plume is no problem. Again, scheduling of the RCS burns can be used to avoid heating degradation.

Erosion by Particulate Matter

Solid particles propelled in the rocket exhaust stream bombard and erode a surface, similar to sand blasting. Several possible sources of solid particles have been postulated including ice, eroded and ablated engine material, and propellant impurities. This leads to the conclusion that solid rockets and ablative rockets are the most damaging; however, radiantly-cooled liquid fuel rockets similar to those in the SM RCS are also damaging.

Etheridge and Boudreaux[17] reported test results using a small 22-lb attitude control rocket and an MMH-$N_2O_4$ propellant. Optical glass samples, exposed to parallel and perpendicular plume flow for 90 seconds, exhibited transmittance losses ranging from 6% to 99%. Etheridge and Boudreaux concluded that the damage resulted primarily from propellant impurities called "tramp metals". Their study, which included computer analysis of the plume equilibrium composition, showed that other particle sources are not significant. The propellant, which met military specifications, had a 120 parts per million tramp-metal concentration.

At least two other investigators in this field are not yet ready to accept the Etheridge and Boudreaux conclusion on tramp metals. P. J. Martinkovic,[18] whose work on the contamination effects of small hypergolic rockets will be discussed later, does not feel the sand blasting effect is well enough understood at this time to make any definite statement on the cause. R. C. Stechman,[19] whose has been analyzing such rocket engines at the Marquardt Company, suggests that ice particles might form in the plume due to the low static temperature (temperature measured while moving at plume gas velocities), although he has not analyzed the problem. Such ice particles would quickly increase in temperature when decelerated at the surface, but erosion could occur before they melt and evaporate.

It appears very likely that the SM RCS exhaust contains particles of some kind; however, the sand-blasting effect depends on geometry. The SM RCS rocket engines are mounted several inches away from the SM hull, and they are canted 10° outboard. In addition, no nearby surfaces are angled perpendicular to the flow. These geometrical factors should greatly reduce the sand-blasting effect, especially since most of the particles probably travel in the continuum region near the plume center. This is substantiated by the Apollo 9 samples, described earlier. Smith and Luedke[9] did not report any of the pitting or erosion typically attributed to the sand-blasting effect. Therefore, it appears that surface erosion by particulate matter in the exhaust stream is not a problem for the Skylab mission case.

Direct Deposition

Rocket exhaust products can be deposited directly on a surface and alter thermal radiation properties by simple masking or chemical reaction with surface materials. The degree of contamination on the affected surface depends on the chemical composition of the exhaust, the dynamic condition of the plume flow field, the chemical composition of the surface coating, and temperatures before and after firing. The situation is complex from both an engine firing standpoint and a surface deposition and degradation standpoint.

Stechman's description[11] of the physical-chemical aspects of an R-4D firing illustrates the role of the engine itself:

> The chemical composition of the plume varies considerably with time in the preignition-burn-shutdown sequence. The plume produced by a typical $N_2O_4$/hydrazine-type engine is composed first of propellant vapors, then probably of reaction intermediates before the complete products of combustion appear. After shutdown, the plume will consist of fuel vapors and may contain the decomposition or evaporation products of nitrate deposits. The plume flow field also varies during the sequence due primarily to pressure changes.

Therefore, the way in which an engine is fired directly determines the degree and type of degradation. It determines the chemical composition of the plume, and to a large degree, the condition of pressure, temperature, and velocity that control deposition at the affected surface.

With respect to contamination effects, rocket engine firings can be divided into two categories: 1)pulse firings dominated by transient, inefficient combustion, and 2)steady-state firings dominated by efficient, fully-developed combustion. The exact demarcation between pulse and steady-state firings is not clear. Figures 5A and 5B show thrust histories for a typical steady-state firing and for the minimum impulse. This gives some indication. In general, pulse firings are in the 0 to 200 millisecond range. Firings of more than 1 second are definitely steady-state. The important difference is whether steady-state combustion has proceeded far enough to eliminate transient effects.

During steady-state firings, combustion is efficient, and plume composition can be predicted from equilibrium thermodynamics. Table II lists the composition of the SM RCS engine steady-state plume as calculated by the Marquardt Company. Secondary reactions between these constituents are very unlikely at the high plume temperatures; therefore, relatively harmless, dissociated gaseous molecules of the chemicals listed in Table II probably do not affect the 92-007 coating. Over-pressures due to flow deflection at the spacecraft surface might cause some localized condensation, but the high surface temperatures in these areas will cause rapid evaporation once the plume stops. Some condensation outside the high temperature plume center area, especially where the free molecular region impinges, can occur if spacecraft surfaces are cool enough. However, where thermal control is needed on the sun-side of the SM, surface temperatures are relatively high. Therefore, from these considerations alone, it appears that steady-state firings are not harmful from a deposition contamination standpoint.

There is little worthwhile test data now available to support any theory on the deposition contamination effects of steady-state firings. Ground tests for extended firings of even small rockets are of uncertain value because a suitable vacuum cannot be maintained with the influx of combustion products. Without a good vacuum, plume flow characteristics, residue evaporation, and any chemical reaction processes are altered to the extent of making data unacceptable. The Apollo 9 samples are not acceptable either, because the effect of exhaust deposition cannot be separated from the other forms of contamination.

Pulse firings differ in almost every respect with the steady-state firings. Pulse firings are inefficient, not easily analyzed, but some good data exist for small rocket engines. Before discussing some of the data, it should be noted again that the present Skylab schedule includes only a few thousand pulse firings. The Apollo lunar missions typically involved 50,000 firings, many in the worstcase 16 to 18 millisecond range; and

TABLE II. STEADY STATE COMPOSITION OF THE

R4D PLUME FLOW FIELD FROM

THE MARQUARDT COMPANY

| SPECIES NAME | MOLE FRACTION | WEIGHT FRACTION |
|---|---|---|
| $H_2O$ | 0.4130 | 0.3254 |
| $N_2$ | 0.3305 | 0.4050 |
| CO | 0.0954 | 0.1109 |
| $H_2$ | 0.0773 | 0.0068 |
| $CO_2$ | 0.0749 | 0.1441 |
| HO | 0.0068 | 0.0050 |
| H | 0.0050 | 0.0002 |
| NO | 0.0011 | 0.0014 |
| $O_2$ | 0.0006 | 0.0008 |
| O | 0.0003 | 0.0002 |
| OTHERS | TRACE | TRACE |

NOTE: MARQUARDT VALUES HAVE BEEN ROUNDED OFF TO 4 DECIMAL PLACES.

the SM coatings apparently did not degrade appreciably. Since no samples were returned from the lunar mission, no direct data exists, but thermal control in flight obviously succeeded. If the Skylab and Apollo missions were not so different, as outlined in the Introduction, it could be concluded rather quickly that pulse firings are no problem. However, in light of the mission differences as well as the distinct possibility for change in the firing timeline, especially in later Skylab missions, the effect of pulse firings bear examination now.

Transient, pulse-type firings can produce intermediate reaction products as well as unreacted fuel and oxidizer. Borson and Landsbaum[20] in a review of rocket plume contamination results presented in October, 1968, stated that "nitric acid, MMH nitrate, and ammonium nitrate are materials which can be produced and could react chemically with spacecraft materials." Water is also a possible product and when reacted with the nitrogen tetroxide oxidizer will quickly result in a corrosive nitric acid mixture. The MMH nitrate and ammonium nitrate products apparently form during and after the combustion process.

The Bureau of Mines Explosives Research Center[21,22] experimentally investigated preignition and post combustion non-flame characteristics of several hydrazine-type fuels reacted with $N_2O_4$. In the first test series, condensed phase combustion products were collected from the walls of a 2-dimensional, clear plastic model of an R-4D engine. In later tests, fuel and oxidizer were metered into a long glass tube, and the gaseous reaction products were analyzed. In both cases, the reaction products consisted primarily of fuel nitrate, water, ammonium nitrate, unreacted fuel, nitrous oxide, and nitrogen. In a single glass tube run, using MMH under an $N_2O_4$ rich condition, a product they believed to be MMH nitrite formed. However, this appears to be a special case, and the MMH nitrate is a more likely combustion product.

The chemical constituents found in the Bureau of Mines investigation only indicate what might exist in an engine before or after firing. Further chemical reactions, altered by combustion and long term residence in vacuum, might conceivably result in different chemical constituents, or, at least, a different distribution of the already measured constituents.

Juran and Stechman[23] calculated propellant evaporation times for an MMH fuel in a "small hypergolic rocket." They solved three simultaneous equations describing heat transfer through the liquid layer, vapor flow through the exhaust nozzle, and evaporation from the liquid surface. Their results showed that liquid films a few thousands of an inch thick, which is "equivalent to the amount of fuel in the dribble volume of the injector," can require many seconds to evaporate. For example, at a 40°F wall temperature, a 0.010 inch film requires 5 seconds to evaporate. Apparently this means the unreacted fuel deposits and other constituents remain in the engine long enough for intermediate reaction products to form, but it is very unlikely the fuel itself remains in the space environment long enough to affect any spacecraft surface.

Martinkovic[24] carefully conducted some small rocket tests, which correspond in several aspects to the Skylab SM RCS case. A Marquardt 22 pound R-1E engine was pulse fired in a vacuum chamber to study the formation and dispersion of firing residues. The propellant combination was $N_2O_4$ and MMH. Each test series consisted of 2000 firings at the minimum pulse width of 16.5 millseconds with an off time of 20 seconds between firings. Except during the first 15 pulses, when the vacuum degraded from an initial 400,000 foot altitude, a 225,000 to 235,000 foot altitude was maintained throughout the test.

Before describing Martinkovic's results, differences in design and performance for the R-1E and the R-4D engines are worth noting. The R-1E engine has a single doublet injector that mixes fuel and oxidizer in two converging streams. An asymmetrical plume results - fuel rich on one side and oxidizer rich on the other. The R-4D engine has a complex injector assembly that produces a symmetrical plume with the outer regions relatively rich in the propellant, used as a film coolant. The smaller R-1E engine operates more efficiently than the R-4D at the short pulse firing levels. Although the two engines differ as described, combustion products are similar, and much of the R-1E test data can be used to estimate the contamination effects of the R-4D.

Based on visual observation and camera coverage, Martinkovic described the test results as follows: "...a reddish brown, viscous material forms on the inner surface of the engine nozzle following a long series of engine pulses. Subsequent engine pulsing forces this material to the nozzle lip where it is ejected in directions outside the primary gas flow." Figure 6, taken from Martinkovic's report, indicates the ejection of this material from a rocket nozzle. Post-test analysis revealed that the "reddish brown, viscous material" was MMH nitrate with some absorbed water.

To make in-place weight measurements during each test, Martinkovic mounted a collector ring in the plane of the exhaust nozzle, which intercepted the emitted contaminant represented by the arrows in Figure 6. In a more complete vacuum, this collector ring would be located in the free molecular region, and even at 235,000 feet, it should not interfere with development of the plume flow field.

The temperature of the collector ring was 75 ± 5°F for all tests. This is noteworthy since contaminant condensation and dwell time at a surface decrease at high temperatures. The SM surfaces most likely to receive this kind of contamination are outside the primary impingement zone and therefore receive no plume heating. Temperatures for these SM surfaces depend on the space-thermal environment and, for a 0.5 α-value, are often at or below the 75°F level.

Figure 7 presents three plots of contaminant weight on the collector ring versus total pulse count for three engine injector temperatures: 40°F, 75°F, and 110°F. As might be expected, contaminant weight increases linearly with pulse count. It is also reasonable to expect less contaminant formation at higher injector temperature because smaller quantities of fuel and combustion products can condense and chemically react in the engine. This suggests that the contaminant formation can be minimized by maintaining high engine temperatures. One way of doing this is to decrease the off time between pulses thus permitting combustion heating to maintain high temperatures. Juran and Stechman[23] demonstrated by test and analysis that residue formation can be eliminated even for short pulse widths if the off time is very short also. However, Stechman[19] says that for a series of pulse-type firings, contaminant deposition from the R-4D reaches a maximum for off times around 3 seconds. For very short off times, high engine temperatures prevent residue formation, as discussed above, and for very long off times, residues can evaporate in the engine between pulses before build-up occurs.

Martinkovic has recently completed a second series of tests, his "Phase II" tests, which are now documented with release as an Air Force technical document expected soon. Under conditions similar to the first test series, several spacecraft functional surfaces were exposed to what would be the continuum portion of an R-1E engine exhaust plume under more complete vacuum conditions. Thermal control coatings, including the 92-007 coating, exhibited very little degradation after 400 pulse firings at parallel plume impingement. However, being located in the continuum portion of the plume, these samples were not subjected to the kind of depositio of viscous MMH nitrate shown by the arrows in Figure 6. Martinkovic also exposed some solar array material and optical samples to direct plume impingement in the second series of tests. A white, frost like crystalline layer collected on these samples, which were located 5 feet from the nozzle exit. This frost-like layer, clearly visible after 150 to 200 firings, was analyzed as pure MMH nitrate. After exposure to moisture, the pure crystalline MMH nitrate quickly reverts to the viscous form found in Martinkovic's earlier tests.

Other investigators besides Martinkovic have found MMH nitrate as a residue from transient $N_2O_4$ - MMH firings. For example, Etheridge and Boudreaux[17] conclude that MMH nitrate is the principal condensate produced in such firings. They compared the infrared transmission spectra of rocket combustion residues collected by Burch with the spectrum of a known MMH nitrate sample and found the two spectra almost identical. They also referenced 6 other studies indicating similar results.

It is not clear why only MMH nitrate is found without any measurable quantities of other possible reaction products. Martinkovic reports observing a reaction of the contaminant on the collector ring during the test. The reaction, which was in the form of bubbling at the surface of a residue puddle, continued for at least 2 hours, but after 16 hours it had subsided. Martinkovic offers no explanation. However, the reaction might be due to the formation of MMH nitrate from other residue constituents. This, plus some evaporation of non-reacted constituents, might explain why only MMH nitrate was found in post-test analysis. Another possibility is that the bubbling is due to boiling only, and no chemical reaction takes place.

R. C. Stechman and T. A. Thonet have recently completed a series of tests[19], now being documented for presentation at the 12th JANNAF Liquid Propulsion Meeting. An R-1E 22 pound engine was fired in a vacuum chamber (235,000 feet) at various on-off cycles (0.008 to 3 cps) and various engine on times (16.5 milliseconds to 5 seconds). Thermal control coating samples were mounted on two plane surfaces. One surface canted 10° from the exhaust centerline received almost parallel impingement. The other surface, mounted perpendicular to the exhaust centerline several inches behind the engine, received radial impingement. Coating temperatures varied from -118°F to 80°F, depending on whether cryogenic conditioning was used. Samples were located at various positions up to 78 inches from the R-1E engine. In general, very little degradation occurred. For example, for the white coating, McDonnell Douglas MD-22, $\alpha$ increased from 0.16 to 0.20 after 6,300 firings at a 17 milliseconds pulse width and a 0.5 cps frequency.

H. Mark and J. Cassidy[25] are now beginning a series of tests at the Lewis Research Center that will probably answer many of the questions concerning plume deposits. In a small, but very efficient vacuum chamber, transient, in place, mass spectrography and thermal radiation reflectance ($\alpha$ and $\epsilon$) measurements are being made for various coating samples exposed to the pulse firings of a 5-pound hypergolic rocket. These tests are unique because it is the first time such transient, in place measurements have been made, and although the rocket is small, much of value to the Skylab program can be learned about surface conditions after deposition occurs.

To judge accurately whether contamination from pulse firings is a problem for the Skylab mission, tests using the 100-pound R-4D engines are probably needed, but it is almost impossible to satisfactorily conduct such tests. Even tests using the small 20 to 25 pound engines typically lack good altitude simulation. Martinkovic maintained 225,000 feet ($6.0 \times 10^{-2}$ torr), which is comparatively good; the Skylab orbit is 235 nautical miles or 1,428,800 feet ($1.5 \times 10^{-9}$ torr). Since the chemical reactions leading to harmful residue formation increase at the higher pressures, ground tests probably yield pessimistic results for a given rocket. However, this is offset somewhat in tests using the R-1E engine, since it is more efficient than the R-4D at pulse firings levels.

Summarizing the pulse firing data, it seems very possible that several thousand pulse-type firings can result in the deposition of a residue on the SM surface in the critical RCS door area. There might be significant quantities of MMH nitrate deposited; and, for some period of time, other constituents such as nitric acid and ammonium nitrate might exist also. The currently available test data on coatings exposed to parallel impingement indicate only minimal degradation occurs. However, more data is needed, especially for coatings exposed to MMH nitrate deposition near the exhaust nozzle.

Engine firing timelines are the determining factor. Residue formation can be reduced or eliminated for even long pulse trains if high engine temperatures are maintained; therefore, when possible, such firings should be conducted in a series of closely spaced pulses, preferably when engines are warmed by solar exposure.

The current Skylab mission requires relatively few randomly initiated pulse-type firings, and residue deposition probably is minimal. The effect of such residues on the 92-007 coating and other coatings will be discussed later.

Secondary Condensation from a Cloud

Gaseous molecules in the rocket plume travel at high velocities, even for the pulse-type firings. These molecules very rapidly disperse, and a cloud never really forms. However, some of the residues formed during pulse firings might slowly detach from the engine nozzles and form a lingering cloud of droplets or particles, probably consisting of MMH nitrate.

Judging from the quantities of rocket residue produced, primarily during pulse firings, only a very low density cloud can form. If some portion of the cloud condenses on a surface, the degradation will be much less than that caused by direct impingement, and it is probable that other spacecraft contamination sources, such as urine dumps, overshadow the effects of any rocket produced cloud.

Chemical Reaction with Coating Materials

Pulse firings produce several constituents that can react chemically with typical spacecraft coating materials given enough exposure time under proper conditions. For example, nitric acid and water solutions are very corrosive, and ammonium nitrate can be damaging also. The studies currently being conducted by Mark and Cassidy might determine whether such chemical reactions damage coatings under space conditions. However, except for the MMH nitrate, other constituents have not been measured from surface test samples, and they might disappear, through some chemical reaction-evaporation process, before seriously damaging the surface. The MMH nitrate, at least, can remain in contact with surface materials for extended periods allowing ample opportunity for chemical reaction.

MMH nitrate has been studied briefly as a possible monopropellant, but apparently only a few basic properties have been determined.* As mentioned earlier, pure MMH nitrate is a crystalline material but can quickly absorb moisture and change to a viscous form. From some tests conducted at the United States Bureau of Mines[22], the MMH nitrate crystalline form melts at 104°F (40°C); it thermally decomposes at 455°F (235°C); and it is somewhat impact sensitive with a 136% TNT equivalence. In general such nitrates can be corrosive, especially in contact with a porous organic material like the SM cork layer, however, it might not react with

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*In addition to a singularly unsuccessful literature search for MMH nitrate data, several discussions in person and by telephone were held with a number of people knowledgeable in areas related to propellant properties and material properties.

the 92-007 coating. Simple tests could easily determine material compatibility. Also, since simple masking is possible, $\alpha$ and $\epsilon$ measurements of the deposit are needed.

Stechman[19] has often worked with the viscous form of MMH nitrate. On one occasion, he threw a test tube containing a few grams of it against a wall. No explosion occurred indicating the viscous form probably poses no explosive impact danger. He has also tasted MMH nitrate on the tip of his tongue, and although it was bitter, he suffered no ill effects. However, he may have been fortunate to taste only a very small amount because MMH nitrate is toxic. In a recent Apollo directive[28], flight crew procedures during extra vehicular activities were modified to avoid a toxicological hazard from MMH nitrate deposits picked up from astronaut handrails. Simple washing procedures were judged adequate to safely limit exposure.

## V. CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

1. When fired for extended durations, the SM RCS rocket exhausts can cause surface damage by overheating. For the RCS doors, surface breakdown begins after approximately 114 seconds for an initial tangential jet burn and after 41 seconds for an initial axial jet burn. Surface damage from overheating can be avoided by limiting firing durations or, to an extent, by increasing cork thickness.

2. The relatively inefficient pulse firings can deposit several potentially damaging chemicals on the surface, especially during a series of several hundred firings at low engine temperatures. Apparently MMH nitrate is the one deposited plume product that persists in a vacuum. When pure, it is a white crystalline material, but when exposed it can quickly absorb water and become viscous. Its effect on spacecraft materials has not been established.

3. The deposition of plume combustion products is not a problem for steady-state firings.

4. Erosion by particulate matter (sand blasting effect) probably is not a problem.

5. Except for a few droplets or particles of MMH nitrate released with negligible velocity, RCS exhaust products quickly disperse and no significant lingering cloud is formed.

6. Since the present Skylab SM RCS firing schedule does not include long continuous firings (except possibly after separation) or a long series of short pulse type firings, the SM RCS very likely will not degrade the 92-007 coating on the critical RCS sun side door much beyond a 0.5 absorptance value. According to North American, an absorptance below 0.6 is needed. Surfaces other than the SM RCS door will be affected even less since either tight thermal control is not needed or plume impingement is relatively minor.

Recommendations

1. For the currently configured Skylab mission, further tests, other than those being conducted by Mark and Cassidy, are not needed.

2. If future uses of the SM RCS indicate possible coating damage, full scale testing with an R-4D engine and an SM simulated geometry should be considered, but only as a last resort. Such a test would be expensive, difficult to perform accurately, and possibly prove inconclusive anyway. Instead, RCS firing situations that are expected to cause degradation should be avoided.

3. If a series of pulse firings from one rocket is ever needed, shorten the off time between firings to raise engine temperatures and evaporate combustion residues.

4. Material compatibility tests, especially with MMH nitrate, should be made when there is any possibility of deposition by the RCS engines.

5. When possible, shield critical surfaces from exhaust impingement.

6. Consider the use of different coating materials, which can resist all the various forms of degradation including RCS exhaust exposure. For example, the Z-93 white coating, one of the Apollo 9 samples, seems to resist degradation better than the 92-007. Also, B. Seidenberg[2] feels the silver coated teflon now in use on the OSO-F satellite is a very good candidate because of its thermal radiation properties ($\alpha$=0.07, $\varepsilon$=0.89) and its resistance to degradation.

George Yanizeski

1022-GMY-mef G. M. Yanizeski

Attachments

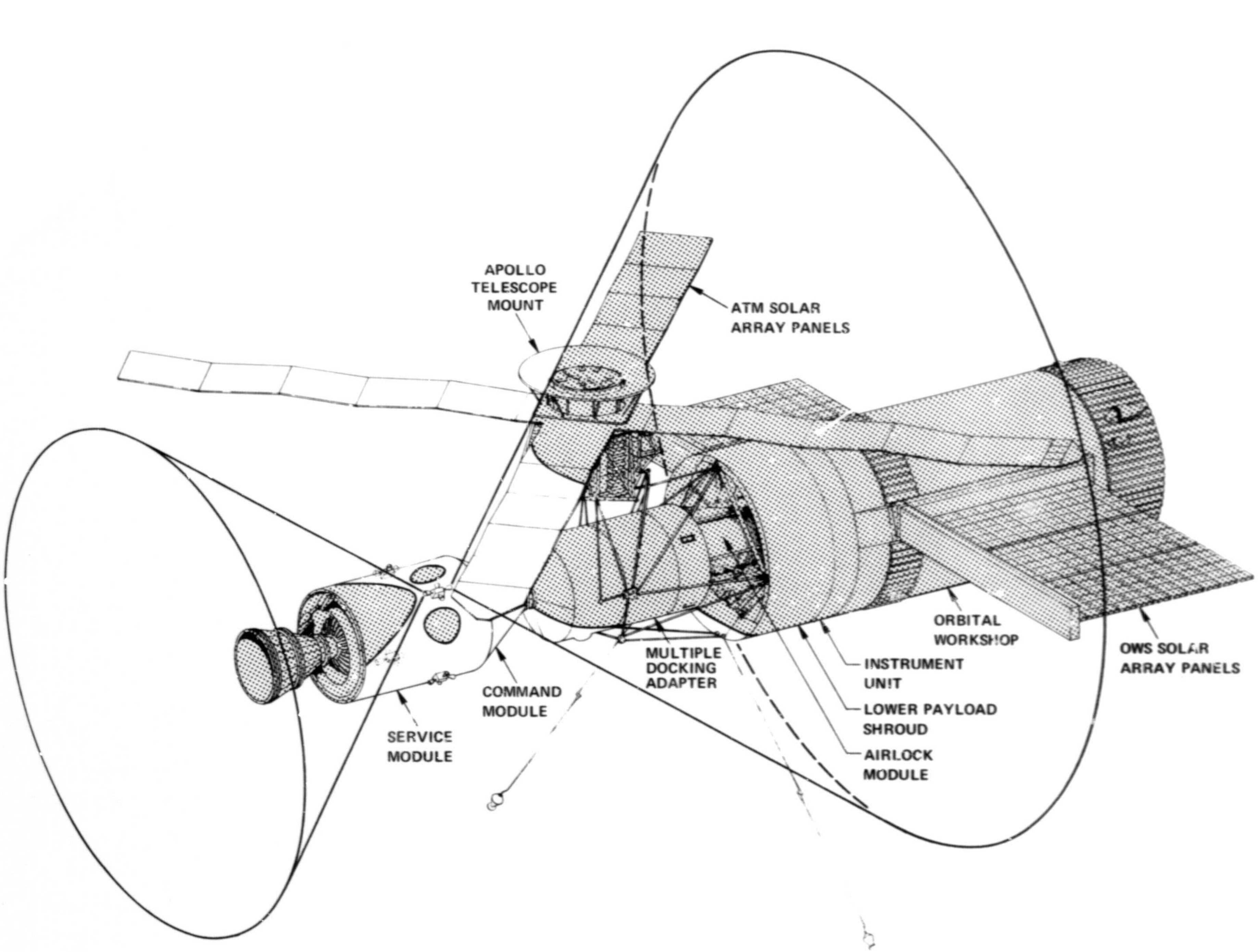



FIGURE 1 - SATURN V WORKSHOP AREAS AFFECTED BY ONE RCS QUAD - SHADED AREAS LIE WITHIN THE CONES BOUNDING 90.7% OF THE MASS FLOW

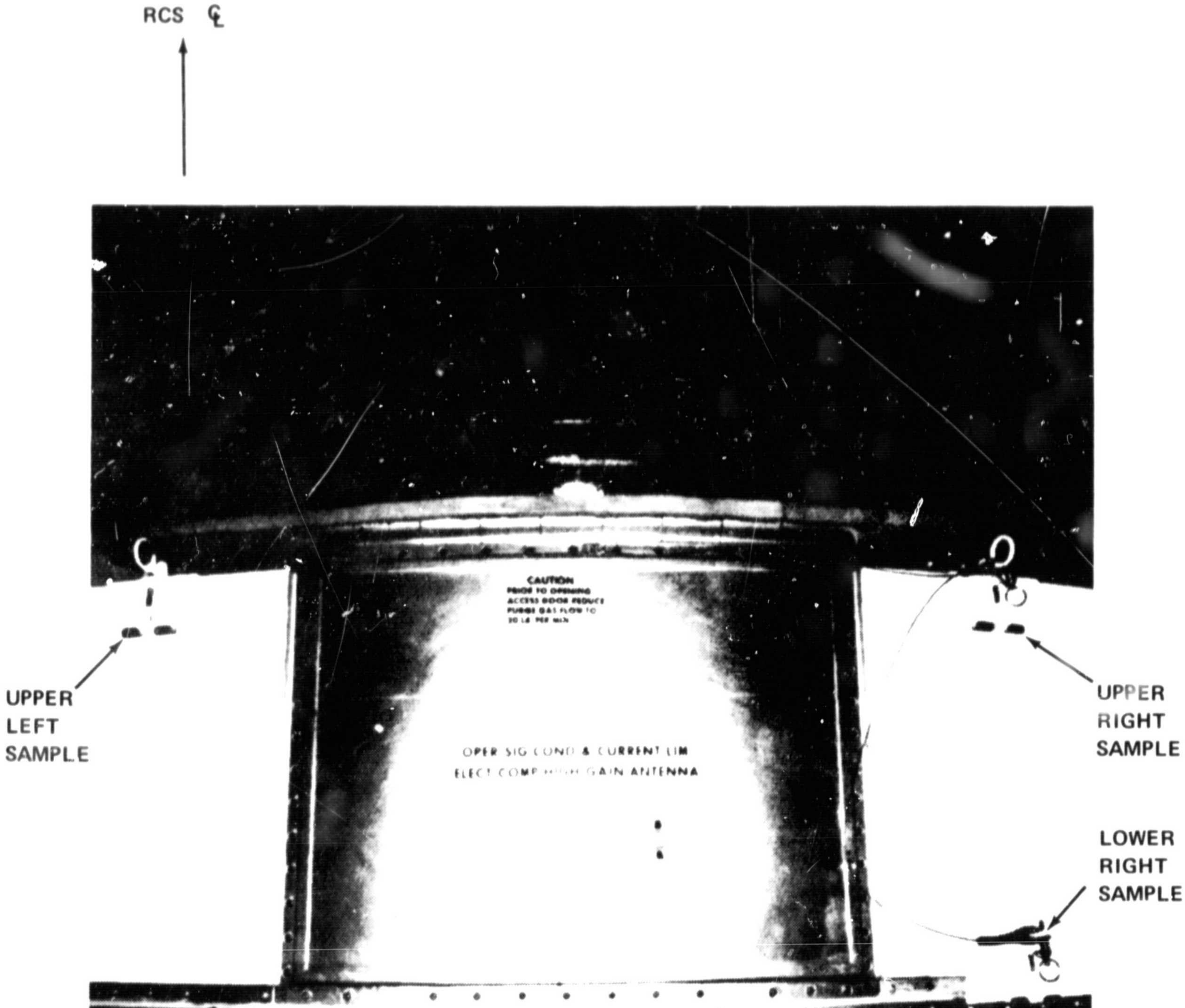
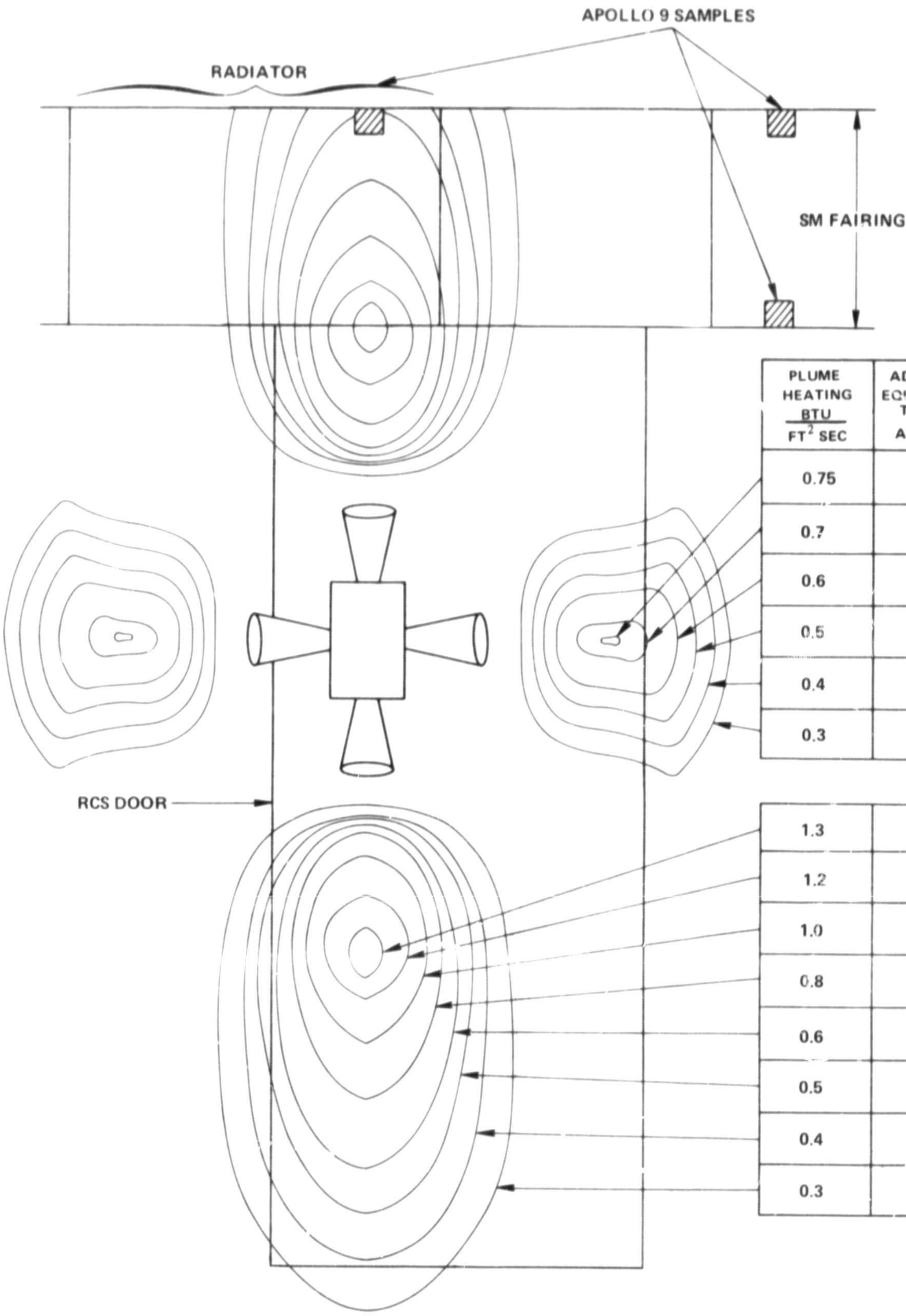



FIGURE 2 - PREFLIGHT INSTALLATION OF THE SERVICE-MODULE THERMAL SAMPLES AND TETHER. (FIGURE 3, REFERENCE 9)




| PLUME HEATING $\frac{BTU}{FT^2\ SEC}$ | ADIABATIC EQUILIBRIUM TEMPERATURE °F | TIME TO 500 °F SEC |
|---|---|---|
| 0.75 | 690 | 114 |
| 0.7 | 670 | 144 |
| 0.6 | 628 | 234 |
| 0.5 | 579 | 406 |
| 0.4 | 523 | — |
| 0.3 | 455 | — |

| | | |
|---|---|---|
| 1.3 | 860 | 41 |
| 1.2 | 834 | 47 |
| 1.0 | 776 | 64 |
| 0.8 | 709 | 102 |
| 0.6 | 628 | 271 |
| 0.5 | 579 | 725 |
| 0.4 | 523 | — |
| 0.3 | 455 | — |

FIGURE 3 – PLUME IMPINGEMENT LINES OF CONSTANT HEATING MAPPED ON A FLAT DEVELOPMENT OF THE SM SURFACE (FROM NORTH AMERICAN DATA, REFERENCE 27)

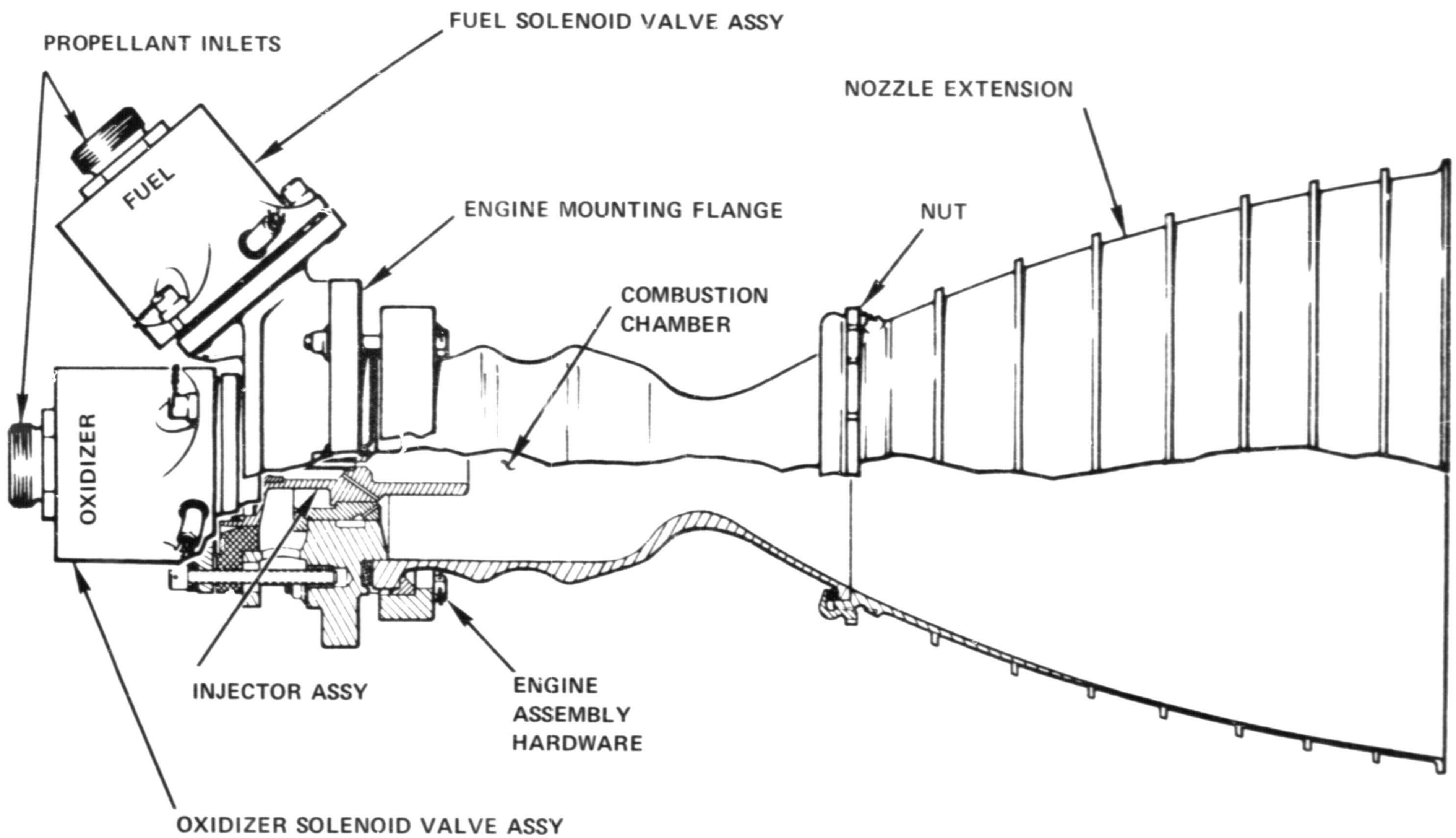



FIGURE 4 - SM RCS ENGINE CUTAWAY

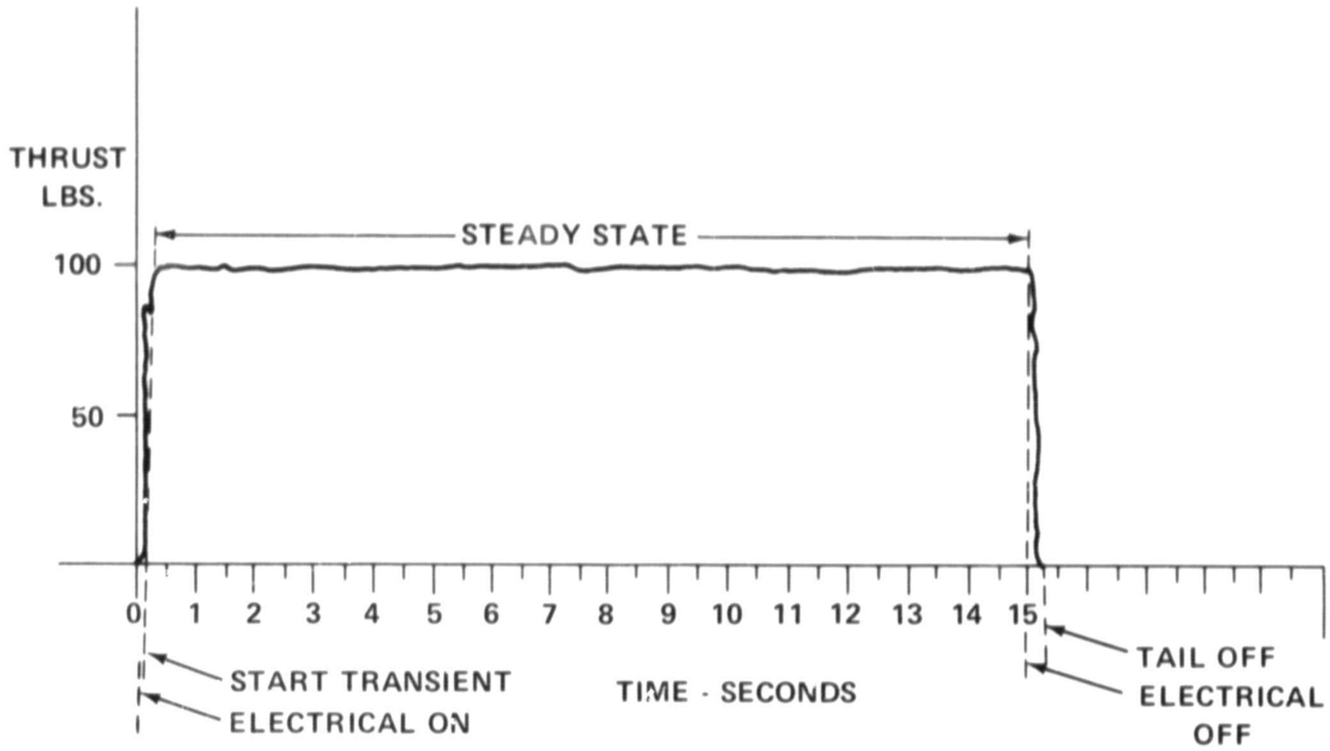



FIGURE 5A - SM RCS STEADY STATE OPERATION–TYPICAL
(FROM REFERENCE 26)

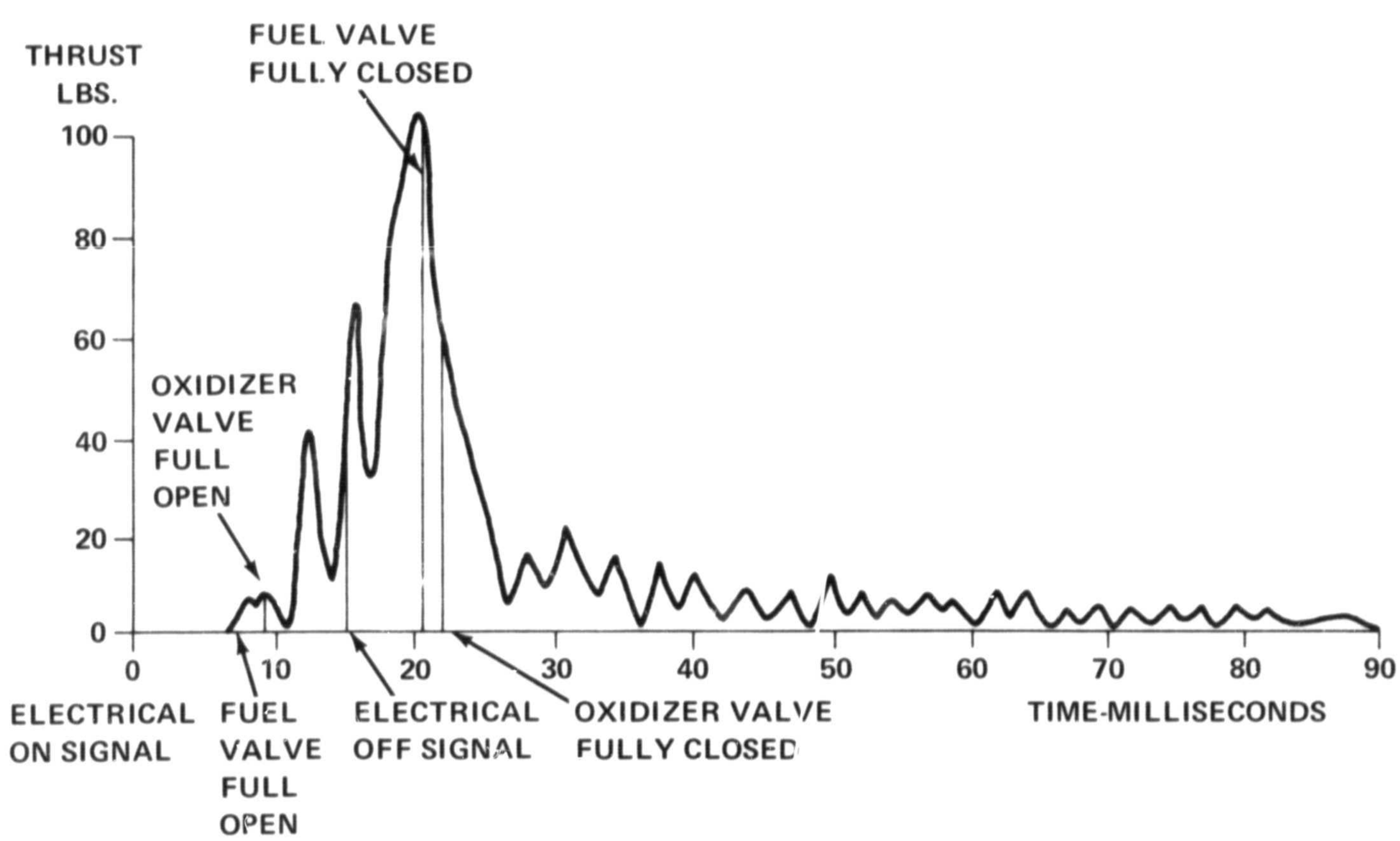



FIGURE 5B - SM RCS ENGINE MINIMUM TOTAL PULSE (FROM MARQUARDT COMPANY QUALIFICATION
TEST CONDUCTED NOVEMBER 23, 1965)

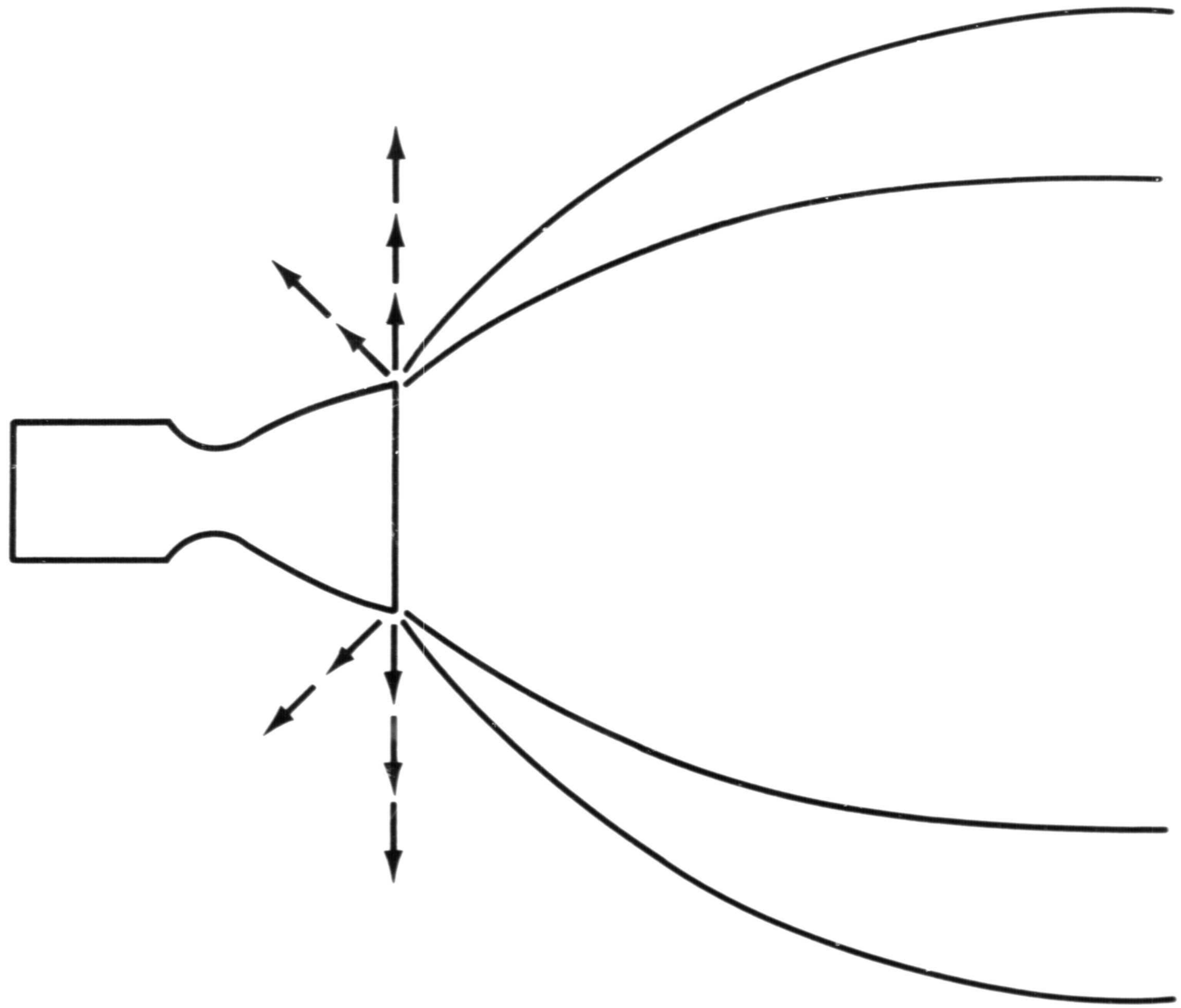


FIGURE 6 - SIMULATED BIPROPELLANT ACR EXHAUST PLUME. (FIGURE 1, REFERENCE 24)

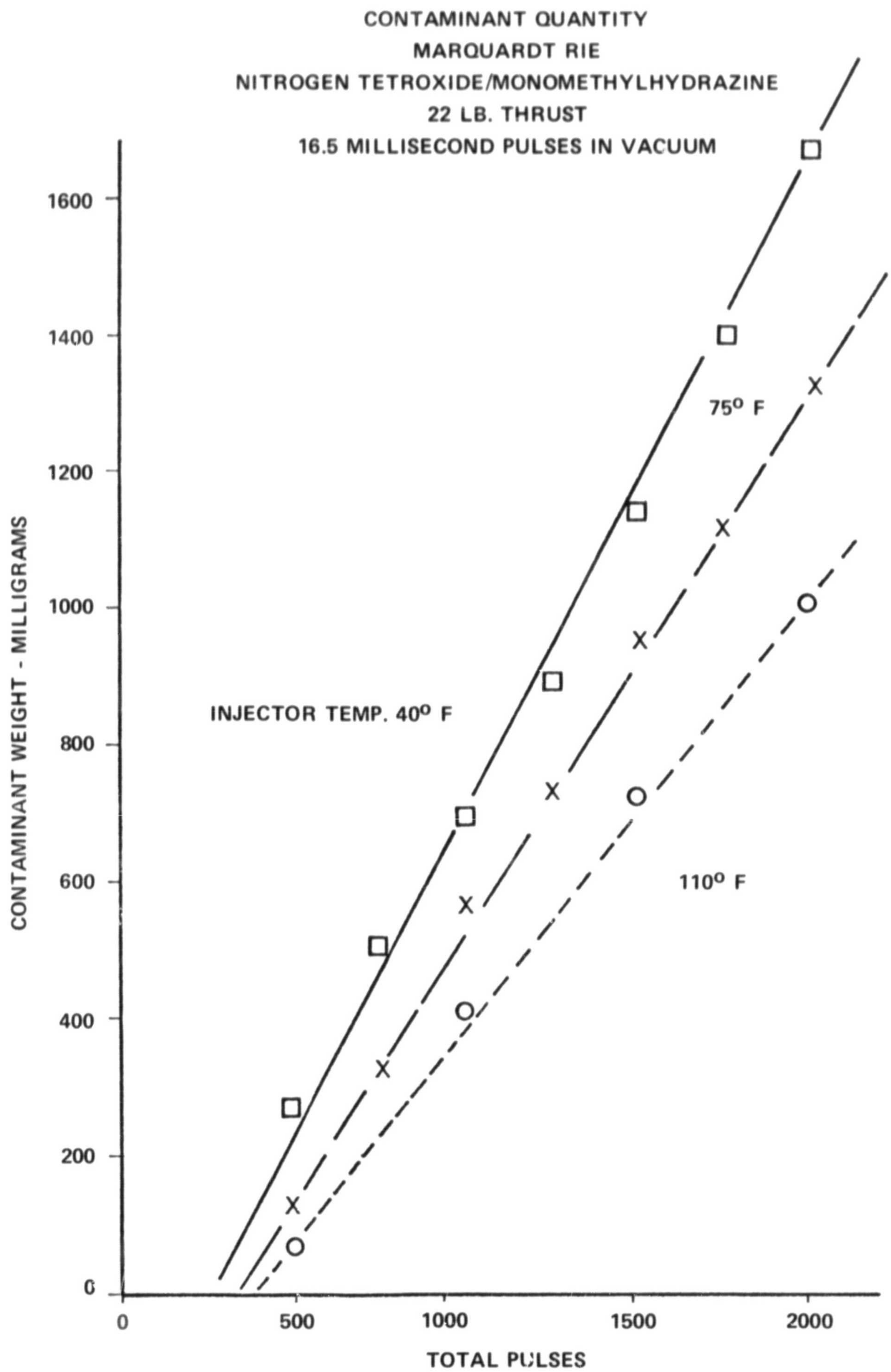



FIGURE 7 - CONTAMINANT WEIGHT VERSUS PULSES (FIGURE 6, REFERENCE 24)

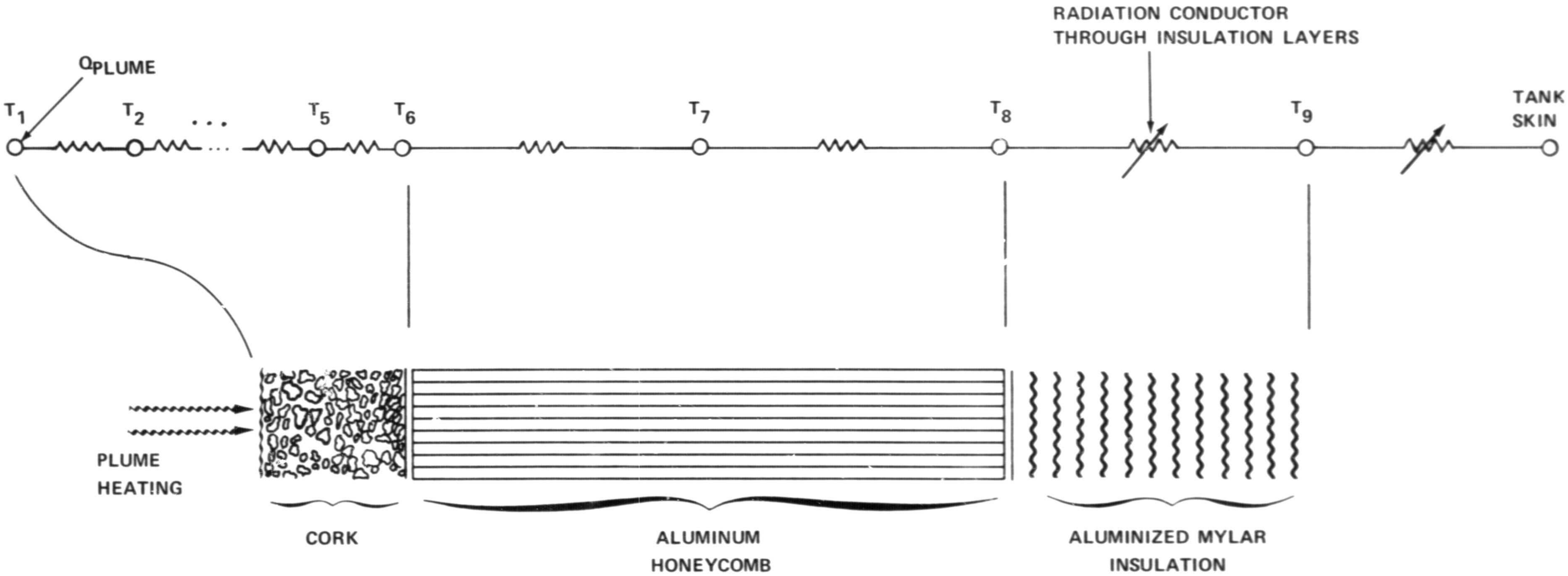



FIGURE 8 - SERVICE MODULE HULL CROSS SECTION AND NODAL BREAKDOWN

## Appendix: One-Dimensional Thermal Model of the SM Hull

Figure 8 shows a typical cross section of the SM hull for those areas receiving RCS plume heating. The cross section consists of a 1-inch layer of aluminum honeycomb covered externally with a layer of cork and internally with 30 layers of aluminized mylar radiation-barrier type insulation. The cork layer varies in thickness; the 0.6-inch and 0.155-inch thicknesses used in this analysis correspond to areas on the RCS doors located beneath the axial jet plume and the tangential jet plume respectively.

The finite difference thermal model of the SM hull is represented by a single chain of nodes and conductors in Figure 8. Rocket plume heating is applied to the first node of 5 representing the cork layer. Heating rates, listed in Figure 3, represent North American's best available data.

Node 1 at the cork surface radiates to deep space with a 0.9 emittance value. Heat is transferred through nodes 1 to 8 by conduction, and the insulation layers between nodes 8 and 9 are represented by a single composite radiation conductor. Since the aluminized mylar super insulation is very effective in limiting heat transfer, almost no heat is transfered beyond node 9 in the time required to exceed the 500°F limit at the cork surface.

By using a single chain of nodes to represent the SM hull, it is assumed that heat transfer through the hull, in a direction perpendicular to the surface, dominates. This assumption holds best for high plume heating rates and thick cork layers because plume heating does not appreciably penetrate the low conductance cork layer before the surface temperature exceeds the 500°F limit. For the hottest portion of the axial plume impingement zone, $T_5$ is still at 105.0°F, the initial temperature for all nodes, when $T_1$ exceeds 500.0°F. As a comparison, for the hottest portion of the tangential plume impingement zone, $T_5$ increases to 225.5°F as $T_1$ increases to 500.0°F. However, it should be noted that this one-dimensional analysis represented in the single chain of nodes produces conservative results because heat dissipation away from localized hot areas is not included.

To calculate transient temperatures, a CINDA* computer model of the nodes and conductors was solved using a forward

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*Chrysler Improved Numerical Difference Analyzer computer program designed for thermal analysis of physical systems presented in the characterestic network of nodes and conductors.

differencing time stepping technique. Figure 3 presents the results as the time required to exceed the 500°F surface temperature limit at various plume heating rates.

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