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Task III
Supporting
Tests

SS/RCS Surface Tension Propellant Acquisition/Expulsion Tankage Technology Program

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MARTIN MARIETTA

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PROPELLANT ACQUISITION/
EXPULSION TANKAGE
TECHNOLOGY PROGRAM

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FOREWORD

This interim report is submitted to the National Aeronautics and Space Administration, Johnson Space Center, by Martin Marietta Corporation, Denver Division, under Contract NAS9-13709, "SS/RCS Surface Tension Propellant Acquisition/Expulsion Tankage Technology Program." This work was administered under the technical direction of Mr. Dale Connelly, NASA-JSC Technical Monitor. Mr. Dale Fester, Chief, Thermodynamics and Fluid Mechanics Section, Propulsion Department, was the Martin Marietta Program Manager. Mr. Preston E. Uney directed the Task III activity.

SUMMARY

An evaluation of published propellant physical property data together with bubble point tests of fine-mesh screen in propellants, was conducted. The effort consisted of: (1) the collection and evaluation of pertinent physical property data for hydrazine (N_2H_4), monomethylhydrazine (MMH), and nitrogen tetroxide (N_2O_4); (2) testing to determine the effect of dissolved pressurant gas, temperature, purity, and system cleanliness or contamination on system bubble point; and (3) the compilation and publishing of both the literature and test results. The space shuttle reaction control system (SS/RCS) is a bipropellant system using N_2O_4 and MMH, while the auxiliary power system (SS/APU) employs monopropellant N_2H_4. Since both the RCS and the APU use a surface tension device for propellant acquisition, the propellant properties of interest are those which impact the design and operation of surface tension systems.

Information on propellant density, viscosity, surface tension, and contact angle was collected, compiled, and evaluated. Both NASA and DOD literature searches plus personal contacts with government agencies and industry were employed. With the exception of contact angle, the data were obtained as a function of propellant temperature. Some data were obtained showing the effects of pressure on propellant viscosity and density. Information on the effect of propellant purity and contamination on propellant surface tension was also collected and evaluated.

Screen bubble point was chosen as the parameter to be measured in the test program. The propellant acquisition systems proposed for the SS/RCS employ fine-mesh screen in their design. For these fine-mesh screen systems, screen bubble point in the propellant rather than propellant surface tension is the primary design para-

meter (Ref. 3). Therefore, the bubble points of three fine-mesh screen, Dutch-twill weaves (325 x 2300, 200 x 1400, and 165 x 800) in N_2O_4, MMH, and N_2H_4 were measured as a function of propellant temperature and system pressure. Tests were also conducted with purified N_2H_4 to investigate the effect of propellant purity. Contamination and screen cleaning effects were also investigated. Excellent agreement between measured and predicted screen bubble points was obtained with N_2O_4 and MMH. However, anomalous and inconsistent screen bubble point data were obtained with the two grades of hydrazine.

As a result of the anomalous data on screen bubble point in hydrazine, an IR&D test program was conducted to evaluate the surface tension of N_2H_4, its contact angle with metals, and its bubble point with 325 x 2300 fine-mesh stainless steel screen (Ref. 1). This test program was performed as part of Martin Marietta's IR&D activities, since the information is of general interest for designing surface tension systems. The results of the Reference 1 IR&D program, discussed in Chapter III of this report, showed that high contact angles will be obtained with N_2H_4 unless special metal surface cleaning methods are employed. Methods found effective were flame cleaning and chromic acid cleaning. The testing also showed that the high contact angles produced low surface tension values, when measured with a tensiometer, and low screen bubble point values.

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I. INTRODUCTION AND BACKGROUND

The objective of this technology program is to analyze, design, fabricate, and test surface tension propellant acquisition/expulsion tankage that satisfies the requirements of the Space Shuttle Reaction Control System (SS/RCS). The technical effort to meet this objective is composed of five tasks, as follows:

Task I - Design Definition;

Task II - Analysis;

Task III - Supporting Tests;

Task IV - Preliminary Design and Similitude Testing; and

Task V - Full-Scale Tankage.

This report documents the results obtained from the Task III Supporting Tests.

The specific objectives of Task III were: (1) to collect and evaluate pertinent physical property data for hydrazine (N_2H_4), monomethylhydrazine (MMH), and nitrogen tetroxide (N_2O_4), with respect to the RCS and APU system criteria; (2) to conduct testing, as required, to determine the effect of dissolved pressurant gas, temperature, purity, and system cleanliness or contamination on system bubble point; and (3) to compile and publish the results. The RCS uses N_2O_4 and MMH and the auxiliary power unit (APU) uses N_2H_4.

To achieve the objectives, Task III was divided into four specific subtasks:

Subtask III-1: Data Collection - Under this phase of the main task, propellant physical property data of interest to the overall program (density, viscosity, surface tension, and material-propellant contact angle) were updated through literature

searches and personal contacts;

Subtask III-2: Data Evaluation - Data collected under Subtask III-1 were evaluated with regard to the RCS design criteria. Based on this evaluation, the amount and depth of testing to be conducted was determined;

Subtask III-3: Support Testing - The actual supporting tests were conducted under this subtask; and

Subtask III-4: Data Compilation - Under this phase, all data obtained from the task were compiled and documented in this interim report.

The effort conducted under Subtask III-3 consisted of tests to determine the effects of temperature, dissolved pressurant gas purity, and cleanliness on screen bubble point. Determination of screen bubble point was chosen for this evaluation since this is the most important design parameter for surface tension systems, giving the best indication of actual system operation. In this manner, the performance of the screen material to be used can be determined.

In general, surface tension propellant acquisition systems can be divided into two general classifications: those which employ fine-mesh screen, and those which do not (Ref. 2). For those systems which do not employ fine-mesh screen, such as capillary-pumping concepts similar to the Viking Orbiter system, the prime design parameters of interest are propellant surface tension (σ) and the liquid-to-solid surface contact angle (θ). However, for surface tension systems which employ fine-mesh screen, such as the SS/RCS, the primary design parameter is the pressure retention capability (ΔP_c) or bubble point of the screen in the propellant to be used (Ref. 3). The pressure re-

tention capability of a porous material is given in general by the Young-Laplace equation (Ref. 3):

$$\Delta P_c = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \qquad (1)$$

where:

ΔP_c = pressure difference across the liquid/gas interface at any point.

σ = liquid/gas surface tension.

r_1 & r_2 = principal radii of curvature at that point.

If the interface is spherical, as in a circular pore, the pressure difference becomes more simply

$$\Delta P_c = \frac{2\sigma}{r_s} \qquad (2)$$

where r_s is the curvature of the interface ($r_s = r_1 = r_2$).

The capillary pressure difference can be related to a dimension other than the radius of curvature that is easily determined, such as the pore radius R and a second parameter, the liquid-to-solid contact angle θ. This is done by introducing the geometric relationship between R, θ, and r_s, as shown in Figure 1. Using this approach, equation (2) becomes

$$\Delta P_c = \frac{2\sigma}{R}\cos\theta \qquad (3)$$

Experimental verification of the pressure retention for circular pores, as determined by bubble point measurement, agrees with values obtained from the above equation (Ref. 3). Good agreement has also been achieved for square-weave screen, assuming that R is one-half the length of a side of the square pore. However, for the twilled metal cloth, such as Dutch-weave, the

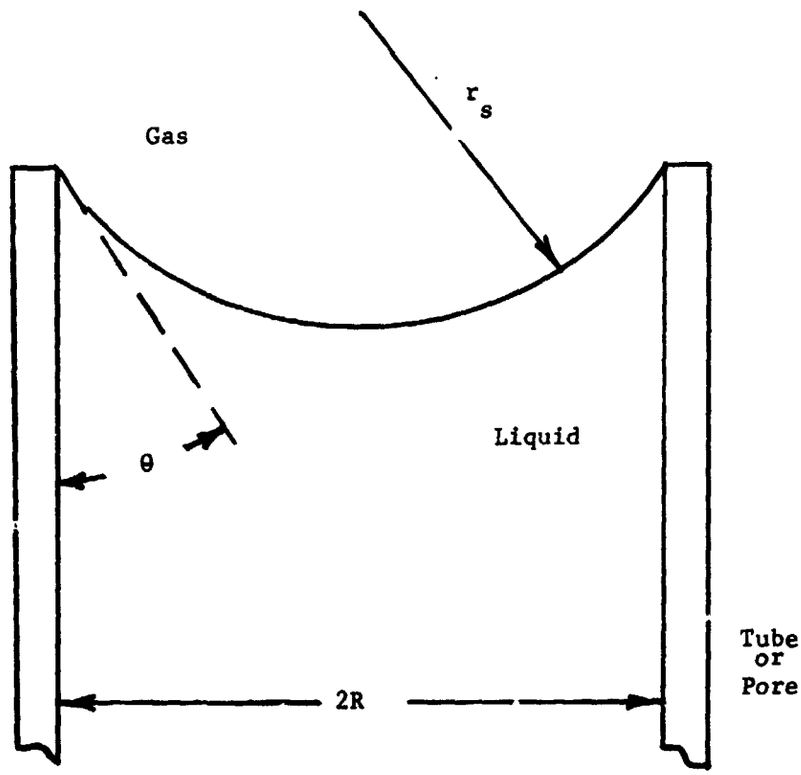

Figure 1: Relationship Between Pore Radius, Contact Angle, and Radius of Curvature for a Liquid-Gas Interface in a Circular Pore or Tube

complex pore geometry is difficult to define in terms of a pore radius. In addition, the effect of contact angle may not be accurately represented by $\cos\theta$ for fine-mesh, Dutch-twill screen. To obtain an accurate representation for fine-mesh screen, the Young-Laplace equation would have to be solved employing the complex geometry of the screen. As a practical alternative, the pressure retention capability of fine-mesh screen is usually determined empirically with a referee fluid having well-established pertinent properties such as isopropyl alcohol or methanol (Ref. 3). Equation (3) is then employed to obtain

$$\frac{\Delta P_{c1}}{\Delta P_{c2}} = \frac{\sigma_1}{\sigma_2} \tag{4}$$

Equation (4) can be used to obtain the bubble point ΔP_c for the actual propellant assuming that either $\theta = 0$ or that $\theta_1 = \theta_2$. If θ is not zero or is different for the referee fluid and the propellant, equation (4) will give incorrect results.

As demonstrated by equation (3), the effect of a non-zero contact angle on a porous material is to lower the pressure retention capability of the material. In theory, the value of contact angle primarily depends on the liquid surface tension and the solid boundary's surface energy (Ref. 4). The latter can be expressed as a so-called "critical surface tension." If the liquid surface tension is less than this critical value, the contact angle is zero. If the surface tension is greater than the critical value, the contact angle will be non-zero and in direct proportion to the difference between the liquid surface tension and the critical surface tension. Clean metal surfaces have high critical surface tensions and the propellants should completely wet them. However, maintaining a contaminant-free

surface is difficult to achieve. Most monolayer contaminant films (except fluorocarbons) have critical surface tensions between 20 and 45 dynes/cm (Ref. 5). Even clean surfaces, exposed to an atmosphere with a relative humidity as small as 0.6% form a monolayer of H_2O that lowers the critical surface tension to 45 dynes/cm (Ref. 6). This should have little effect on the wettability of N_2O_4 and MMH because of their low surface tension values. However, unless proper cleaning procedures are employed and moisture limited, non-zero contact angles resulting in off-nominal bubble point values could be obtained with screens in hydrazine which has a high surface tension.

As indicated by the above discussions, the use of equation (4) to calculate the bubble point of fine-mesh screens from surface tension data is limited to cases having near-zero contact angle. Therefore, the knowledge of the effects of dissolved pressurant gas, temperature, propellant purity, and contamination on propellant surface tension does not enable the accurate determination of the effect these parameters have on the bubble point of fine-mesh screen. Only by direct measurement of the bubble point in the propellant can these effects be accurately determined.

The results obtained from Task III of the contract are discussed in Chapter II. Pertinent propellant physical property data compiled from the literature and personal contacts are presented first. This is followed by a detailed discussion of the bubble point test program.

During the tests, anomalous bubble point data were obtained with N_2H_4. In an effort to gain a better understanding of the cause of the low bubble point measured in N_2H_4, a test program was conducted with N_2H_4 to evaluate surface tension, contact angle

with different metals, and bubble point of fine-mesh screens. This test program was performed as part of Martin Marietta's IR&D activities (Ref. 1), since it was of general interest for surface tension system design and was not part of this contract. Since the problem was uncovered under the contract, however, and the results are of interest, the IR&D tests are presented in Chapter III. A discussion of contract and IR&D results is presented in Chapter IV and conclusions and recommendations are presented in Chapter V. References are contained in Chapter VI.

II. CONTRACT TESTING

A. DATA COMPILATION

As stated in Chapter I, one of the specific objectives of Task III was the collection and evaluation of pertinent physical property data for the propellants N_2H_4, MMH, and N_2O_4 with respect to the SS/RCS and APU system criteria. Propellant physical properties of particular interest to the design of a surface tension propellant acquisition system contact angle are density, viscosity, surface tension, and contact angle (Ref. 3).

NASA and DOD literature searches were conducted to update our collection of physical property data for N_2O_4, N_2H_4, and MMH. In addition, personal contacts were made with both government agencies and industry. The results of the data collection and evaluation are discussed in this section.

Density

Data obtained on the density of N_2H_4, MMH and N_2O_4 are shown as a function of temperature in Figures 2, 3 and 4, respectively. The data shown are for a pressure of 10 N/cm^2 (one atm), except as noted. Source of the data is indicated on the plots. For N_2H_4, the maximum variation in the reported data is only 0.45% while for MMH it is 0.37%. The maximum N_2O_4 data scatter is about 1% if the CPIA data (Ref. 8) are included. Not considering the CPIA data, the data scatter is less than 0.2%, except at higher temperatures. Also included in Figure 4 is the effect of pressure on N_2O_4 density, as reported by Bell (Ref. 13). For a system pressure of 345 N/cm^2 (500 psi) the increase in N_2O_4 density over that at 10 N/cm^2 (one atm) is approximately 0.3%. Assuming a linear relationship between system pressure and density, the increase in N_2O_4 density for the SS/RCS tankage at a system pres-

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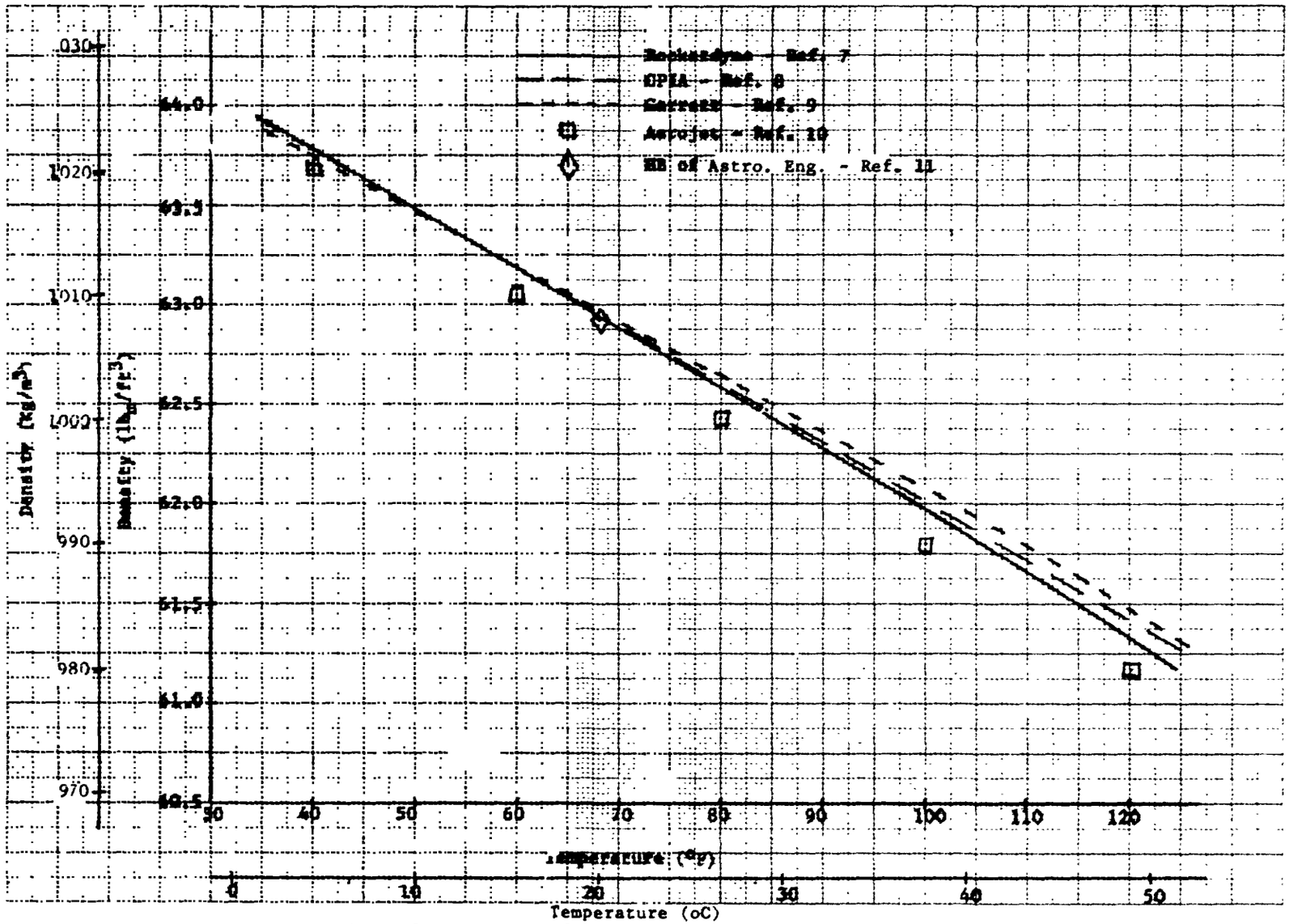

Figure 2: Density of N_2H_4 as a Function of Temperature

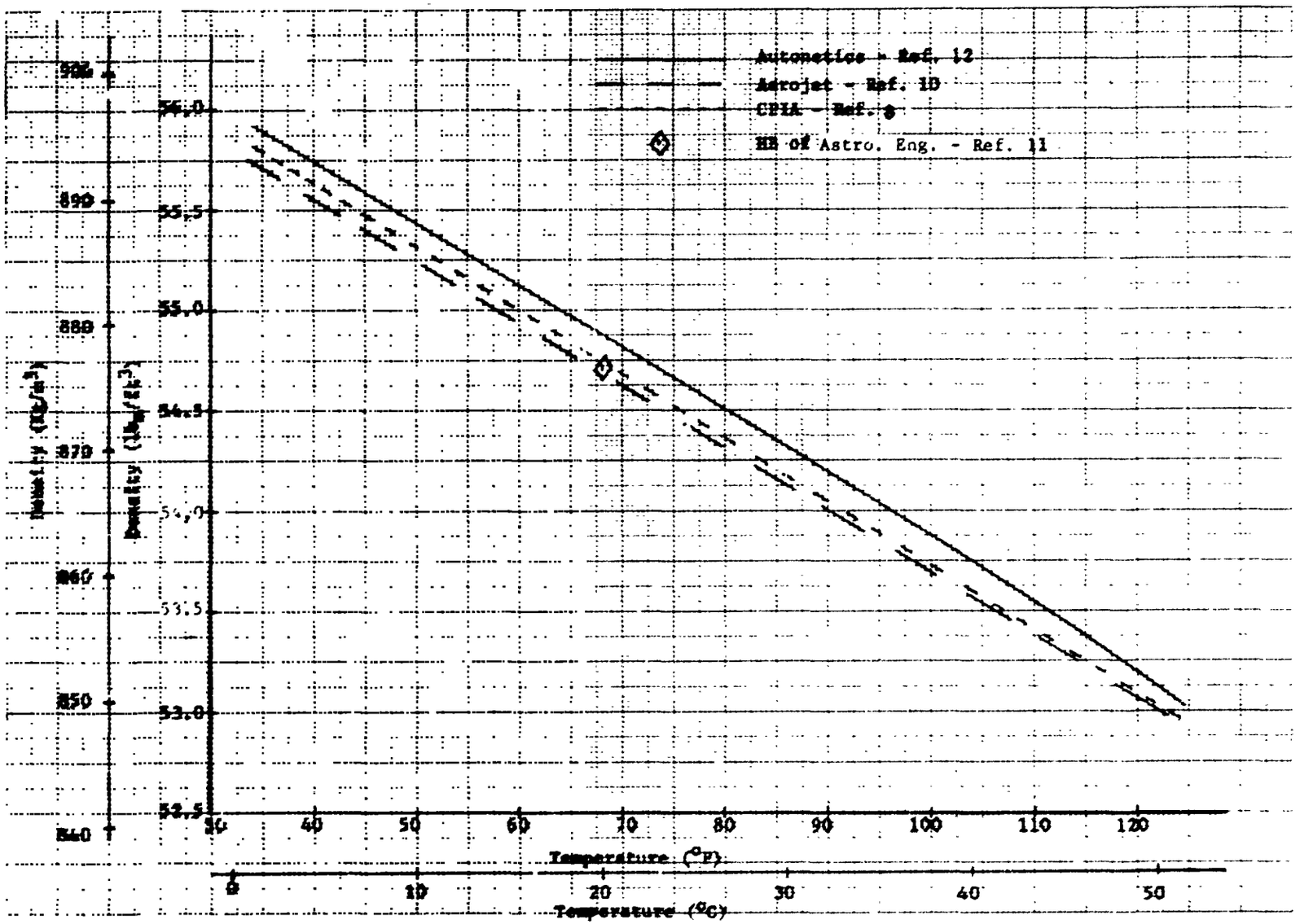

Figure 3: Density of MMH as a Function of Temperature

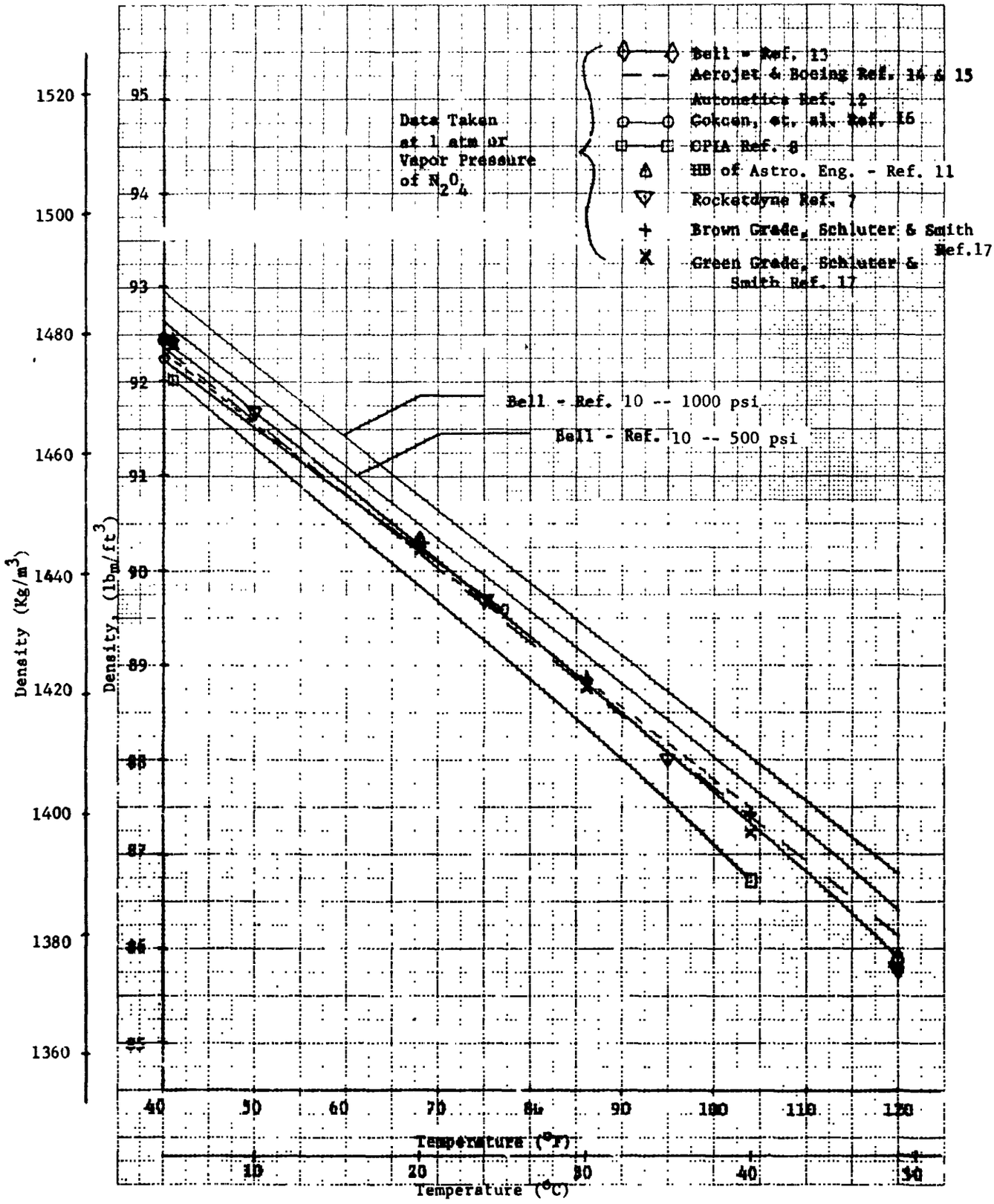

Figure 4: Density of N_2O_4 as a Function of Temperature

sure of 193 N/cm^2 (280 psi) would only be about 0.17% over that at 10 N/cm^2 (one atm). This is less than the variation in the reported data.

2. Viscosity

Data compiled on the viscosity of N_2H_4, MMH and N_2O_4 are presented as a function of temperature in Figures 5, 6 and 7, respectively. Unless indicated on the plots, the data are assumed to be for a pressure of 10 N/cm^2 (one atm). The maximum variation in the N_2H_4 viscosity data (Figure 5), discounting the Rocketdyne results (Ref. 7) is 2.4%. Including the Rocketdyne data, the variation is as much as 9.7% at the lower end of the temperature range. Although the high pressure data obtained from two references do not agree with one another, it can be seen that there is a definite increase in viscosity with pressure. Assuming a linear dependency of viscosity with pressure at constant temperature, the increase in N_2H_4 viscosity for a RCS tank pressure of 193 N/cm^2 (280 psi) would be only 0.5% over that at 10 N/cm^2 (one atm) at 20°C (68°F).

For MMH, the reported viscosity data presented in Figure 6 varies by as much as 10.5% at the higher temperatures. No data was found at elevated pressures, but the effect should be minimal. For N_2O_4, the amount of scatter in the viscosity data, shown in Figure 7, is much less than for either N_2H_4 or MMH. At the higher temperatures (lowest value of viscosity), the maximum variation in the reported data is less than 3%. The viscosity of N_2O_4 also increases with pressure; again, the effect would be minimal, approximately 0.8% at 20°C (68°F).

3. Surface Tension

The surface tension data compiled for N_2H_4, MMH, and N_2O_4 are presented in Figures 8, 9, and 10, respectively. The data

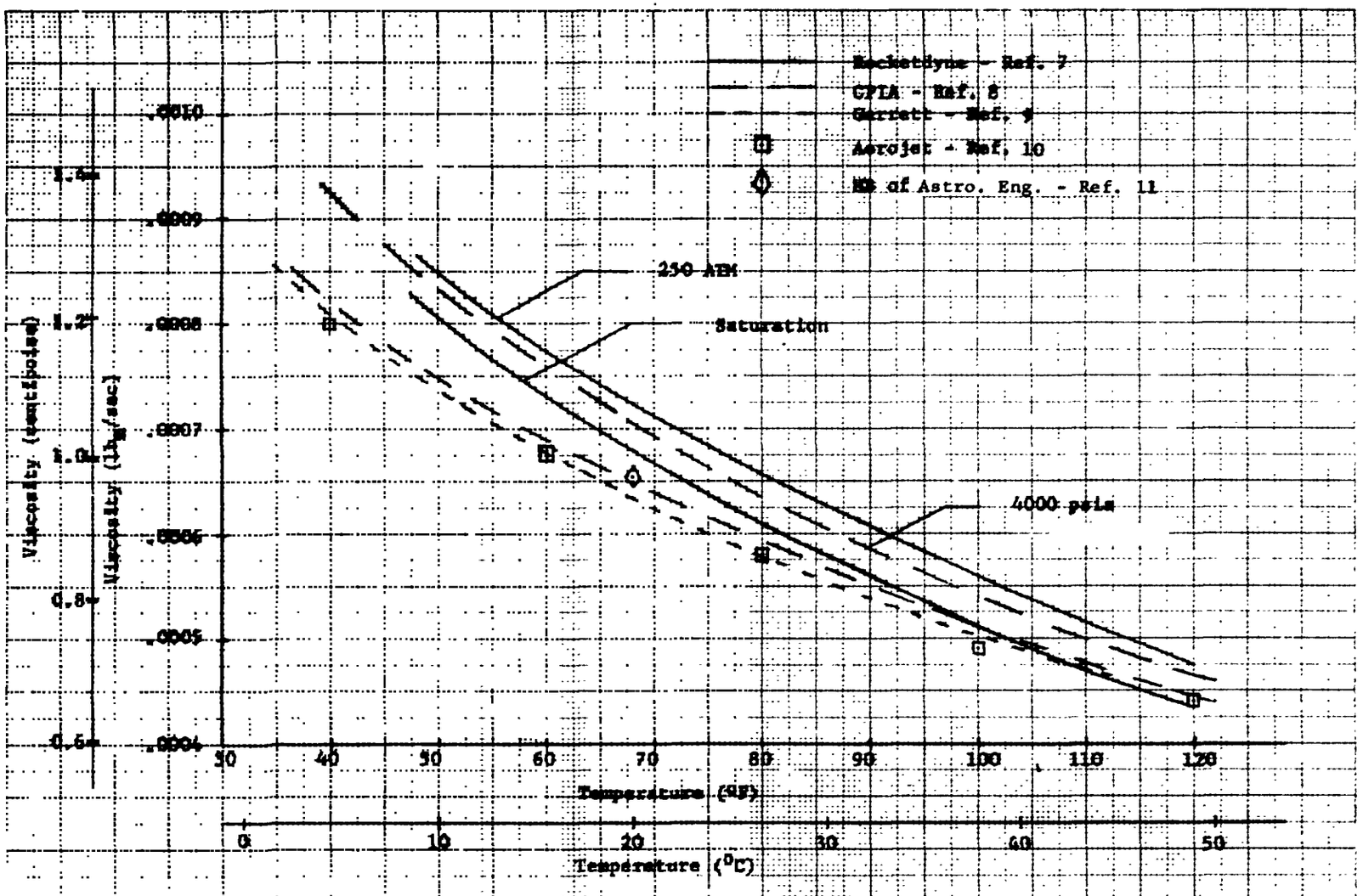

Figure 5: Viscosity Data for N_2H_4 as a Function of Temperature

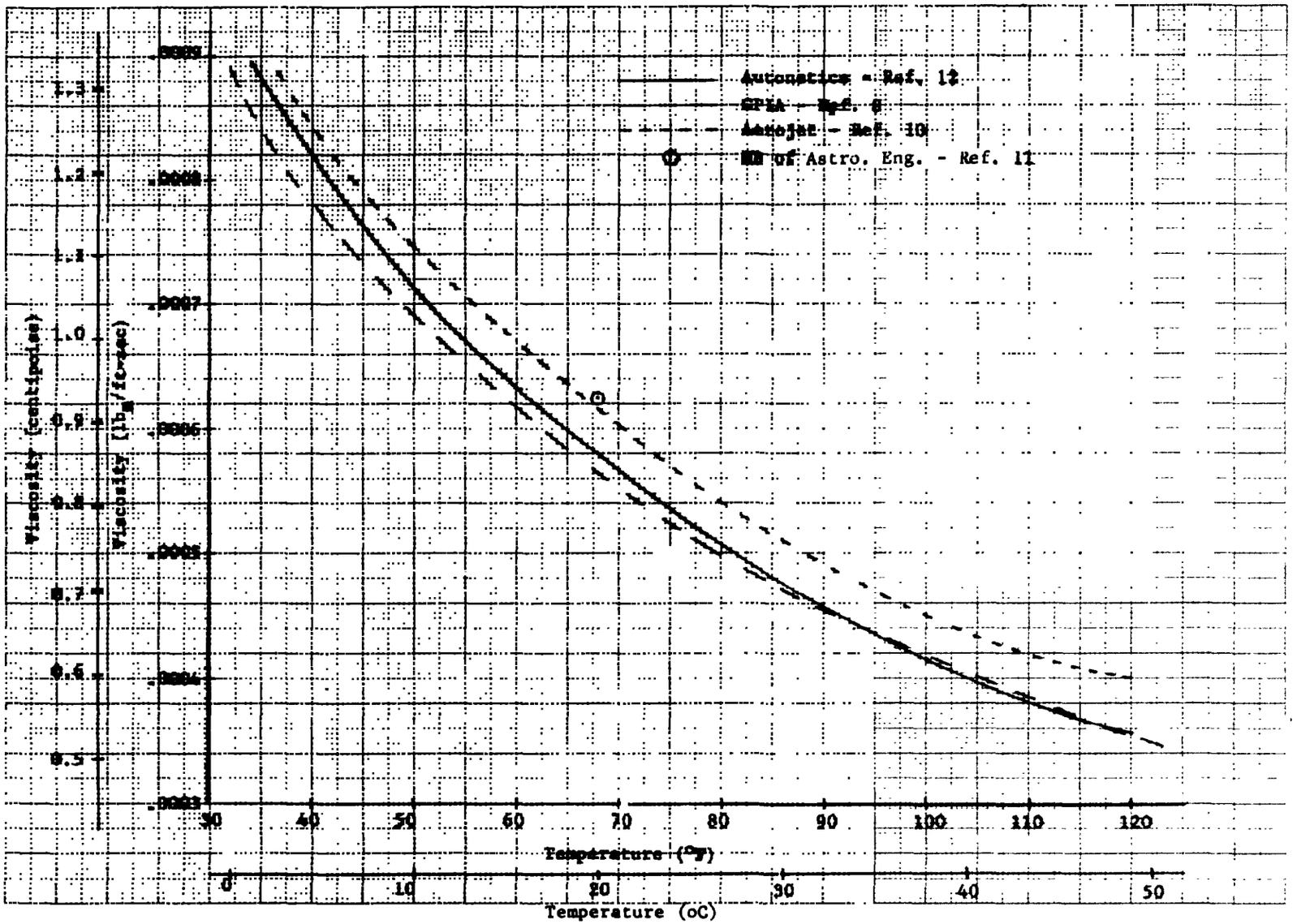

Figure 6: Viscosity Data for MMH as a Function of Temperature

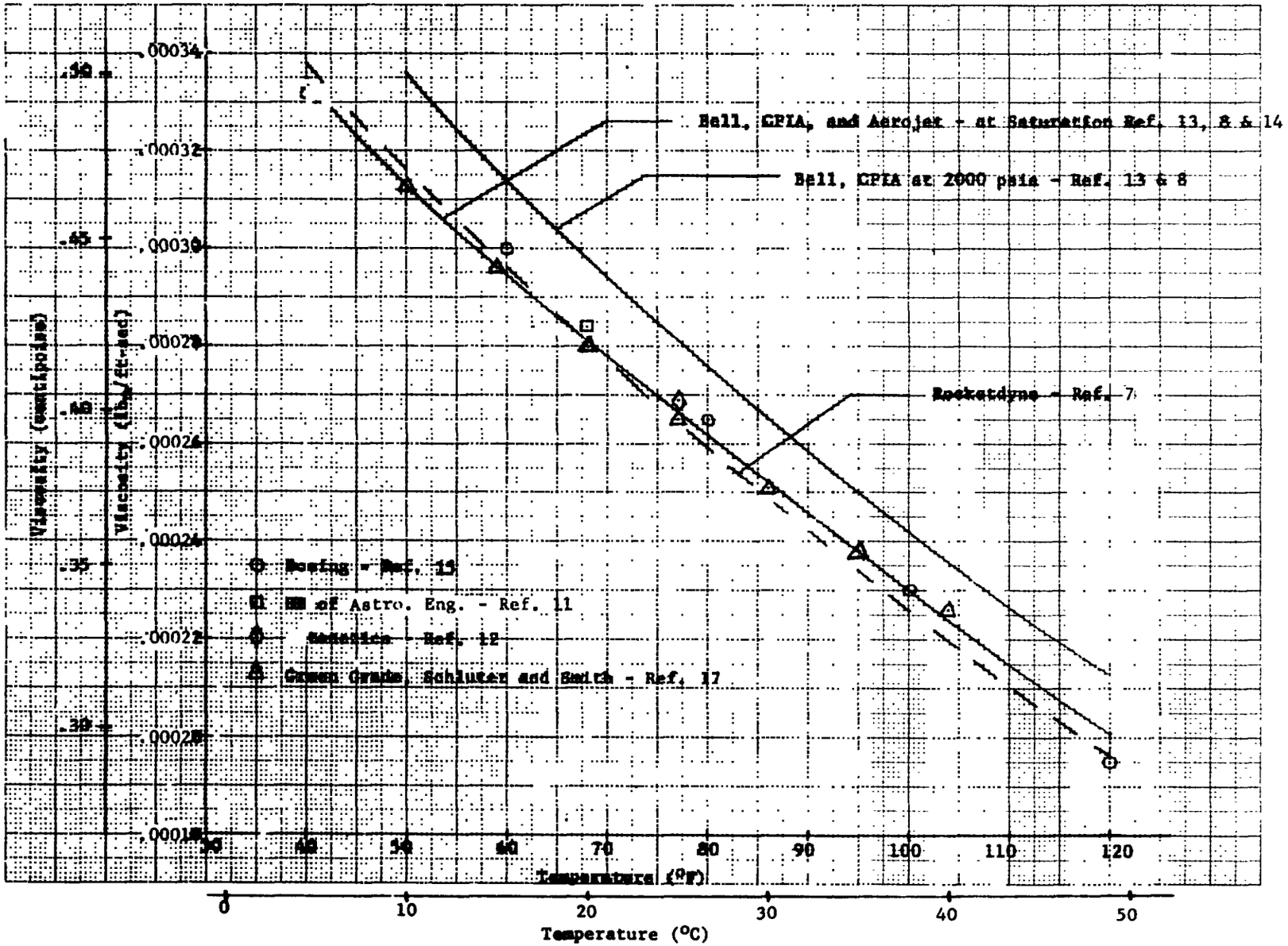

Figure 7: Viscosity Data for N_2O_4 as a Function of Temperature

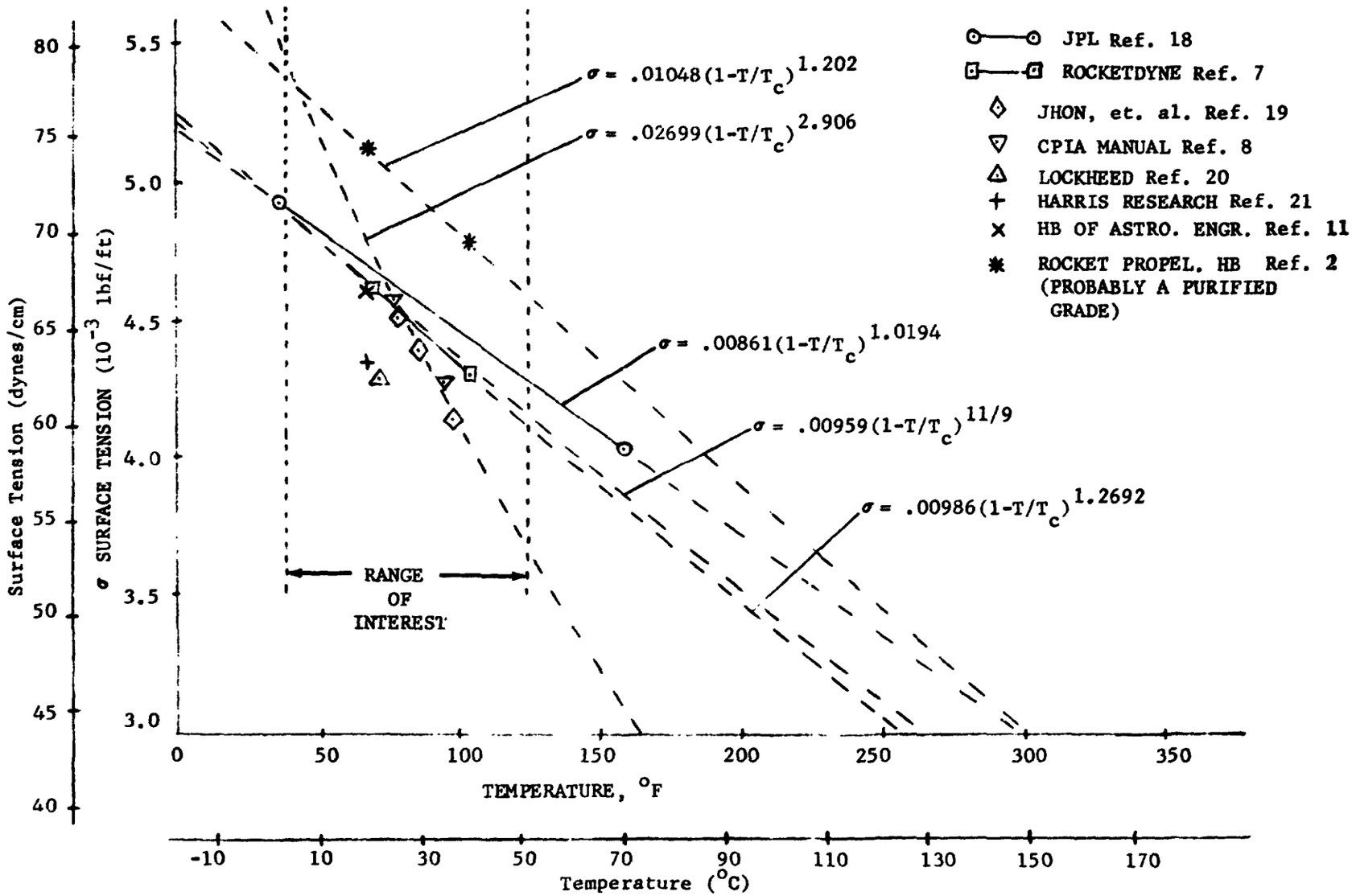

Figure 8: Surface Tension Data for N_2H_4 as a Function of Temperature

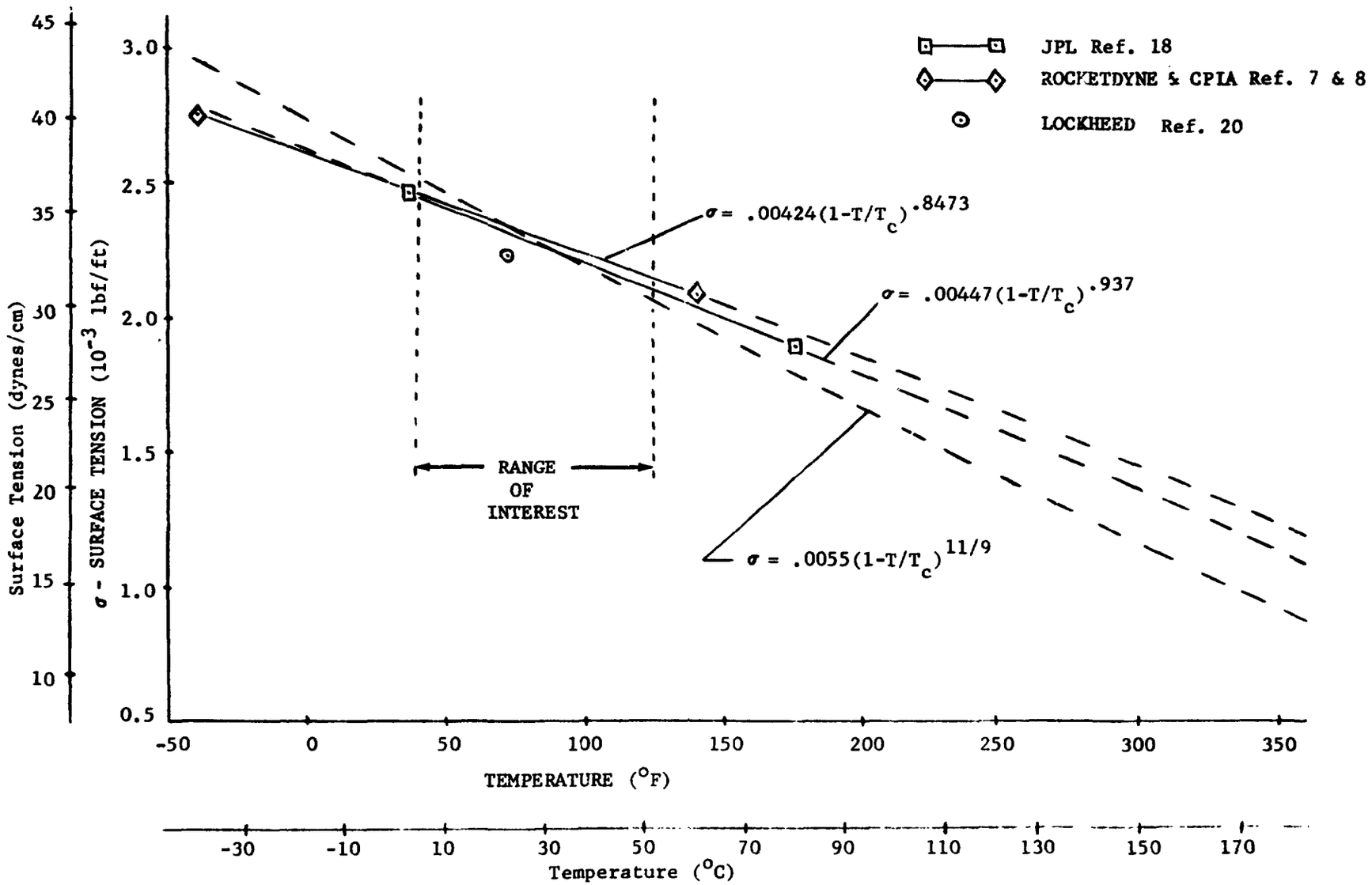

Figure 9: Surface Tension Data for MMH as a Function of Temperature

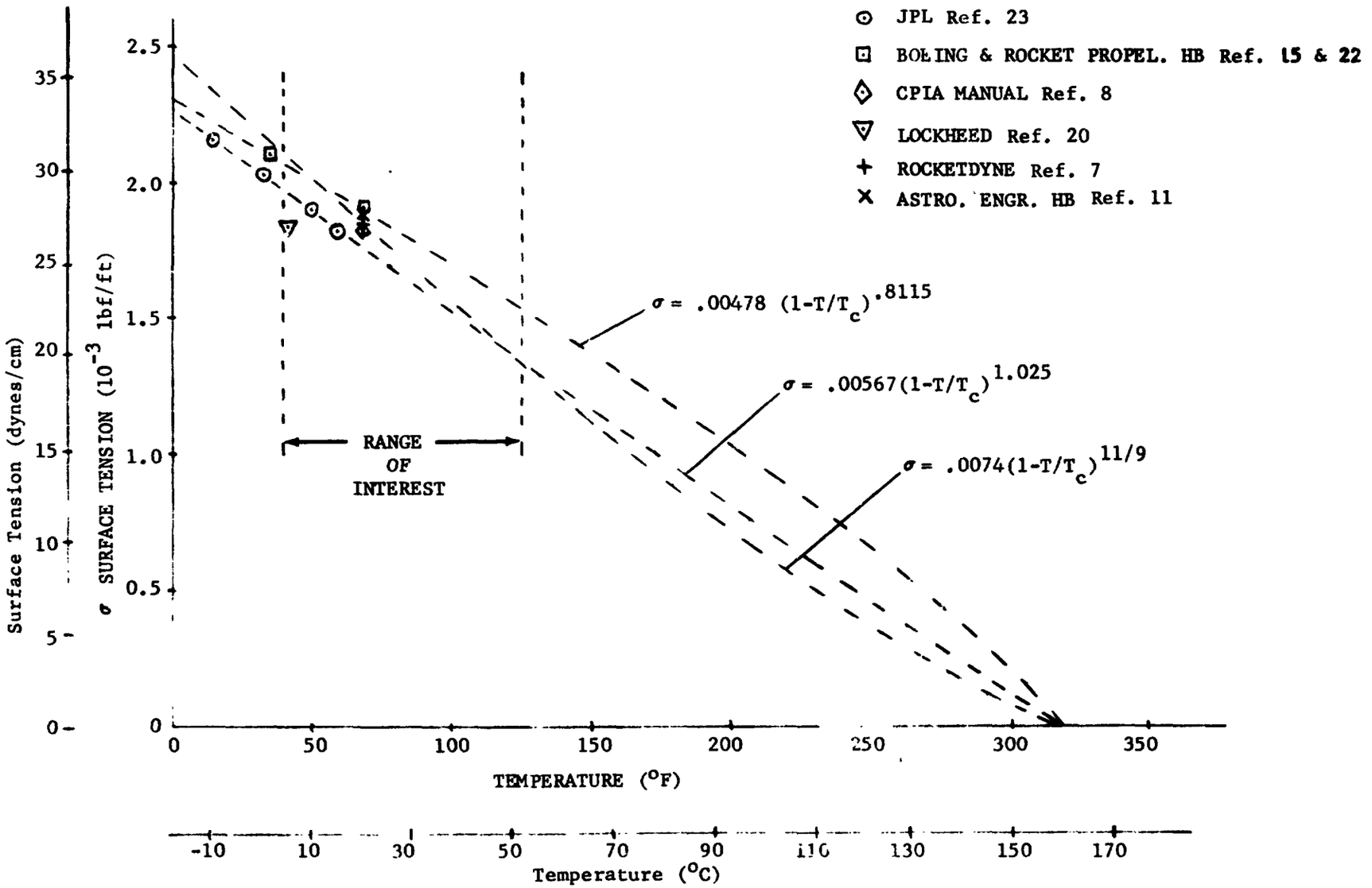

Figure 10: Surface .ension Data for N_2O_4 as a Function of Temperature

are presented as a function of temperature and represent values for a pressure of 10 N/cm^2 (one atm). It should be noted that in most cases no indication was made of the pressure at which the surface tension measurements were made. The temperature range of interest for the SS/RCS is also indicated in the figures. Where feasible individual data points are presented. However, where the individual points were too numerous to be presented without confusion, or where the data were reported in the form of a curve rather than individual points, a solid curve is used to represent the data. Also included in the figures are dashed-line curve fits for the reported data, based upon the standard accepted temperature dependency for surface tension (Ref. 18):

$$\sigma = \sigma_o \left[1 - \frac{T}{T_c} \right]^r \tag{5}$$

where:

σ = surface tension

σ_o = the "so-called" surface tension at absolute zero (a constant)

T = temperature (absolute)

T_c = propellant critical temperature (absolute)

r = a constant

For N_2H_4, the reported data varies as much as 22%, if data obtained from the Rocket Propellant Handbook (Ref. 22) are included. However, as indicated in Figure 8, the data obtained from Reference 22 are probably for a purified grade of hydrazine rather than for Military Specification (Mil. Spec.) N_2H_4. This is based on the fact that the references used for the Rocket Propellant Handbook data are fairly old (pre-1956 with some as old as 1928) and primarily from chemistry handbooks. In addition, JPL found that the surface tension of purified N_2H_4 is higher than that for Mil.

Spec. N_2H_4. Eliminating the Reference 22 data from consideration still leaves a 12% maximum variation in the data. In addition, values of N_2H_4 surface tension differing as much as 20% can be obtained over the temperature range of interest using the curve fit equations presented in Figure 8.

A plot of equation (5) with r set equal to 11/9 is included in Figure 8 for comparison purposes. In theory, r should be equal to 11/9, based upon the principle of corresponding states (Ref. 18). The value of σ_o shown in Figure 8 for the 11/9 power curve was determined by taking the average of the data reported at 20°C (68°F) and substituting this value of σ into equation (5) to solve for σ_o. All of the equations presented in Figure 8 employ σ_o in English units; to obtain values in dynes/cm, the σ_o must be multiplied by 14,595. It is seen that the curve-fit equations presented in Figure 8 all have temperature dependencies which differ somewhat from the 11/9 power. This is not surprising since the 11/9 factor is for a hypothetical situation only.

The surface tension data for MMH, presented in Figure 9, exhibit a maximum variation over the temperature range of interest of about 5%. This is less than half the scatter exhibited by the Mil. Spec. N_2H_4 data. Curve fits for the reported data, based on equation (5) are also included in Figure 9, and an 11/9 power curve is presented. Neither the JPL data (Ref. 18) nor the Rocketdyne/CPIA data (Ref. 7 and 8) agree with the 11/9 power temperature dependency.

For N_2O_4, the maximum scatter in the reported surface tension data is around 8%. However, curve fits for the reported data result in surface tension values differing by as much as 15% (Figure 10). Also, the temperature dependency of the curve-fitted data differ from the 11/9 power.

From the foregoing, it is seen that data showing the effect of temperature on surface tension are available (Figures 8, 9, and 10). In addition, the effect of propellant purity on surface tension (hydrazine) was investigated by Razouk (Ref. 18). However, no actual data could be found showing the effect of dissolved pressurant gas on surface tension. Estimates based on dilution theory predict a reduction in the surface tension at 10 N/cm^2 (one atm) of only 0.0058%, 0.045%, and 0.14% for N_2H_4, MMH, and N_2O_4, respectively, when saturated with helium at a total pressure of 193 N/cm^2 (280 psi) (Ref. 24 through 26).

Recent data on contamination effects on surface tension have been reported by JPL (Ref. 23). The data, presented in Figure 11, show that the effect of Krytox 143AB, a commonly used valve lubricant, on N_2O_4 surface tension does not become significant until the lubricant concentration reaches 10 ppm. At a concentration of 100 ppm, the reduction in surface tension reaches 17%. For MMH, JPL reported little effect, if any, on surface tension, since Krytox 143AB is relatively insoluble in MMH. Based on these data, the use of lubricants in the space shuttle RCS and APU (and OMS) must be approached with caution to preclude degradation of propellant surface tension or screen bubble point.

4. Contact Angle

The angle formed by the intersection of the gas-liquid interface with a solid surface is an important parameter in the design of many capillary propellant management systems. However, very little data exist on the contact angle of N_2O_4, MMH, and N_2H_4 with various metals. The most recent data were reported by Martin Marietta (Ref. 27 through 29). To confirm the Martin Marietta capillary propellant management device design for the Viking Orbiter 1975 propulsion system, the contact angles of both MMH

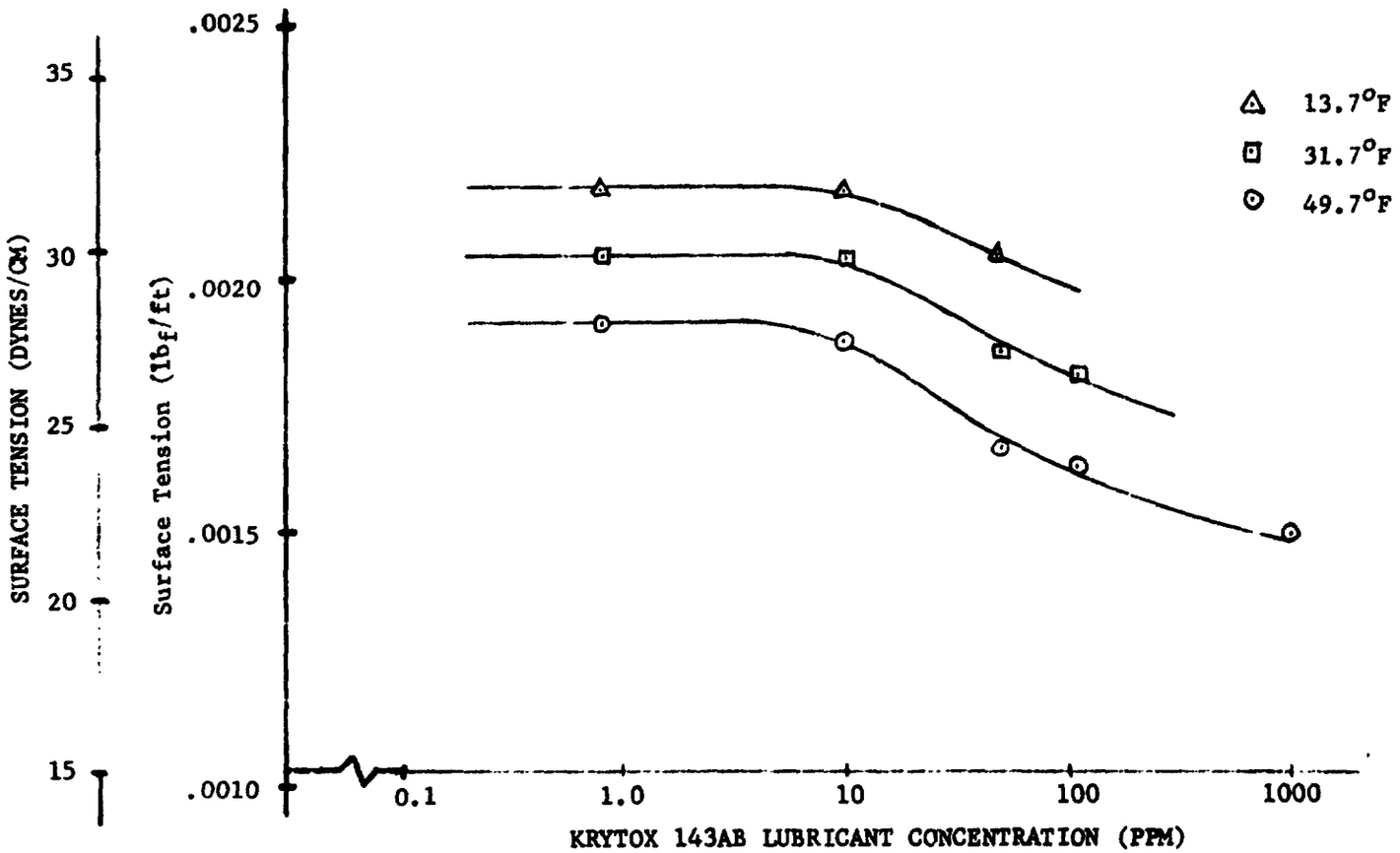

Figure 11: Effect of Krytox Contaminant on the Surface Tension of N_2O_4 (Ref. 23)

and N_2O_4 with titanium surfaces exposed to various environments were measured. The metal test samples consisted of 2.54 cm (one-inch) square segments of sheet stock and chemically-milled titanium (6Al-4V), cleaned by a standard Martin Marietta procedure for earth-storable propellants. These test samples were then tested either in the freshly cleaned condition or in a Krytox 143AB, Freon PCA, or isopropanol contaminated condition. The specific propellant grades used were MIL-P-27404A, Amendment 2, 11 June 1970, for MMH and MSC-PPD-2B, 1 August 1968, for N_2O_4. In addition, measurements were also made with both a nitrogen tetroxide-Krytox 143AB solution prepared by allowing nitrogen tetroxide to stand over Krytox 143AB for a period of six hours at 5°C, and with a MMH-Krytox 143AB solution prepared by allowing MMH to stand over Krytox 143AB for a period of one week at room temperature. The results of the contact angle measurements are summarized in Table I. Both the Mil. Spec. MMH and MMH-Krytox 143AB solution spread on or wet, the freshly-cleaned and isopropanol-rinsed specimens. However, the contact angle was increased by exposure of the solid surface to both Krytox 143AB lubricant and Freon PCA. Similar results were obtained for both the MSC Spec. N_2O_4 and N_2O_4-Krytox 143AB solution.

JPL has also reported some data on the effect of aging on contact angle of N_2O_4 and MMH (Ref. 30). As part of JPL's continuing long-term compatibility tests, various materials (stainless steels, aluminums, titaniums, plastics and others) stored in contact with different propellants (hydrazine, MMH, nitrated hydrazine and N_2O_4) are periodically analyzed to assess the compatibility of these materials with the propellants. As part of this assessment, the contact angle of these propellants with the particular material being tested is measured. To date, JPL has reported no variation in the contact angle between N_2O_4 and

Table I: Contact Angles of MMH and N_2O_4 on 6Al-4V Titanium, in Degrees (Ref. 29)

Propellant	MMH		MMH-Krytox 143AB Solution	
Surface	Sheet Stock	Chem Milled	Sheet Stock	Chem Milled
Cleaned	0	0	0	0
Krytox 143AB Film	8	8	9	8
Freon PCA Rinse	0	12	2	0
Isopropanol Rinse	0	0	0	0

Propellant	Nitrogen Tetroxide		N_2O_4-Krytox 143AB Solution	
Surface	Sheet Stock	Chem Milled	Sheet Stock	Chem Milled
Cleaned	2	2	2	3
Krytox 143AB Film	10	4	4	2
Freon PCA Rinse	3	3	8	3
Isopropanol Rinse	Spreads	Spreads	Spreads	Spreads

MMH and the various test materials, from a value of near-zero, over a period of 33 months.

Harris Research Laboratories have also reported contact angle data for the propellants of interest (Ref. 21). These data are summarized in Table II and include both advancing and receding contact angles. A receding contact angle is defined as the angle made between a liquid drop reducing in volume and a metal surface, while an advancing contact angle is the angle made by a drop increasing in volume and thus spreading out against the metal surface. It should be pointed out that for the Martin Marietta and JPL data, the propellant drops measured were neither advancing nor receding, but were stationary. The cleaning procedures employed by Harris Labs differed depending on whether the test specimen was metal or glass. The two procedures are listed below.

Metal Specimen Cleaning -- Polished or satinized metal specimens were washed with Tide and running hot tap water using a camel's hair brush. A final Tide wash and rinse was done with boiling conductivity water. The residual water film was allowed to flash off the hot specimen, which was then placed in the contact angle test cell.

Glass Specimen Cleaning -- Glass specimens were stored in a mixed nitric-sulfuric acid bath at room temperature. For use, they were rinsed with boiling conductivity water, then heated by placing them in a container of boiling conductivity water. The specimens were then withdrawn from the boiling conductivity water while maintaining a continuous flush with boiling conductivity water. This technique insured the rapid flash of residual water from the glass specimen when dried in air.

The data reported by Harris Research Laboratories indicate that near-zero contact angles should be obtained for both N_2O_4

Table II: Contact Angles of Liquid Propellants and Water Against High-Energy Surfaces (Ref. 21) in Degrees

Type of Surface / Liquid	Pyrex Glass		Type 6061 T6 Aluminum				ASTM B348-59T Grade 6 Titanium Alloy				Type 301 Stainless Steel			
			Polished		Satinized		Polished		Satinized		Polished		Satinized	
	Advancing	Receding	Advancing	Receding	Advancing	Receding	Advancing	Receding	Advancing	Receding	Advancing	Receding	Advancing	Receding
Water	2	1	2	2	2	1	2	1	2	1	2	1	2	1
Hydrogen Peroxide, 90%	2	1	2	1	2	1	2	1	2	1	2	1	2	1
Absolute Ethanol	1	0	1	0	1	0	2	0	2	1	2	1	2	1
Di-nitrogen Tetroxide	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Fuming Nitric Acid Type IIIB	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Hydrazine	2	1	2	1	2	1	2	1	2	1	0	0	2	1
UDMH (Unsymmetrical Dimethyl-hydrazine)	2	1	2	1	2	1	2	1	2	1	2	1	2	1
Aerozine 50- (0.5/0.5) N_2H_4/UDMH	2	1	2	1	2	1	2	1	2	1	0	0	0	0

and N_2H_4 on metal and glass surfaces cleaned according to the above cleaning procedures. However, the data are somewhat suspect based on the reported test procedure. Harris used the standard sessile drop method employing a goniometer; however, the measurements were made in air instead of under an inert atmosphere, such as GN_2 or GHe. When exposed to air, N_2H_4 immediately starts to react and decompose. In addition, N_2H_4 is highly hygroscopic and readily absorbs CO_2. Therefore, at least for N_2H_4, the measurements obtained might have been made for a liquid whose properties could have been altered by exposure to air.

B. TEST PROGRAM

The purpose of the tests was to determine the effects of temperature, dissolved pressurant gas, propellant purity, and system cleanliness or contamination on the bubble point of representative fine-mesh screens in N_2H_4, N_2O_4, and MMH. The effect of temperature on screen bubble point was determined by measuring the bubble point of the screen test specimens in propellant conditioned to temperatures within the range of interest, 4.4 to 48.9°C (40 to 120°F). Tests to determine the effect of dissolved pressurant gas on system bubble point were conducted with one screen mesh. Gaseous helium was the pressurant, since it is the pressurant for the Shuttle orbiter systems. Bubble point of the fine-mesh screen was determined over a pressure range from zero to 275.8 N/cm^2 gage (0-400 psig) with helium saturated propellant. Propellant purity effects were investigated using hydrazine since both Mil. Spec. N_2H_4 and a highly purified N_2H_4 were readily available. The specification grade met the MIL-P-26536C requirements, while the purified grade was manufactured for the Viking program with contaminants reduced to <0.01% H_2O, <3.5 ppb analine and <1.0 ppm other volatile impurities. Finally, the effect of system cleanliness or contamination was determined by evaluating the impact of

various cleaning procedures on screen bubble point. These tests were conducted using the purified N_2H_4 since it should be the most sensitive to contamination effects.

The test procedure for the screen bubble point tests is presented in Appendix A of this report. The planned test matrix is presented in Figure I and the test system schematic is presented in Figure II of the Appendix. Testing was planned with four screen mesh sizes, which were: 325 x 2300, 200 x 1400, and 165 x 800 Dutch-twill weave, and 180 x 180 square weave stainless steel screen. These four are representative of screen which could be used in the SS/RCS capillary propellant acquisition system. The 325 x 2300 screen was used for the propellant purity and screen cleaning evaluations. The cleaning procedures used in the evaluation are listed in Table III.

Some deviation from the planned tests occurred when problems were encountered or where the change would provide an improvement. Testing from a remote location precluded the use of the 180 x 180 mesh square weave screen, since successful wetting could only be accomplished by physically spreading liquid over the surface.

The specially fabricated bubble point test apparatus is shown in Figures 12 through 14. It consists of an inner test vessel contained in an outer pressure bomb capable of withstanding internal pressures of 414 N/cm^2 gage (600 psig). This allowed testing at pressures up to 276 N/cm^2 gage (400 psig). The inner test vessel holds the screen specimen and provides both a propellant reservoir on top of the screen and a GHe reservoir below the screen. The pressure in the gas space below the screen is increased until gas just begins to bubble through the screen; the difference at which this occurs is known as the bubble point (uncorrected). As can be seen in Figure 13, a small overflow port was included in the inner

Table III; Screen Cleaning Methods

A. Chemical Method No. 1

1) Acetone Rinse

2) Diversey 909 Alkaline Cleaner (9 oz./gal.)
15 min. at 160-190°F in ultrasonic cleaner.

3) Demineralized H_2O rinse checking PH.

4) Diversey Everite Deoxidizer (40% by Vol.)
3 min. at 70°F.

5) Demineralized H_2O rinse checking PH.

6) Isopropanol Rinse

7) GN_2 dry - 70°F

B. Chemical Method No. 2

1) Degrease - Trichlorethylene

2) Ultrasonic detergent clean - 100°F soap/H_2O solution.

3) Isopropanol Rinse

4) Demineralized H_2O Rinse

5) Isopropanol Rinse

6) Hot GN_2 dry

C. Vacuum Annealing

1) 2050°F for 30 min. under high vacuum.

2) Cool to room temperature maintaining vacuum.

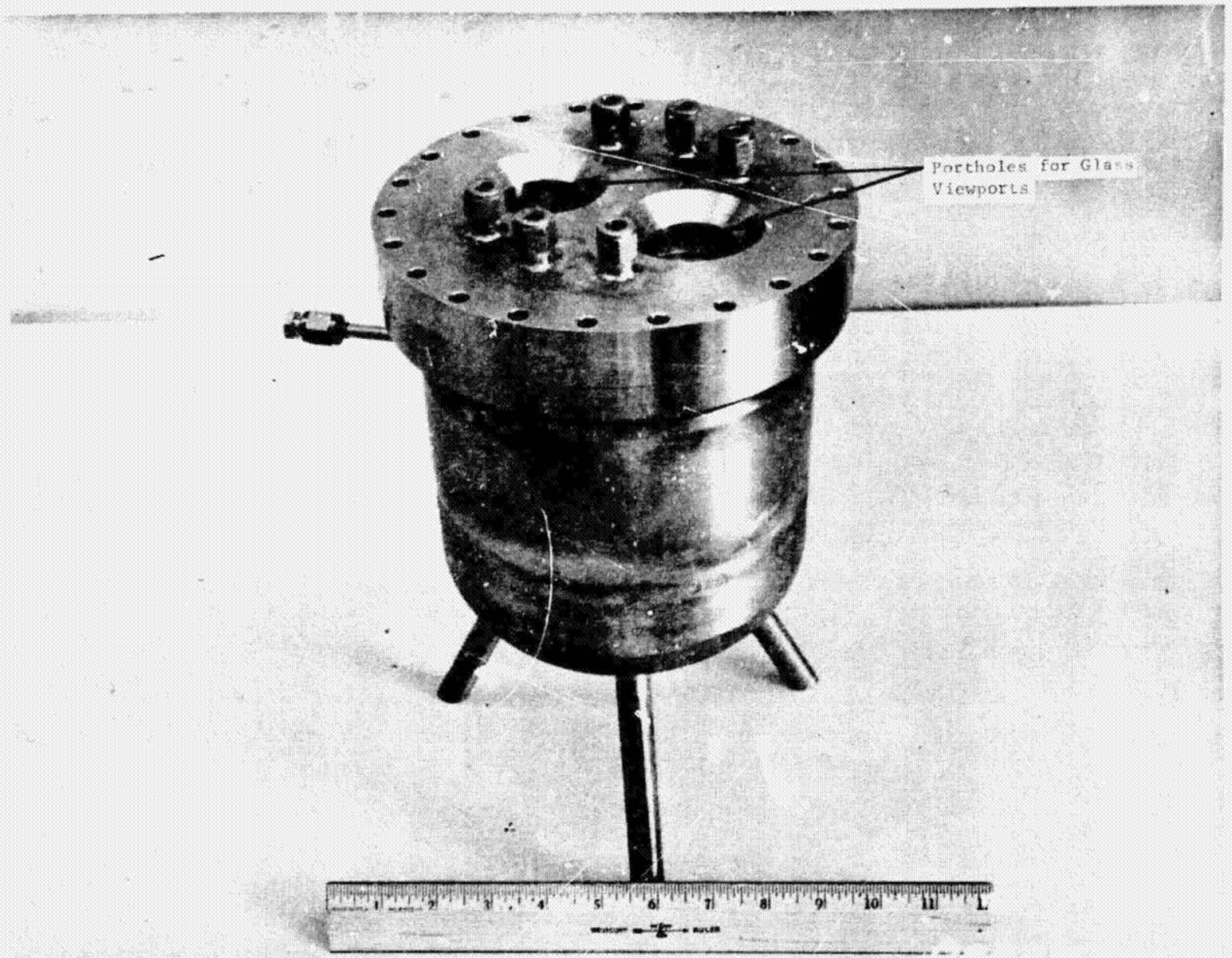

Figure 12: Propellant Bubble Point Test Fixture

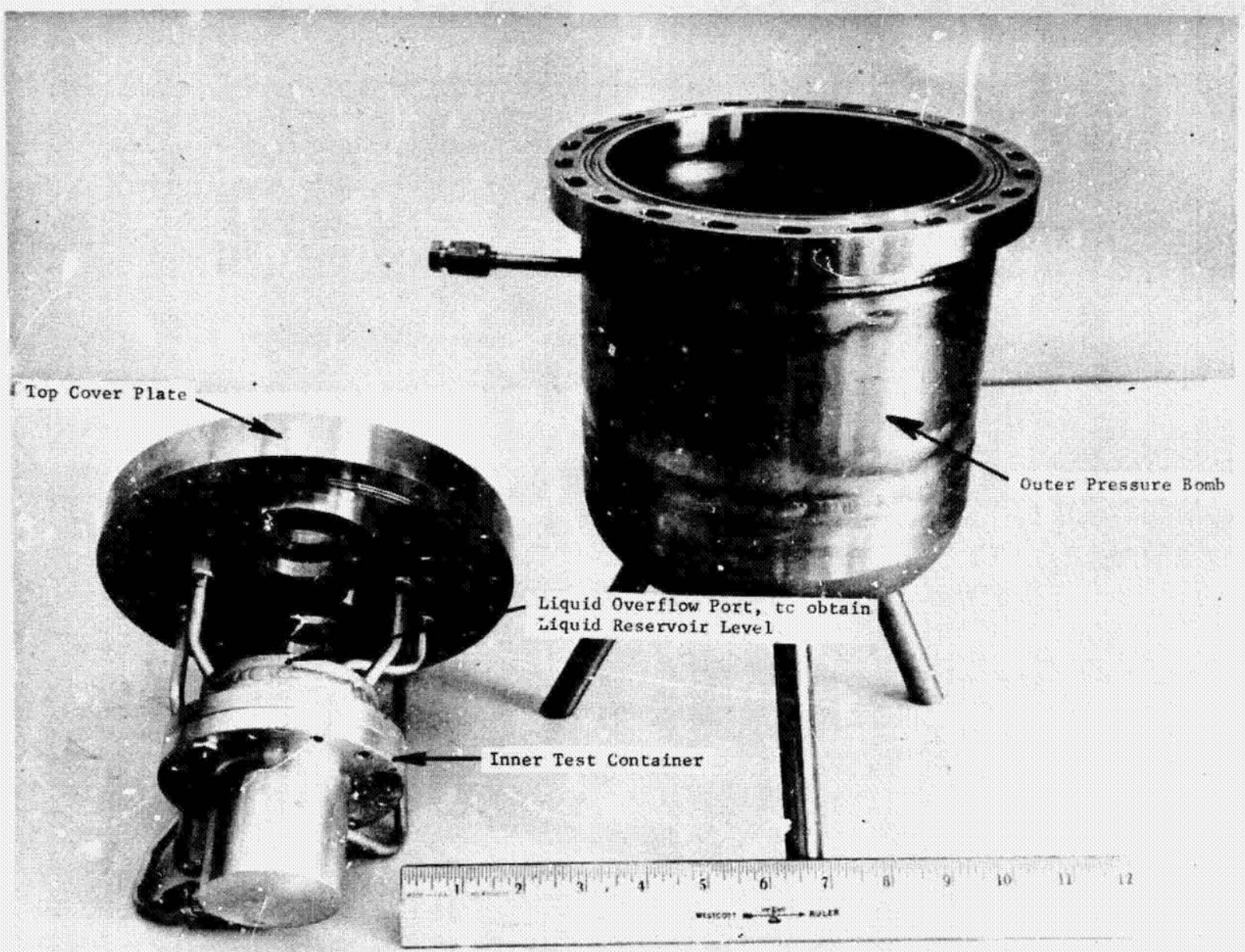

Figure 13: Disassembled Outer Pressure Bomb

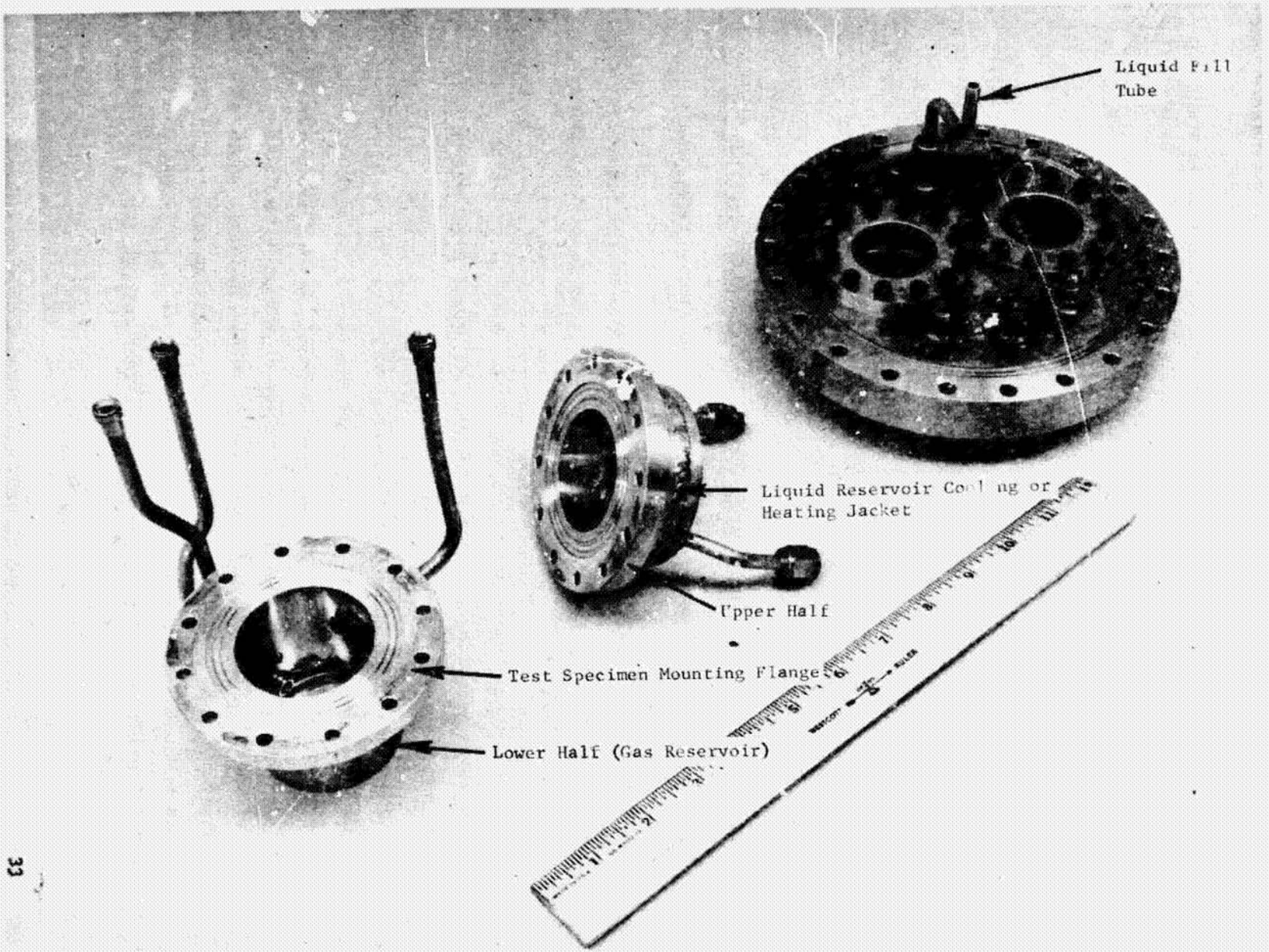

Figure 14: Disassembled Inner Test Vessel

container to provide a constant propellant hydrostatic head in the liquid reservoir. Therefore,

$$\Delta P_{MEASURED} = \Delta P_c + \Delta P_h \tag{6}$$

where:

ΔP_c = bubble point (actual)

ΔP_h = hydrostatic head (ρgh)

ρ = density of propellant

g = acceleration due to gravity

h = height of propellant above screen specimen

By always filling the liquid reservoir to the same level, the hydrostatic correction was kept constant for each propellant tested.

The test temperature of the propellant was controlled to the desired level by circulating a methanol/H_2O mixture from a temperature conditioning unit through the jacketed-walls of the liquid reservoir portion of the inner test container. The inner test container was aluminum to provide good heat transfer characteristics.

Three of the screen specimens tested are shown in Figure 15. They consist of a screen disc seam welded to a solid metal washer which was clamped between the test vessel mounting flanges.

The bubble point test system is shown in Figures 16 and 17. Figure 16 shows the control panel located outside of the test cell while the actual test hardware is shown installed in the test cell in Figure 17. To allow visual confirmation of screen bubble point, two viewports were included in the test fixture. The lamp, shown in Figure 17, was focused through one of the viewports onto the screen surface. A mirror was positioned above the other viewport so the illuminated screen surface could be seen through the

Figure 15: Bubble Point Screen Test Specimens

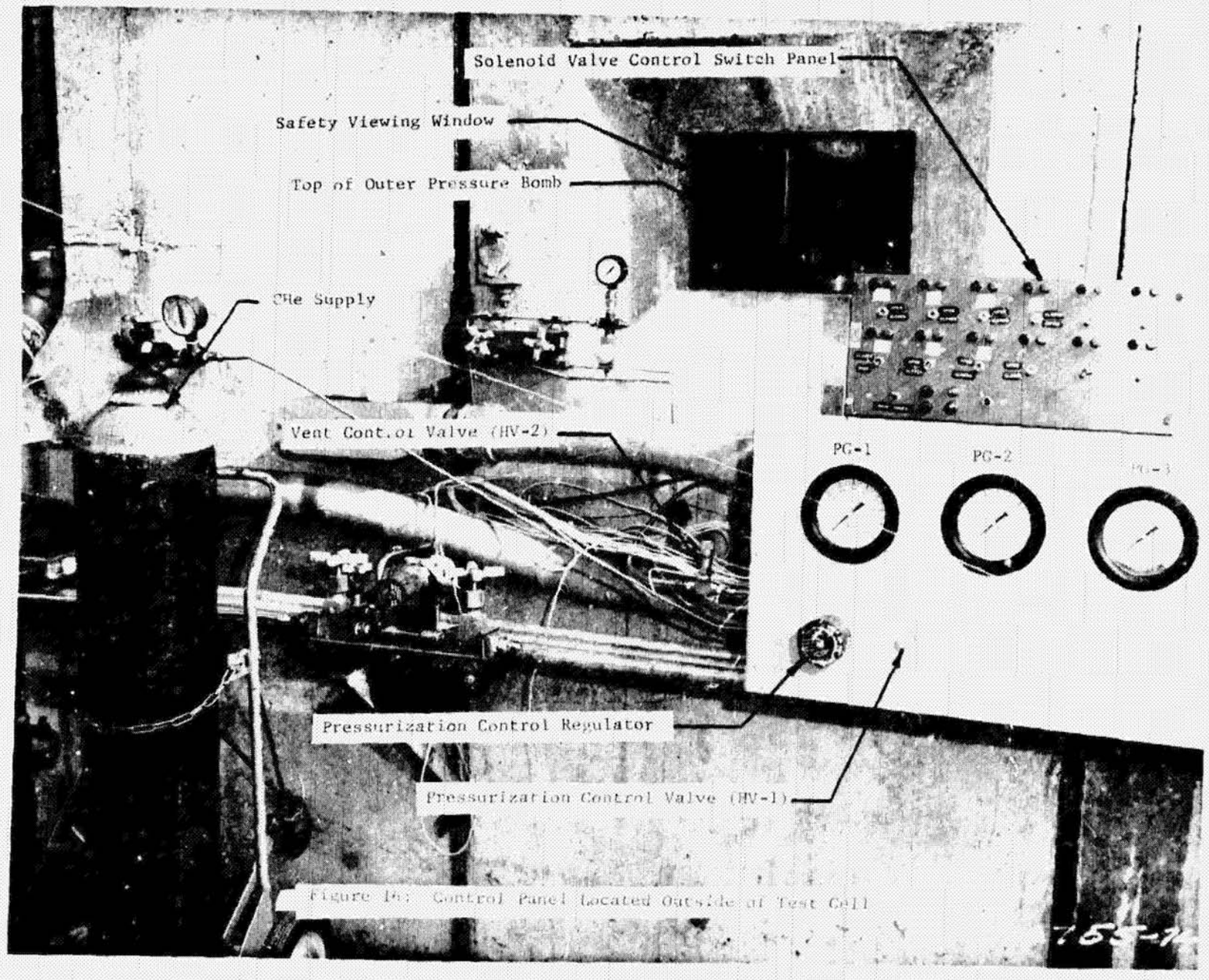

Figure 16: Control Panel Located Outside of Test Cell

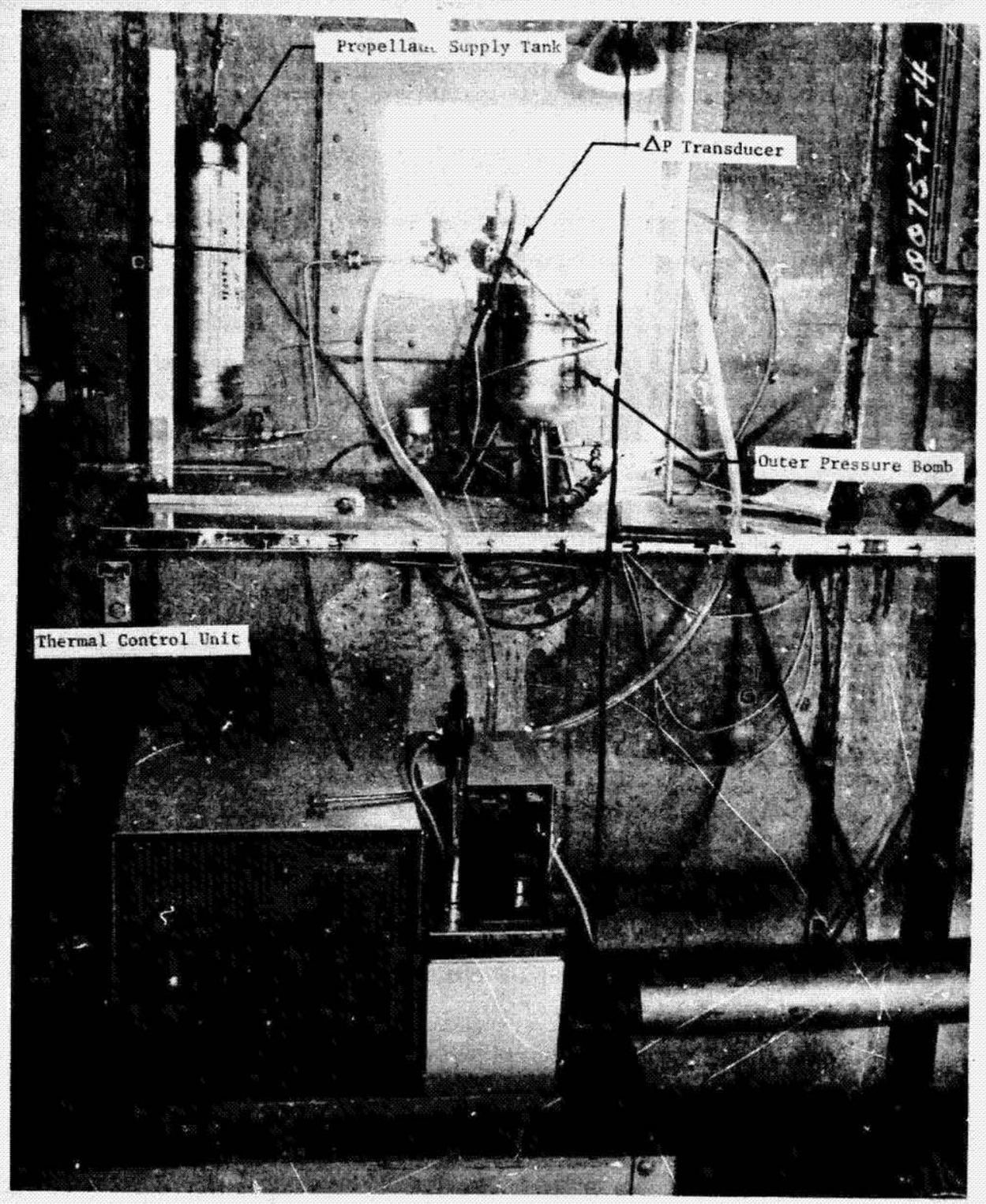

Figure 17: Bubble Point Test System Within Test Cell

window in the test cell. The test results are discussed by propellant in the following paragraphs.

1. Purified Hydrazine

The data obtained from the bubble point tests using the purfied N_2H_4 are presented in Table IV and Figure 18. These data are presented in two different manners. First, the measured bubble point data are compared in Table IV, with values calculated for Mil. Spec. N_2H_4 using equation (4). Each of the measured values presented in Table IV represent an average of at least 5 measurements. Calculations were made for Mil. Spec. N_2H_4, since surface tension data for the purified N_2H_4 were not available. The measured bubble point values for the referee fluid (isopropyl alsohol) used in the calculations are also presented in Table IV. The isopropyl alcohol surface tension values used in equation (4) were obtained from Reference 32. The values of surface tension for Mil. Spec. N_2H_4 were obtained from the representative literature data presented in Figure 18. This plot of surface tension as a function of temperature was selected as most representative of the compiled data presented previously in Figure 8. This was weighted toward the more recent consistent data.

The second manner used was to calculate surface tension values from the bubble point data by use of equation (4). The results are presented in Figure 18 where they are compared to two curves obtained from the literature: one a representative curve for Mil. Spec. N_2H_4, as discussed above, and the other for a purified grade of hydrazine tested by JPL (Ref. 18).

Considering the data presented in Table IV first, all of the measured 325 x 2300 mesh screen bubble point values with purified N_2H_4 are well below those values calculated for Mil. Spec. N_2H_4. In at least two cases, screen bubble points more than 55% below calculated values were measured. In addition, the screen cleaning

Table IV: Measured Bubble Point Data for Purified N_2H_4

Sample	Type of Cleaning Performed Prior to Test	Test Number	Test Temperature °C ±1.6°C (°F ±3°F)	Test Pressure N/cm²/Gage ±3.4 N/cm² (psig ±5 psig)	Measured Isopropanol Bubble Point Adjusted to 20°C (68°F)	Measured Purified N_2H_4 Bubble Point N/cm² ±.021 N/cm² (psi ±.03 psi)	Calculated Mil. Spec. N_2H_4 Bubble Point at Test Temperature N/cm² (psi)
Pre-Cleaning Results							
No. 1 325 x 2300	Isopropanol Rinse	1	22.5 (72.5)	0	.634 (.92)	1.45 (2.11)	1.94 (2.82)
No. 2 325 x 2300	Isopropanol Rinse	1	18.3 (65.0)	0	.634 (.92)	1.36 (1.98)	1.96 (2.85)
No. 3 325 x 2300	Isopropanol Rinse	1	20.0 (68.0)	0	.634 (.92)	1.46 (2.12)	1.96 (2.84)
No. 4 325 x 2300	Iropropanol Rinse	1	20.0 (68.0)	0	.593 (.86)	1.22 (1.77)	1.83 (2.66)
Post-Cleaning Results							
No. 1	Isopropanol Rinse	1	6.7 (44)	0	.614 (.89)	.924 (1.34)	1.97 (2.86)
		2*	6.7 (44)	0	.614 (.89)	1.00 (1.45)	1.97 (2.86)
		3	13.9 (57)	0	.614 (.89)	.800 (1.16)	1.92 (2.79)
No. 2	Method No. 1	1	16.1 (61)	0	.607 (.88)	.848 (1.23)	1.90 (2.75)
No. 3	Vacuum Annealed				.572 (.83)		
No. 4	Method No. 2	1	21.1 (70)	0	.593 (.86)	.944 (1.37)	1.83 (2.65)

*Soaked in N_2H_4 approximately 1 1/2 hours before testing.

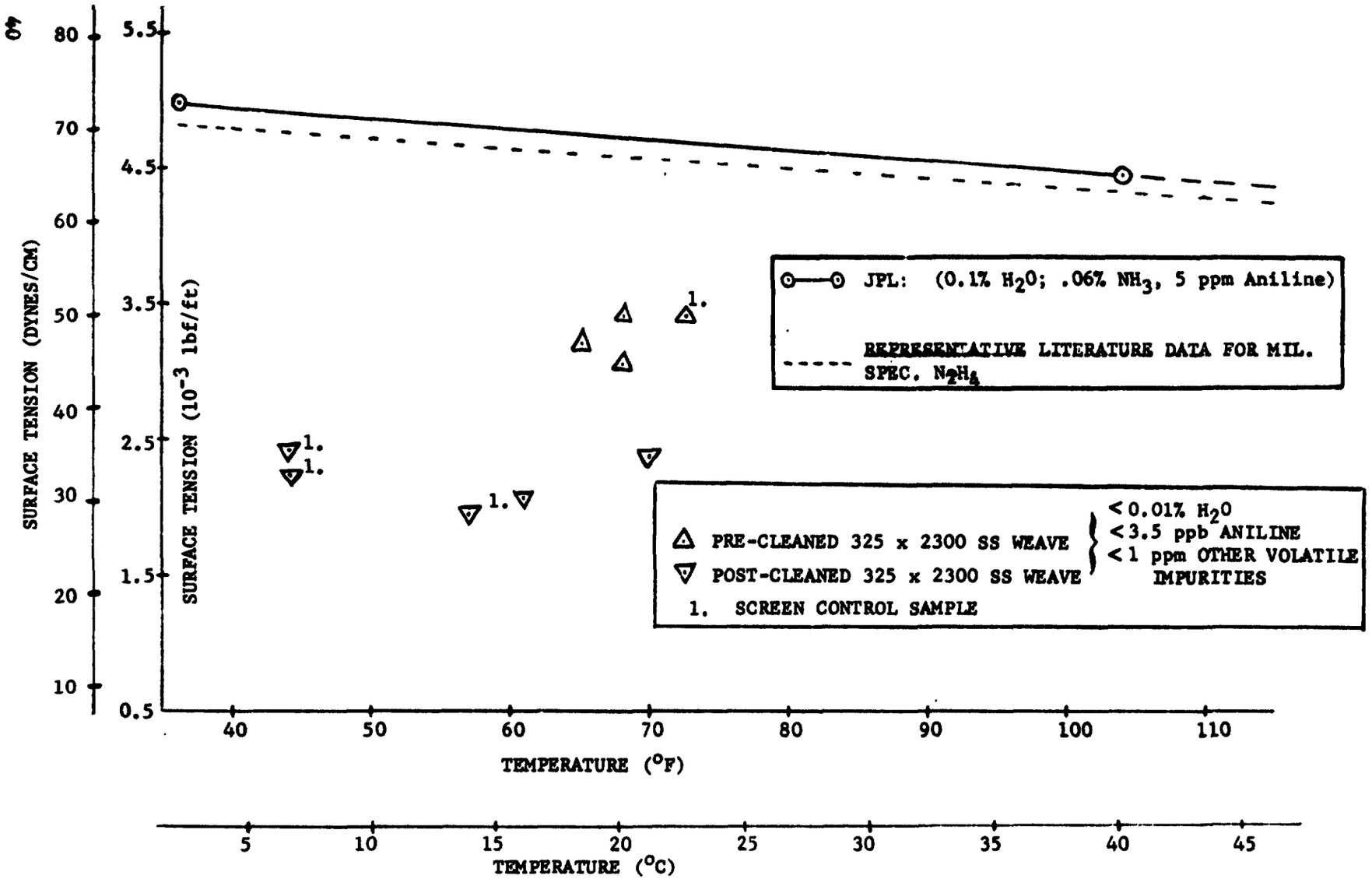

Figure 18: Comparison of Published and Measured Surface Tension Data for Purified N_2H_4

procedure evaluation produced unexpected results. Samples tested in the "as received" condition (except for an isopropyl alcohol rinse) had bubble points 25 to 33% below the values calculated for Mil. Spec. N_2H_4. These low values were not unexpected since no cleaning procedures were performed on the screens prior to testing, and it was thought that these low measurements were a result of contamination. However, as shown in Table IV, cleaning did not improve the results. Instead, the bubble points after cleaning were significantly lower than those measured before cleaning. The control sample (sample 1) also produced a significantly lower value even though no cleaning procedure had been performed on it, except for another isopropanol rinse prior to testing. For this reason, no assessment could be made of the relative impact of the individual cleaning procedures on screen bubble point in purified hydrazine (including the simple isopropanol rinse). It did appear, however, that the cleaning was detrimental.

In summary, the surface tension values derived from the bubble point data are all well below the literature values, as shown in Figure 18. Also, the post-cleaning measured values are significantly below the values obtained prior to cleaning. The data presented in Figure 18 also points up another interesting fact. Purification of N_2H_4 seems to increase its surface tension; therefore, the purified N_2H_4 bubble point values should have been higher than the calculated values shown in Table IV. Just the opposite was true, however,

Based on the bubble point test results with the purified N_2H_4, it was felt that the cause of these anomalous results could have been due to the propellant itself. Further testing with purified N_2H_4 was terminated and testing with Mil. Spec. N_2H_4 was begun to determine if the problem was limited to the purified form or was more general in nature. Because of this, the vacuum annealed sample (sample 3) was not tested with purified fuel.

2. Mil. Spec. Hydrazine

The data for Mil. Spec. N_2H_4 is presented in Table V and Figure 19. Measured bubble point values of the screen in Mil. Spec. N_2H_4 are compared with values calculated from published surface tension data in Table V while surface tension values derived from the Mil. Spec. N_2H_4 bubble point data are compared with representative literature data in Figure 19. In general, the data are well below expected values (measurements 65% below the calculated or literature values, in some cases). In addition, the data are inconsistent. Tests 9, 10, and 11 with sample 6, for instance, produced values approximately 0.69 N/cm^2 (1 psi) below other measurements made with the same sample (Table V).

Because of the anomalous results obtained with Mil. Spec. N_2H_4, a precise determination of temperature effects on screen bubble point in hydrazine was not possible. The data presented in Figure 19 does form a trend with temperature if each group of data at the three general temperatures tested is considered, rather than considering individual points. However, all that can be said about this trend is that it seems to have the proper slope, i.e., surface tension or bubble point decreasing with increasing temperature.

The effect of dissolved helium pressurant on screen bubble point was also investigated using Mil. Spec. N_2H_4. As shown in Table V, bubble points were measured at elevated pressures with each of the three screen meshes tested (325 x 2300, 200 x 1400, and 165 x 800). In each instance, the propellant was saturated with helium prior to measuring screen bubble point. Some increase in bubble point with system pressure and dissolved helium concentration could be inferred. However, this increase appears negligible in comparison to the data scatter.

Table V: Measured Bubble Point Data for Mil. Spec. N_2H_4

Sample	Measured Isopropanol Bubble Point N/cm^2 (psi)	Test Number	Test Temperature $^oC \pm 1.6^oC$ ($^oF \pm 3^oF$)	Test Pressure N/cm^2 Gage ± 3.4 N/cm^2 (psig ± 5 psig)	Measured Mil. Spec. Bubble Point N/cm^2 $\pm .021$ N/cm^2 (psi $\pm .03$ psi)	Calculated Mil. Spec. N_2H_4 Bubble Point at Test Temperature N/cm^2 (psi)
No. 6 325 x 2300 SS	.555 @ 23.3°C (.805 @ 74°F)	1	7.8 (46)	0	1.56 (2.26)	1.81 (2.62)
		2	20.0 (68)	0	1.44 (2.09)	1.74 (2.53)
		3	48.3 (119)	0	1.23 (1.79)	1.60 (2.32)
		4	20.8 (69.5)	0	1.21 (1.76)	1.74 (2.52)
		5	21.1 (70)	297.8 (432)	1.74 (2.52)	1.74 @ 0 Gage (2.52 @ 0 psig)
		6	20.0 (68)	231.0 (335)	1.56 (2.26)	1.74 @ 0 Gage (2.53 @ 0 psig)
		7	27.2 (81)	0	1.27 (1.84)	1.71 (2.48)
		8	19.7 (67.5)	284.0 (412)	1.39 (2.02)	1.74 @ 0 Gage (2.53 @ 0 psig)
		9	21.1 (70)	67.6 (98)	.614 (0.89)	1.74 @ 0 Gage (2.52 @ 0 psig)
		10	21.1 (70)	146.8 (213)	.620 (0.90)	1.74 @ 0 Gage (2.52 @ 0 psig)
		11	21.1 (70)	202.0 (293)	.765 (1.11)	1.74 @ 0 Gage (2.52 @ 0 psig)
No. 7 200 x 1400 SS	.383 @ 24.4°C (.555 @ 76°F)	1	Set for 21.1 (70)*	0	.944 (1.37)	1.20 (1.74)
		2	Set for 21.1 (70)*	143.4 (208)	.903 (1.31)	1.20 @ 0 Gage (1.74 @ 0 psig)
		3	Set for 21.1 (70)*	273.7 (397)	.855 (1.24)	1.20 @ 0 Gage (1.74 @ 0 psig)
		4	Set for 4.4 (40)*	73.1 (106)	1.05 (1.53)	1.25 @ 0 Gage (1.82 @ 0 psig)
		5	6.7 (44)	0	.931 (1.35)	1.25 (1.81)
		6	23.3 (74)	0	.917 (1.33)	1.19 (1.73)
		7	51.1 (124)	0	.827 (1.20)	1.10 (1.60)
No. 3 325 x 2300SS	.563 @ 23.9°C (.816 @ 75°F)	1	23.3 (74)	0	1.28 (1.86)	1.75 (2.54)
No. 10A 165 x 800SS	.172 @ 24.4°C (.249 @ 76°F)	1	Set for 21.1 (70)*	0	.476 (0.69)	.538 (0.78)
		2	Set for 21.1 (70)*	137.2 (199)	.441 (0.64)	.538 @ 0 Gage (0.78 @ 0 psig)
		3	Set for 21.1 (70)*	273.7 (397)	.490 (0.71)	.538 @ 0 Gage (0.78 @ 0 psig)
		4	Set for 51.7 (125)*	273.7 (397)	.393 (0.57)	.496 @ 0 Gage (0.72 @ 0 psig)
		5	7.8 (46)	0	.524 (0.76)	.558 (0.81)
		6	22.8 (73)	0	.393 (0.57)	.538 (0.78)
		7	51.7 (125)	0	.386 (0.56)	.496 (0.72)
		8	30.5 (87)**	0	.503 (0.73)	.524 (0.76)

*Temperature variation $\pm$ 2.8°C ($\pm$ 5°F).

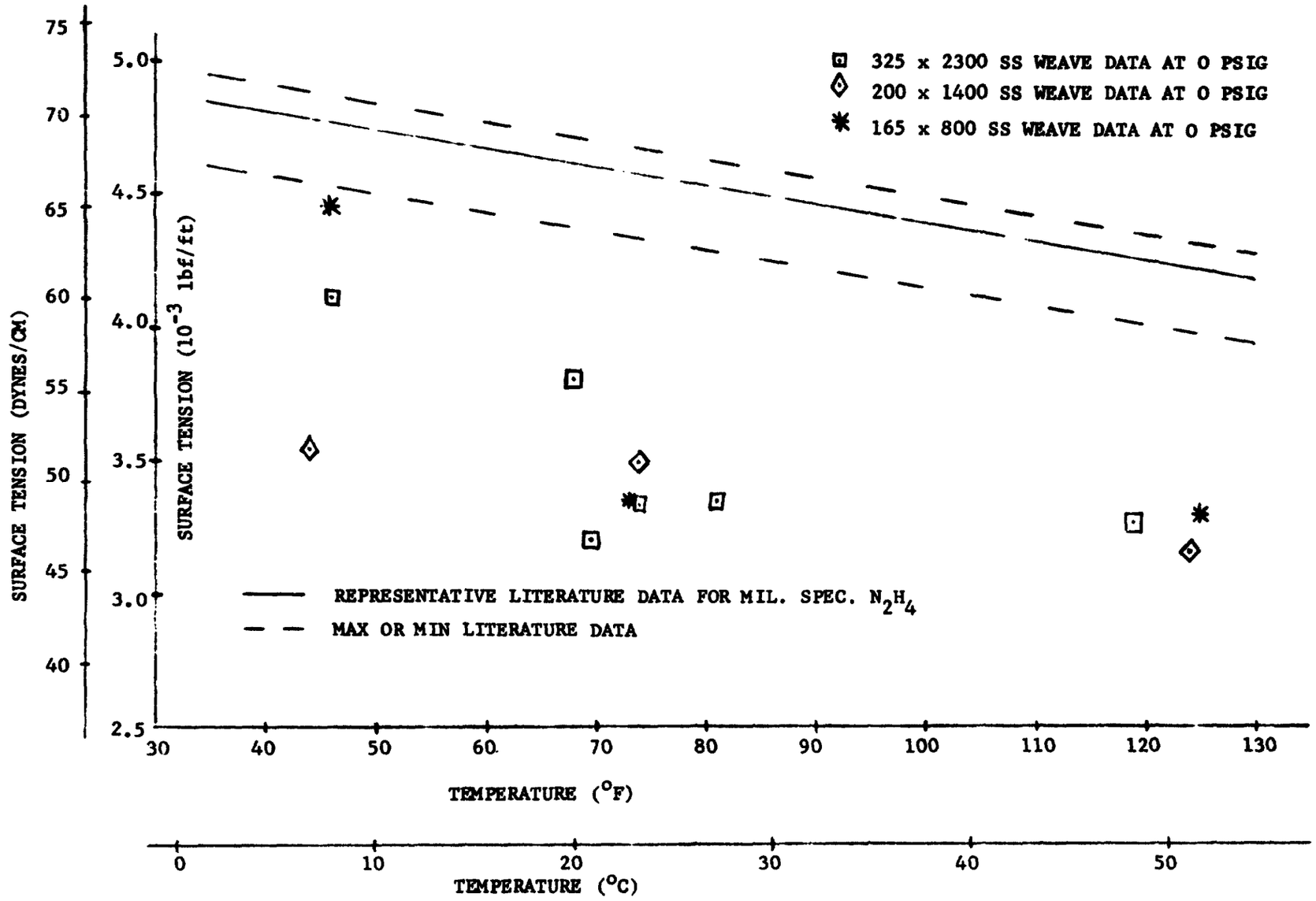

Figure 19: Comparison of Published and Measured Surface Tension Data for Mil. Spec. N_2H_4

3. Monomethylhydrazine

The screen bubble point data obtained with MMH are presented in Table VI and Figure 20 in the same manner as was done for the two grades of N_2H_4. The MMH used in the testing met Mil. Spec. MIL-P-27404A. The agreement between measured and calculated or literature values is excellent. In addition, the data shows the expected trend with temperature (Figure 20). Tests conducted at elevated pressures with helium saturated MMH showed negligible pressure and dissolved helium concentration effect on screen bubble point (Table VI).

4. Nitrogen Tetroxide

The screen bubble point data obtained with N_2O_4 are presented in Table VII and Figure 21. As was done for the other propellants tested, Table VII compares the measured bubble point values with calculated values, while Figure 21 compares values calculated from the measured bubble point data with surface tension values from the literature. The N_2O_4 used in the measurements was the brown or Mil. Spec. grade MIL-P-26539C. Due to the relatively high vapor pressure of N_2O_4, all measurements were conducted under a positive helium pressure.

The data show excellent agreement with the calculated or literature values. The bubble point decreases with increasing temperature, as expected. No effect of pressure and dissolved helium pressurant is apparent from the tests with N_2O_4 saturated with helium over the pressure range investigated.

The data obtained with the RCS propellants, N_2O_4 and MMH, were as expected. They showed excellent agreement with the literature and prove the value of the equation (4) relationship. The results obtained with both purified and Mil. Spec. hydrazine, however, were anomalous and inconsistent.

Table VI: Measured Bubble Poin :a for Mil. Spec. MMH

Sample	Measured Isopropanol Bubble Point @ 24.2°C (75.5°F) N/cm² (psi)	Test Number	Test Temperature °C ± 1.6°C (°F ± 3°F)	T :t Pre.:ure N/cm² Gage ± 3.4 N/cm² (psig ± 5 psi)	Measured MMH Bubble Point N/cm² ± .021 N/cm² (psi ±.03 psi)	Calculated MMH Bubble Point at Test Temperature N/cm² (psi)
No. 5A 325 x 2300	.574 (.832)	1	7.8 (46)	0	1.00 (1.45)	.958 (1.39)
		2	22.2 (72)	0	.958 (1.39)	.910 (1.32)
		3	49.4 (121)	0	.876 (1.27)	.834 (1.21)
		4	6.7 (44)	0	.944 (1.37)	.958 (1.39)
		5	23.3 (74)	0	.951 (1.38)	.910 (1.32)
		6	22.8 (73)	77.9 (113)	.972 (1.41)	.910 @ 0 Gage (1.32 @ 0 psig)
		7	22.2 (72)	137.9 (200)	.979 (1.42)	.910 @ 0 Gage (1.32 @ 0 psig)
		8	21.1 (70)	266.2 (386)	1.01 (1.46)	.917 @ 0 Gage (1.33 @ 0 psig)
No. 8 200 x 1400	.389 (.564)	1	21.7 (71)	0	.620 (0.90)	.620 (0.90)
		2	23.3 (74)	137.9 (200)	.676 (0.98)	.620 @ 0 Gage (0.90 @ 0 psig)
		3	23.3 (74)	265.4 (385)	.70[illegible] (1.02)	.620 @ 0 Gage (0.90 @ 0 psig)
		4	51.1 (124)	269.6 (391)	.641 (0.93)	.558 @ 0 Gage (0.81 @ 0 psig)
No. 11 165 x 800	.185 (.268)	1	5.6 (42)	0	.255 (0.37)	.310 (0.45)
		2	21.1 (70)	0	.290 (0.42)	.296 (0.43)
		3	48.9 (120)	0	.269 (0.39)	.276 (0.40)

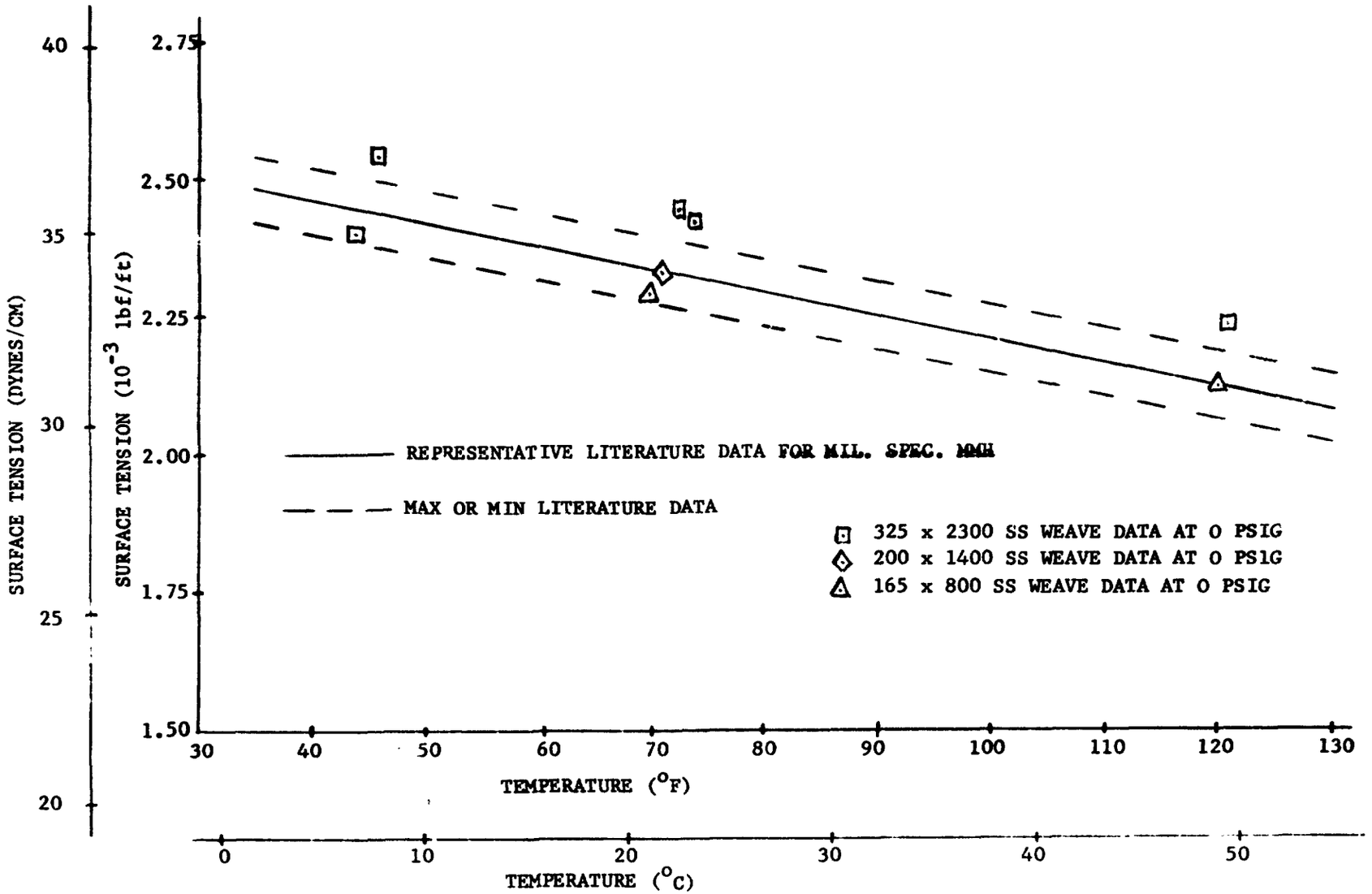

Figure 20: Comparison of Published and Measured Surface Tension Data for Mil. Spec. MMH

Table VII: Measured Bubble Point Data for N_2O_4 (MIL-P-26539C)

Sample	Measured Isopropanol Bubble Point @ 23.9°C (75°F) N/cm² (psi)	Test Number	Test Temperature °C ±1.6°C (°F ± 3°F)	Test Pressure N/cm² Gage ± 3.4 N/cm² (psig ±5 psig)	Measured N_2O_4 Bubble Point N/cm² ±.021 N/cm² (psi ±.03 psi)	Calculated N_2O_4 Bubble Point at Test Temperature*, Based on σ's from Literature Survey N/cm² (psi)
NTO-1 325 x 2300	.563 (.816)	1	5.0 (41)	9.6 (14)	.786 (1.14)	.772 (1.12)
		2	20.0 (68)	29.0 (42)	.689 (1.00)	.703 (1.02)
		3	21.1 (70)	140.6 (204)	.724 (1.05)	.696 (1.01)
		4	21.1 (70)	266.8 (387)	.703 (1.02)	.696 (1.01)
		5	51.7 (125)	70.3 (102)	.531 (0.77)	.558 (0.81)
NTO-2 200 x 1400	.385 (.559)	1	2.2 (36)	15.2 (22)	.524 (0.76)	.538 (0.78)
		2	21.7 (71)	30.3 (44)	.441 (0.64)	.476 (0.69)
		3	21.1 (70)	197.9 (287)	.455 (0.66)	.476 (0.69)
		4	52.2 (126)	71.0 (103)	.379 (0.55)	.379 (0.55)
NTO-3 165 x 800	.139 (.202)	1	6.7 (44)	11.0 (16)	.193 (0.28)	.193 (0.28)
		2	21.7 (71)	34.5 (50)	.179 (0.26)	.172 (0.25)
		3	21.1 (70)	241.3 (350)	.213 (0.31)	.172 (0.25)
		4	21.1 (70)	34.5 (50)	.186 (0.27)	.172 (0.25)
		5	3.3 (38)	5.5 (8)	.193 (0.28)	.193 (0.28)
		6	51.1 (124)	69.6 (101)	.145 (0.21)	.139 (0.20)

*All values for 0 Gage system pressure.

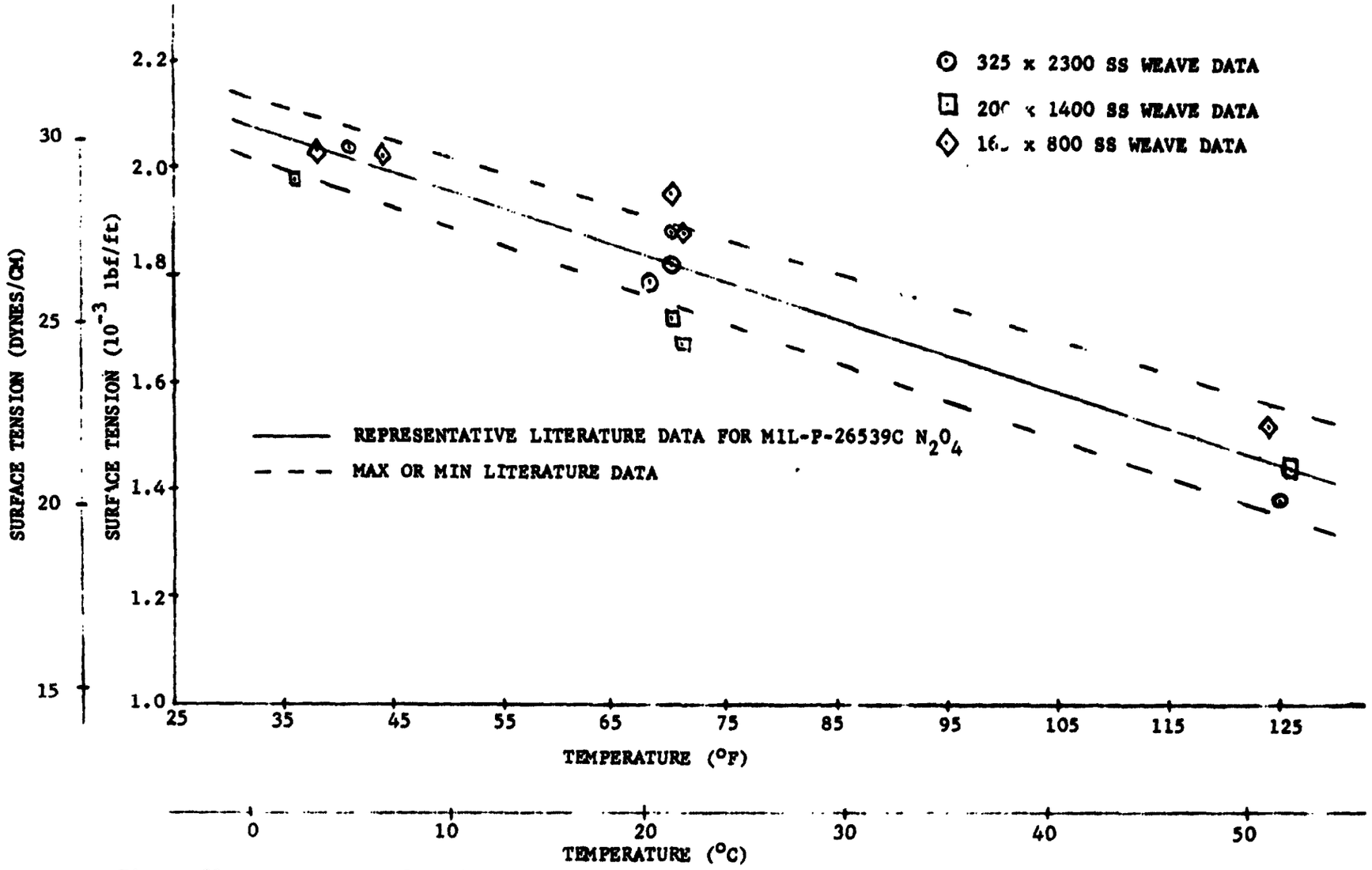

Figure 21: Comparison of Published and Measured Surface Tension Data for MIL-P-26539C N_2O_4

III. IR&D TEST PROGRAM

Due to the concern over the low bubble point measurements obtained under the contract and because of our continuing interest in propellant acquisition systems, a test program was conducted under Martin Marietta IR&D Task Authorization 48714 to determine the causes of the anomalous results with hydrazine. As discussed previously, bubble point measurements below those calculated with equation (4) can be obtained if either the contact angle is not zero or the propellant surface tension is lower than the value employed. Because of these possibilities, three types of tests were conducted under the IR&D test program. These were: 1) measurement of propellant surface tension using a standard DuNouy Tensiometer; 2) measurement of contact angle using a Rame'-Hart goniometer; and 3) bubble point measurement with fine-mesh stainless steel screen.

A. PRELIMINARY TESTING

The initial IR&D tests were conducted to measure surface tension and contact angle of the two grades of hydrazine used in the contract bubble point testing. If the hydrazine were contaminated, the surface tension values could be lower than expected, which would explain the lower bubble point values. If significant contact angles existed, this would produce the low bubble point values.

1. Surface Tension Measurements

A standard Cenco DuNouy tensiometer was used to measure the surface tension of both the purified and Mil. Spec. hydrazine used in the bubble point testing conducted under Contract NAS9-13709. This instrument, shown in Figure 22, was installed within a glove box for all testing. A GN_2 atmosphere was maintained within the

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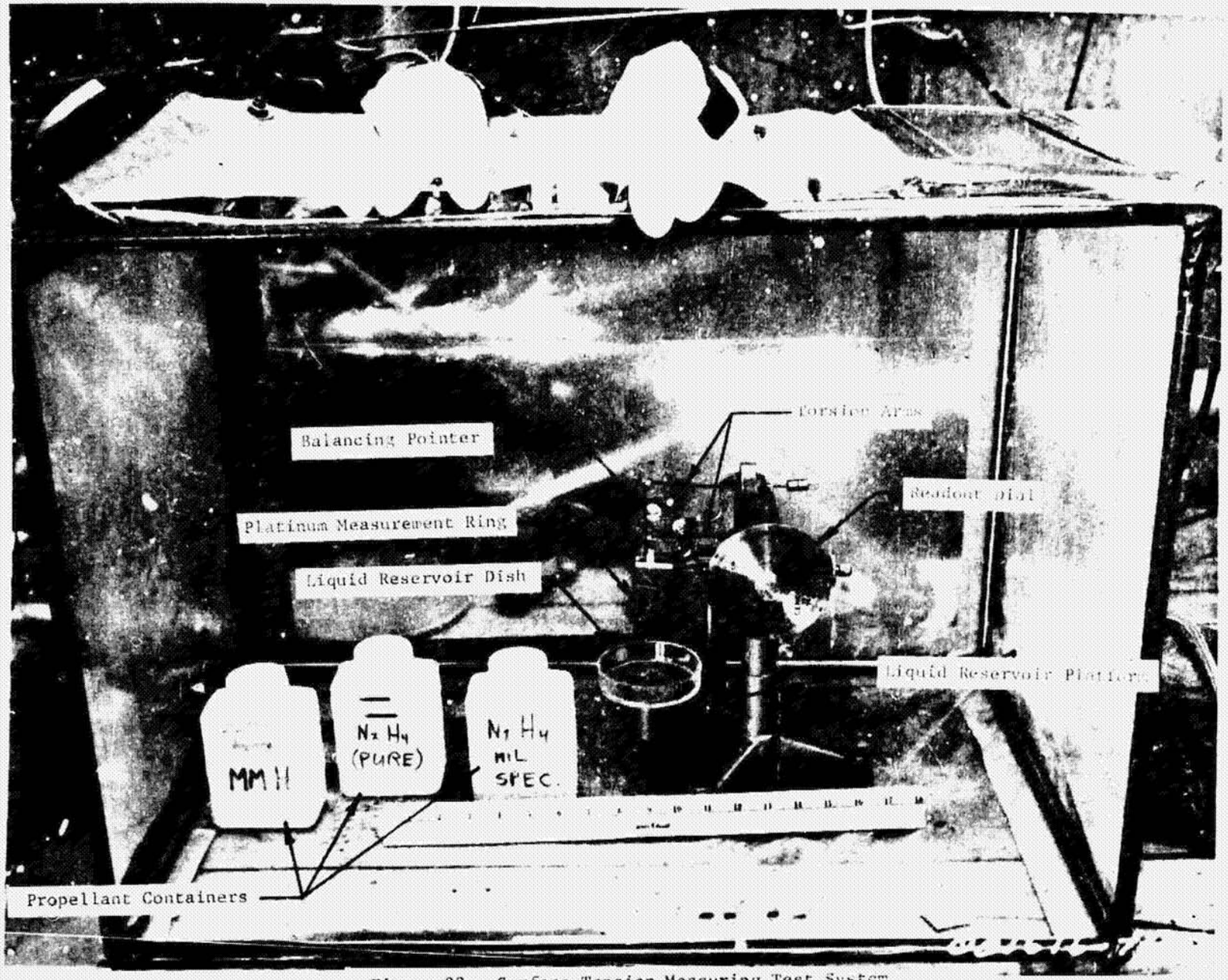

Figure 22: Surface Tension Measuring Test System

glove box to prevent air contamination. Prior to testing, the instrument was calibrated using the dead-weight method. An accurately known weight was mounted on the platinum ring, and the instrument was nulled. Nulling, or balancing, the instrument consisted of applying a force sufficient to raise the platinum ring and bring the pointer to the null position (see Figure 22). This force is read directly on the readout dial in dynes/cm. If this value did not agree with the force produced by the known weight, the length of the torsion arms controlling the force distribution was changed until agreement was obtained.

Following this initial calibration, the accuracy of the instrument was checked by measuring the surface tension of known standard fluids. Both chemically pure isopropyl and methyl alcohols, with known surface tensions, were checked with the instrument. The values obtained showed the instrument to be reading in error by about one dyne/cm. This correction factor was later applied to all of the measurements.

Prior to any measurements, both the dish used to hold the propellant and the platinum measuring ring were cleaned. Cleaning consisted of first immersing the articles in a strong alkaline cleaner (Diversey 909), followed by a water rinse, a rinse in isopropyl alcohol, and air drying. This cleaning procedure is similar to chemical cleaning method no. 2 (Table III), which was used on the screen bubble point test specimens.

The procedure used to measure propellant surface tension was as follows:

1) Following calibration, the instrument was placed in the glove box and leveled to assure that the liquid reservoir platform was parallel with the platinum measuring ring.

2) The supply of test liquid in a sealed container was placed in the glove box and the instrument was checked to make sure it was nulled or balanced properly (pointer in the null position with the dial reading 0 dynes/cm.

3) The glove box was then sealed and purged of all air using GN_2.

4) The propellant container was opened and a small quantity of propellant was placed in the dish located on top of the liquid reservoir platform.

5) The platform was then raised until the platinum measuring ring was submerged in the liquid and the pointer was again in the null position.

6) For the actual measurement, the platinum ring was raised and liquid reservoir platform was simultaneously lowered while keeping the pointer in the null position. This was continued until the liquid adhering to the measuring ring separated from the bulk liquid surface. The amount of force required to raise the ring to this point was the liquid surface tension.

The data obtained with the tensiometer are presented in Table VIII. In addition to measuring the surface tension of N_2H_4, the surface tension of MMH and four other fluids generally employed as bubble point referee fluids (water plus three types of alcohol) was also measured for comparison purposes. The values shown in Table VIII have been adjusted using the previously discussed correction factor. Also included in Table VIII are literature values obtained from the indicated references. As can be seen, all liquids exhibited excellent agreement between experimental and literature values except the two grades of N_2H_4. For Mil. Spec. N_2H_4, values about 20 dynes/cm (.00137 lbf/ft) below those reported in the literature were measured. Surface tension values for the Martin

Table VIII: Surface Tension of Various Liquids Measured with a DuNouy Tensiometer

Fluid	Test Temperature °C ± 1.1°C (°F ± 2°F)	Average Measured Value of Four Measurements Dynes/cm (lbf/ft)	Literature Value Dynes/cm (lbf/ft)	Reference
Purified N_2H_4*	23.9 (75)	50.2 (.00343)	-----	----
Mil. Spec. N_2H_4	22.8 (73)	47.7 (.00326)	67.9 (.00464)	18
Mil. Spec. MMH	22.2 (72)	35.2 (.00241)	33.6 (.00230)	18
H_2O	17.8 (64)	72.6 (.00496)	73.0 (.00499)	32
99% Isopropanol	20.6 (69)	22.1 (.00151)	21.6 (.00148) For Pure Isopropanol	32
Commercial Grade Methanol	12.2 (54)	24.5 (.00168)	23.4 (.00160) For Pure Methanol	32
95% Denatured Ethanol Plus 5% Isopropanol	18.9 (66)	23.2 (.00159)	22.1 (.00151) For Pure Ethanol	32

* <0.01% H_2O
<3.5 ppb Aniline (theoretical value)
<1 ppm other volatile impurities

Marietta purified N_2H_4 have not been reported previously. However, according to Razouk of JPL (Ref. 18), purifying N_2H_4 should increase its surface tension. In surface tension testing conducted at JPL with both Mil. Spec. N_2H_4 and a purified grade of N_2H_4, Razouk measured values 1 to 2% higher for the purified grade compared to the Mil. Spec. grade (Ref. 18). The purified grade used by Razouk contained 0.1% H_2O, 0.06% NH_3, and 5 ppm aniline. Therefore, if purification of N_2H_4 has the effect of increasing its surface tension, the value of surface tension measured with the tensiometer for the purified grade of N_2H_4 should have been at least 2% higher than the literature value for Mil. Spec. N_2H_4 presented in Table VIII. Instead, the measured surface tension of the purified N_2H_4 was 26% below that given in Reference 18. It should be noted, however, that the measured surface tension of N_2H_4 was 5% higher than that of the Mil. Spec. N_2H_4.

The low hydrazine surface tension measurements obtained with the tensiometer could indicate that something in the propellants themselves could have caused the anomalous bubble point results reported in Chapter II. Either due to contamination or some other factor, the surface tension of the hydrazine could have been degraded. However, the DuNouy tensiometer method of measuring surface tension is not free of contact angle constraints. If a non-zero contact angle existed between the liquid surface and the platinum measuring ring of the tensiometer, the amount of force required to lift the ring free of the liquid would decrease (the liquid would not have completely wetted the ring). Therefore, the low surface tension values presented in Table VIII could have resulted from a non-zero contact angle. Because of this, an assessment of contact angle, discussed in the following subsection, was undertaken.

2. Contact Angle Measurements

A Rame'-Hart Model A-100 goniometer was employed for the contact angle measurements. This instrument is basically a telescope with a special eye piece which enables the operator to measure the angle a liquid drop makes with a solid surface. The instrument also includes a special specimen enclosure or sample box which allows the measurement to be made in a controlled atmosphere. To measure the liquid/metal contact angle, the metal sample to be tested is placed in the sample box and the box is purged with the atmosphere desired (GN_2, GHe, propellant vapor, etc.) until all air is removed. Following this, a drop of the test liquid is placed on the metal surface, the telescope is focused on the drop, and the angle the drop makes with the surface is measured using the locating lines contained in the eye piece.

Initial contact angle measurements were made with the purified N_2H_4. The metal samples were 2.54-cm (one-inch) square by 0.254-cm (0.1-inch) thick, 304L stainless steel plate. The pretest cleaning procedure for these samples was identical to that used for the tensiometer tests.

Purified N_2H_4 contact angle test data are presented in Table IX. Relatively high contact angles were obtained. In addition, there appeared to be a passivation of the surface in contact with the propellant drop. After a period of one to three minutes, the initially measured angles dropped to lower values. The final angles obtained, however, were still relatively high, e.g., Figure 23. The airfoil shape is due to the reflection of the propellant drop by the metal surface. As also indicated in Table IX, introduction of air into the sample box caused the contact angle to decrease to a significantly lower value. Reaction with air causes N_2H_4 to immediately start to decompose. In

Table IX: Purified N_2H_4 Contact Angle Data

Fluid/Surface	Test No.	θ	Remarks
Purified N_2H_4/ 304L SS Polished Surface	1	35.0°	Held for approximately 5 minutes, then decreased.
	2	27.0°	
	3	33.0°	
	4	33.0°	
	5	33.5°	For these three runs θ dropped within 1 minute to approximately 23°.
	6	33.5°	
	7	34.5°	
	8	14.0°	Didn't use isopropanol rinse (detergent then tap H_2O).
	9	24.0°	Isopropanol rinse restored.
	10	18.0°	
	11	12.0°	
	12	28.5°	Changed N_2H_4 sample (possible air contamination).
	Two Drops 13A	35.0°	
	Two Drops 13B	25.0°	
	14	25.0°	
	15	33.5°	Initial (held for approx. 1 min.)
		30.0°	Held for 11 minutes
		22.0°	Stabilized value.

NOTES: Run in a closed GN_2/N_2H_4 vapor atmosphere.

Sample rinsed with isopropanol prior to testing, except as noted.

For each test, θ dropped to approximately 2° - 10° as soon as air was introduced into system.

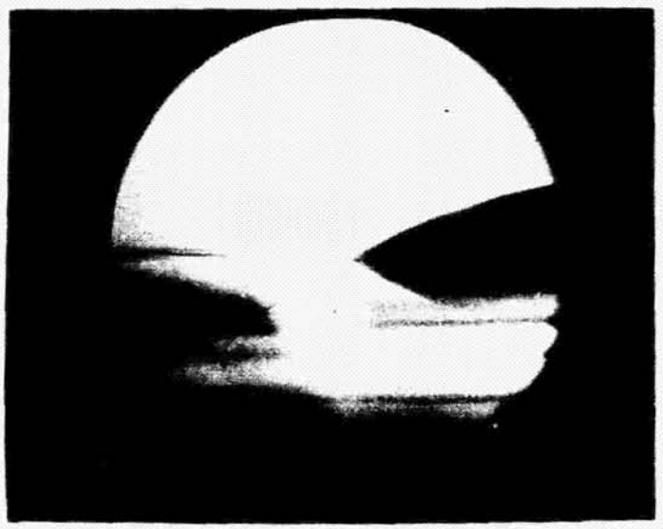

Figure 23: 33.5° Contact Angle for a Purified N_2H_4 Drop on a 304L SS Surface

addition, the purified N_2H_4 is highly hydroscopic and also readily absorbs CO_2. Therefore, the physical properties of the hydrazine may have been altered significantly after exposure to air, resulting in the lowered contact angles.

B. CLEANING PROCEDURE EVALUATION

The preliminary IRAD tests showed that relatively high contact angles resulted between the purified hydrazine and the stainless steel samples. In addition, it was concluded that the high contact angles caused the low measured surface tension values. Since non-zero contact angles result if the metal surface is contaminated, it was further concluded that some sort of contaminant film was causing the problem. Also, because the cleaning procedures used for the goniometer, tensiometer, and bubble point testing were similar, it was postulated that contaminants causing the non-zero contact angle are not removed by these cleaning methods or remain as a cleaning residual.

Based upon the above hypotheses, further tests were conducted to (1) verify that the anomalous bubble point results were caused by a contaminant film on the metal surface, (2) investigate the effects of these contaminants on materials other than stainless steel, and (3) determine means by which fine-mesh screen can be cleaned to remove any contaminant film causing non-zero contact angles with hydrazine. To accomplish these objectives, additional contact angle and bubble point tests were conducted. Contact angle measurements were used to evaluate the effectiveness of various cleaning procedures in producing near-zero contact angles with hydrazine. The bubble point tests were conducted to verify that any cleaning procedures which did produce near-zero contact angles on the sample surfaces would yield near-nominal bubble point values for fine-mesh screen in N_2H_4.

1. Contact Angle Measurements

Various cleaning procedures were evaluated by cleaning the sample metal surfaces and then measuring the contact angle of N_2H_4 with the Rame'-Hart Model A-100 goniometer. The cleaning procedures employed in the evaluation are listed in Table X. All of the procedures listed, except for III, VII, and X, are representative of aerospace methods for earth-storable propellants. Procedures III and X are more stringent, being representative of chemical laboratory methods. Procedure VII was included to investigate possible passiation effects. The metal samples were 2.54-cm (one-inch) square by 0.254-cm (0.1-inch) thick pieces of 304L stainless steel, 6061 aluminum, and 6Al-4V titanium plate. The surfaces of the samples were in the "as received" condition, i.e., no surface preparation such as grinding or polishing was used.

The measurements were made in either a helium or nitrogen atmosphere. For all M and H samples (see Table XI, presented later, for description of metal samples), GHe was used; GN_2 was used for all of the other samples tested. As the data presented in Table XI show, for any particular cleaning procedure, there was no significant difference between the contact angles measured in helium or nitrogen.

Contact angles obtained with Mil. Spec. N_2H_4 and metal samples, cleaned per the procedures listed in Table X, are presented in Table XI. Tests were conducted with MMH for comparison. The values shown are initial angles only. The data indicate that all of the cleaning procedures, except III and X, produced contact angles greater than 10°. For many of these procedures, angles as great as 55° were measured. For procedures III (flame cleaning) and X (chromic acid cleaning solution), the resulting contact angles were reduced to less than 10°. When air was introduced

Table X: Metal Sample Cleaning Procedure

Procedure 1

1) Concentrated HNO_3 (21°C [70°F])
2) Tap H_2O Rinse
3) Isopropanol Rinse
4) GN_2 Dry in Air

Procedure II

1) Concentrated HNO_3 (21.1°C [70°F])
2) Tap H_2O Rinse
3) GN_2 Dry in Air

Procedure III

1) Soap/H_2O Solution (21.1°C [70°F])
2) Tap H_2O Rinse
3) Concentrated HNO_3 (21.1°C [70°F])
4) Tap H_2O Rinse
5) Isopropanol Rinse
6) Propane/Air Flame
7) Air Cool

Procedure IV

1) Diversey 909 Alkaline Cleaner (21.1°C [70°F])
2) Tap H_2O Rinse
3) Isopropanol Rinse
4) Heat in Air to Dry

Procedure V

1) 100°C (212°F) Diversey 909 Solution
2) 100°C (212°F) Distilled H_2O Rinse
3) Air Dry

Procedure VI

1) 100°C (212°F) Diversey 909 Solution
2) 20°C (68°F) Distilled H_2O Rinse
3) Concentrated HNO_3 -21.1°C (70°F)
4) 100°C (212°F) Distilled H_2O Rinse
5) Air Dry

Procedure VII

1) Procedure VI
2) Soak 3-4 Days in Propellant to be Tested
3) GN_2 Dry in Air

Procedure VIII

1) Concentrated HNO_3 -21.1°C (70°F)
2) 100°C (212°F) Distilled H_2O Rinse
3) Freon TF Rinse
4) Air Dry

Procedure IX

1) Concentrated HNO_3 -21.1°C (70°F)
2) 100°C (212°F) Distilled H_2O Rinse
3) Isopropanol Rinse
4) Heat in Air to Dry

Procedure X

1) 100°C (212°F) Chromic Acid Cleaning Solution (K_2CrO_4/H_2O Solution Dissolved in Concentrated H_2SO_4)
2) Distilled H_2O Rinse and Soak (20°C [68°F])
3) Heat in Air to Dry

Table XI: Measured Contact Angles

Sample	Metal Surface	Propellant	Cleaning Procedure	Test No.	Drop No. On Surface	θ (Degrees)
AA	304L SS	Mil. Spec. N_2H_4	I	1	1	18
					2	14
				2	1	38
				3	1	15
				4	1	15
BB	304L SS	Mil. Spec. N_2H_4	II	1	1	31
				2	1	33
				3	1	26
			I	4	1	16
					2	26
CC	304L SS	Mil. Spec. N_2H_4	III	1	1	4
				2	1	7
1	304L SS	Mil. Spec. N_2H_4	VI	1	1	44
				2	1	21
				3	1	31
				4	1	14
				5	1	11
					2	11
2	304L SS	Mil. Spec. N_2H_4	V	1	1	20
3	304L SS	Mil. Spec. N_2H_4	VII	1	1	13
				2	1	10
4	304L SS			3	1	17
				4	1	14
5	304L SS			5	1	14
6	304L SS			6	1	13
					2	12
7	304L SS	Mil. Spec. N_2H_4	X	1	1	7
					2	6
8	304L SS			2	1	8
					2	7
9	304L SS			3	1	9
					2	6

Table XI (continued)

Sample	Metal Surface	Propellant	Cleaning Procedure	Test No.	Drop No. On Surface	θ (Degrees)
1G	304L SS	Mil. Spec. N_2H_4	VIII	1	1	42
				2	1	55
					2	45
			IX	3	1	37
					2	50
M1	304L SS	Mil. Spec. MMH	IX	1	1	3
					2	3
				2	1	1
					2	2
					3	5
					4	2
			VIII	3	1	6
					2	7
					3	5
H1	304L SS	Mil. Spec. N_2H_4	IX	1	1	35
					2	35
				2	1	46
					2	39
H2	6Al-4VTi	Mil. Spec. N_2H_4	IX	1	1	34
					2	34
				2	1	26
					2	29
				3	1	25
					2	27
H3	6Al-4VTi	Mil. Spec. N_2H_4	III	1	1	4
					2	4
				2	1	4
H4	6061 Al	Mil. Spec. N_2H_4	IX	1	1	17
					2	32
				2	1	7
					2	13
H5	6061 Al	Mil. Spec. [illegible]	III	1	1	3
					2	1

Table XI (concluded)

Sample	Metal Surface	Propellant	Cleaning Procedure	Test No.	Drop No. On Surface	θ (Degrees)
H6	6Al-4VTi	Mil. Spec. N_2H_4	X	1	1	4
					2	4
					3	4
H7	6Al-4VTi			2	1	4
					2	8
H8	6Al-4VTi			3	1	7
					2	4
H9	6Al-4VTi			4	1	7
H10	6061 Al	Mil. Spec. N_2H_4	X	1	1	6
			VIII	2	1	19
H11	6061 Al		X	3	1	4
					2	4

into the sample box, a significant reduction in contact angle occurred in every instance. This phenomena also occurred, as indicated in Table IX, during the preliminary contact angle tests with purified N_2H_4.

The data presented in Table XI tend to verify the existence of a contaminant film which causes relatively high contact angles with N_2H_4. The data also indicate that these films are either not removable by standard earth-storable propellant cleaning procedures or may result from contaminants introduced during the cleaning procedure. With Freon TF (procedure VIII), a contaminant film was apparently deposited on the test samples during cleaning. This is indicated by the 42 to 55° contact angles obtained from sample 10 (Table XI). Passivation of the metal surface by immersion in N_2H_4 for three to four days did not remove the contaminant. The only cleaning procedures which appeared effective for removing the contaminant film were flame cleaning and chromic acid cleaning (procedures III and X). As shown by the data, essentially the same results were obtained with titanium, aluminum, and stainless steel samples.

The contaminants affecting the wettability of N_2H_4 had little impact on MMH wettability, as indicated by the low contact angles measured with MMH (Table XI). With its lower surface tension, the wettability of MMH is less constrained by surface contaminants (i.e., the MMH surface tension is less than the "critical surface tension" of the contaminated surface). Contaminant films which reduce the "critical surface tension" of a metal surface to produce non-zero contact angles for N_2H_4 should also produce non-zero contact angles for fluids such as water, which also has a very high surface tension value (~72 dynes/cm [.00492 lbf/ft]). However, the surface tension value for H_2O, as measured with the tensiometer, agreed with values reported in the literature (see Table VIII).

This indicates that the contaminants which resulted in non-zero contact angles for N_2H_4 do not appear to cause problems with H_2O.

2. Bubble Point Tests

The apparatus, shown schematically in Figure 24, was used to measure the bubble point of fine-mesh screen. It consists of two cylindrical sections connected by a flange which holds the screen specimen. The test system is shown in Figure 25. To exclude air, the bubble point apparatus and the ΔP transducer were both located in the same glove box used for the surface tension measurements. The screen bubble point, ΔP_c, was read directly in psi on a calibrated voltmeter having an accuracy of $\pm .021$ N/cm^2 ($\pm .03$ psi). To perform a measurement, the screen specimen is wetted with a thin, 1.6-mm (1/16-inch) layer of propellant and the region beneath the screen is slowly pressurized until the first bubble breaks through the wetted screen. The pressure differential at which this occurs is the bubble point.

The results of the cleaning evaluation indicated that only two of the procedures produced near-zero contact angles; therefore, the fine-mesh screen samples were cleaned using these two procedures. If bubble point values near those calculated by equation (4) were obtained ($\theta = 0^o$), then the effectiveness of these cleaning procedures would be verified. To further aid in this evaluation, a cleaning procedure similar to those which produced the relatively high contact angles was also used to clean one of the screen specimens to provide comparative data.

The screen material used in the bubble point testing was 325 x 2300 mesh, stainless steel, Dutch-twill screen. The test specimens were similar to those shown in Figure 15. A total of four such samples was prepared for testing. Three were chromic acid cleaned while the fourth was flame cleaned. One of the

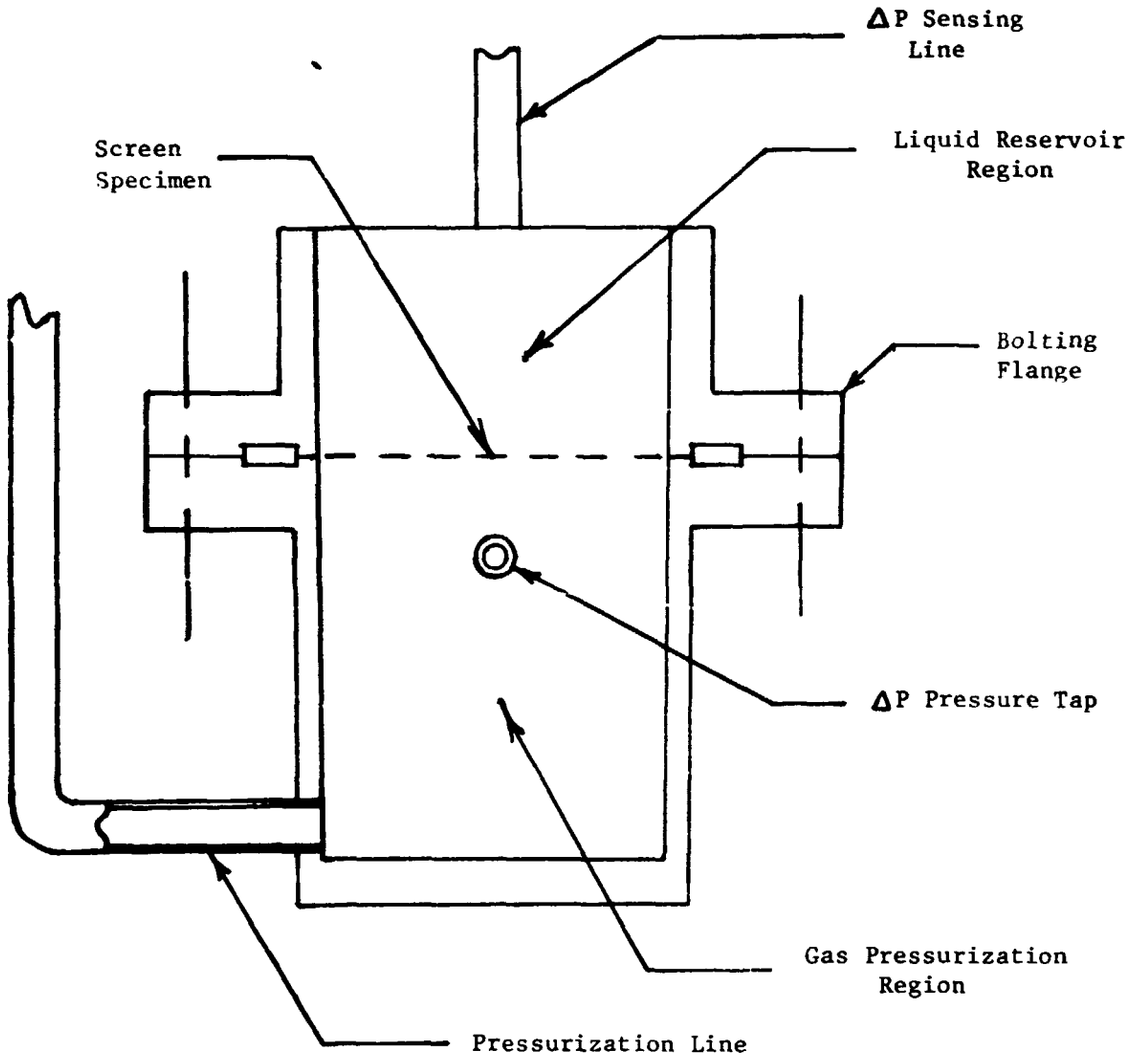

Figure 24: Schematic of IR&D Bubble Point Apparatus

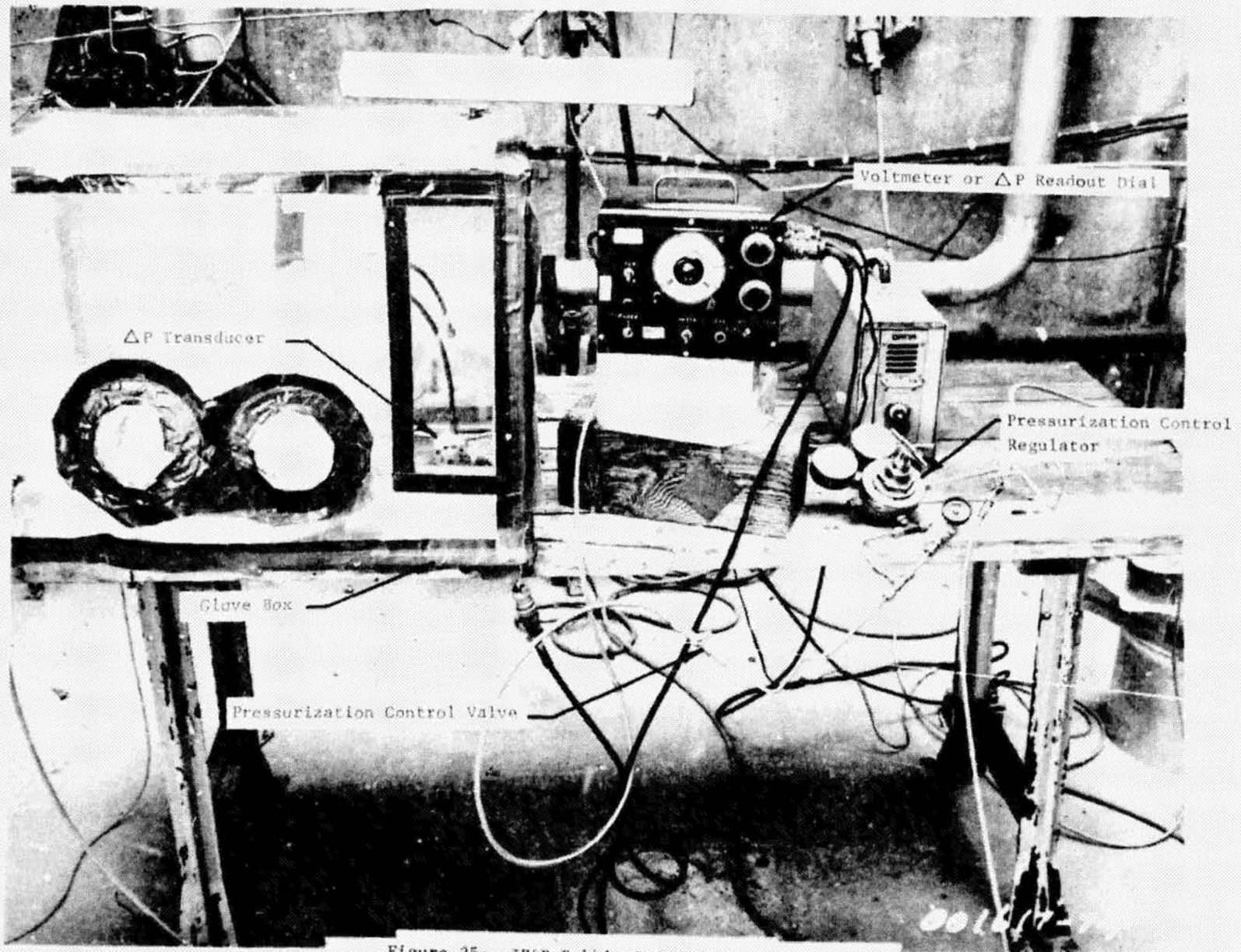

Figure 25: IR&D Bubble Point System

chromic acid cleaned samples was recleaned using procedure IV (see Table XI) after testing in hydrazine.

The bubble point data obtained with the 325 x 2300 screen in Mil. Spec. N_2H_4 are presented in Table XII. Screen bubble points measured in isopropanol are also included in the table. These values were used in equation (4) to calculate theoretical N_2H_4 bubble points. The surface tension value of isopropanol at the N_2H_4 test temperature was obtained by taking the tensiometer value listed in Table VIII and adjusting it for temperature variation. The surface tension variation with temperature was obtained from Reference 32. The surface tension value of N_2H_4 was obtained from Reference 18.

As stated previously in Chapter I, equation (4) is only valid if the contact angles are zero or equal. Isopropanol has a zero contact angle since it is totally wetting (a drop will spread completely over a metal surface). Therefore, the calculated values presented in Table XII represent the N_2H_4 bubble points assuming the hydrazine totally wets the screens ($\theta = 0^o$). The results show good agreement between the measured and calculated bubble point values when cleaning procedures III and X were used, thereby indicating a zero or near-zero contact angle. However, when cleaning procedure IV was used the measured value was approximately 16% below the calculated value, showing the existence of a larger contact angle.

Table XII: IR&D Bubble Point Test Results with Mil. Spec. N_2H_4

Sample	Isopropanol Bubble Point (psi)	Test Temperature °C ± 1.1°C (°F ± 2°F)	Cleaning Procedure*	Measured Bubble Point N/cm² ±0.021 N/cm² (psi ±0.03 psi)	Calculated Bubble Point N/cm² (psi)
A 325 x 2300 SS	.606 at 21.1°C (0.88 at 70°F)	20.0 (68)	III	1.78 (2.58)	1.83 (2.66)
B 325 x 2300 SS	.620 at 22.8°C (0.90 at 73°F)	18.9 (66)	X	1.77 (2.57)	1.90 (2.75)
		20.0 (68)	IV	1.58 (2.30)	1.89 (2.74)
C 325 x 2300 SS	.613 at 20.3°C (0.89 at 68.5°F)	17.8 (64)	X	1.69 (2.45)	1.86 (2.70)
D 325 x 2300 SS	.600 at 19.4°C (0.87 at 67°F)	20.0 (68)	X	1.82 (2.64)	1.80 (2.61)

*Per Table X

IV. DISCUSSION OF RESULTS

A discussion of the propellant physical property data compiled from the literature and personal contacts is presented in this chapter, together with an assessment of adequacy of the available properties. This is then followed by a discussion of the test results.

A. DATA COMPILATION

The propellant physical property data obtained from the literature was presented in Chapter II. In considering the data compiled, it appears that sufficient data on density are available for all the propellants for SS/RCS design purposes. The maximum scatter in the data is less than 0.5%. The collected viscosity data, although having as much as a 10.5% data scatter at 20°C (68°F), also seems quite adequate for SS/RCS propellant acquisition design purposes, since the variation in viscosity of MMH is 55% over the temperature range of interest. The density and viscosity data, presented in Figures 2 through 7, also indicate a negligible effect of pressure over the SS/RCS range of interest.

Surface tension data for both MMH and N_2O_4 also seem adequate for SS/RCS design purposes. The maximum variation in the reported data is about 5% for MMH and around 8% for N_2O_4. Based upon the compiled MMH and N_2O_4 surface tension data shown in Figures 9 and 10, a representative curve plus maximum and minimum value curves were developed. These curves, presented in Figures 20 and 21, should be employed for SS/RCS design purposes. The maximum and minimum curves, represent the variation in reported MMH or N_2O_4 surface tension data. The slopes of the representative data curves agree with the temperature dependencies shown by the reported data. Representative, maximum, and minimum surface tension curves were also developed for Mil. Spec. N_2H_4 (Figure 19). As shown by

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these curves, the variation in the reported data at 20°C (68°F) is almost as great as the variation in N_2H_4 surface tension over the SS/RCS temperature range of interest. While showing more scatter than MMH and N_2O_4, the surface tension data for N_2H_4 still appear adequate.

Very little contact angle data were found for MMH and N_2O_4. However, the data available indicate that near-zero contact angles can be obtained with N_2O_4 and MMH using ordinary earth-storable propellant cleaning procedures (Ref. 27, 28, and 29). However, cleaning procedures which employ Freon as a final rinse should be avoided. Both the contract and the IR&D test results substantiate near-zero contact angles for MMH and N_2O_4. Excellent agreement was obtained between measured and calculated bubble points of fine-mesh screen in MMH and N_2O_4, indicating near-zero contact angles (Chapter II). In addition, contact angles less than 4° were measured for MMH using a typical earth-storable propellant cleaning procedure while angles as large as 7° were measured when a cleaning procedure incorporating a Freon TF final rinse was employed (see Table XI).

The only data found in the literature on contact angle with N_2H_4 were reported by Harris Research Laboratories (Ref. 21). However, the report seems to indicate that their data were taken in an air atmosphere and may, therefore, be invalid.

B. TEST PROGRAM

The results of the screen bubble point tests conducted under the contract were presented in Chapter II. These results were excellent for N_2O_4 and MMH, the primary SS/RCS propellants, but anomalous and inconsistent bubble points were obtained with purified and Mil. Spec. N_2H_4. Screen bubble point in MMH and N_2O_4 followed the same temperature dependencies exhibited by published surface tension data. Tests conducted at pressures up to 276 N/cm^2 (400

psia) indicated that dissolved GHe has little or no effect on the screen bubble point in either MMH or N_2O_4. Also, because the measured N_2O_4 and MMH bubble point values showed excellent agreement with values calculated by equation (4), the contact angles of these propellants on the screen were near-zero. Therefore, the normal cleaning procedures employed were sufficient for N_2O_4 and MMH screen systems.

Unlike MMH and N_2O_4, the bubble point test results for both purified and Mil. Spec. N_2H_4 were anomalous and inconsistent. The IR&D test program investigated causes of the anomalies with N_2H_4 and showed the most likely cause to be a contaminant film on the screen surface. This contaminant caused relatively high contact angles for hydrazine (purified or Mil. Spec.) which in turn produced the anomalous bubble point measurements. The results from the IR&D test program also indicated that normal chemical aerospace cleaning methods either did not remove the high contact angle contaminant or were the source of this contaminant. However, two cleaning procedures (III and X of Table X) were found which could remove the contaminant. Subsequent IR&D tests demonstrated that these two cleaning procedures would clean fine-mesh screen and provide near nominal bubble point values with N_2H_4. This is shown in Figure 26 where surface tension values calculated from the IR&D bubble point data are compared against the representative, maximum, and minimum literature values. Screen samples cleaned with either procedure III or X produced surface tension values which compare favorably with the literature data. For cleaning procedure IV (similar to the chemical cleaning methods used in the contract bubble point tests), a surface tension considerably below the literature data was obtained (indication of contamination).

The tensiometer tests conducted under the IR&D test program seemed to verify that purification of N_2H_4 increases surface tension and thus bubble point value for fine-mesh screen (if $\theta = 0$). This agrees with the JPL data presented in Figure 18 (Ref. 18).

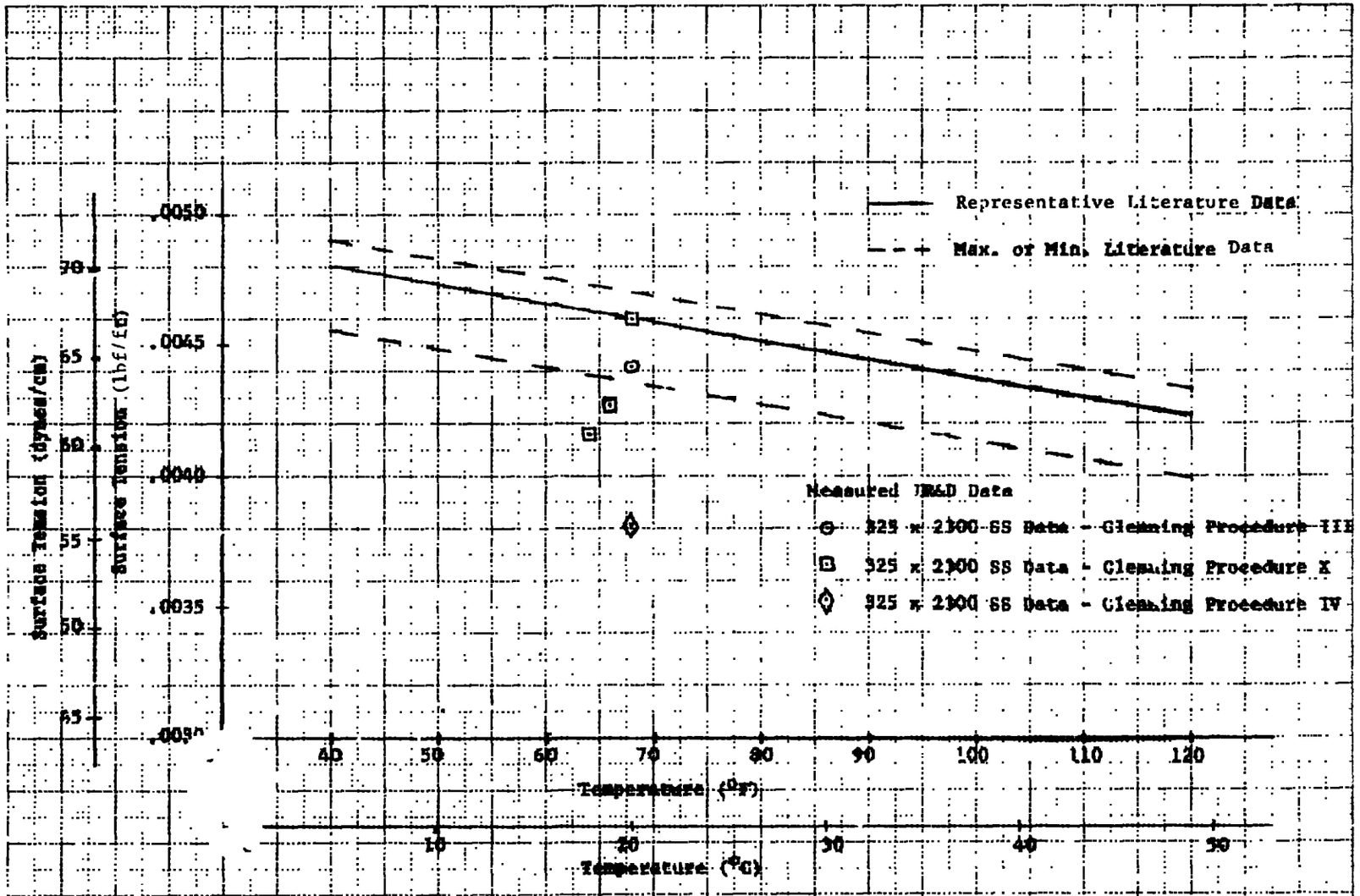

Figure 26: Comparison of Published and Measured Surface Tension Data for Mil. Spec. N_2H_4 (IR&D Data)

V. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the results obtained during the program.

The density, viscosity and surface tension data available in the literature for the SS/RCS and SS/APU propellants (N_2O_4, MMH, and N_2H_4) seem adequate for propellant acquisition system design purposes. Information on the contact angles for N_2O_4 and MMH also seems adequate; the data are insufficient for N_2H_4, however. Based on the N_2O_4 and MMH contact angle data reported in the literature, near-zero contact angles can be obtained for these propellants using typical earth-storable propellant cleaning procedures. The only exception are cleaning procedures employing Freon as a final rinse. The contact angles measured in the IR&D test program substantiate these conclusions. Published data also indicate that the effect of pressure on the viscosity and density of N_2H_4, N_2O_4, and MMH is insignificant at pressures up to 276 N/cm^2 (400 psia).

Several conclusions can also be drawn from the results obtained in the contract and IR&D test programs. Fine-mesh screen bubble points measured in MMH and N_2O_4 were in excellent agreement with calculated values. Typical earth-storable propellant cleaning procedures are suitable for use with fine-mesh screen to be used in these propellants. Anomalous screen bubble points resulted with both purified and Mil. Spec. N_2H_4 in the contract testing, however. The effect of dissolved helium and pressure level on screen bubble point in N_2H_4, MMH and N_2O_4 is insignificant over the range of system pressures tested, i.e., up to about 276 N/cm^2 (400 psia). Measured bubble point (surface tension) decreased with increasing temperature, also as expected.

Complementary IR&D testing conducted to investigate the reasons for the anomalous N_2H_4 contract results showed that contact angles from 15 to 50° can be obtained in a saturated helium or nitrogen atmosphere with both purified and Mil. Spec. N_2H_4 on various metal surfaces (6061 Al, 6Al-4V Ti, 304L stainless steel) unless cleaning methods more stringent than normal aerospace procedures for earth-storable propellants are employed. These relatively high hydrazine contact angles can result in low surface tension values measured with a DuNouy tensiometer and low (14 to 65% below predicted) and inconsistent bubbl poi's for fine-mesh screen. These high contact angles for N_2H_4 resulted from a contaminant film remaining on the metal surface following normal earth-storable propellant cleaning operations. This film may have been present prior to cleaning or may have been deposited during cleaning. No high contact angles were encountered between MMH, N_2O_4, or H_2O and metal samples cleaned in the normal earth-storable manner, indicating that the contaminant presents no problem to the wettability of these liquids. High contact angles are not obtained when measurements are made in air.

Passivation of metal surfaces by immersion in N_2H_4 for periods up to four days does not remove the contaminant film; it does have some effect, however, since the contact angle is reduced by the passivation. Finally, bubble point (surface tension) increases as propellant purity is increased.

The following recommendations are made for further work based on the results obtained during the program.

1) For any selected SS/RCS propellant acquisition design, adequate testing (contact angle and bubble point) should be conducted to verify that possible contaminants such as valve lubricants like Krytox 143AB will not cause contact angle or screen bubble point problems with MMH, N_2O_4, and N_2H_4.

2) Additional N_2H_4 contact angle and bubble point testing should be conducted to further investigate cleaning procedures. The results of the IR&D test program (Chapter III) identified only two applicable cleaning procedures for N_2H_4. As part of this investigation, vacuum annealing should be investigated as a means of cleaning fine-mesh screen. In theory, this type of cleaning procedure should be capable of cleaning fine-mesh screen as well as the flame cleaning procedure.

3) Further work is needed to identify the contaminants causing the contact angle problems with N_2H_4.

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APPENDIX A

TEST PROCEDURE

(Revision 1)

PROPELLANT BUBBLE POINT

TEST PROGRAM

Contract NAS9-13709

Task III

January, 1974

Approved by: Porter Uney
P. E. Uney
Test Conductor Leader
Task III

Approved by: R. O. Harvey
R. Harvey
Safety

Approved by: Dale A. Fester
D. A. Fester
Program Manager

1.0 TEST OBJECTIVE

The objective of these tests is to measure the bubble point of four typical fine-mesh screens in four earth storable propellants (MIL-Spec. N_2H_4, purified grade N_2H_4, MMH, and N_2O_4) under various conditions of propellant temperature, and He gas saturation levels. In addition, an assessment of the effect various cleaning methods would have on screen bubble point is also to be made. Figure I presents the test matrix to be followed during the tests. This matrix indicates the types of screens to be tested as well as the propellants employed and the test temperatures and pressures to be used.

2.0 TEST EQUIPMENT

The equipment to be used in the test is shown schematically in Figure II. This apparatus consists primarily of a bubble point assembly enclosed in a pressure vessel, a propellant conditioning unit, propellant supply tank and associated plumbing. The pressure vessel has two view ports on the top for visual observation of the bubble point assembly. Instrumentation will be provided to monitor and control test operations and to record pertinent data.

3.0 SAFETY REQUIREMENTS

3.1 All personnel authorized to work in the test area during propellant transfer and tests will wear safety equipment, as specified by the Safety Department.

3.2 All personnel at the Propulsion Research Laboratory or authorized personnel in the test area must have a propellant physical or obtain

Screen Type	Propellant	Type of Screen Cleaning	Approx. 32°F			Approx. 70°F				Approx. 125°F			Temperature
			1 atm	6 atm	20 atm	1 atm	6 atm	20 atm	28 atm	1 atm	6 atm	20 atm	Pressure
325 x 2300 Dutch Twilled Stainless Steel	N_2H_4 (Purified)	Alcohol Rinse				X							
		Vacuum Annealed				X							
		Chem. Cleaning Method No. 1				X							
		Chem. Method No. 2	X			X		X		X			
	N_2H_4 (MIL Spec)	Method No. 2	X			X	X	X	X	X			
	MMH	Method No. 2	X			X		X		X			
	N_2O_4	Method No. 2	X			60°F	X	X			55psi		
200 x 1400 Dutch Twilled	N_2H_4 (MIL Spec)	Method No. 2				X							
	MMH	Method No. 2				X							
	N_2O_4	Method No. 2				60°F							
165 x 800 Dutch Twilled SS	N_2H_4 (MIL Spec)	Method No. 2				X							
	MMH	Method No. 2				X							
	N_2O_4	Method No. 2				60°F							
180 x 180 Twilled Square Weave SS	N_2H_4 (MIL Spec)	Method No. 2	X			X				X			
	MMH	Method No. 2	X			X				X			
	N_2O_4	Method No. 2	X			60°F					55psi		

Figure I: Propellant Bubble Point Test Matrix

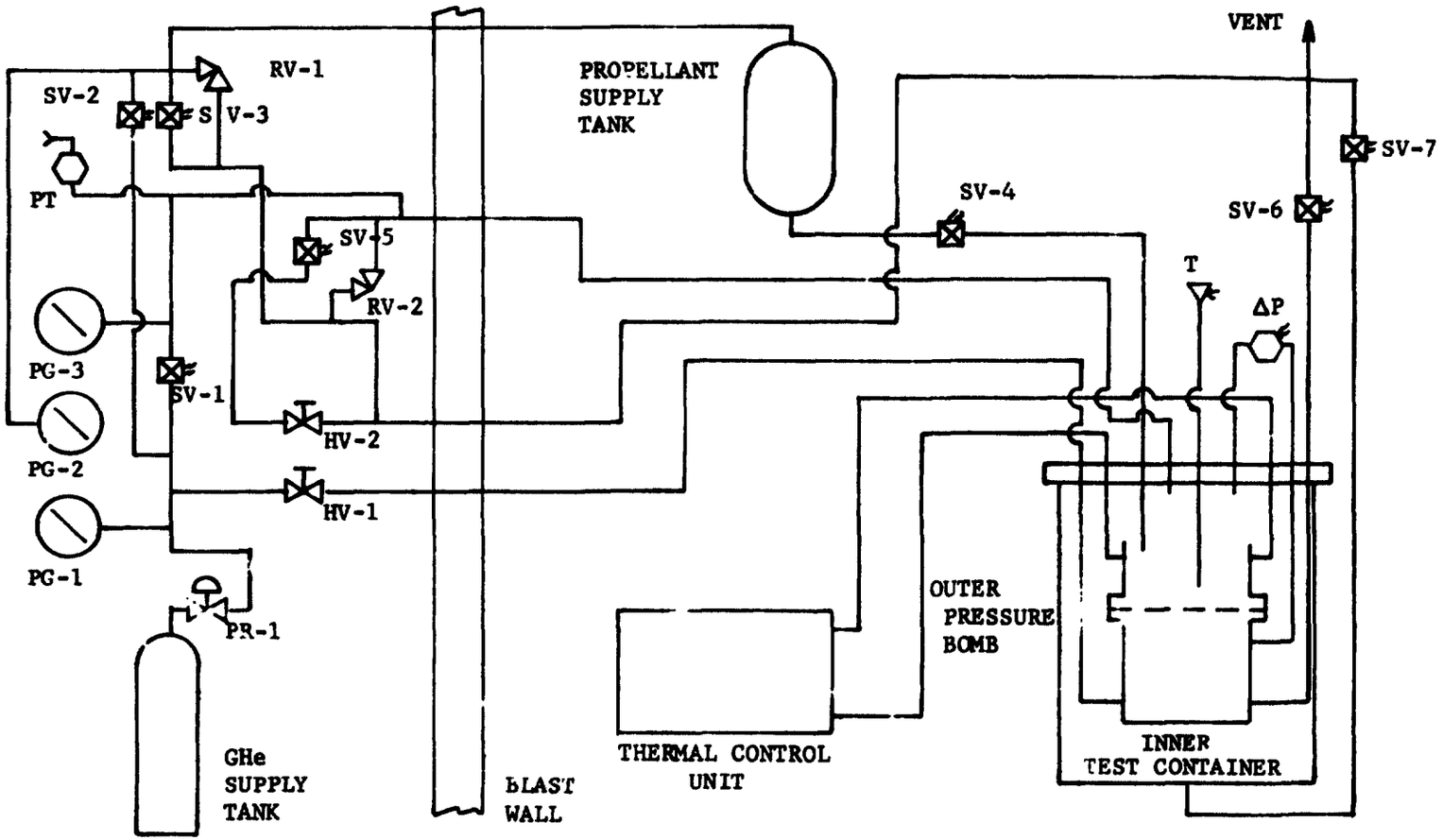

Figure II: Bubble Point Test System Schematic

an approval from the Safety Department to be in the area during the test program.

3.3 Prior to each testing day notify the Safety Department of intent to test.

3.4 Verify the test equipment is grounded, prior to propellant transfer.

4.0 GENERAL INFORMATION

4.1 Purge and Pressurization Gases Pressures

At all times during the test, the pressurization and purge gases upstream of their respective shutoff valves shall always exceed the downstream pressure. This precaution shall be taken to prevent propellant vapors from backflowing into the purge and pressurization gas systems and contaminating them.

4.2 System Components

Verify all components in the system are rated to operate at pressures greater than 400 psig.

4.3 Vent Disposal System

Verify that when venting N_2O_4 no visible vapor is coming out of vent stack (all propellant vapors will be diluted by GN_2).

5.0 SYSTEM LEAK CHECK

5.1 Verify all solenoid and hand valves are closed.

5.2 Set the GHe pressure regulator to 50 $\pm$ 5 psig.

5.3 Open solenoid valve SV-4.

5.4 Open solenoid valve SV-2 and pressurize the system to 50 $\pm$ 5 psig, then close the valve.

5.5 Leak check all fittings, connections and components, using bubble test solution.

5.5.1 If any leakage is seen, make repairs as required.

5.6 Increase the GHe pressure regulator to 450 $\pm$ 50 psig.

5.7 Open solenoid valve SV-2 and pressurize the system to 400 psig, then close the valve.

5.8 Leak check all fittings, connections and components, using bubble test solution.

5.8.1 If any leakage is seen, make repairs as required, after system has been vented to ambient.

5.9 Once it has been determined the system is leak tight, open solenoid valve SV-7 and vent the system to 10 ± 5 psig, then close the valve.

5.10 Close solenoid valve SV-4.

5.11 Back-off the GHe pressure regulator.

6.0 AMBIENT PRESSURE TEST PROCEDURES

6.1 Purge System of Air Using GHe

1) Verify valves SV-1, SV-2, SV-3, SV-4, SV-5, SV-6, SV-7, HV-1 and HV-2 are closed.

2) Set GHe pressure regulator to 50 ± 5 psig.

3) Open valves HV-1 and SV-1 to pressurize system to 30 ± 5 psig.

4) Open valves SV-5 and HV-2 to blowdown system.

5) Close SV-5 and HV-2 and pressurize again to 30 ± 5 psig.

6) Open valve SV-6 to blowdown.

7) Close SV-6 and again pressurize to 30 ± 5 psig.

8) Open SV-7 for blowdown.

9) Repeat above sequence a number of times to insure no air is in test system.

10) After last purge sequence, shut all valves except HV-1, HV-2 and SV-5 to maintain a He purge on system. GHe flow through HV-1 should be minimal as to not pressurize test container.

6.2 Propellant Loading and Test Conduction

1) Safe test area and put test area in red condition. Notify Safety of intent to test.

2) Start chill unit to condition test system.

3) Set relief valves RV-1 and RV-2 at 10 $\pm$ 1 psig.

4) When proper test temperature has been reached, open valve SV-2 and pressurize propellant tank to 5 $\pm$ 1 psig.

5) Cycle valve SV-4 to load system maintaining He flow through valve HV-1 so as to bubble He through the screen test specimen.

6) When required liquid level is reached, terminate cycling of valve SV-4, maintaining it in the closed position.

7) Reduce He flow below screen by use of valve HV-1 until He no longer bubbles through screen specimen and until ΔP transducer indicates 1 to 2 in of H_2O across screen.

8) Increase ΔP across screen by opening up valve HV-1 until bubble point of screen specimen is reached.

9) Repeat steps 7 and 8 until required number of bubble point measurements are made.

10) If temperature is to be changed for more measurements, change temperature setting of chill unit. To change temperature, propellant tank will first be safed by opening Valve SV-3. Once temperature setting has been changed inside the test cell, valve SV-3 can be shut and SV-2 opened to again pressurize propellant tank to 5 $\pm$ 1 psig.

11) When proper temperature has been reached, repeat steps 5 and 6 if propellant topping is required.

12) Repeat steps 6, 7 and 8 to obtain bubble point measurements.

13) If no more measurements are to be made with this propellant and screen specimen, safe system as specified in Section 6.3.

6.3 System Safing or Unloading

1) Verify vent stack purge is on.

2) Shut valves SV-5, HV-1 and HV-2.

3) Cycle valves SV-6, SV-7 and open valve SV-1 to blow out propellant. Cycling of SV-6 and SV-7 is needed to preclude relatively large amounts of propellant being vented at one time.

4) Verify valve SV-2 is closed.

5) Open valve SV-3 to vent propellant tank to 5 ± 1 psig.

7.0 PRESSURIZED TEST PROCEDURES

7.1 System GHe Purging

(Same as for Ambient Pressure Procedure)

7.2 Propellant Loading and Test Conduction

1) Shut valves SV-5 and HV-2.

2) Set GHe pressure regulator to 450 ± 50 psig.

3) Set relief valve RV-1 50 ± 10 psig higher than intended propellant tank pressure

4) Set relief valve RV-2 50 ± 10 psig greater than system test pressure.

5) Pressurize test container up to test pressure by use of valves HV-1 and SV-1. Shut HV-1 and SV-1 after system pressure is reached.

6) Open valve SV-2 and pressurize propellant tank up to a pressure greater than test pressure.

7) Cycle valve SV-4 to load system. In addition, open valve HV-1 to bubble GHe through the screen in order to mix the propellant and saturate it with GHe.

8) After system is loaded to required level, shut SV-4.

9) Reduce pressure below screen specimen by use of valve HV-1 and by cycling valve SV-6 until GHe bubbling through screen stops and ΔP transducer indicates 1 to 2 in. of H_2O across screen.*

10) Measure bubble point by use of steps 7 and 8 of ambient pressure procedures.

11) Safe and unload system per Section 6.3.

7.2.1 <u>Alternate Bubble Point Measurement Procedure</u>

1) Use steps 1 through 9 of Section 7.2 to load and prepare the test system for a bubble point measurement.

2) Open solenoid valve SV-5 maintaining HV-2 in the closed position.

3) Slowly open HV-2 to degrease the system pressure or pressure above the screen's surface.

4) Continue to degrease system pressure until the bubble point of the screen specimen is reached.

5) If another measurement is to be made, close HV-2 and SV-5 and bring the system pressure up to test pressure by use of valves HV-1 and SV-1.

6) Use step 9 of Section 7.2 to reduce the pressure below the screen specimen if required.

*Prior to step 10), a hold period of up to half an hour should be maintained in order to guarantee that the propellant is saturated with GHe.

7) Repeat steps 2 through 4.

6) Safe and unload system per Section 6.3.

7.3 <u>System Safing or Unloading</u>

(Same as for Ambient Pressure Procedure)

NOTE: If pressurized test follows an ambient test directly, steps 6 through 8 of Section 7.2 will be employed as a topping procedure if needed.