NATIONAL BUREAU OF STANDARDS REPORT

9976

COMPATABILITY OF PROTECTIVE COATINGS, MATERIALS, AND LIQUID PROPELLANTS

QUARTERLY PROGRESS REPORT NO. 12

October 1 to December 31, 1968

For

Picatinny Arsenal Project
Order No. A1-8-RF034-01-D1-GG

To

Commanding Officer
Picatinny Arsenal, Dover, N.J. 07801
Attn: Code SMUPA DL-2
Liquid Rocket Propulsion Laboratory

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT 3120465

January 1, 1969

NBS REPORT 9976

COMPATABILITY OF PROTECTIVE COATINGS, MATERIALS, AND LIQUID PROPELLANTS

By

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COMPATIBILITY OF PROTECTIVE COATINGS, MATERIALS, AND LIQUID PROPELLANTS

A. Objectives of Project

1. To investigate the effect of various coatings and materials for their ability to withstand the corrosive effects of hydrazine fuels and oxidizers, and for freedom from catalytic effect on the decomposition of fuels and oxidizers.

2. To develop procedures for applying coatings, disclosed as satisfactory under part (1), to the interior surfaces of rocket and missile fuel tanks of complex shape.

B. Summary of Progress in Preceding Quarter

1. Decomposition of MHF-3 fuel in contact with various materials

a. Decomposition rates due to various metals at 160°F

The activity of metals in contact with MHF-3 listed in Table 1 did not undergo significant changes. The units containing AM355 stainless steel and stainless Maraging steel were still giving considerably different rates for comparable units and a third unit for each had been set up. Electroless nickel from the alkaline bath gave a lower rate in a second unit after special pretreatment of the specimen but was still higher by a factor of 20 than the rate for standard electroless nickel. Heat-treated standard electroless nickel gave no increase in rate of fuel decomposition above that for a similar untreated deposit. The rate for Teflon coated Maraging steel decreased to about one-half its initial value indicating decreasing reactivity of the coating or its components with time.

2. Results of experiments on kinetics of fuel decomposition

a. Effect of porosity of coatings

The activity of the cadmium-plated Maraging steel containing synthetic pores and of the half-plated specimen decreased further, confirming the protective action of the cadmium. A Maraging steel specimen with one-half plated with electroless nickel was put under test.

b. Effect of ratio of metal area to fuel volume

No significant changes were observed for units for which the range of area to volume was from 0.5 to 6.8, having rates still in the normal range for nickel.

3. Decomposition of Aerozine-50 fuel at 160°F

The background rate for this fuel decreased by a factor of over 40 percent for the period. Two units, one containing Teflon coated 7075-T6 aluminum and one Maraging steel were disassembled and the fuel replaced to see if the high rate is confirmed with the new change of fuel.

4. Exposure of materials to oxidizers at 160°F

The pressure in units containing IRFNA increased sharply near the end of the quarter and they were disassembled and the oxidizer replaced. Slight increases in rate were shown by units containing NTO.

5. Examination of specimens and MHF-3 fuel after tests at 160°F

Both specimens examined were bare 18% Maraging steel. One had been exposed to fuel in a stainless steel bomb and one in a glass test unit. There was no apparent attack of the surface and negligible weight

loss but microscopic examination of the surface revealed coloration believed to be oxide.

Salts in the fuel were about three times greater for the fuel in the stainless steel bomb unit than for that in the glass unit, indicating pick up from the walls and fittings of the bomb.

C. Progress During Current Report Period

1. Decomposition of MHF-3 fuel in contact with various materials at 160°F

a. "Background" rate

The average rate of evolution of gas from MHF-3 fuel in blank (no specimen) mercury manometer test units Hg-2 and Hg-15 has decreased slightly from 0.0041 cm^3/day at the end of the preceding quarterly period to 0.0039 cm^3/day for the present period.

b. Effects of various metals

Table 1 and Figure 1 contain the cumulative results to the end of December 1968. The relative reactivity of the various specimens is as follows:

> Low activity: silver, cadmium, 50/50 lead-tin solder, electroless nickel (standard acid bath), zinc, tin-nickel alloy, tin, 347 stainless steel, tungsten, aluminum, lead, titanium alloys 6Al-4V and 3Al-11Cr-13V, and Teflon coated Maraging steel.
>
> Moderate activity: gold, nickel, stainless Maraging steel, electroless nickel (Prop. borohydride bath), and chromium.
>
> High activity: cobalt, 18% Maraging steel, molybdenum, iron, AM 355 stainless steel, electroless nickel (alkaline bath), Inco-718.

(1) Behavior of recent units

The units listed in Table 1 containing AM 355 stainless steel (Hg-44, Hg-54) and stainless Maraging steel (Hg-43, Hg-55) are still giving considerably different rates of reactivity for comparable units. The third unit for each type of steel, under test during the past quarter, gave no confirmation of the rates previously obtained. There is some indication that variation in the oxide film on the specimens may be responsible for different rates of fuel decomposition for the same type of steel.

(2) Oxidized metals

Three specimens were oxidized in air at a low temperature (about 300°C) for several hours until the clean metal surface had acquired a light straw-colored film. The metals were AM 355 stainless steel, electrolytic nickel and stainless Maraging steel. These specimens were set up in units Hg-74, 75, and 76, respectively. Although the units have been under test for too short a time to obtain confirmed results, initial indications are that the thermally oxidized surfaces of AM 355 stainless steel and nickel are considerably less reactive with MHF-3 than clean or chemically oxidized surfaces.

(3) Other new tests

Test units containing solid electroless nickel and solid electroplated cadmium are being set up at the request of Mr. Ng of Picatinny Arsenal. Four other test units containing phosphatized Maraging steel, Maraging steel oxidized in air, thin (0.0001") cadmium and electroless nickel plated on Maraging steel will soon be ready for test.

2. Results of experiments on the kinetics of fuel decomposition

a. Effect of the porosity of coatings

There was a further decrease in the rate of fuel decompos of the cadmium plated Maraging steel specimen with one-half of the Maraging steel surface exposed (Hg-51) and the cadmium plated Maraging steel specimen with "pores" drilled to expose the Maraging steel (Hg-63). This indicates continued excellent protection by the cadmium in electrical contact with the exposed areas of Maraging steel.

The specimen consisting of electroless nickel on Maraging steel with one-half of the Maraging steel surface exposed (Hg-71) gave a higher rate during its first period of testing than that for either Maraging steel or electroless nickel alone.

b. Effect of ratio of metal area to fuel volume

Continued observation of units listed in Table 3, for which there is a range of area to volume of 0.5 to 6.8, has shown no significant changes. The rate coefficients are still in the normal range for nickel, independent of the variation of the area to volume ratio.

During the current period, data have been obtained on the rate of fuel decomposition in a unit in which a large area of electroless nickel of the standard type is exposed to fuel (Unit No. 70, Table 3). The area to volume ratio in this unit is 6.0, in comparison with the ratio of 0.5 and 0.8 in units 4 and 12 which were tested early in the program. In spite of the large variation of A/V, the rate coefficient is nearly the same for the three units, namely, 0.0017, 0.0016,

and 0.0012 $cm^3/day/cm^2$, respectively. Thus, the independence between the rate coefficient and A/V is confirmed for another kind of metal.

3. Decomposition of Aerozine-50 fuel in contact with various materials at 160°F

Results of the exposure tests are given in Table 4. The background rate for this fuel in a test unit without a specimen has continued to decline from a previous value of 0.0087 cm^2/day to 0.0063. No new data are given for Maraging steel (Hg-59A) and Teflon coated aluminum (Hg-69A). Although the units were disassembled and reassembled with new fuel the fuel decomposition rates were still so high that reliable readings could not be obtained.

4. Exposure of various materials to oxidizers at 160°F

Results of the nine bomb-type test units are given in Table 5 and Figure 2. The two oxidizers used are NTO (nitrogen tetroxide inhibited with 0.6±0.2% of nitric oxide) and IRFNA (red fuming nitric acid inhibited with 0.7±0.1% of hydrogen fluoride).

During this period the units containing IRFNA again underwent a rapid increase in pressure 60 to 90 days after the oxidizer had previously been renewed. Renewal of only the inhibitor did not retard the reaction, probably because of the metal salts in solution. Apparently the inhibitor is gradually consumed at the 160°F test temperature and then attack on the walls and fittings of the bombs causes the sharp pressure rise and build up of salts in the oxidizer. Renewal of the complete oxidizer after cleaning the unit, including the fittings, restores the original rate of pressure rise. It is apparent that at the test

temperature of 160°F, inhibitor is consumed fairly rapidly and that after 60 to 90 days, severe attack of stainless steel occurs. Since the ratio of the area of the specimen to that of the stainless steel of the bomb is small, it becomes impossible to reliably evaluate the rate of gas formation due to contact of the oxidizer with the specimen. The latter effect is swamped by the much larger factor of attack on the bomb. At the end of some period, corrosion of the specimen can be evaluated, but even this might be affected significantly by presence in the oxidizer of salts derived from the bomb.

It thus appears that a different test method for evaluating IRFNA must be developed.

D. New Work

1. Tests of special metals

About a dozen modifications of, or coatings on, metals of special interest are being readied for test. Other metals and coatings will be set up for testing as requested.

2. Tests with oxidizers

The NBS Safety Office has furnished material containing directions and safety precautions for handling CTF (chlorine trifluoride) oxidizers and does not object to the use of small quantities in the laboratories. Tests using this oxidizer can start when the materials to be tested are decided upon and test units are available.

3. Examination of terminated units

Fuel and metals in units for which there is no need for further testing will be examined as necessary.

4. Coating fuel tanks

Two one-half scale fuel tanks have been modified in the NBS shops and are now being heat treated. They will be plated, one with electroless nickel and one with cadmium, when shop work has been completed.

TABLE 1

Summary of Test Data for Materials

Exposed to MHF-3 at 160°F

Test unit number	Specimen	Area of specimen cm^2	Time under test days	Gas evolved cm^3 *	Rate coefficient * $cm^3/day/cm^2$ previous	present	Calculated tank pressur after 1 year psig **
Hg-2	Background	--))av.	771	2.81	0.0041	0.0039	--
Hg-15	Background	--)					
Hg-12	Electroless nickel	22.2	696	15.1	0.00098	0.00098	10
Hg-14	347 Stainless steel^{a}	13.2	705	0	0.00004	Zero	Zero
Hg-16	Cadmium (thin)	9.4	678	7.9	0.001	0.0012	13
Hg-22	Silver (thin)	16.0	629	104.2	0.0089	0.0104	109
Hg-27	Cadmium (thin)	10.6	537	5.2	0.0010	0.0009	10
Hg-28	347 Stainless steel^{a}	6.5	533	7.1	0.0023	0.0020	21
Hg-29	Silver	14.5	534	1.8	0.0002	0.0002	2
Hg-30	Titanium^{a,b} (13V,11Cr.3Al)	15.0	364	0	Zero	Zero	Zero
Hg-31	Cadmium	14.7	522	0.6	0.00005	0.00008	1
Hg-32	Tin	13.0	524	23.6	0.0038	0.0035	37
Hg-33	Solder 50/50 lead-tin^{a}	15.3	522	Zero	Zero	Zero	Zero
Hg-39	Inco 718^{a}	12.0	390^{xx}	180.7	0.1001	0.1120	1183
Hg-43	Stainless Maraging steel^{a}	15.0	434	37.5	0.0060	0.0058	61
Hg-44	Stainless steel type AM 355^{a}	11.4	306^{xx}	133.9	0.0792	0.0883	932
Hg-45	Titanium alloy^{a} (6Al, 4V)	13.3	386	Zero	Zero	Zero	Zero
Hg-48	Aluminum^{a,c}	12.5	383	0.7	0.00022	0.00015	2

TABLE 1 (cont.)

Summary of Test Data for Materials

Exposed to MHF-3 at 160°F

Test unit number	Specimen	Area of specimen cm^2.	Time under test days	Gas evolved cm^3 [*]	Rate coefficient cm^3/day/cm^2 [*] previous	present	Calculated tank pressur after 1 year psig [**]
Hg-49	Electroless nickel (Alkaline bath)	12.6	369[xx]	152.4	0.236	0.228	2409
Hg-50	Chromium	17.0	390[xx]	91	0.0203	0.0199	210
Hg-52	Electroless nickel (Alkaline bath)	13.0	228[xx]	39.7	0.0303	0.0187	197
Hg-54	Stainless steel[a] AM 355	11.5	306[xx]	57.7	0.0198	0.0335	353
Hg-55	Stainless Maraging steel[a]	16.6	306[xx]	63.1	0.0203	0.0176	186
Hg-57	Nickel	14.0	313	21.8	0.0067	0.0050	53
Hg-58	Electroless nickel (Propri- (Proprietary borohydride)	14.2	298	83	0.0184	0.0196	207
Hg-61	Electroless nickel (Heated to 800°C)	12.2	229	3.1	0.0011	0.0011	12
Hg-68	Teflon (on Maraging steel)	14.2	198	11.4	0.0058	0.0041	43

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[*] Cumulative total, corrected for background rate and to 1 atm. pressure.

[**] Based on a tank in the form of a cube, 1 cu. ft. volume, 10% ullage.

[x] Discontinued

[xx] Total days under test are not equal to number of days during which gas was collect due to temporary leaks, or to interrupted collection due to high rate.

[a] These specimens are solid metal. All others are coatings on 18% Maraging steel.

[b] Titanium alloy, 13% V, 11% Cr, 3% Al. Similar to alloy B120VCA.

[c] Vapor-deposited foil from Commonwealth Scientific Corp.

TABLE 2

Data on Decomposition of MHF-3 Fuel at 160°F in Special Test Units

Effect of Porosity in Coatings of Cadmium on Maraging Steel

Test unit number	Description	Time under test days	Gas evolved cm^3	Rate coefficient[*] $cm^3/day/cm^2$ previous	present
Hg-51	Cadmium on Maraging steel with 1/2 of MS surface exposed - 8 cm^2	339	27.8	0.012	0.013
Hg-63	Cadmium on Maraging steel with 200 0.026" diam. pores. MS area 1.04 cm^2	218	6	0.03[**]	0.027
Hg-71	Electroless nickel on Maraging steel with 1/2 of MS surface exposed - 14 cm^2	13	55.6	0	0.355[x]

[*] Rate coefficient is calculated on basis of exposed Maraging steel only.

[**] Rate coefficient based on pore area: 1.04 cm^2.

[x] Highest rate for either Maraging steel or electroless nickel alone was 0.098.

TABLE 3

Effect of Variation of Ratio of Metal Area to Fuel Volume at 160°F

Test unit number	Description				$\frac{A}{V}$	Time under test	Gas evolved	Rate coefficient
	Coating or metal	Volume (V)		Metal Area (A)				
		Liquid cm^3	Vapor cm^3	cm^2	cm^{-1}	days	cm^3	$cm^3/day/cm^2$
Hg-46	Nickel[a]	27	15.7	100	3.7	129	737	0.057
Hg-65	ditto	16	18.7	100	6.8	53	317	0.0598
Hg-66	ditto	28	6.5	100	3.6	42	265	0.063
PA-26	ditto	32	3.2	16	0.5	283	343	0.054
347-Ni	ditto	45	42	82	1.8	456	1193	0.033
Hg-70	El nickel on Ni wire coil	18	6	108	6.0	62	11.2	0.0017
Hg-4	El nickel on MS	37	4.7	19.6	0.5	458	14.5	0.0016
Hg-12	El nickel on MS	29	5.9	22.2	0.8	696	15.1	0.0012

[a] Electroformed sheet.

TABLE 4

Test Data for Materials Exposed to Aerozine-50

at 160°F

Test unit number	Coating or metal	Area of speci-men cm^2	Time under test days	Gas evolved[*] cm^3	Rate coefficient[*] cm^3/day/cm^2 previous	present	Calculated tank press after 1 ye psig
Hg-53A	301 Stainless steel[a] (cryogenic form)	14.7	154	65.6	0.0257	0.0290	306
Hg-56A	None (Background)		276	1.73	0.0087	0.0063	--
Hg-59A	Maraging steel steel[a,b]	15.2	0.8	41.2	--	3.39	35,760
Hg-60A	Titanium[a]	14.5	278	Zero	Zero	Zero	Zero
Hg-62A	Teflon (TFE)[a]	17.5	278	0.1	0.00003	0.00002	Zero
Hg-69A	Teflon coated 7075-T6 Al[b]	14.2	0.33	9.4	--	2.01	21,170

[*] Cumulative total, corrected for background rate and to 1 atm. pressure.

[**] Based on a tank in the form of a cube, 1 cu. ft. volume, 10% ullage.

[a] These specimens are uncoated, solid material.

[b] Gas evolved too rapidly to obtain accurate reading this quarter.

TABLE 5

Results of Tests of Materials Exposed to Oxydizers at 160°F in Stainless Steel Bomb-Type Test Units

Bomb unit number	Specimen	Area of specimen cm^2	Time under test days	Gas evolved[*] cm^3	Rate[*] coefficient $cm^3/day/cm^2$		Calculated[**] tank pressur after 1 year psig
					previous	present	
			Inhibited red fuming nitric acid				
RFN-1	Teflon (TFE)	14.5	145	15.5	0.0189	0.0074[xx]	78
RFN-2	Stainless steel (301 Cryogenic form aged)	14.7	153	9.4	0.0135	0.0042	44
RFN-3	Maraging steel	13.6	158	Zero	Zero	Zero	Zero
RFN-4	Teflon on 6061-T6 Al	15.1	165	6.5	0.0012	0.0026	28
RFN-5	None (Background)	--	32	1.27	--	0.038	--
			Nitrogen tetroxide				
301-NTO[x]	Stainless steel (301 Cryogenic form un-aged)	338	210	Zero	Zero	Zero	Zero
NTO-1	None (Background)	--	115	5.8	--	0.0417	--
NTO-2	Teflon (TFE)	19.9	184	24.1	0.0120	0.0066	69
NTO-3	Stainless steel (301 Cryogenic form aged)	14.7	207	3.8	0.0028	0.0013	13
NTO-4	Maraging steel	13.6	180	2.4	0.0015	0.00099	10
NTO-5	Titanium (6Al, 4V)	13.4	77	1.0	0	0.00097	10

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[*] Cumulative total, corrected for background rate and to 1 atm. pressure.

[**] Based on a tank in the form of a cube, 1 cu. ft. volume, 10% ullage.

[x] Tested at 90°F.

[xx] These lower rates for IRFNA were obtained after a sharp pressure rise due to attack on the surface of the bomb by the oxidizer because of apparent depletion of the inhibitor at 160°F required replacement of the oxidizer and inhibitor as explainted in the text.

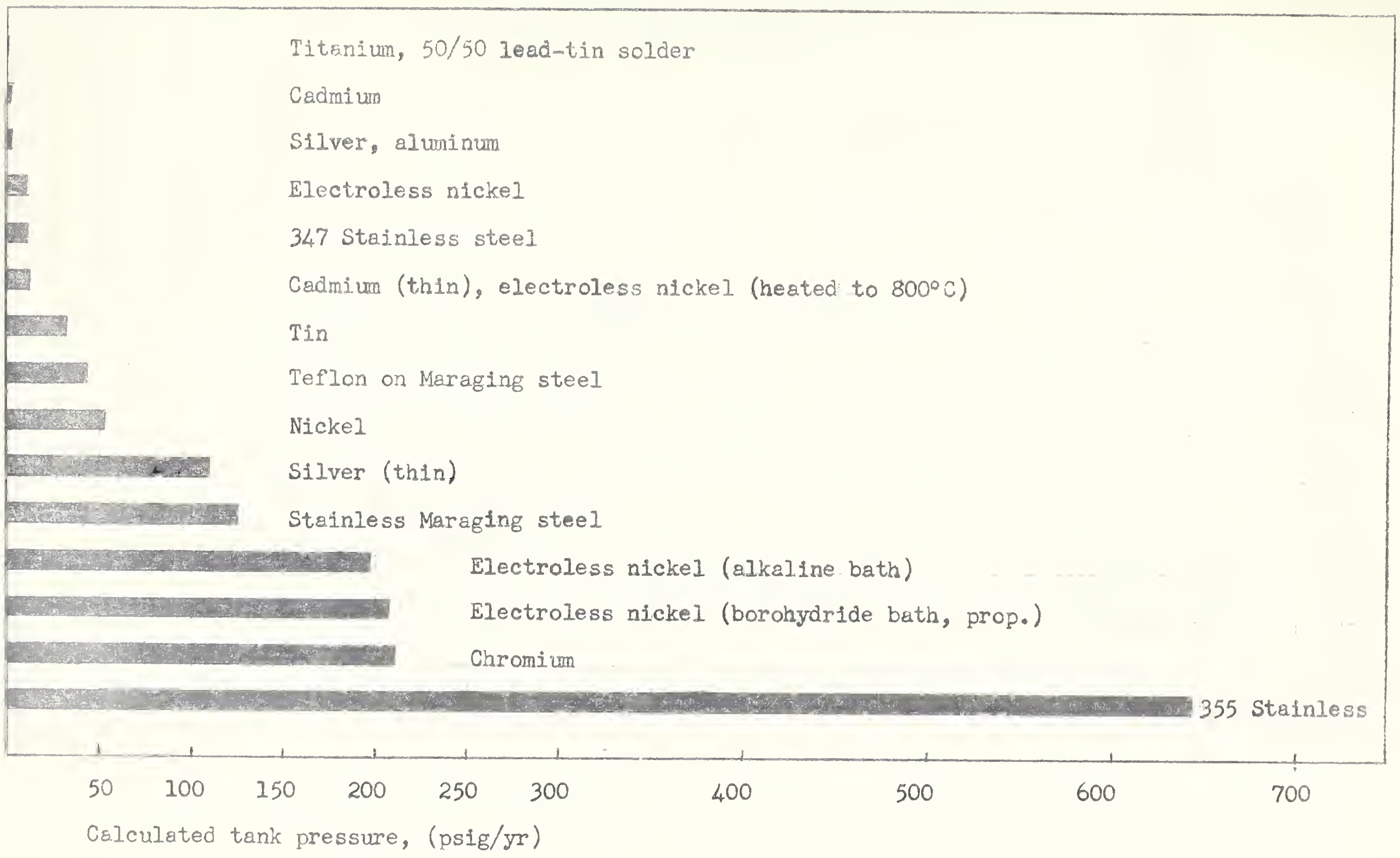

Figure 1

Rate of gas evolution from MHF-3 in contact with indicated metals and Teflon at 160°F.

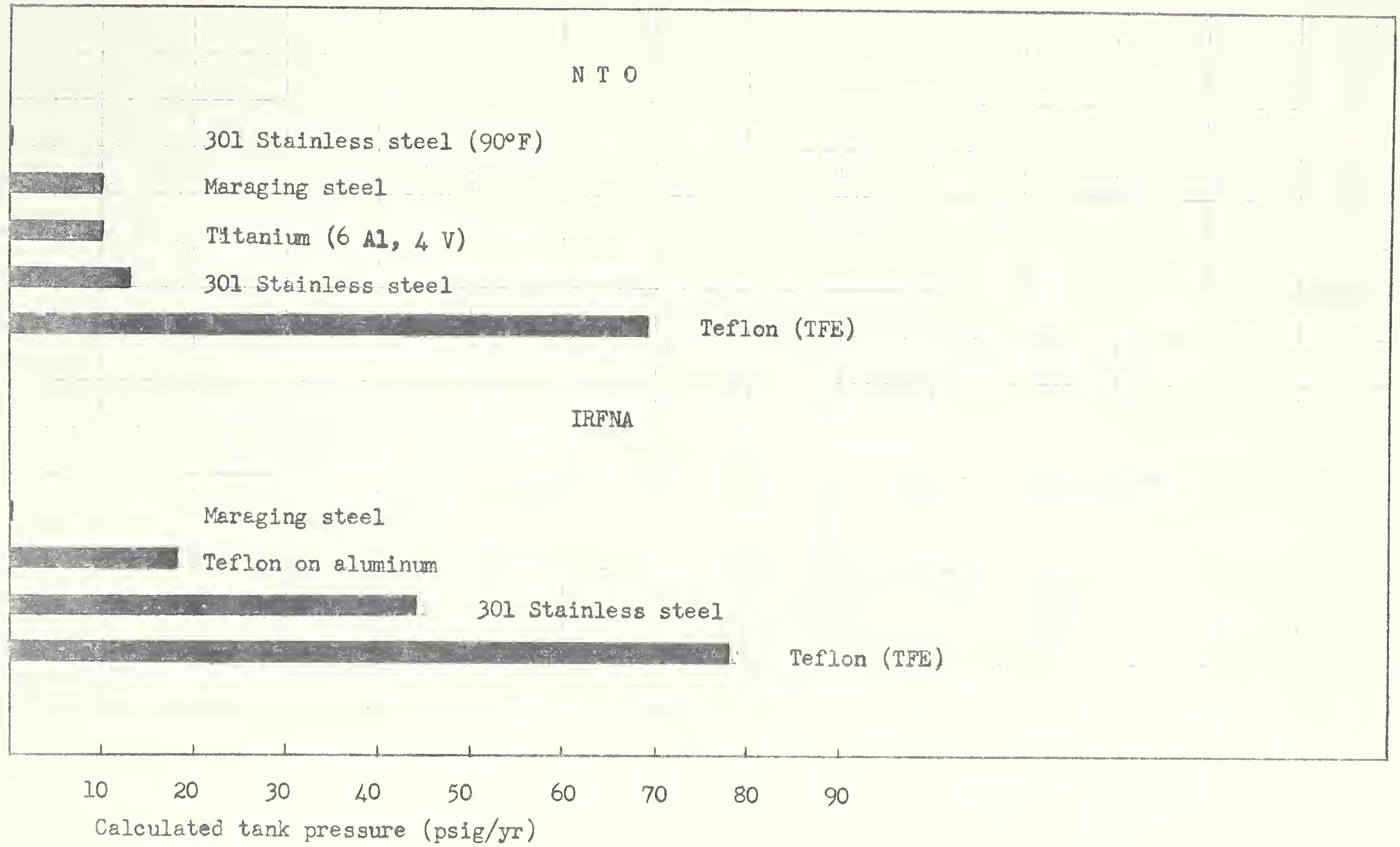

Figure 2

Cumulative gas evolution as indicated by pressure increase resulting from contact of above materials with NTO and IRFNA at 160°F.

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