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COMPATIBILITY AND HYPERGOLICITY STUDIES WITH HNP (U)

by

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for the
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ABSTRACT. Hydronitracidium perchlorate (HNP) is a potential candidate as an igniter material for JP-5 filled firebombs. Hypergolicity tests of HNP with JP-5 were attempted using pool-drop and spray-ignition methods. Neither was found to be suitable as an indicator of the reaction found in full-scale firebomb testing.

Compatibility studies were conducted of HNP with 14 materials from which firebomb igniters could be made. Teflon (TFE) and Kel-F were nonreactive. All metals tested were attacked to varying degrees. (UNCLASSIFIED)

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA * DECEMBER 1967

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M. R. Etheridge, Capt., USN ..... Commander
H. G. Wilson ..... Technical Director (Acting)

FOREWORD

This report is a facsimile of a contractor's report to this Center on the compatibility of hydronitracidium perchlorate with 14 materials of which firebomb igniters could b made, and on tests of methods by which the hypergolicity of HNP with firebomb fuels might be readily determined without the necessity of full-scale testing of fuel in use or proposed for use.

The investigation was performed by the Callery Chemical Company, Callery, Pa., during Fiscal Year 1967 under Contract No. N60503-12654. This contract is in support of the Firebomb Improvement Program, Warhead Supporting Research (Surface Targets) under the technical coordination of J. B. King, Firebomb Improvement Program manager. It was funded by Task Assignment A35-350-004/216-1/F008-08-06.

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SUMMARY

Compatibility studies of hydronitracidium perchlorate (HNP) were conducted on samples of 14 materials of construction under two sets of conditions: (1) accelerated storage at +165°F for 30 days; and (2) cyclic storage, from dry-ice temperature to +165°F, using a modified MIL-STD-304 procedure.

Teflon (TFE) and Kel-F were completely compatible with HNP under military storage conditions.

Stainless steel was slightly attacked, but still may be suitable as a container. Steel welds were not obviously affected, while other types of materials used for fabrication joints, silver solder, and brazing compound reacted grossly.

All types of aluminum were incompatible at elevated temperatures. However, anodized aluminum appeared to be compatible with HNP at ambient temperature for greater than 3 months.

The hydrocarbon-based polymer, polyvinylchloride, reacted with HNP at the onset of the storage tests.

Hypergolicity studies of HNP with JP-5 were attempted using pool-drop and spray-ignition tests. The spray-ignition tests were unsuccessful.

In pool-drop tests, the mixture of HNP (5 grams) with JP-5 (85 grams) was not hypergolic at 90°F. At 113°F an extremely hazardous mixture was obtained which exploded after 29.2 seconds.

As expected, ignition delays in the NP/JP-5 system were a function of surface area and treatment. Near-instantaneous ignition was obtained with nitronium perchlorate powder and JP-5 at 90°F. A short ignition delay of 0.05 second occurred with NP granules, and a delay of 0.48 second occurred with NP granules treated with 10-mole-percent water.

INTRODUCTION

Nitronium perchlorate, NO_2ClO_4, is well established as perhaps the most energetic solid oxidizer in existence. Its reactivity with fuels, and especially its tendency to ignite or detonate almost any hydrocarbon containing available electrons (e.g. olefins, amines, and ethers), is well-documented. For most applications this extreme reactivity--far from being an asset--has hampered widespread use of the chemical. However, at the same time this reactivity makes nitronium perchlorate (NP) ideal for use in incendiary applications.

As a pure compound, nitronium perchlorate has stability limits which fail to meet the military storage standards at 165°F. However, recent studies have shown that the stability of NP is increased by the addition of small quantities of water. Water hydrolyzes NP according to the equation:

$$NO_2ClO_4 + 2H_2O \longrightarrow HNO_3 + H_3OClO_4$$

The presence of hydronium perchlorate, H_3OClO_4, in the nitronium perchlorate prevents a catalytic decomposition of the bulk sample and thus imparts a dramatic increase in stability.

HNP, the material under test in this study, is a modification of water-stabilized NP. When treated mole-per-mole with water and the resulting HNO_3 removed, an equimolar mixture of NP and H_3OClO_4 results. This mixture forms a mixed-crystal system which, when originally observed, was thought to be a new compound called "hydronitracidium perchlorate," $[H_3NO_3(ClO_4)_2]$. Although the formulation is probably wrong, the name--and thus the designation HNP--is used for this NP-H_3OClO_4 crystal modification.

In laboratory tests, the properties of HNP were much the same as NP, but it has a much slower rate of decomposition. HNP was observed to be hypergolic with JP-5 when an excessive amount of the oxidizer was used and in tests in which the oxidizer was detonated into the fuel. Subsequent tests at the Naval Weapons Center, China Lake, Calif. confirmed its hypergolicity with gelled fuel.

As a result of these promising observations for its use as an igniter in incendiary applications, this program was initiated to obtain data on its compatibility with potential construction materials and a closer insight into its ignition characteristics. Because of the decreased reactivity of this material--heretofore unnoticed--some of

the projected hypergolicity tests could not be performed. This information is valuable in itself. In addition, NP in several forms was tested, although not originally proposed. Thus, comparable data were obtained which may be of use in the selection of a suitable igniter modification.

RESULTS AND DISCUSSION

COMPATIBILITY OF HNP WITH MATERIALS OF CONSTRUCTION

The compatibility of "hydronitracidium perchlorate" (HNP) with various materials of construction, under military storage conditions, was investigated. To provide significant storage data within a limited test-time, two procedures were followed: (1) accelerated storage at +165°F for 30 days; and (2) cyclic storage, from dry-ice temperature to +165°F, using a modified MIL-STD-304 procedure.

The bases for the selection of test samples were availability and suitability for igniter construction, using knowledge gained from experience with nitronium perchlorate. The materials tested were:

Aluminum 6063-T5	Kel-F
Aluminum 6061-Y6	Polyvinylchloride (PVC)
Aluminum 3003-H14	Stainless Steel 304
Aluminum Teflon (TFE), cased	Stainless Steel 304, brazed strip
Aluminum, anodized	Stainless Steel 304, silver solder
Aluminum Silicon, rod-weld	Stainless Steel 304, welded strip
Carbon Steel Teflon (TFE), cased	Stainless Steel 316
Carbon Steel Teflon (FEP-100), coated	Teflon (TFE)

Test sample sizes were approximately one-half inch wide, 6 inches long, and one-eighth inch thick. About half the sample was placed into the HNP, and the other half was exposed to vapor. A bend and scratch were placed at each end of the metal samples to induce stress points.

Prior to examination the specimens were washed in detergent and rinsed alternately with water, cleaning solution, water, methanol, chlorethene, and finally water; then oven-dried at 90°C. The cleaned specimens were then examined visually, weighed, and photographed.

The storage containers for the tests were Fischer-Porter 3-ounce aerosol compatibility tubes equipped with Ashcroft stainless-steel pressure gauges, and stainless-steel fittings and hoke valves. The various parts were degreased and cleaned in the same manner as the specimens.

The tubes were filled to a depth of 3 inches with HNP and the specimen inserted. The apparatus was assembled and leak-tested at 125 psig, with nitrogen. Tubes loaded with HNP without specimens served as standards, or control samples.

After the tests were terminated, the Fischer-Porter tubes were opened and placed in a large volume of water. The HNP dissolved and the specimens were removed, rinsed with water, and oven-dried at 90°C. The specimens were weighed, examined visually, and photographed.

Accelerated Storage Test

The procedure consisted of maintaining the test specimen in a cabinet held at 165°F for 30 days. The purpose of the accelerated test was to provide an indication of the effect of HNP on construction materials during long-term storage at ambient conditions.

The data logged were as follows:

1. At 0900 each morning, excluding weekends, recorded pressure of each tube.

2. Noted and recorded changes in the appearance of the HNP and test specimens.

3. Terminated the testing of any specimen, if the pressure in the tube exceeded 100 psig.

The recorded pressures and visual observations are summarized in Table 1.

TABLE 1. HNP Compatibility, Accelerated Storage Test at 165°F

SPECIMEN	Pressure (Psig) and Visual Observation of Tube Contents																													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
PVC	0 a	100 b																												
Carbon Steel Coated Teflon (FEP 100)	0 a	0 b	15	26	34	40	52	58	71	80	100																			
Aluminum 6063-T5	0 a	36 b	36	32	37	35	37	38	40	44	45[i]																			
Aluminum 3003-H14	0 a	19 b	55	77	90	91	93	96	100	100	103																			
Aluminum 6061-T6	0 a	55 b	75	86	92	95	97	101	103	107	107																			
Aluminum Welded with Silicon Rod	0 a	41 b	66	79	87	91	94	98	100	103	106																			
Aluminum Anodized	0 a	0 b	10	18	20	25	30	35	44	52	61	70	79	87	93	100														
Stainless Steel 304	0 a	0 b	0	<10	18	29	36	45	54 c	61	70 d	75	82	88	95	100														
Carbon Steel Cased in Teflon (TFE)	0 a	<10 b	10	22	28	34	38	44	48	52	60	63	68	72	75	78	78	82	89	90	93 f	95	98	100						
Stainless Steel 304, Braze Strip	0 a	0 c	0 e	0	0	0	0	0	0	60	65	68	70	74	76	80	82	85	87	87	92 f	94 g	95	100						
Aluminum Cased in Teflon (TFE)	0 a	0 b	<10	10	20	25	30	35	38	43	47	53	55	60	65	67	73	80	80	83	85	87	92	94	100					
Teflon (TFE)	0 a	0 b	8	9	20	27	30	34	38	42	45	50	55	57	60	65	68	72	76	78	80	83	85	87	90	100				
Stainless Steel 304, Silver Solder Strip	0 a	<10 b	<10	10	19	22	25	28	32	35	37	42	45	46	50	52	55	60	64	65	73	76	79	84	55	45	49	51	55	60
Stainless Steel 304, Welded Strip	0 a	0 b	7	21	30	34	42	49 c	55	63	68	75	80	85	90	95	90	87	85	85	85	82	83	70	73	75	75	75	75	74
Stainless Steel 316	0 a	0 b	7	20	28	32	40	47 c	54	62	68	75	80	85	90	55	60	62	70	71	50	45	48	51	60	67	71	60	60	65
Kel-F	0 a	0 b	6	17	22	29	32	36	36	40	45	45	50	55	63	63	65	67	69	71	73	74	75	80	90	92	95	95	97	102
HNP only	0 a	0 a	<10 a,b	10 a,b	8 b	15	18	20	20	24	26	30	35	35	38	42	43	45	45	50	55	55	55	55	55	55	55	55	55	55

Number designates the pressure (psig)
Letter - description of the contents of the Fisher Porter tube.

a - white solid
b - yellow slush
c - yellow and green color in HNP
d - brown green color in HNP
e - blue green color in HNP
f - brown gas
g - dark blue liquid
h - darker color of the specimen
i - Terminated fearing a leak had developed, and all other samples of aluminum had attained 100 psig.

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In general, visual observations of the conditions of the specimens in the Fischer-Porter tubes during the test were unsatisfactory. The attack on the specimens could not be seen due to the presence of the solid HNP. No noticeable attack was observed on the portion of the specimen in contact with the vapors during the tests nor after the specimen had been removed. Brown gas was observed in all of the tubes containing metal specimens after completion of the test, but in most cases the color was too faint to observe because of the dark background of the oven.

The control or standard--which contained HNP alone--developed higher pressures more rapidly in the Fischer-Porter system than previously observed in an all-glass system. A change in color of HNP from white to yellow, observed after a short storage period at +165°F, is also unusual with HNP in an all-glass system. These changes are indicative of a reaction of HNP with the Fischer-Porter system, perhaps more especially with the metal parts which contact the HNP vapors, and were taken into account when comparing test data.

Only 4 of the 16 specimens tested completed the 30-day accelerated test at +165°F. The others were terminated when the pressure reached 100 psig. The length of time each specimen was subjected to HNP at +165°F is illustrated in Fig. 1. The weight loss of the specimens, shown in Table 2, verified that reaction occurred with all materials tested, except Kel-F and Teflon (TFE). The results are summarized as follows.

Kel-F and Teflon (TFE) were not attacked by HNP throughout the duration of the test, no weight loss was found, and no changes in their appearance were observed. Photographs of Kel-F before (12C, Fig. 3) and after (12D, Fig. 3) the accelerated test show no changes in the specimens. The excessive pressure observed from contact of these materials with HNP is not readily explainable.

Stainless steel showed excellent resistance to attack although it was obviously not passive. The attack of stainless steel specimens by HNP was noticeable as a color change in the solid and an increase in pressure. The weight loss of the specimens verified the observations. The 316 stainless was more resistant to attack than 304. The weight loss of 316 stainless was 666 mg or 1.20 wt percent after 30 days, while the weight loss of 304 stainless was 592 mg or 1.27 wt percent after only 16 days. This difference in compatibility is even more striking when based on percent weight loss per day, 0.04 for 316 versus 0.08 for 304. It also indicates that other types of stainless steel might be even more resistant to attack by HNP.

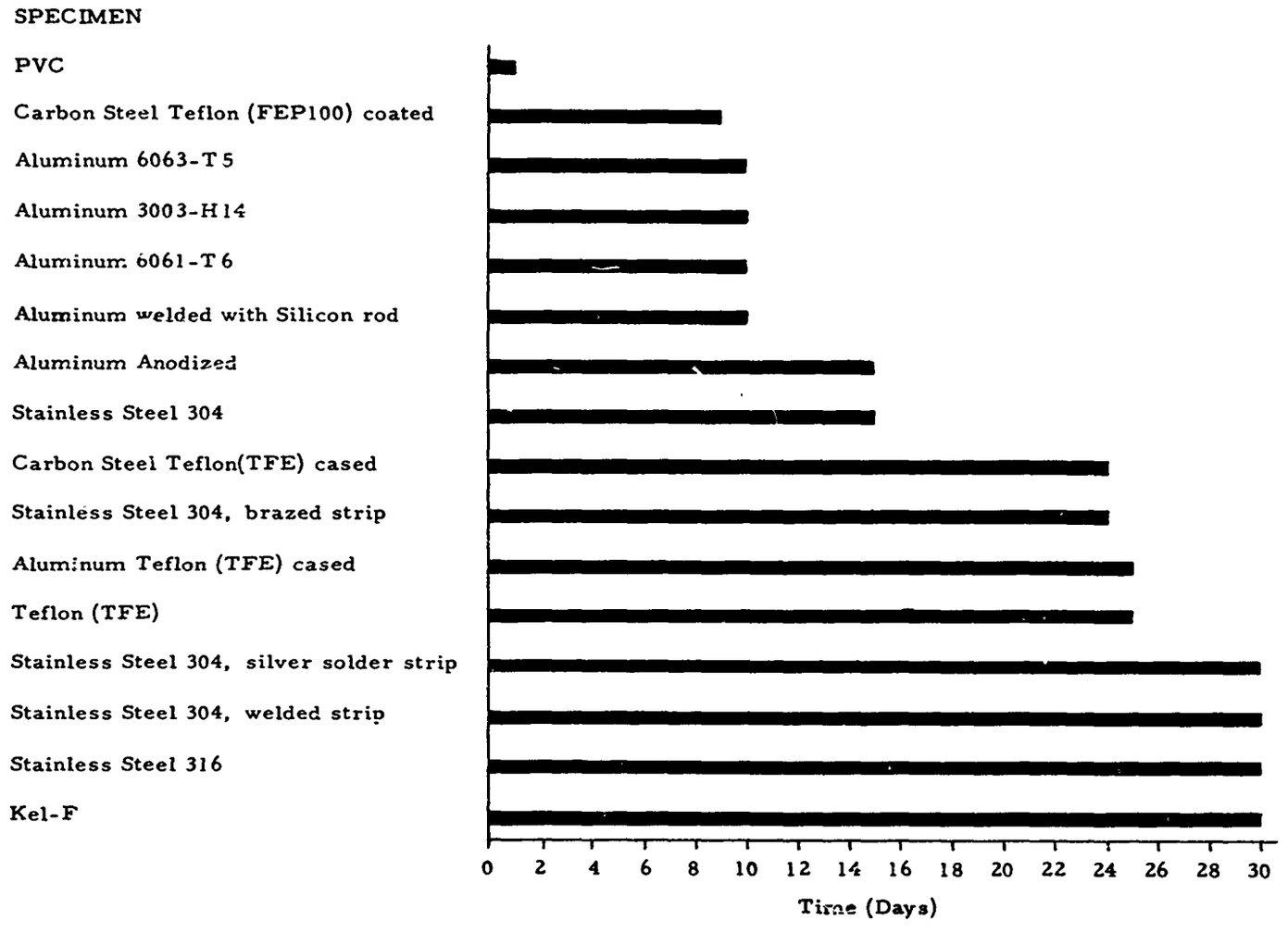

FIG. 1. Time Until Accelerated Test at 165°F Was Terminated.

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TABLE 2.

Specimen	Weight loss, mg	
	Accelerated	Cycle
Aluminum 6063-T5	677	758
Aluminum 3003-H14	507	718
Aluminum 6061-T6	683	654
Aluminum, welded with silicon rod	670	632
Aluminum, anodized	474	424
Aluminum Teflon (TFE), cased	0	0
Carbon Steel Teflon (TFE), cased	0	0
Carbon Steel Teflon (FEP 100), coated	Not valid[a]	Not valid[a]
Stainless Steel 304	592	589
Stainless Steel 316	666	358
Stainless Steel 304, welded strip	998	574
Stainless Steel 304, silver solder strip	1,323	876
Stainless Steel 304, brazed strip	1,341	1,077
Kel-F	0	0
Teflon (TFE)	0	0

[a]Coating failed and metal was attacked.

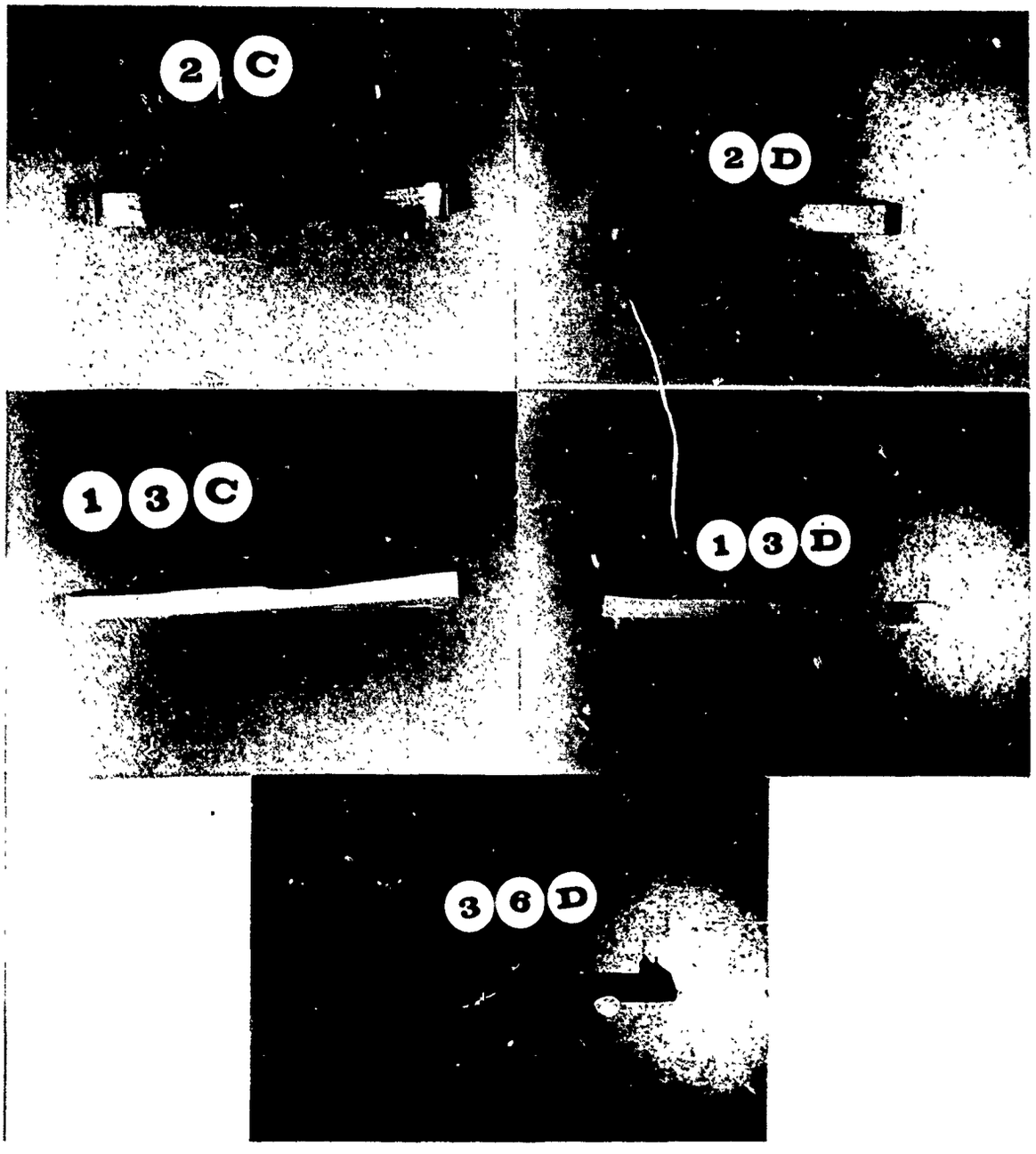

FIG. 2. Compatibility Tests With HNP.

The 304 Stainless with welded strips lasted the 30 days and had a weight loss of 998 mg or 2.22 wt percent. The great difference in pressure build-up in the tubes containing 316, 304, and 304 welded stainless--and therefore, the length of time each was subjected to the test--may be due to leaks developed in the tubes under the test conditions. The pressure increased in the container with the 304 specimen to the sixteenth day and the test was terminated. However, the pressure of the 316 and 304 welded stainless specimens dropped and did not approach the 100 psig limit. It is also possible that an error was made in identifying the specimen for the weld, and that the weld was made on 316 rather than 304 stainless. The weight loss of the specimen, however, appears to confirm that the weld was made on 304 stainless.

In all cases the stainless-steel specimens imparted a green color to the solids, indicative of a reaction with HNP to produce iron nitrates. After the completion of the tests, the specimens were examined and found to have a dull black appearance which remained even after they were thoroughly cleaned. Photographs before (2C, Fig. 2) and after (2D, Fig. 2) the test show this condition for the 304 specimens. The surfaces appeared to be just slightly rougher after the test than for the original specimens. The formation of the coating may, in effect, inhibit further reaction of HNP with the metal and account for some of the discrepancies of the pressures observed.

Silver solder and braze material reacted almost completely with HNP as shown by the photographs--silver solder (7C and 7D, Fig. 3), and braze material (9C and 9D, Fig. 3). The steel near the braze strip had a high lustre in contract to the dull surface of the other parts. However, no significance can be attached to the condition of this surface toward compatibility with HNP. The rapid color change of the HNP to blue-green in the presence of the braze strip specimen, as well as the low pressures observed at the beginning of the test, reflect reaction of the system. However, considering the pressures of the other specimens and the control sample, this abnormality may also be due to a malfunction of the gage. The reaction of these materials is further substantiated by the excessive weight loss of the specimens.

The aluminum specimens were all readily attacked by HNP. The pressure rose rapidly during the test and forced termination after only 11 days for the untreated metals and 16 days for anodized aluminum. The specimens were all badly pitted from contact with HNP as shown by photographs before (13C, Fig. 2), and after (13D, Fig. 2). The weight loss for anodized aluminum was 474 mg or 2.8 wt percent of the specimen after 16 days. For aluminum 6061-T6, the weight loss of 683 mg represents 5.0 wt percent of the original specimen.

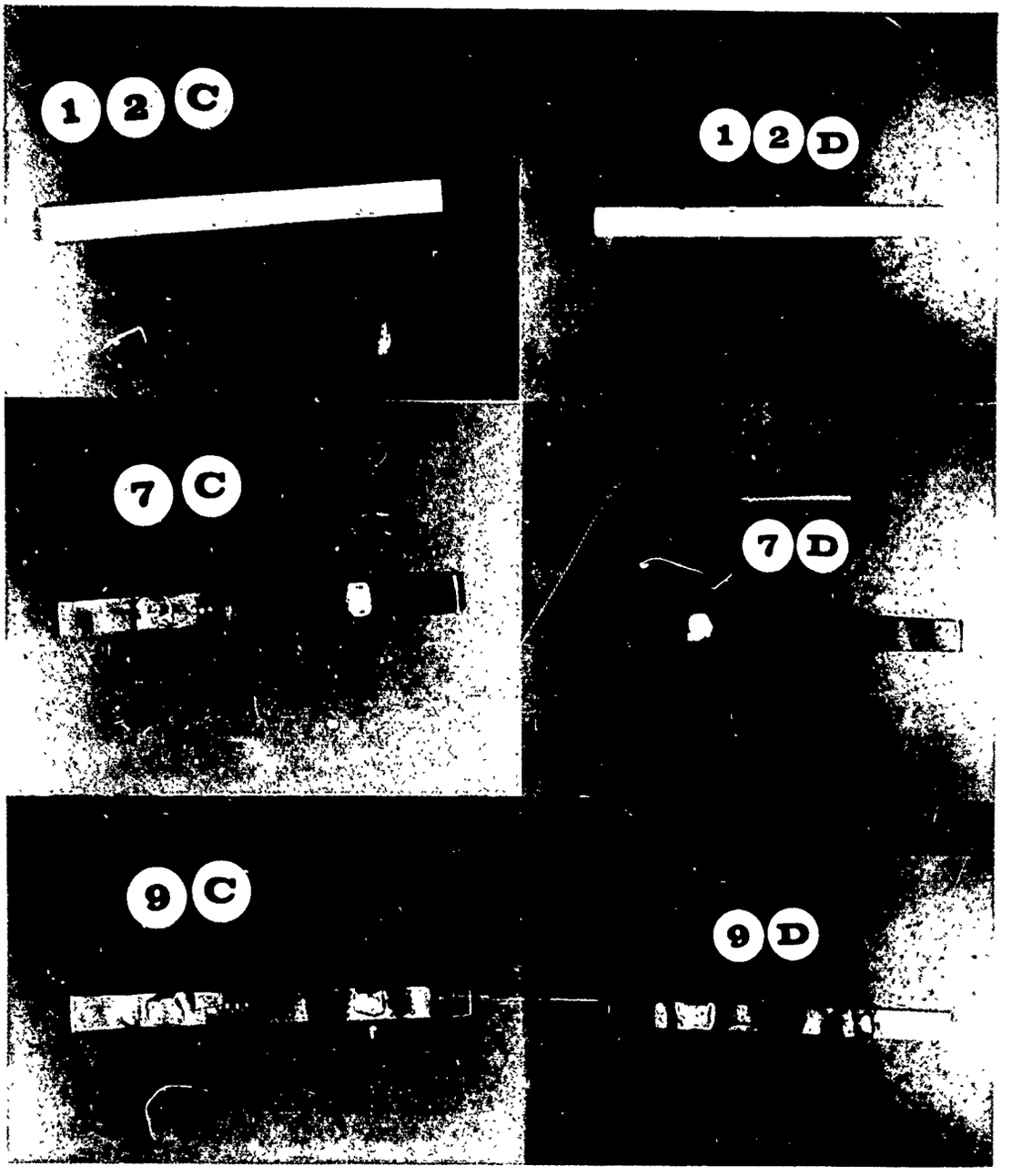

FIG. 3. Compatibility Tests With HNP.

An igniter made of anodized aluminum, welded at the base and soldered (aluminum) around the detonator chamber, was loaded with 0.5 pound of HNP for compatibility and stability tests. At ambient temperatures, 32 to 86°F, no pressure was observed during 15 days. The igniter, after 21 days at +165°F, reached 110 psig at which point the test was terminated. The igniter was cut open and found to be badly pitted at the bottom around the weld and on the sides where contact was made with HNP, similar to the results obtained with the Fischer-Porter system.

The Teflon (FEP-100) coating on carbon steel failed and the steel was attacked. The coating along the edge of the specimen separated and the sides peeled from the steel (photograph 36D, Fig. 2). The bared carbon steel had the reddish appearance of iron oxide. The test was terminated after 11 days due to the high pressure. Carbon steel, therefore, appears to have about the same resistance to HNP as aluminum.

Polyvinylchloride was extremely unsuitable. Reaction appeared to take place at the onset of the test. Pressure exceeded the limit of 100 psig after 24 hours and the test was terminated without further evaluation.

JAN Cyclic Storage Tests

The cyclic testing procedure was a modification of the test procedure outlined in Section 5, MIL-STD-304, Military Standard-Temperature and Humidity Test for use in Development of Fuzes, dated 6 July 1951. The following changes were made:

1. The temperature range was -62°F (dry-ice temperature) to +165°F instead of -65 to +165°F.

2. No control on the relative humidity in the cabinet was necessary since sealed storage containers were used.

The test procedure used is described below.

1. First Week

Monday:

(a) Store sample at dry-ice temperature for 2 hours (1400-1600 hours).

(b) At 1600 hours place samples in 165°F cabinet.

Tuesday:

(a) Remove from 165°F cabinet at 0800 and allow to set at room temperature.

(b) Store in dry ice at 1400.

(c) Remove at 1600 and place in 165°F cabinet.

Wednesday, Thursday and Friday:

(a) Repeat the operations carried out on Tuesday. On Friday evening, place the samples in the 165°F cabinet and maintain this condition until 0800 on the following Monday.

2. Second Week

(a) After 0800 Monday, the sequence of operations described above for Tuesday of the first week was carried out and repeated daily until Friday of the second week.

(b) Samples stored in dry ice at 1400 and this condition maintained until 0800 Monday of the third week.

Comments:

(a) The sequence of temperature conditions described above constitutes one JAN temperature cycle. Two such cycles were applied in testing compatibility of HNP with materials of construction.

(b) The second cycle was completed on Monday of the fifth week at 0800, at which time the samples were allowed to return to ambient temperature. The Fischer-Porter tubes were then disassembled and the specimens examined.

The following data were logged.

1. Pressures and temperatures of the tubes were recorded at 0800 starting on Tuesday of the first week and every morning thereafter, excluding weekends, for the entire cycle.

2. Any changes in appearance of the HNP and test specimens were recorded.

3. The testing of any specimen was terminated if the pressure in the tube exceeded 100 pounds.

After the tests were terminated, the Fischer-Porter tubes were handled in the same manner as the accelerated tests. The data obtained from the tests are presented in Table 3.

In the JAN cycle test, as in the accelerated test, a change in color of the control sample was observed. However, excessive pressure did not develop in the control sample during this test.

All of the test specimens, with the exception of polyvinylchloride (PVC), completed two JAN cycles in the presence of HNP. The test with PVC was terminated after 24 hours due to obvious reactions with HNP and pressure exceeding 100 psig. A summary of the results follows.

Kel-F and Teflon (TFE) were not attacked by HNP during this test. The increase in pressure was not as rapid as in the accelerated test, as might be expected. However, the same trend is present during the 2-day heating period of the cycle.

Stainless steel specimens again showed excellent resistance to attack. As in the accelerated test, a color change occurred in the solid HNP. A difference in color from that observed during the accelerated test is probably due to changes of state of the products, since the containers were observed at lower temperatures. The loss of weight of the specimens were 358 mg or 0.75 wt percent for 316 stainless, and 589 mg or 1.11 wt percent for 304 stainless steel. The weight loss is 53 percent of the loss that occurred during the accelerated test. Again, 316 stainless was more resistant to attack than 304 stainless. The weight loss and the pressure developed is consistent with the results obtained in the accelerated test. The loss in weight of the specimen containing the welded strip is comparable to 304 stainless rather than 316 stainless steel.

Silver solder and braze material reacted almost completely with HNP during the JAN cycle test. Pressure developed in the tube with the braze material as early as with other specimens, which supports the assumption that a malfunction of the gage occurred during the accelerated test. Upon completion of the test, the specimens were similar in appearance to those of the accelerated test and also had an excessive loss in weight.

The aluminum specimens were all badly pitted from contact with HNP. However, the pressure was not indicative of the gross reaction that occurred. The weight loss that occurred from the JAN cycle test was as great as--and in some cases greater than--the accelerated test. This result is assumed to be due to the longer contact time of the specimens with HNP.

TABLE 3. HNP Compatibility, JAN Cycle Test, -62 to +165°F

SPECIMEN	1st Cycle																													
	Wed		Thur		Fri		Sat		Sun		Mon		Tue		Wed		Thur		Fri		Sat		Sun		Mon		Tue		Wed	
	0800	1600	0800	1600	0800	1600	0800 oven +165°F		0800 oven +165°F		0800	1600	0800	1600	0800	1600	0800	1600	0800	1600	0800 -62°F ICC		0800	1600	0800	1600	0800	1600	0800	1600
PVC	0 a	0 a		34 b	>100																									
Carbon Steel Coated Teflon (FEP 100)	0	0	0	0	0	0	10		15		21	13	25	13	26	17	35	20	40	23	23		23		23	23	48	28	49	32
Aluminum 6063-T5	-----		-----		-----		-----		-----		-----		0* a		63 b		77		86		0		0		0		50		56	
Aluminum 3003-H14	-----		-----		-----		-----		-----		-----		0* a		31 b		59		69		0		0		0		48		53	
Aluminum 6061-T6	-----		-----		-----		-----		-----		-----		0* a		35 b		58		70		0		0		0		30		41	
Aluminum Welded With Silicon Rod	-----		-----		-----		-----		-----		-----		0* a		37 b		55 c		68		20		15		18		68		75	
Aluminum Anodized	0 a	0	0 a,b	0	0 b	0	0		8		11 b,d	0	15	0	16	5	18	7	25	8	8		8		10	10	30	14	33	15
Stainless Steel 304	0 a	0	0 a,b	0	0 b,d	0	7		15		18 d,e	13	24 c,d,e	13	26	14	30	16	40	17	17		17		18	18	47	24	50	28
Carbon Steel Cased in Teflon (TFE)	0 a	0	0 a,b	0	0 b	0	5		12		17	0	20	6	21	7	24	9	28	12	12		12		12	12	33	15	34	17
Stainless Steel 304 Braze Strip	0 a	0	0 a,b	0	0 e	0	13		25		33	16	35	16	37	17	41	20	44	19	19		19		19	19	50	25	50	25
Aluminum Cased in Teflon(TFE)	0 a	0	0 a,b	0	0 b	0	0		10		12	0	15	0	17	0	19	0	24	5	5		5		5	5	26	9	28	10
Teflon (TFE)	0 a	0	0 a,b	0	0 b	0	0		10		15	0	20	6	22	9	24	11	31	16	16		16		16	16	40	20	41	22
Stainless Steel 304, Silver Solder Strip	0 a	0	0 a,b	0	0 b	0	0		8		10 b,d,e	0	14	0	15	0	17	6	23	7	7		7		7	7	25	8	26	10
Stainless Steel 304 Welded Strip	0 a	0	0 a,b	0	0 b	0	2		11		17	7	24 c,d,e	9	25	10	31	14	41	18	18		18		18	18	50	26	52	30
Stainless Steel 316	0 a	0	0 a,b	0	0 b	0	3		13		14 d,e	0	18 c,d,e	6	19	9	23	11	29	13	13		13		13	13	37	19	40	21
Kel-F	0	0	0 a,b	0	0 b	0	5		15		20	11	23	11	25	14	28	16	36	20	20		20		20	20	43	24	44	25
HNP only	0 a	0	0 a,b	0	0 b	0	0		9		12		0		0	0	7	0	11	0	0		0		0	0	7	0	0	0

Number designates pressure (psig)
Letter - description of the contents of the Fisher Porter Tube.

0800 Time sample was removed from the oven
1600 Time sample was removed from dry ice

* Cycle started
a white solids
b yellow color
c orange pink color
d blackened metal
e green color
f blue green color

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TABLE 3. (Continued)

SPECIMEN	2nd Cycle																																					
	Thur		Fri		Sat		Sun		Mon		Tue		Wed		Thur		Fri		Sat		Sun		Mon		Tue		Wed		Thur	Fri	Sat	Sun	Mon
	0800	1600	0800	1600	0800	oven +165°F	0800	oven +165°F	0800	1600	0800	1600	0800	1600	0800	1600	0800	1600	0800	ICC -62°F	0800	ICC -62°F	0800	1600	0800	1600	0800	1600	0800	0800	0800	0800	0800
PVC																																						
Carbon Steel Coated Teflon (FEP 100)	54	34	56	34	65		70		75	35	--	29	47	30	47	32	47	30	-----		-----		30	29	42	29	40	--					
Aluminum 6063-T5	59		61		63		65		67	+	69		73		75		76		-----		-----		22		55		57		62	66	67	71	73
Aluminum 3003-H14	27		28		28		30		33	+	35		40		41		37		-----		-----		5		25		25		27	28	30	35	43
Aluminum 6061-T6	22		24		25		28		30	+	32		38		54		52		-----		-----		0		20		21		22	24	30	38	33
Aluminum Welded With Silicon Rod	50		51		54		56		58	+	60		64		90		93		-----		-----		25		45		47		50	67	84	87	90
Aluminum Anodized	37	18	42	19	48		58		64	34	--	27	57	30	59	21	60	35	-----		-----		35	25	52	26	54	--					
Stainless Steel 304	56	30	60	29	67		75		83	43	--	47	85	48	82	49	83	60	-----		-----		60	49	86	49	82	--					
Carbon Steel Cased in Teflon (TFE)	27	18	39	18	45		49		52	26	--	27	53	29	50	30	50	33	-----		-----		33	29	49	29	50	--					
Stainless Steel 304 Brazed Strip	52	28	54	29	60		65		65	34	--	38	68	35	65	36	66	47	-----		-----		47	37	65	37	65	--					
Aluminum Cased in Teflon (TFE)	32	12	33	12	36		40		45	20	--	19	45	22	44	23	44	25	-----		-----		25	22	43	23	42	--					
Teflon (TFE)	42	25	45	25	52		57		62	34	--	36	58	38	57	38	57	42	-----		-----		42	38	55	39	55	--					
Stainless Steel 304 Silver Solder Strip	28	11	29	11	35		35		37	17	--	19	40	21	40	23	41	26	-----		-----		26	22	40	23	40	--					
Stainless Steel 304 Welded Strip	59	30	63	27	60		70		76	19	--	12	35	15	34	16	35	22	-----		-----		22	16	35	18	35	--					
Stainless Steel 316	45	24	49	25	60		62		70	38	--	42	70	44	69	44	70	52	-----		-----		52	45	69	45	70	--					
Kel-F	45	23	42	17	40		45		50	14	--	14	27	16	27	17	28	18	-----		-----		18	17	27	18	28	--					
HNP only	0	0	0	0	6		10		15	0	--	0	0	0	0	0	0	0	-----		-----		0	0	0	0	0	--					

+ End of the first cycle

0800 Time sample was removed from the oven

1600 Time sample was removed from dry ice

The Teflon (FEP-100) coating remained on the carbon steel throughout the test, but was badly perforated. The steel had the reddish appearance of iron oxide, indicative of reaction with HNP.

Conclusions

As expected, Teflon and Kel-F were completely resistant to attack by HNP. Stainless steel, although obviously affected, showed very little weight loss. Type 316 stainless steel was more resistant than type 304, which indicates that a further study of the various stainless steels may reveal a more resistant type. Aluminum, carbon steel, PVC, and Teflon-coated (vapor-deposited) samples all appear unsuitable for HNP service.

HYPERGOLICITY STUDIES

The hypergolicity characteristics of HNP with JP-5 at temperatures up to +127°F were obtained. Although not requested in the Purchase Order, similar data were also obtained for nitronium perchlorate powder, granules, and granules containing 10-mole-percent water for comparison with HNP.

In general, the hypergolicity of JP-5 and HNP was considerably less than expected. The projected program called for hypergolicity studies with the JP-5 temperatures of 0, 45 and 90°F in the following tests:

1. Pool-drop tests, in which HNP was projected into a small pool of JP-5.

2. Spray-injection tests, in which HNP was injected into a spray of JP-5 to simulate field conditions.

The pool-drop test results showed that HNP did not ignite JP-5 at temperatures of 90°F or below. Therefore, failure of the spray-injection tests to ignite at these temperatures was not surprising. In addition, pool-drop tests were thus limited to temperatures higher than those proposed for the study.

The original scope of the program was broadened somewhat to include the more reactive nitronium perchlorate (NP). Results of these tests, gathered only on the pool-drop apparatus, showed that the reactivity of NP with JP-5 is essentially a function of the concentration of surface nitronium (NO_2^+) ions.

Pool-Drop Tests

Pool-drop tests were conducted in a test cell which provided 0.25-inch steel plate as protection for the operator. The HNP was weighed and loaded--in a dry, inert atmosphere--into a 0.5-inch OD stainless steel tube. One end of the tube was sealed with aluminum foil. The other end was attached to a solenoid valve in the test assembly. Discharge of the HNP was controlled remotely by ejecting dry nitrogen pressure through the solenoid valve and rupturing the foil seal.

The JP-5 was weighed, placed in a glass container and floated on a water bath beneath the HNP tube. The fuel temperature was controlled by circulating the water through an external heat exchanger. The JP-5 was protected, by a cover, from accidental ejection of the HNP until immediately before the test.

A 16-mm camera, placed in a protected area, recorded the experiments at 64 frames/second. Ignition delays were obtained from the film and are given in Table 4. The film is submitted as part of the final report.

TABLE 4. Summary of Pool-Drop Hypergolicity Tests

Oxidizer	JP-5		Ignition delay	Comments
	Quantity, gm	Temp, °F		
HNP (5 grams)	85	90	---	No ignition
HNP (5 grams)	85	90	---	No ignition
HNP (5 grams)	85	90	---	No ignition
HNP (5 grams)	85	113	29.2 sec	Explosion, no flame
HNP (5 grams)	85	128	15 sec	Ignition, then explosion
HNP (20 grams)	8	90	Instantaneous	---
NP Powder (5 grams)	85	90	Instantaneous	---
NP Granules (5 grams)	85	90	0.05 sec	---
NP (+10 mole % water) (5 grams)	85	90	0.58 sec	---

Our projected program was to test the hypergolicity of HNP (5 grams) with JP-5 (85 grams) at 0, 45, and 90°F. Tests at 90°F, however, were run three times without ignition. A slow reaction resulting in a black, gummy residue was the extent of combustion. These results negated the projected tests at the lower temperatures.

Tests were made at higher temperatures to establish an area where the two would form a hypergolic mixture. At 113°F, the mixture of HNP (5 grams) and JP-5 (85 grams) exploded after 29.2 seconds without evidence of a flame. At 128°F, JP-5 ignited in approximately 15 seconds after the addition of HNP, then exploded. These explosions produced a substantial shock wave, but the JP-5 which splashed onto the surrounding areas burned only when a flame had originated prior to the explosion.

Increasing the oxidizer-to-fuel ratio gave more favorable results. HNP (20 grams) and JP-5 (8 grams), at about 90°F, ignited almost instantaneously.

Because of the lack of ignition of JP-5 with HNP at the lower temperatures, the hypergolicity of NP and water-treated NP was investigated using the same conditions. Pool-drop tests of NP powder, NP granules, and NP granules treated with 10-mole-percent water (5 grams each) with JP-5 (85 grams) at 90°F gave dramatic results. Spontaneous ignition occurred with NP powder; an ignition-time delay of 0.05 seconds occurred with NP granules; and an ignition-time delay of 0.48 seconds was obtained with NP granules treated with 10-mole-percent water.

Spray-Injection Tests

The injection of HNP into a JP-5 fuel spray was also conducted remotely in a metal cell, with one end removed to accommodate the spray. A schematic of the equipment is presented in Fig. 4. The JP-5 was heated in the fuel reservoir and delivered through a spraco monofan nozzle adjusted to deliver droplets of 420 to 840 microns. A spray of 10-12 feet in length was produced by a nitrogen pressure of approximately 50 pounds.

The HNP was loaded as described for the pool-drop tests and ejected into the length of the fuel pattern by nitrogen pressure. A wire pattern over the end of the HNP gun served to break up the HNP. The HNP particle size, however, was presumably still rather large when compared to NP powder.

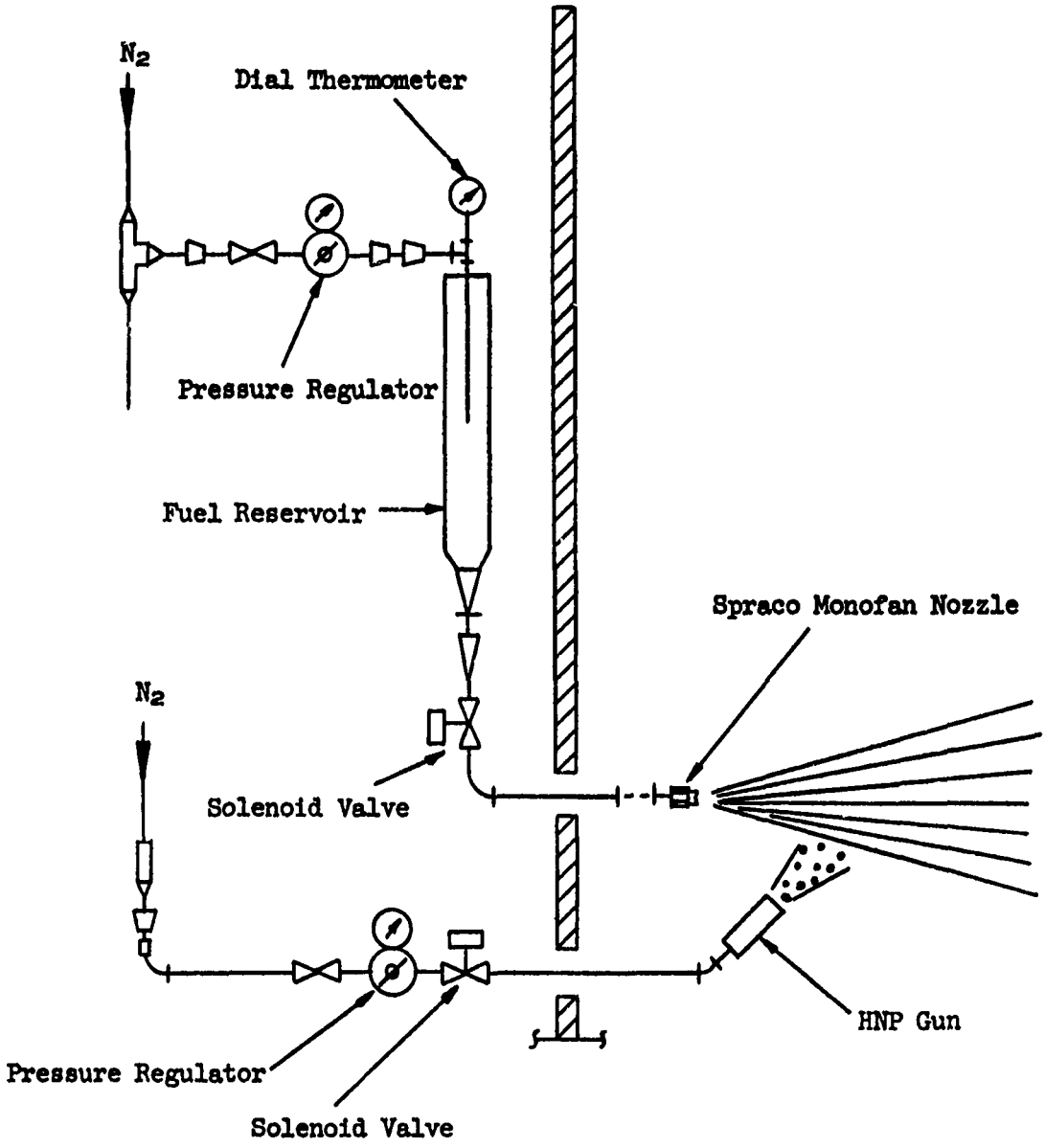

FIG. 4. Schematic of JP-5 Fuel-Spray Ignition Facility.

The tests were run by first activating the spray, and then ejecting the HNP into the fuel pattern. At fuel temperatures of 90°F, some smoke was observed, indicating that ignition may have been achieved either at higher fuel temperatures or longer contact time. Because of the negative pool-drop tests at the lower temperatures, no tests at the lower temperatures seemed advisable.

Conclusions

The results of the pool-drop tests summarized in Table 4 show a definite increase in hypergolicity with increasing NO_2^+ ion surface exposure. Decreasing the surface area of NP by granulation, or hydrolyzing a portion of the surface NO_2^+ (as noted with 10-mole-percent water) and ultimately further hydrolysis to HNP, dramatically increases the ignition delay under identical conditions, until ignition no longer occurs. It is obvious also that the oxidizer-to-fuel ratio affects the hypergolicity. This is undoubtedly related through reaction heat and ignition temperature of the fuel. Although slow to react, HNP, if present in sufficient quantity will ultimately raise the temperature of JP-5 to cause ignition.

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13. ABSTRACT

Hydronitracidium perchlorate (HNP) is a potential candidate as an igniter material for JP-5 filled firebombs. Hypergolicity tests of HNP with JP-5 were attempted using pool-drop and spray-ignition methods. Neither was found to be suitable as an indicator of the reaction found in full-scale firebomb testing.

Compatibility studies were conducted of HNP with 14 materials from which firebomb igniters could be made. Teflon (TFE) and Kel-F were nonreactive. All metals tested were attacked to varying degrees. (UNCLASSIFIED)

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Compatibility and Hypergolicity Studies With HNP (U), by M. D. Marshall (Callery Chemical Company). China Lake, Calif., NWC, December 1967. 20 pp. (NWC TP 4468), CONFIDENTIAL.

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