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NRL Report 6157

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An Evaluation of Certain Materials and Techniques for Handling Accidentally Released Chlorine Trifluoride Mixed Hydrazines Propellant

H. E. Moran, Jr., J. C. Burnett, and E. I. Smith, Jr.

Engineering Research Branch
Mechanics Division

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ABSTRACT

Damage control procedures for spills of high energy missile propellants, especially CTF (chlorine trifluoride), have been examined. The usefulness of some shipboard firefighting equipment and protective clothing now available was evaluated, and some new methods and materials for handling spilled propellants are proposed.

Powdered inorganic fluorides may be used as absorbents to prevent spreading of pools of liquid CTF and to facilitate removal of the CTF for disposal. None of the fluorides tested showed any tendency to form compounds with CTF and thus lower the vapor pressure of CTF in a closed container. Water spray from the Navy L-11 fog head, as well as finer sprays, is effective in dissipating CTF by controlled chemical reaction. Sodium and potassium bicarbonate based dry chemical powder fire extinguishants produced enough heat of reaction that their principal effect was to cause rapid vaporization of pools of CTF.

Materials now used in making propellant handlers' protective clothing as well as other damage control gear were found to be readily ignited by contact with liquid or gaseous CTF. Samples of two varieties of fabric formed from highly fluorinated polymers showed promise for making coveralls which could give reasonable protection from gaseous CTF and splashes of liquid CTF. MHF (mixed hydrazines) fuel fires were found to be comparable to gasoline fires in ease of extinguishment with dry chemical extinguishing powder. Protein base mechanical foam also was effective in extinguishing burning MHF fuel, but there was greater breakdown of the foam bubbles than occurs with similar foam in contact with gasoline.

PROBLEM STATUS

This is a final report on one phase of the problem; work on the problem is continuing.

AUTHORIZATION

NRL problems CO5-19 and CO8-28
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CHAPTER 1

BACKGROUND

A liquid propellant system for prepackaged, storable missiles has been proposed, using chlorine trifluoride (CTF), or chlorine trifluoride mixed with bromine pentafluoride (BPF) as the oxidizer, and mixtures of hydrazine, monomethyl hydrazine (MMH), and unsymmetrical dimethylhydrazine (UDMH) as the fuel. (Various combinations of the fuel components are generally known as the mixed hydrazines or MHF series.) A propellant system using these oxidizers and fuels is expected to give significantly better performance than the currently used propellants such as nitric acid-amine or nitrogen tetroxide-amine. The exact proportions of the various components, i.e., whether CTF will be used alone or in admixture with BPF and the ratios of the various hydrazines in the fuel, is undecided until engineering tests on the missile motors are completed. However, the behavior of the two oxidizers and the three hydrazines is so much alike that tests made for damage control information can be applied equally well to any combination. Due to the very reactive nature of these components, especially the CTF and BPF, any shipboard handling mishap resulting in leakage or spillage will present unique damage control problems. The hydrazines are much more toxic and are more easily ignited than hydrocarbon fuels. They are, however, completely miscible with water and they may be rendered nonflammable by dilution. Burning hydrazines may be extinguished with large amounts of water and by most of the agents commonly used on hydrocarbon fires. Chlorine trifluoride and bromine pentafluoride cause spontaneous ignition and vigorous or explosive burning of all ordinary combustibles as well as many other materials, including water, which are usually considered as being noncombustibles. The work reported here was undertaken to show what parts of established damage control methods and equipment are suitable for use when interhalogen-hydrazine propellants are accidentally spilled, those which are not suitable, and additional procedures and materials which can be used.

Hydrazine and its derivatives have been used industrially for several years; they also have been studied in connection with other propellant systems. Hence, methods of handling mixed hydrazines fuel spills and fires have been fairly well established. Aside from the problems of high toxicity and ease of ignition, especially through the action of catalysts such as rust, hydrazine fuel spills and fires can be handled by the techniques commonly used for hydrocarbons. In addition, the complete miscibility of hydrazines and water simplifies cleaning up fuel spills. Interhalogens, on the other hand, are vigorously, often explosively, reactive with many substances. Contact between CTF or BPF and some ordinary materials can be tolerated, but only under especially dry and clean conditions. Interhalogens have not been used extensively in industry, and experience in handling them has been mostly in open areas where ventilation is easily attained, and decontamination of spills is readily handled without too much regard for evolved gases. When missiles containing in the order of 100 lb each of CTF are brought aboard Naval ships, there will be a real danger of accidental release of this oxidizer when the missiles are handled in the confined spaces between the flight deck and the magazines, as well as in the magazines themselves. While special facilities, such as high-capacity water sprays and special ventilating systems could be used to protect magazines, such facilities would scarcely be feasible throughout the normally inhabited spaces where the missiles will be handled when the ship is taking on a supply of missiles, or when missiles are being prepared for a flight mission. The tests reported here were made to define some of the handling hazards associated with the CTF-MHF propellant systems and to point out some

suitable ways to handle spilled propellant. Since the interhalogen oxidizers are the least well known, and, in many ways, the more hazardous of the propellant components, the greater emphasis has been placed on these items. At the start of this project, a mixture of CTF and BPF appeared most likely to be used, and the tests were run on a 50-50 by weight mixture of these. Later, more consideration was given to the use of CTF alone as the oxidizer, and this change is reflected in the nature of the tests made. Except where noted, the tests were made on commercial grade propellant components. Some of the pertinent chemical and physical properties of the propellant components are given in Table 1. Typical properties of gasoline are given for comparison.

Table 1
Chemical and Physical Properties of Propellant Components

	Freezing Point (°F)	Boiling Point (°F)	Vapor Pressure at 80°F (psia)	Flash Point (°F)	Lower Explosive Limit (vol. %)	Upper Explosive Limit (vol. %)	Auto-ignition Temper-ature (°F)
Hydrazine	36	236	0.31	126	4.7	100	518
Mono methyl hydrazine	-62	190	1.0	62	2.5	92-98	382
Uns-Dimethyl hydrazine	-71	146	3.1	5	2.3	45	452-482
Gasoline	< -40	300-575	---	-36	1.5	7.5	< 850
CTF	-105	53	26.7	---	---	---	---
BPF	-81	105	8.5	---	---	---	---

Work reported previously in NRL Memorandum reports* has been augmented by additional tests of a similar nature. Some of the data from the earlier work are included in this report for the sake of completeness.

*H. E. Moran, Jr. and J. C. Burnett, "Reactivity of Various Damage Control Protective Clothing Materials with Chlorine Trifluoride," NRL Memorandum Report 1434, June 1963, and H. E. Moran, Jr. and J. C. Burnett, "Water Spray as a Damage Control Agent for Chlorine Trifluoride," NRL Memorandum Report 1162, April 1961.

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CHAPTER 2

ABSORPTION OF CTF SPILLS WITH POWDERS

When CTF is released in considerable quantity, evaporation cools a portion of the agent below its boiling point (53°F) and a pool of liquid CTF is formed. Spreading of the liquid over a relatively warmer surface will result in continued evaporation of the CTF, thus increasing the amount of this hazardous material in the atmosphere. The use of powdered materials to absorb liquid CTF has been proposed to stop the spreading of pools and to facilitate mechanical transfer of the CTF to containers for final disposal. The use of a reactive material to convert CTF to a less active compound does not appear feasible. Examination of the heats of reaction between most materials and CTF shows that sufficient heat would be released to volatilize a large proportion of the CTF, and it seems impractical to apply a powdered agent in a layer thick enough to insure trapping substantially all of the CTF by chemical reaction. Thus, reliance must be placed on physical rather than chemical absorption. In addition to being nonreactive, an absorbent should also have the following properties: (a) be wetted by liquid CTF, (b) have substantial capacity to soak up CTF, (c) should not be made sensitive to CTF by slight contamination, (d) be readily obtainable, and (e) be storable without change in properties over a reasonable period of time.

Numerous candidate absorbents were tested for compatibility with liquid CTF. Three series of tests were made using equipment set up in the laboratory fume hood. The first series consisted of applying liquid CTF slowly to a sample of the powder and noting the visual and audible results; the second consisted of dumping a batch of powder into a small pool of liquid CTF; the third was similar to the second, except that water spray was applied to CTF-powder mixtures which did not appear to react spontaneously. An additional series of tests was run on some of the more promising powders to determine their ability to retain CTF when applied to pools of this material.

TEST PROCEDURE AND RESULTS - LIQUID CTF APPLIED TO POWDERS

In the first test series, the prospective absorbent was spread out in a layer about 1/4 in. deep in a 2-1/2 in. diameter by 1/2 in. deep glass dish. CTF was released slowly from an inverted lecture cylinder equipped with a short delivery tube until self-refrigeration caused drops of liquid CTF to form. These were allowed to fall onto the powder until liquid started to accumulate. If no reaction occurred up to this point, the CTF flow was increased and the powder was well wetted. The nature of any reaction was noted in terms of appearance (fuming or flaming), and sound (quiet, vigorous, or explosive). Burning accompanied by no more than a mild hissing noise was considered quiet; that producing a "blow torch" sound was called vigorous. Those materials which exploded produced a sharp cracking noise and scattered the reactants, but there was seldom any damage to the test dish. If no reaction was observed in 2 min the test was considered negative. The results of the test series are given in Table 2.

Table 2
Compatibility of Some Absorbent Powders with Liquid CTF

Powder	Reaction
Kaolin	Ignited. Burned with a quiet, white flame, producing white smoke.
Infusorial earth	Ignited. Burned with a slight hissing, white flame producing white smoke.
Bentonite 200	Ignited. Powder glowed bright yellow.
Linde molecular sieve No. 5A	Ignited. Burned with quiet, yellow flame, producing white smoke.
Silica gel, untreated	Ignited. Burned quietly with bright yellow glow, producing white smoke.
Silica gel, dried by heating at 300°C	Ignited. Burned quietly with bright yellow glow, producing white smoke.
Tricalcium phosphate	Ignited. Burned with quiet pink flame, producing white smoke.
Talc	No reaction. (Later tests under somewhat different conditions showed that talc may ignite and burn in CTF.)
ABC type dry powder fire extinguishant*	Ignited immediately giving a tall, green flame with white smoke.
PKP extinguishant†	Ignited. Burned with a slightly hissing, purple flame; some bright sparks were emitted.
CDC extinguishant‡	Ignited. Burned with a low, yellow flame; some bright sparks were given off.
Calcium fluoride (native)	No reaction.
Cryolite (natural)	No reaction.
Sodium fluoride	No reaction.
Lithium fluoride	No reaction.
Magnesium oxide	Brilliant yellow glow in powder with some scintillation.
Pyrogenic silica	Brilliant yellow glow.
Calcium carbonate (porous granules from respirator cartridge)	Dull red glow.

*Principally ammonium phosphate.
†Potassium bicarbonate powder with agents added to keep the powder free-flowing.
‡Sodium bicarbonate powder with agents added to keep the powder free-flowing.

TEST PROCEDURE AND RESULTS - POWDER ADDED TO POOLS OF LIQUID CTF

A series of tests was run in which the powder to be tested was dropped into a pool of liquid CTF. By this method a substantial portion of the powder was immediately wetted, as it would be in actual practice. The apparatus consisted of a 2-1/2-in.-diameter petri

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dish to hold the CTF, and a cylindrical container mounted on the end of a rod so that its contents could be dumped into the CTF by rotation of the rod. The rod was supported on bearings that allowed it to be moved laterally, as well as rotated (Fig. 1). In carrying out a test, 10-20 gm of the powder was placed in the holder and kept to one side to avoid premature contact with CTF vapor. CTF was run into the dish until the initial boiling and fast evaporation subsided and a layer of liquid CTF 1 or 2 mm deep was obtained. The powder holder was then centered over the CTF and inverted to drop the powder, all at once, into the CTF. The resulting reaction was described, as before, according to appearance and sound.

Fig. 1 - Apparatus for dropping powders into a pool of liquid CTF and for applying water spray to the CTF-powder mixture

Since CTF vapor as well as the liquid agent can ignite ordinary combustible material, water (probably as a spray or fog) may be used in the vicinity of CTF spills. Some of the powders which did not react immediately on contact with liquid CTF were subjected to water spray to determine whether the absorbent powder would modify the reaction between liquid CTF and water. A small, single fluid spray nozzle was mounted above the test dish and slightly off center so that it would not drip into the sample at startup or shutdown. The nozzle produced a solid cone spray of droplets less than 1 mm in diameter in a pattern large enough to cover the CTF-powder sample. The results of these tests are given in Tables 3a and 3b.

Table 3a
Compatibility of Various Powdered Absorbents with Pools of CTF

Powder	Reaction
Fuller's earth, untreated	Ignited at several points and fire then spread throughout the sample, forming a tall, quiet flame. A large proportion of the powder was expelled from the dish.
Fuller's earth, dried by prolonged heating at 250°C	Ignited. Powder glowed a dull red and there was a quiet, yellow flame about 1 in. high accompanied by a few bright sparks.
Sodium aluminate	Ignited and burned quietly
Aluminum fluoride hydrate	Ignited and burned quietly
Zirconium dioxide	Ignited and burned quietly
Magnesium trisilicate	Ignited and burned quietly. A large portion of the powder was expelled from the dish.
Boric acid	Ignited and burned quietly
Mica	Ignited and burned quietly
Sodium carbonate	No visible reaction
Sodium bicarbonate (reagent grade)	Ignited and burned with a very low, green flame visible only in partially darkened room.
CDC dry powder fire extinguishant*	Most of powder was rapidly ejected from dish, accompanied by numerous glowing particles.
PKP dry powder fire extinguishant†	Same as CDC powder
ABC dry powder fire extinguishant‡	Ignited. Burned with tall green, hissing flame.
Talc, clean	Variable. In several trials, CTF gradually evaporated without apparent reaction. In other trials, talc ignited at one or more points and fire spread throughout the powder; the powder became red hot and there was a low, bright yellow flame.
Talc, contaminated§	Ignited at contaminant and fire spread slowly as above.
Talc, wet¶	Exploded on contact with CTF
Polytetrafluoroethylene (Teflon) powder	Ignited and burned quietly

*Compatible dry chemical fire extinguishing powder. Principally sodium bicarbonate with a small percentage of additives to make the powder free flowing.
†Similar to CDC powder, except potassium bicarbonate is used in place of sodium bicarbonate.
‡Principally ammonium phosphate.
§This sample of talc contained a few very small flecks of dark material, composition unknown, which ignited with a bright flash on contact with CTF.
¶Four percent by weight of water was mixed with clean talc just before the test.

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Table 3b
Compatibility of Various Powders with Pools of CTF in the Presence of Water Spray

Powder	Reaction
CTF only	Burned quietly with a green flame
Sodium fluoride	Water spray produced low, hissing, green flame
Lithium fluoride	Same
Cryolite*	Same
Aluminum oxide	Water spray produced a roaring, green flame
Sodium carbonate, anhydrous	Water spray produced burning and vigorous spattering
Calcium carbonate	Water spray produced a weak explosion followed by a steady, roaring flame
Calcium fluoride†	Water spray produced a brief burning with a green flame, terminated by an explosion
Mixture of 75 wt% calcium fluoride and 25% sodium carbonate	Water spray produced very quiet green flame
Mixture of equal parts by wt of calcium fluoride, cryolite, calcium carbonate	Water spray produced an initial weak explosion followed by a brief period of quiet burning
Talc	Water spray produced sputtering without visible flame
Mixture of 90 wt% talc, 10% fine aluminum powder	No reaction without water. Water spray produced quiet burning.
Same	Ignited and burned quietly without water spray
Mixture of 80 wt% talc, 20%, 20 mesh aluminum granules	Ignited and burned without water spray

*Natural mineral (sodium aluminum fluoride).
†Natural mineral.

DISCUSSION

Of the materials examined in the preceding tests, only the inorganic fluorides were compatible with CTF. The other candidate adsorbents either reacted promptly and vigorously or, possibly due to scattered particles of sensitive material, could be ignited at separate points, after which reaction spread through the mass of the powder. In view of the high heats of formation of fluorides in comparison with other compounds, and the requirement that the absorbent be used in powdered form (which would tend to promote rapid reaction), it appears unlikely that materials other than inorganic fluorides will be found suitable for absorbing liquid CTF.

CHAPTER 3

EFFECT OF ABSORBENT POWDERS ON THE EVAPORATION RATE OF POOLS OF CTF

Tests were made on three inorganic fluorides to determine their effect on the rate of evaporation of shallow pools of liquid CTF, and to determine their influence on the reaction between liquid CTF and water spray which most surely will be used in case of propellant spills. The powders used were ground natural calcium fluoride (fluorspar, CaF_2), ground natural cryolite ($Na_3Al\ F_6$), and technical grade sodium fluoride (NaF). Occasionally, reagent grade chemicals were used for comparison. Anhydrous sodium carbonate, sodium bicarbonate, and potassium bicarbonate base dry powder fire extinguishing agents were included in some of the tests, since these materials have been proposed as absorbents and decontaminants for CTF.

TEST PROCEDURE AND MATERIALS FOR MEASURING EVAPORATION RATES

The apparatus used for measuring the effect of the powders on the evaporation rate of CTF comprised a stainless steel, circular dish 6-3/8 in. in diameter by 1 in. deep placed on a single-pan balance, a supply tank of CTF supported to discharge liquid CTF into the pan, and a cup which could be manipulated to drop the absorbent powder into the

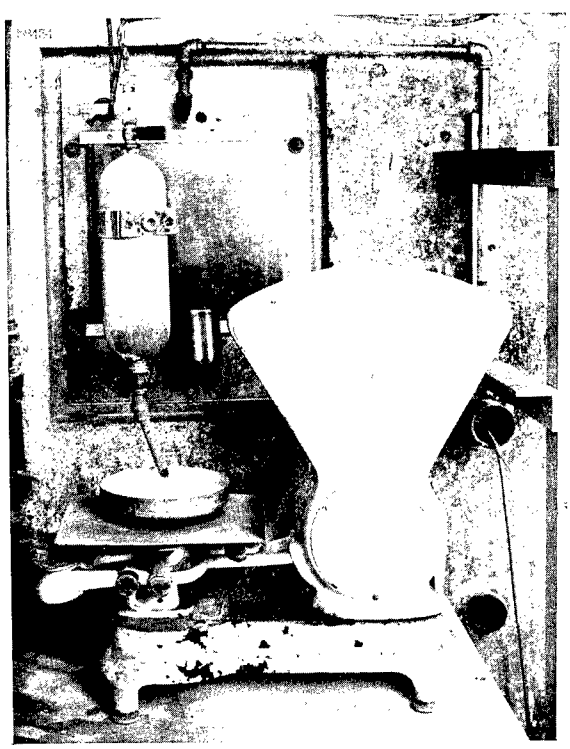

Fig. 2a - First apparatus used for measuring evaporation of CTF from absorbent powders. (The face of the scale was visible from the operators side of the test facility.)

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dish. The equipment was placed behind a barricade, under a fume hood which produced a slow (50 cfpm) sweep of air over the sample holder. Initially, a springless balance was used for weighing, as shown in Fig. 2a. The evaporation pan was supported by three 1/2-in.-thick spacers to permit circulation of air on the underside of the pan. This balance, however, deteriorated rapidly in the corrosive CTF fumes and required frequent overhaul to maintain its ability to weigh within 1 gm accuracy. It was replaced by a strain gage weighing device whose corrosion sensitive parts could be kept away from the CTF vapor. This device consisted of a 1/4 by 1 in. rectangular aluminum cantilever beam with four foil type strain gages cemented near the center of the free length of the beam. The strain gages were arranged and connected to form a temperature compensated bridge whose output was fed to a manually operated strain indicator. The evaporation pan was held by a wire frame suspended by a pivot near the free end of the beam (see Fig. 2b). The beam, except for a small portion near the pivot end, was covered with a loose fitting wrapper of thin Teflon sheeting for protection from CTF fumes. The strain indicator was calibrated using laboratory weights, and it was found to respond linearly to weight changes with an accuracy of approximately 1 gm over the required weight range. This device was found to be reliable and it has been used several months without significant deterioration.

Evaporation rate tests were made when the ambient air temperature was below the boiling point of CTF, as well as when it was considerably higher. The absorbent powders were stored in the test room so that they were at substantially the same temperature as the ambient air when the tests were made. The powders of principal interest in

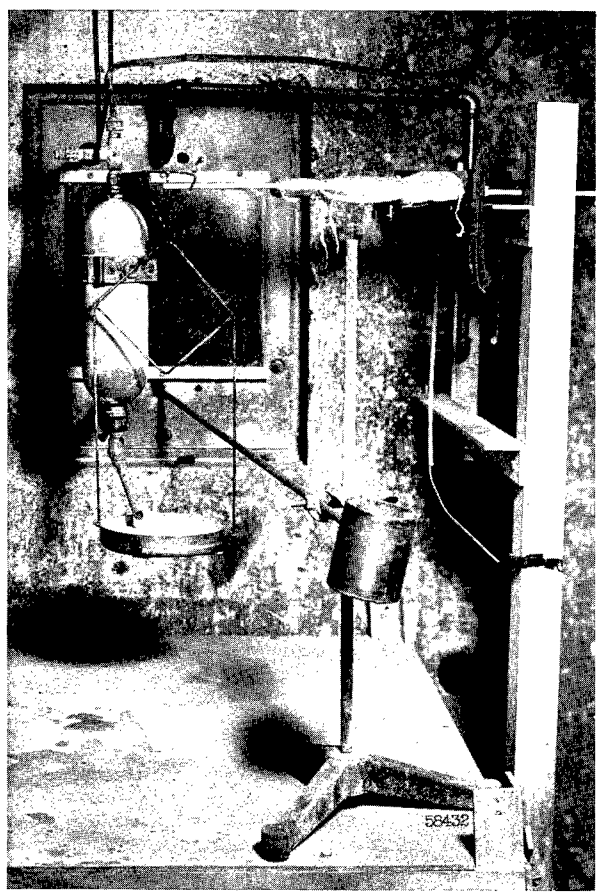

Fig. 2b - Second apparatus used to measure evaporation of CTF from absorbent powders. Strain gages are mounted under a protective wrapper of Teflon sheeting; auxiliary readout equipment is in the operators side of the test facility.

Table 4
Moisture in Absorbent Powders

Material	Moisture (% by wt)
Calcium fluoride	0.017
Cryolite	0.066
Sodium fluoride	0.038

these tests are nonhygroscopic and were used as supplied. The moisture content, measured as the loss of weight on prolonged heating at 110°C, is given in Table 4.

The bulk density and open space (void fraction) in beds of the principal powders was measured. The powder was added in small increments to a graduated cylinder which was dropped on a padded surface several times after each increment to compact the bed. After about 25 cc of powder had been added, the cylinder was dropped repeatedly until there was no further change in volume. The bulk density was calculated from the weight and final volume of the powder. The void fraction (ϵ) was calculated as:

$$\epsilon = 1 - \frac{\text{bulk density}}{\text{true density}} .$$

The results are given in Table 5.

Table 5
Bulk Density and Void Fraction of Powder Beds
Used in Absorption Tests

Material	Bulk Density (gm/cc)	True Density* (gm/cc)	Void Space (fraction of total volume)
Calcium fluoride	1.99	3.18	0.37
Cryolite	1.55	2.98	0.48
Sodium fluoride	1.61	2.79	0.42

*From Chemical Rubber Co. Handbook, 39th Edition.

Particle size of the absorbent powders was measured visually with a microscope equipped with a calibrated grid. The results are given in Table 6.

Table 6
Particle Size Distribution of Absorbent Powders
(microns)

Absorbent Powder	Percent of Total Number of Particles			
	100	90	50	10
Calcium fluoride, native	< 159	< 30	< 9	< 1
Cryolite	< 25	< 3	< 2	< 1
Sodium fluoride, tech	< 19	< 6	< 3	< 1

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In carrying out an evaporation rate test, CTF was run into the evaporation pan until the initially rapid evaporation had subsided to a negligible rate by self-cooling and the pan contained about 80 gm of the liquid. At this point, the desired amount of powder was poured into the pan to form a powder bed as nearly level as possible. The weight was noted at various time intervals until evaporation stopped and constant weight was attained.

The evaporation rates of similar amounts of CTF without an absorbent also were measured, using the same apparatus. Again, approximately 80 gm of liquid CTF were run into the pan until boiling and rapid evaporation subsided, after which time and weight change were noted.

RESULTS OF TESTS

The data obtained for the evaporation of CTF held in absorbent powders were plotted as the logarithm of weight of CTF per unit area of powder bed vs time (log [lb/ft^2] vs min) as shown in Figs. 3-10. When the tests were run in duplicate, a single curve was drawn for the best fit with both sets of data. The data for evaporation of CTF in the absence of an absorbent were plotted on rectangular coordinates as shown in Fig. 11.

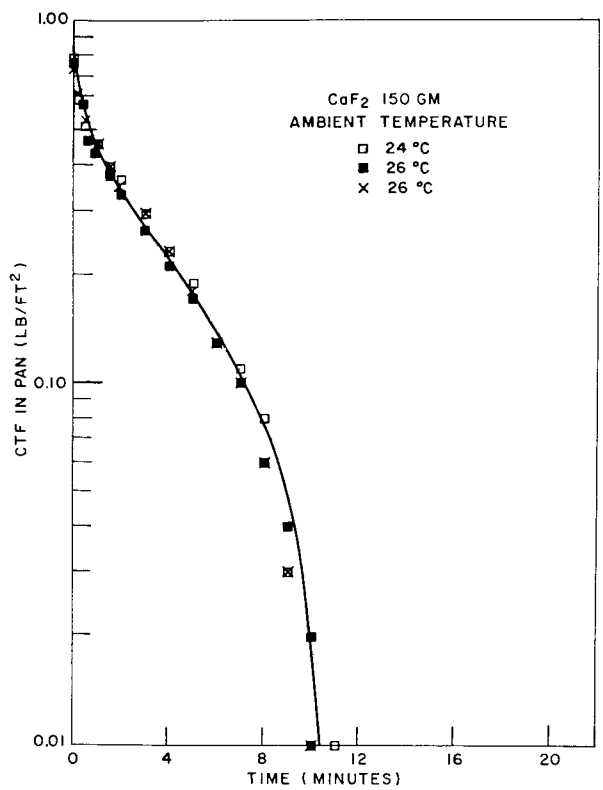

Fig. 3 - Evaporation of CTF from calcium fluoride (native) powder. Powder/CTF ratio of 2.

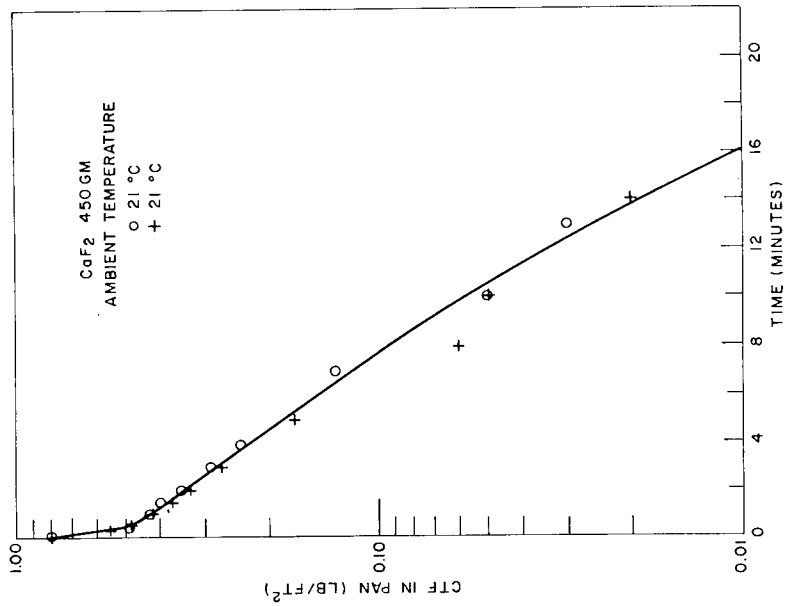

Fig. 5 - Evaporation of CTF from calcium fluoride (native) powder. Powder/CTF ratio of 6.

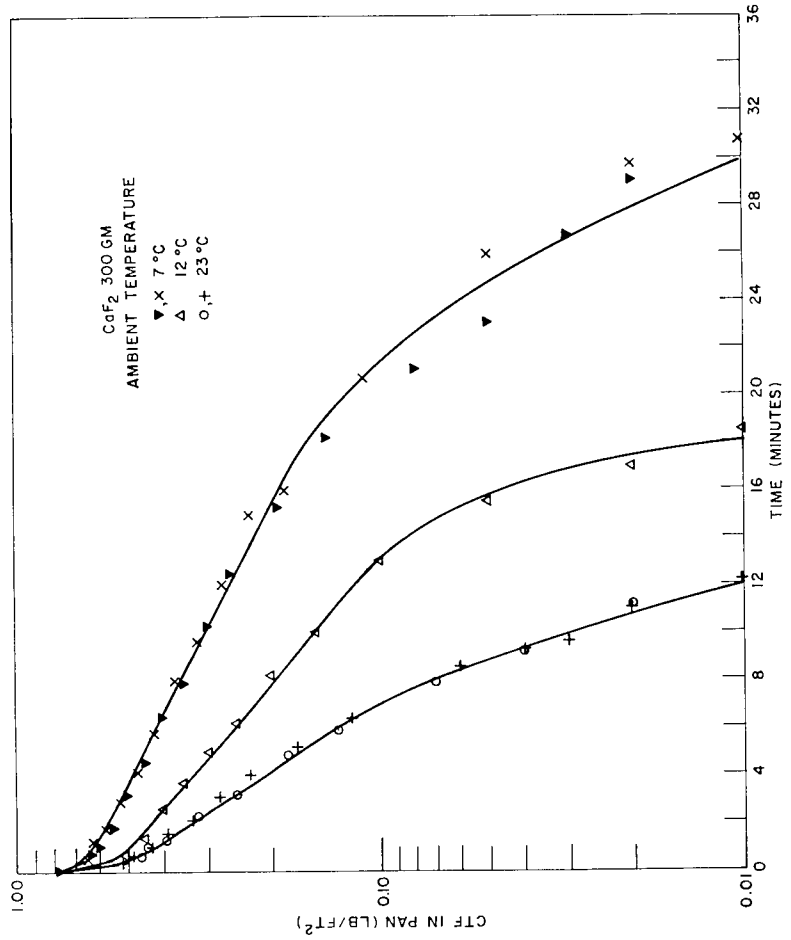

Fig. 4 - Evaporation of CTF from calcium fluoride (native) powder. Powder/CTF ratio of 4.

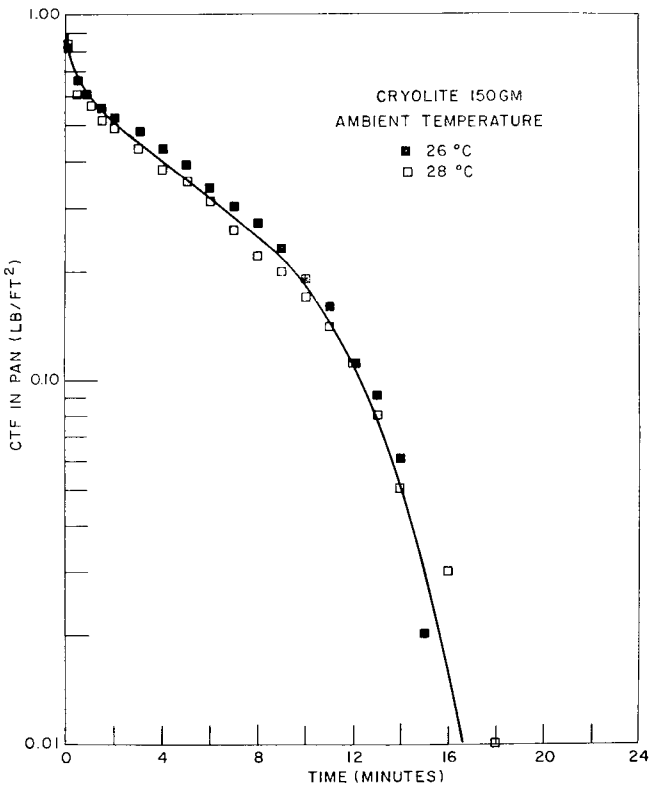

Fig. 6 - Evaporation of CTF from cryolite powder. Powder/CTF ratio of 2.

The loss of CTF was so rapid when the chemically reactive sodium carbonate, sodium bicarbonate, and potassium bicarbonate powder (PKP) estinguishant were used that no time-weight loss measurements could be made. With these three powders, constant weight, indicating the end of evaporation, was attained in less than 1 min. Also, it was noted that substantial amounts of the powders were carried out of the pan by the rush of evolved gases.

SUPPLEMENTARY MEASUREMENTS OF TEMPERATURE CHANGES IN ABSORBENT BED DURING EVAPORATION

In order to understand the effects of the absorbents on the evaporation rate of CTF, it was considered desirable to determine, at least semiquantitatively, the temperature history of the powder beds during absorption and subsequent evaporation. Since CTF reacts with thermocouple wires and most thermocouple sheathing materials, no attempt was made to measure bed temperatures by probes placed directly in the CTF-powder mixture. Instead, a thermocouple was soldered near the center of the outside bottom surface of the pan used in the evaporation rate tests. The thermocouple and pan bottom were shielded from the ambient atmosphere, first by a layer of asbestos paper, and finally an outer sheath of stainless steel. The thermocouple leads were protected from CTF vapors by Teflon tubing. Approximately 80 gm of CTF were put into the pan, and then 300 gm of powder were poured in, as was done in the evaporation rate tests. The temperature of the CTF was noted just before adding the powder (zero time), and at intervals after adding the powder. The time-temperature relationship for the evaporation of CTF in the absence of an absorbent powder also was measured. The temperature

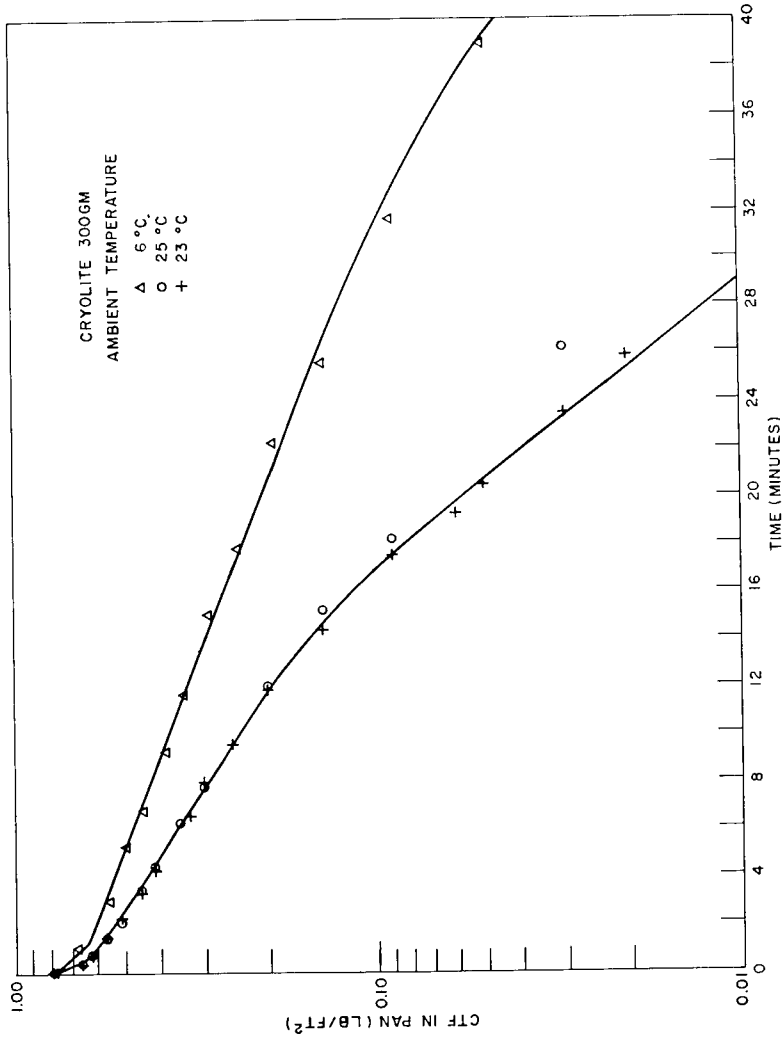

Fig. 7 - Evaporation of CTF from cryolite powder. Powder/CTF ratio of 4.

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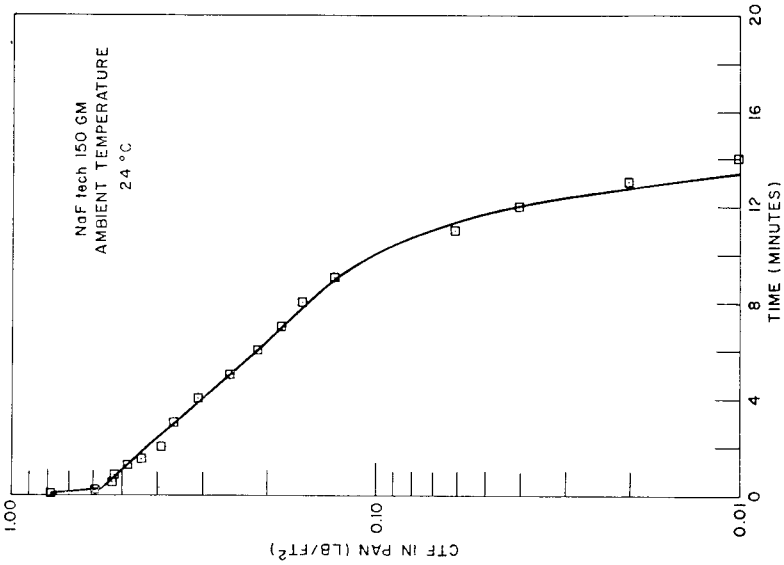

Fig. 9 - Evaporation of CTF from sodium fluoride (technical) powder. Powder/CTF ratio of 2.

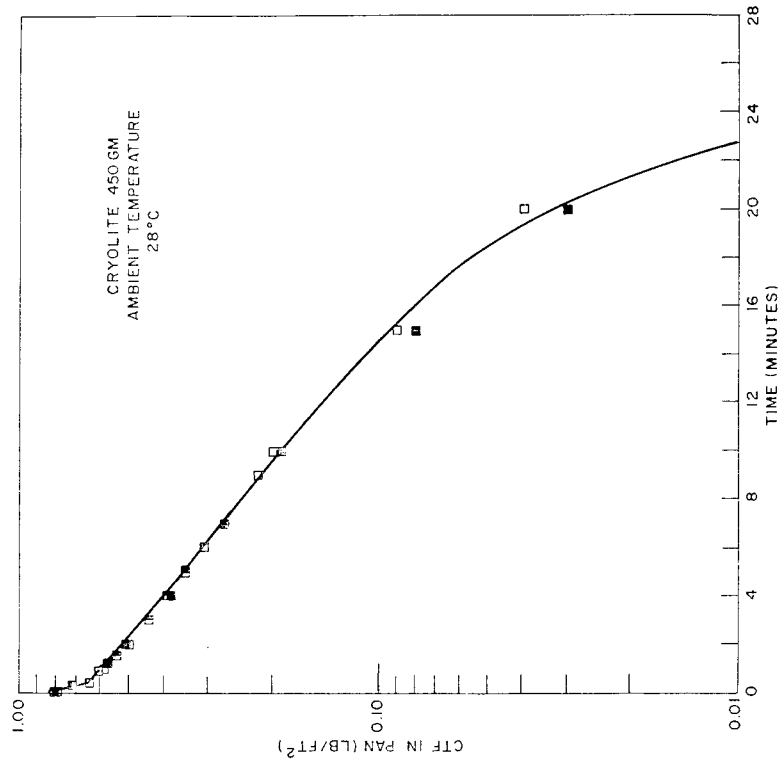

Fig. 8 - Evaporation of CTF from cryolite powder. Powder/CTF ratio of 6.

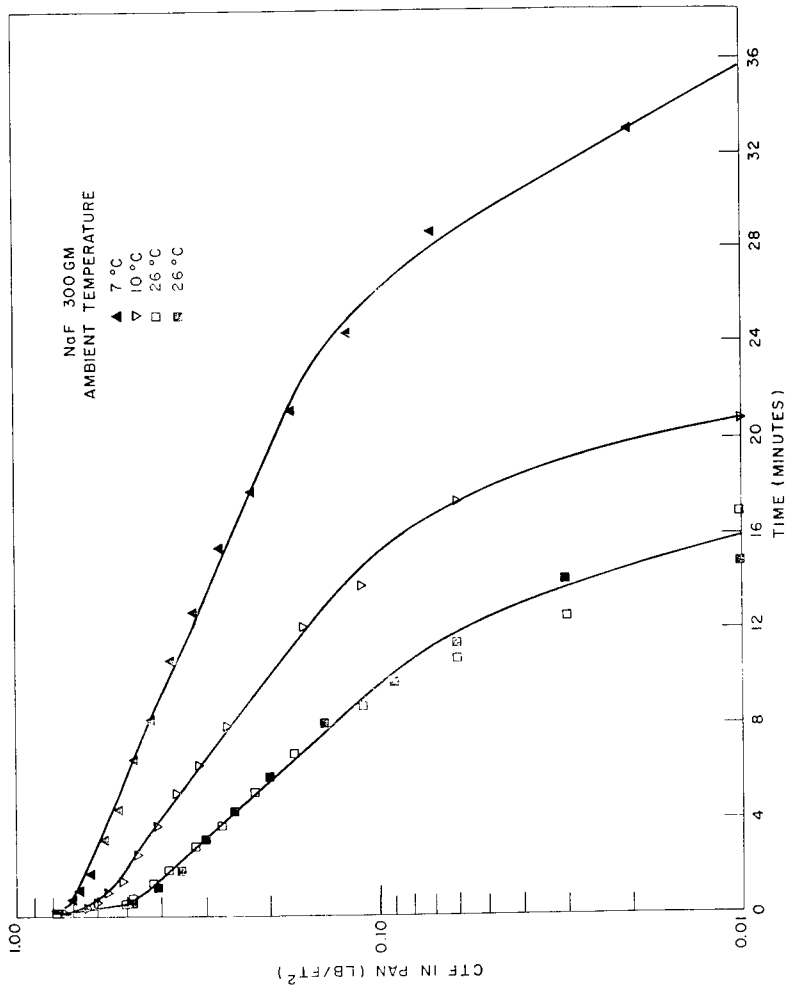

Fig. 10 - Evaporation of CTF from sodium fluoride (technical) powder. Powder/CTF ratio of 4.

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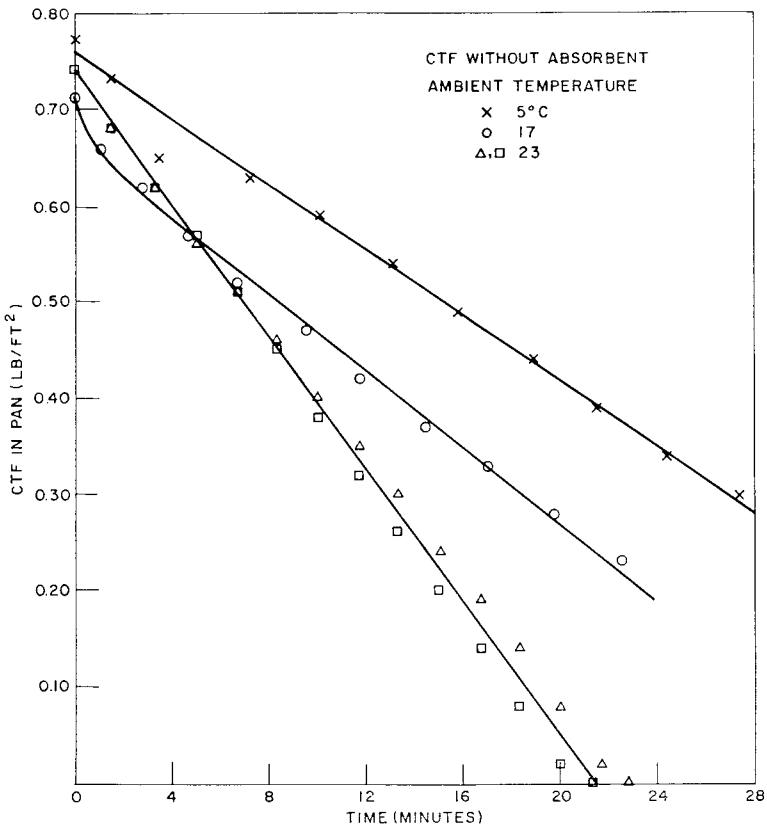

Fig. 11 - Evaporation of CTF without absorbent powder

over the first few minutes was measured continuously to detect any initial temperature rise, after which the temperature measurements were made at convenient time intervals.

All three powders tested, natural calcium fluoride, technical sodium fluoride, and cryolite, gave an initial, sudden temperature rise of considerable magnitude, followed by a rapid decrease to the boiling point of CTF, all within about 2 min after the powder addition. After this, there was a very gradual temperature decrease to a minimum, and then a gradual rise toward ambient temperature, the latter presumably due to depletion of the liquid CTF. The addition of plain CTF to the pan did not produce any initial temperature rise. These results are illustrated in Fig. 12.

EFFECT OF WATER ON CTF-ABSORBENT MIXTURES

The effect of water on the CTF-absorbent mixtures was determined both for water spray, which would be used during shipboard damage control, and for sudden immersion, which might occur on final disposal of the mixture.

Water Spray

For the spray tests, a nozzle producing substantially the same size range of droplets as the Navy L-11 fog head was mounted to discharge a solid cone spray onto the same sample-holding arrangement that was used in the evaporation rate tests. As before,

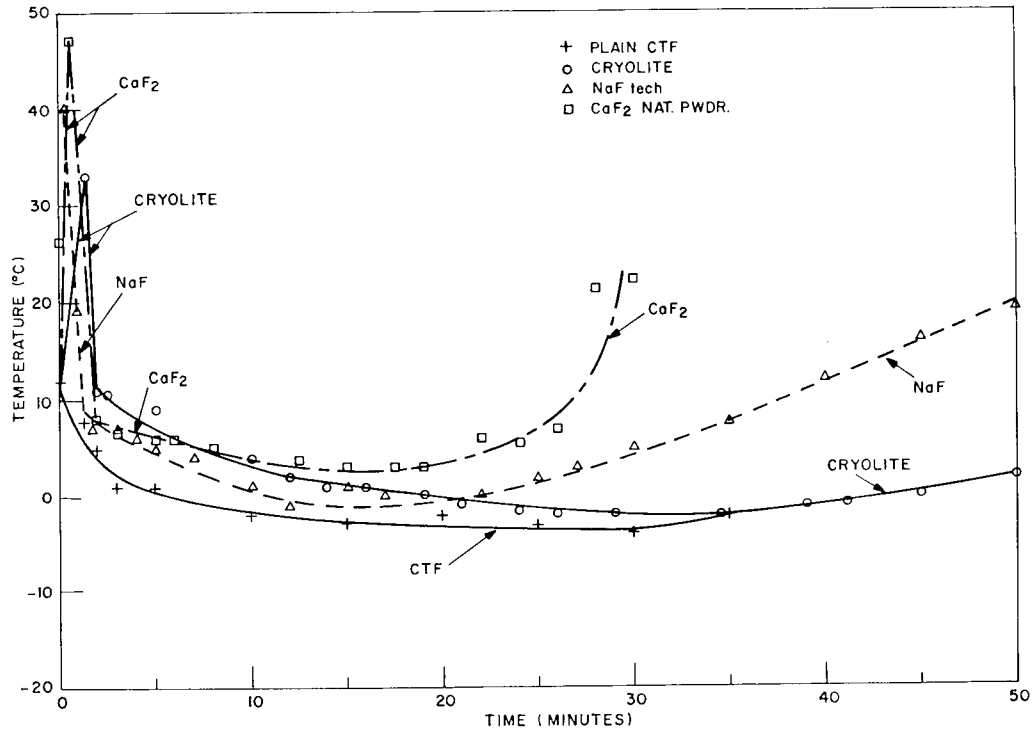

Fig. 12 - Relationship of temperature to time during evaporation of CTF

80 gm of CTF was placed in the pan and 300 gm of powder poured into it. After 0.6 min, while a large part of the CTF was still in the powder, the spray was actuated until the mixture was thoroughly wet and visible reaction ceased. The results are given in Table 7. Heavy fuming was produced with all absorbents tested. In some tests, flames were seen just over the powder; in other tests, flames were not seen, but may have been obscured by the fumes. Accurate timing of the events was not practical; however, all reactions were completed in less than 5 sec.

Immersion

In the CTF-absorbent immersion tests, mixtures of 80 gm of CTF and 300 gm of powder were prepared in the same manner as in the evaporation rate tests. At 0.5 min after mixing, the test dish and contents were held 2 ft above a relatively large (10 gallon) bucket of water and dropped. The dish submerged immediately in all tests. Both the CTF-calcium fluoride and the CTF-cryolite mixtures remained on or close to the surface of water and reacted quietly for about 5 sec, giving a low, yellow flame and very little fumes. The CTF-sodium fluoride mixture appeared to submerge and then immediately react, without visible flames. This reaction was more vigorous than with calcium fluoride or cryolite, and resulted in a spray of water being ejected from the water container. Eighty grams of CTF alone were run through the same test. There was a single vigorous explosion which threw about one fourth of the water out of the container. Much of the water was thrown up against the ceiling (10 ft high) of the test cell, but the explosion was not strong enough to damage the bucket. The preceding tests were repeated with the same results.

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Table 7
The Effect of Water Spray on CTF Absorbed by Various Powders

Absorbent	Reaction
Calcium fluoride, native	Momentary, mild sputtering, followed by heavy fumes; no visible flame.
Calcium fluoride, native	Momentary yellow flames about 6 in. high, followed by heavy fuming.
Cryolite	Mild sputter at start, followed by quiet burning with flames 2 in. high. Fuming was less than with calcium fluoride.
Cryolite	Quiet burning with 1-in.-high flame and fumes as above.
Sodium fluoride, tech	Quiet reaction with momentary 1-in.-high flame at start; heavy fuming.
Sodium fluoride, tech	Quiet reaction with heavy fuming; no visible flame.
CTF without absorbent	Vigorous sputtering at start of spray, and CTF was thrown out of sample holder. Many small fires were observed on floor within about 6 ft of the apparatus. All reactions were complete in less than 1 sec.
CTF without absorbent	Same result

DISCUSSION

Inspection of the curves given in Figs. 3-11 shows that the addition of an absorbent to pools of liquid CTF results in evaporation at a rate greater than that of a confined pool of CTF alone, at the same ambient atmospheric temperature. This is true regardless of whether the ambient atmosphere and absorbent powder are at a temperature either higher or lower than the boiling point of CTF. The evaporation of CTF from an absorbent is shown to take place in three distinct steps.

The first step is a very rapid loss of approximately 13 to 22% of the original amount of CTF present when the ambient temperature is low, and 25 to 46% when the ambient temperature is high. This step lasts less than 1 min and evidently results from heat generated by a rapid reaction between the CTF and the surface of the absorbent particles, and, at higher temperatures, the heat taken up by the CTF in cooling the absorbent below the boiling point of the liquid. (See the temperature-time curve, Fig. 12.) Table 8 was prepared to permit ready comparison of the effects of the various absorbents on the evaporation of CTF pools. The proportion of the CTF evaporated given under the column headed "1 min" is principally that lost during the first step.

The second step is represented by sloping, straight lines in the evaporation curves. This step encompasses 59 to 69% of the original amount of CTF at low ambient temperatures, and 45 to 59% at the higher temperatures. This portion of the evaporation curve shows a dependence of the rate of evaporation on the amount of liquid CTF present. It can be represented mathematically by the expression

$$- \log \frac{W}{W_0} = kt$$

Table 8
Loss cf CTF from Absorbent Powders after Various Time Lapses

Absorbent	Ambient Temp (°C)	Amount of Absorbent (lb/ft²)	CTF Evaporated in Indicated Time, Percent of Initial Amount (by wt)					
			1 min	10 min	15 min	20 min	30 min	40 min
None	5	0	3	10	34	45	--	--
None	17	0	8	34	48	62	--	--
None		0	5	47	70	93	--	--
Calcium fluoride, tech	24-26	1.50	38	97	> 99	--	--	--
	7	3.00	21	61	74	84	99	--
	12	3.00	33	81	92	> 99	--	--
	23	3.00	45	96	> 99	--	--	--
	21	4.50	46	93	98	> 99	--	--
Cryolite	26-28	1.50	25	77	96	> 99	--	--
	6	3.00	18	51	64	73	87	94
	23-25	3.00	26	69	83	92	> 99	--
	28	4.50	27	77	90	96	> 99	--
Sodium fluoride, tech	24	1.50	36	87	> 99	--	--	--
	7	3.00	13	52	65	76	94	--
	10	3.00	22	73	86	97	> 99	--
	26	3.00	44	88	98	> 99	--	--

where W_0 is the amount of CTF initially present (at the beginning of the straight part of the curve), W is the amount evaporated after time lapse t, and k is a constant which depends on the nature of the absorbent and the ambient temperature. The constant k serves as a measure of the effectiveness of the absorbent in retarding evaporation of the CTF — the lower the value of k, the greater the effectiveness of the absorbents. The constant has been calculated for each test and is listed in Table 9.

Table 9
Evaporation Rate Constant (k) for Various Absorbents

Absorbent	Ambient Temp (°C)	Wt of Absorbent (lb/ft²)	Evaporation Constant (k)
Calcium fluoride, native	24-26	1.50	0.099
	23	3.00	0.103
	12	3.00	0.056
	7	3.00	0.036
	21	4.50	0.091
Cryolite	26-28	1.50	0.052
	23-25	3.00	0.043
	6	3.00	0.026
	28	4.50	0.055
Sodium fluoride, tech	24	1.50	0.074
	26	3.00	0.074
	10	3.00	0.050
	7	3.00	0.029

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In the third step, encompassing the final 19 to 23% of the original CTF present at low ambient temperatures, or 12 to 27% at higher temperatures, the amount of CTF evaporated is very nearly linearly proportional to time lapse. This change in the dependence of the evaporation rate on time and amount of CTF present, to dependence on time alone, is probably due to the depletion of the liquid CTF to the point where it is no longer uniformly distributed throughout the powder bed, and CTF vapor is lost by diffusion.

The evaporation of liquid CTF in the absence of an absorbent was found to be directly proportional to time (Fig. 12). This result was to be expected, since it is well established that an open pool of liquid will cool itself by evaporation until an equilibrium is reached between heat lost from the liquid by evaporation and heat gained from the surroundings (principally by conduction in these tests).

Table 7 permits comparison of the rates of loss of CTF from open pools and from the various absorbent powders. The table shows that, in all cases, the addition of an absorbent powder results in a more rapid loss of CTF than occurs in the absence of an absorbent. It should be noted, however, that the plain CTF was confined to a pool of definite area, whereas in an actual accidental spill it is likely that the liquid CTF would be unconfined and would tend to spread out over a larger area, resulting in a much more rapid rate of evaporation. It thus appears that absorbents would be useful in confining liquid CTF. Ventilation of the spill area or neutralization of the CTF vapor would be required with or without an absorbent.

Of the absorbents tested, cryolite generally gave the least evolution of CTF vapor immediately after application, and retained the CTF longer. In addition, the evaporation rate constants (k values in Table 8) were substantially lower for cryolite than for calcium fluoride or sodium fluoride.

The data in Tables 7 and 8 show that the amount of absorbent applied to the CTF pools makes little difference in the quantity of CTF given off in the first rush of vapor or in the time required for evaporation of all of the CTF pool. It should be noted that the void space (Table 5) in the powder beds containing 1.5 lb absorbent/ft^2 is just a little more than sufficient to hold all of the liquid CTF, while at 3.0 and 4.5 there is a substantial excess capacity. Apparently, sufficient powder is needed to prevent existence of a free layer of liquid CTF, while an excess does no harm.

CHAPTER 4

EFFECT OF VARIOUS ABSORBENTS ON THE VAPOR PRESSURE OF CTF

It has been suggested that some of the powders tested for soaking up spills of CTF might form at least partly effective chemical bonds with the oxidizer, thus reducing the vapor pressure of the absorbed CTF below that of the free liquid. If such were the case, missile shipping containers could be packed with absorbent to hold minor CTF leaks. The absorbents previously found useful for soaking up spills of liquid CTF were examined for their effect on the pressure exerted by CTF in a closed container. Lithium and barium fluorides were included in the tests because of their general similarity to calcium and sodium fluorides. Reagent grades of sodium and calcium fluorides were tested for comparison with the technical grades to show whether impurities in the less carefully prepared technical materials significantly affected their compatibility with CTF.

TEST PROCEDURE AND RESULTS

The apparatus consisted of a 500-cc stainless steel cylinder, which served as the powder holder, a 30-cc stainless steel cylinder holding the CTF supply, and a 0 to 2 atm pressure gage graduated in 0.002 atm intervals. (In the few instances when the pressure exceeded 2 atm, an ordinary 0 to 60 psi gage was substituted for the precision gage.) These items were connected with copper tubing, brass fittings, and brass bellows valves, as shown in Fig. 13.

Tests were made with a 4 or 5 to 1 weight ratio of absorbent to CTF. The tests also were repeated at a 20 or 25 to 1 ratio to determine if a large increase in absorbent would affect the results. Approximately 100 gm of absorbent powder was placed in the 500-cc cylinder. The 30-cc cylinder was evacuated, cooled in dry ice, and CTF from the stock tank was distilled into it. (A sodium fluoride pellet bed was inserted in the vapor line to remove any HF present.) A few grams in excess of the desired weight of CTF was collected, and, after warming to room temperature, CTF was vented from the vapor phase to remove the excess and, at the same time, to sweep out noncondensable gases. The two cylinders were attached to the rest of the apparatus, and the entire system, except for the 30-cc cylinder, was evacuated. The CTF was then transferred to the powder holder by distillation, using dry ice around the 500-cc cylinder as a coolant. After transfer of the CTF was completed, the CTF reservoir was closed off from the system and the powder cylinder was held in an ice water bath until the pressure became steady for at least 1 hr. Next, the tank was transferred to a water bath at $20 \pm 0.1°C$ and the pressure was recorded after it remained steady for 1 hr. (When calcium fluoride was used, no equilibrium pressure was attained at either temperature. Instead there was a slow, continuous increase of pressure.) The vapor pressure of the CTF in the absence of absorbents also was determined using the same apparatus and technique. The results are given in Table 10.

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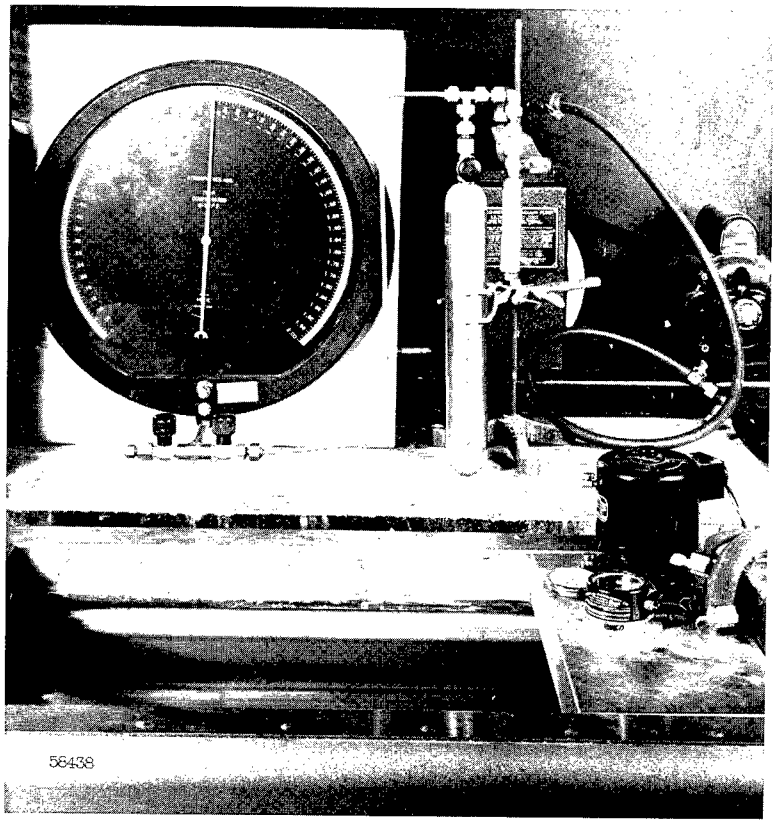

Fig. 13 - Apparatus for measuring vapor pressure of CTF held in absorbent powders. (In actual tests, the 500-cc cylinder was immersed in ice water, or in the constant temperature both in the foreground.)

DISCUSSION

As shown in Table 10, CTF mixed with any of the powders tested gave a pressure higher than that of CTF alone. With the exception of calcium fluoride (either natural mineral or the pure reagent grade), there was an apparent equilibrium pressure reached at both 0° and 20°C (32 and 68°F). The highest pressure reached, 1.582 atm (8.6 psig) was not significantly higher than the normal vapor pressure of CTF (6 psig). Hence, liquid CTF could be soaked up in one of these absorbents and stored in a closed container for subsequent disposal. Calcium fluoride and CTF, on the other hand, did not reach a pressure equilibrium, but continued to show a pressure increase to as much as 4.8 atm (56 psig) after 3 days. While calcium fluoride is useful as an absorbent, its final disposition would have to be made promptly. (Further tests were made on calcium fluoride. These are reported in Appendix A.)

Table 10
Vapor Pressure of CTF over Various Absorbents

Absorbent Powder	Pwd/CTF Ratio	Equilibrium Press. at 0°C (atmosphere)	Equilibrium Press. at 20°C (atmosphere)	Remarks
Barium fluoride, reagent	5:1 20:1	0.642 0.604	1.453 1.428	Powder dried at 120°C
Calcium fluoride, native	4:1 20:1	(1) (1)	(2) (3)	
Calcium fluoride, reagent	5:1 20:1	(1) (1)	(4) (5)	Powder dried at 120°C
Cryolite	4:1 20:1	0.671 0.693	1.582 1.578	Powder dried at 120°C
Lithium fluoride, reagent	5:1 25:1	 0.698	 1.431	Powder dried at 120°C
Sodium fluoride, tech	4:1 20:1	0.693 0.684	1.512 1.518	
Sodium fluoride, reagent	4:1 20:1	0.638 0.639	1.444 1.456	Powder dried at 120°C
CTF without absorbent	---	0.610	1.413	

(1) No equilibrium attained. Pressure still rising after 1 hr.
(2) No equilibrium attained. Pressure was 2.2 atm after 48 hr.
(3) No equilibrium attained. Pressure was 3.7 atm after 144 hr.
(4) No equilibrium attained. Pressure was 4.8 atm after 72 hr.
(5) No equilibrium attained. Pressure was 2.7 atm after 36 hr.

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CHAPTER 5

INCENDIVITY OF CTF IN CONTACT WITH PROTECTIVE CLOTHING AND OTHER MATERIALS

CTF is a much more reactive oxidizer than any other now used in missile propulsion systems and it is recognized that protective clothing currently used for protection against fuming nitric acid or nitrogen tetroxide may ignite on contact with liquid CTF. It should be remembered, however, that direct contact with large amounts of liquid CTF would be unlikely in damage control operations. In the case of gross spills of liquid CTF, the damage control personnel probably would apply water spray or other decontaminant from a reasonable distance, and thus they would be exposed to CTF vapor, which is more or less diluted with air. Contact with the liquid oxidizer would result only from spattering occasioned by contact between liquid CTF and pools of water. In the more probable case of slowly leaking missiles, the problem is, of course, less acute. The following tests were made to demonstrate the relative resistance to ignition of various materials likely to be in contact with CTF in the event of an oxidizer leak. In some tests, the materials were intentionally contaminated with water or oil, since these might well be present during actual damage control operations.

"Armalon"* and "Aclar 33C"† are new products which are purported by their manufacturers to be very resistant to liquid CTF. Neoprene has been recommended by the manufacturers of CTF for protective clothing, but this recommendation evidently did not contemplate the close quarters and confined spaces likely to be met in shipboard handling of missiles, and further examination of this material is needed. Armalon, Aclar, and neoprene showed the most resistance to CTF and were examined more extensively than other candidate materials. Some other materials (paper, missile fuels, lubricants, etc.) that might reasonably be found in missile handling areas also were examined for their behavior with dilute CTF vapor, either separately or in contact with candidate protective clothing materials. The tests were arranged to show also the minimum concentration of CTF in air required to cause spontaneous ignition of these materials.

REACTIVITY OF VARIOUS MATERIALS WITH LIQUID CTF AND UNDILUTED GASEOUS CTF

Test Procedure

Most of the materials tested for compatibility with CTF either were in continuous sheet form or were polymer-coated fabric. They will be described more fully along with the test results. Approximately 3/4 by 2-1/2 in. samples were cut from unused stock. These were freed from dust and lint by wiping with a dry cloth, followed by blowing with a jet of compressed air.

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*Teflon (polytetrafluoroethylene) woven cloth laminated with a continuous sheet of FEP (fluoroethylenepropylene polymer). There may also be a thin layer of aluminum or gold deposited on the smooth side.

†Chlorofluoroethylene and fluorovinylidene polymer. Samples of this material were supplied as continuous sheets laminated with 2 mil thick aluminum foil; woven TFE (polytetrafluoroethylene) cloth impregnated with the polymer; and continuous sheets laminated with woven Teflon cloth.

In carrying out the liquid phase tests, CTF was allowed to fall in a small, steady stream onto the face of a sample placed horizontally on a clean stainless steel surface which had previously been rinsed with liquid CTF to burn off any foreign material which might act as a source of ignition. After initial coverage of the sample was complete, the CTF stream was operated intermittently to keep the sample face thoroughly wet. If ignition did not occur in one min, the test was recorded as negative. All specimens were at room temperature (70 to 90°F) at the start of a test. Likewise, the CTF supply was at room temperature. However, it was necessary that the CTF cool itself by partial evaporation to a temperature below its boiling point (53°F) to form the liquid.

Initially, gas phase compatibility tests were made by a jet of CTF vapor impinging on the sample material. The apparatus was simply a 1/4-in. copper tube from the supply tank, bent to discharge downward. The open end was held about 2 mm above the sample (see Fig. 14). This arrangement released objectionably large amounts of CTF, so a second apparatus was devised in which samples could be immersed in CTF gas. One end of a stainless steel pressure tank was cut off to give a chamber 1-3/4 in. I.D. by 11-1/2 in. inside length. The bottom was connected to the CTF storage cylinder, and a perforated plate diffuser was placed near the bottom (Fig. 15). Air in the chamber was first displaced by CTF gas, and then the test specimen, held by an aluminum wire clip, was lowered well below the rim of the chamber. A slow flow of CTF vapor was maintained during the test. This apparatus permitted exposure of the specimens to undiluted CTF gas with a considerably lower flow of the gas than with the jet. When ignition did not occur in 1 min, the test was recorded as negative. When ignition did occur, it was marked by a burst of flame without any preliminary glowing, and the burning area increased rapidly.

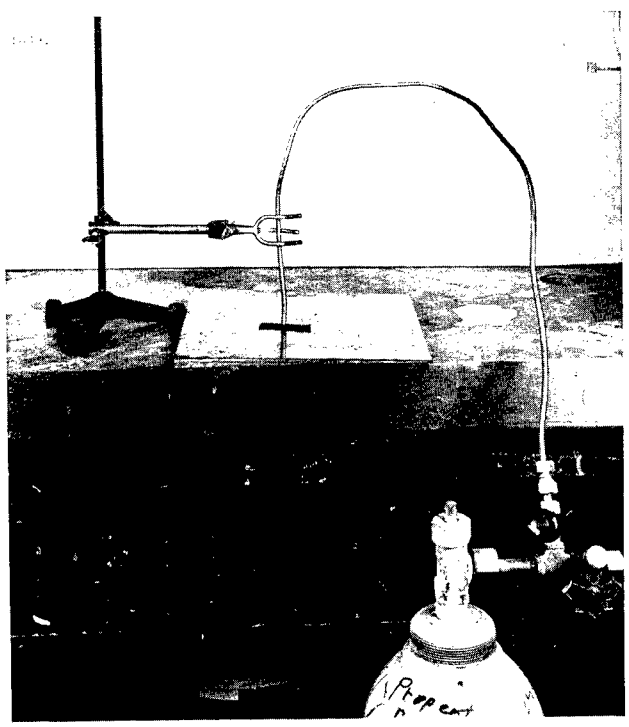

Fig. 14 - Apparatus for exposing samples to a jet of undiluted CTF gas

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Results of Tests

Neoprene (black) — Samples of this material were obtained from black neoprene laboratory gloves. Dry samples exposed to liquid CTF, and to gaseous CTF in both the jet and immersion tests, did not ignite. The only visible effect was a change from shiny to dull luster where the neoprene and liquid CTF were in contact. A piece of the neoprene was wetted with a 0.1-cc drop of water which spread out to cover a 1/4-in.-diameter circle, and a jet of CTF gas was directed onto the water. Ignition occurred in 4 or 5 sec. The wetted portion was immediately destroyed and the remainder burned vigorously as long as it was held in the CTF. A strip sample was smeared over half its length with a thin film of water and immersed in CTF gas in the immersion tube. Ignition was immediate and the fire rapidly spread to the dry portion. A 0.1-cc drop of water was placed on the back of a complete neoprene glove and liquid CTF was poured on the glove at a point 2 in. away from the water so that a substantial part was wet with CTF before ignition occurred at the water spot. The flow of CTF was cut off at the moment of ignition. The fire flashed back quickly over the CTF wetted area of the glove, leaving a hole of corresponding shape. The preceding test was repeated, using a drop of light lubricating oil instead of water. The result was identical. In the same fashion, a drop of oil was placed on a strip sample which then was immersed in CTF gas. Ignition was prompt and the whole sample burned.

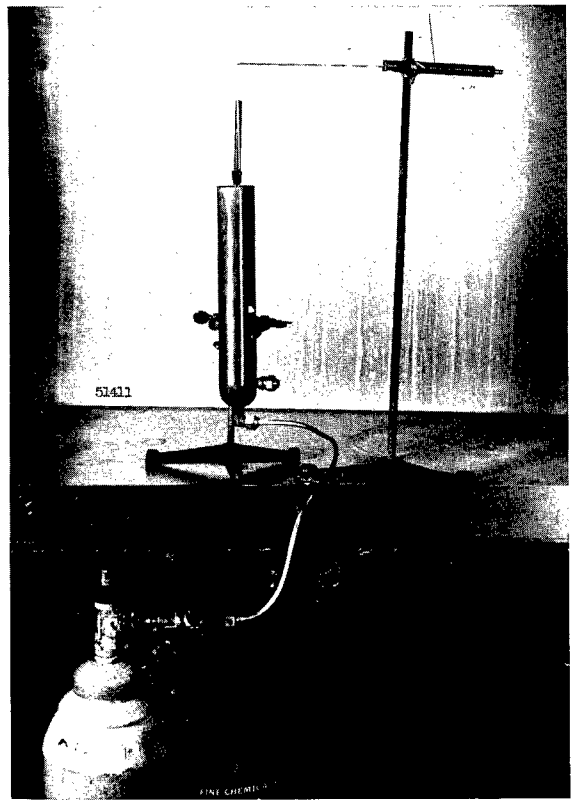

Fig. 15 - Apparatus for immersing samples in undiluted CTF gas. (In actual tests the sample is lowered well below the rim of the test chamber.)

Neoprene (unfilled) — A sheet of neoprene which contained no filler or coloring agent was obtained. Two samples of this material were immersed in CTF vapor. Both immediately ignited along the edges and burned with a very sooty flame. However, the fire did not flash over the faces of the samples.

Four samples of the unfilled neoprene were placed in a horizontal position and a stream of liquid CTF was applied near the center of each sample. One ignited immediately at the point of impact of the CTF and burned outward. One ignited immediately at the edge and burned rapidly inward. The other two remained wet with CTF for 3 and 5 sec, then ignited at an edge and fire flashed over the surface. In all trials the flames were very sooty.

Armalon — Both the Teflon and FEP sides of dry samples of uncoated Armalon and the aluminum side of metallized Armalon were subjected to a jet of CTF gas without producing any visible effect.

A 0.1-cc drop of water was placed on the FEP face of uncoated Armalon and a jet of gaseous CTF was discharged over the water and surrounding Armalon. (Since water does not wet Armalon, the water retained its drop shape.) In two trials out of six, the

water burned away, leaving the Armalon slightly curled. (Curling was subsequently found to be the normal result of heating Armalon.) In the remaining four trials, the water ignited, and a few seconds later the Armalon ignited and continued to burn vigorously as long as the CTF flow was maintained. The preceding tests were repeated on aluminum coated Armalon with similar results. Ignition failed to occur in one trial, and did occur in two trials. It was noted that the drop of water often moved about on the Armalon during a test. When the Armalon was lightly creased in two directions to form a shallow pocket the water drop was held stationary, and the application of gaseous CTF invariably resulted in ignition of the Armalon.

A specimen of uncoated Armalon was placed in a horizontal position with the FEP face upward. This face was kept thoroughly wet with CTF for 1 min without any sign of reaction. The same result was obtained when liquid CTF was applied to the aluminum face of metallized Armalon. However, a piece of paper dropped on one end of the CTF-wetted Armalon served as an ignition source; the samples ignited immediately and burned briskly.

Samples of both uncoated and aluminum coated Armalon were held horizontally, FEP layer upward, and a 0.1-cc drop of water was placed on each. Liquid CTF was then applied. In one trial (uncoated sample) the drop of water slid off the edge of the sample and there was no ignition. In two more trials with uncoated material, and in two with aluminum coated material, ignition took place in a few seconds and the Armalon continued to burn briskly in the CTF.

In the foregoing tests on Armalon, the flow of liquid CTF was shut off, or the samples were removed from the CTF immersion chamber, before the samples were completely consumed. Combustion stopped immediately; i.e., there was no tendency of the samples to continue burning in air alone.

Aclar 33C — Aclar-aluminum laminate, Aclar-TFE cloth laminate, Aclar impregnated TFE cloth, and a sheet of plain Aclar stripped from a piece of foil laminate were all unaffected by liquid CTF and undiluted gaseous CTF.

A sample of plain Aclar was stripped from a foil laminate and a 0.1-cc drop of water was placed on it, and then it was wet with liquid CTF. In two trials, the water was driven off the edge of the sample. In one trial, the Aclar ignited and continued to burn as long as CTF was applied. The fire was self-extinguishing when the CTF was shut off, but the residue was immediately reignited by additional CTF.

Aclar-aluminum foil laminate, Aclar-woven TFE cloth laminate, and Aclar solution impregnated Teflon cloth were wet near one end with 1 drop of light lube oil and immersed in CTF vapor. All ignited immediately and burned with sparkling, sooty flames until the samples were consumed. (The aluminum foil burned, as well as the Aclar.)

Materials of Construction for Oxygen Breathing Apparatus — Samples of the outer covering, liner, and seam reinforcement strips of the breathing bag of the Navy oxygen breathing apparatus (OBA, types A-1 and A-2) were subjected to a jet of CTF gas. The outer covering and the seam reinforcing strip ignited immediately and continued to burn vigorously until the CTF flow was stopped. The elastic liner of the breathing bag, when dry, appeared unaffected after 1 min. exposure to a CTF vapor jet. The same material, moistened with water, ignited immediately and burned vigorously. These materials were ignited immediately by a stream of liquid CTF. A small sample of the material used in the breathing bag of the OBA model A-3 was available for testing. This material is a laminate consisting of rubber impregnated cotton sheeting on the outside and a neoprene layer on the inside. Liquid CTF ignited the test sample immediately. It was not apparent which of the components was most sensitive to ignition. Since the construction of the OBA exposes a cross section of laminate at some points, liquid CTF can cause its ignition.

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Butyl Rubber — Samples of butyl rubber impregnated cloth, cut from "guided missile handlers protective clothing" (Federal stock number 8415-753-6210) were exposed to a stream of liquid CTF and to a jet of gaseous CTF. In both circumstances the material ignited immediately.

Vinyl Coated Cloth — Samples cut from an "acid and fuel resistant propellant handlers protective suit" (MIL-C-12527A (QMC)) made of vinyl polymer impregnated glass cloth, ignited immediately and burned briskly when exposed to either liquid or gaseous CTF.

Fire Hose — A 30-in.-long section of Navy cotton covered, rubber lined, fire hose was subjected to both liquid and gaseous CTF. The CTF was applied to the outside of the hose, near the center, so as to avoid contact between the CTF and the cut and somewhat frayed ends of the sample. Brief (approximately 1 sec) application of a stream of liquid CTF resulted only in slight scorching of the surface of the cotton jacket. The application of a steady stream of liquid CTF for 1 min produced a scorched circle about 4 in. in diameter. The cotton jacket was deeply charred at the point of impact of the CTF, but the rubber liner appeared little damaged. A jet of gaseous CTF scorched a circle 1-1/2 in. in diameter and burned a 1/2-in.-diameter hole through the cotton cover and almost through the rubber. The remaining rubber was so weakened that it was easily punctured with the blunt end of a pencil, and obviously would not be able to withstand normal service pressures.

REACTIVITY OF VARIOUS MATERIALS WITH DILUTE GASEOUS CTF

Test Procedure

CTF-air mixtures of the desired concentrations were prepared in the apparatus shown in Fig. 16. This apparatus comprised a 34-liter stainless steel tank, a pressure gage having a range of 2 atm absolute in 0.002 atm divisions, and an exposure chamber, assembled as shown in the figure. Copper tubing, brass flare fittings, and bellows-sealed brass valves were used in connecting the parts. The exposure chamber is the 1-3/4 by 11-1/2 in. stainless steel chamber described for the earlier tests with undiluted CTF. CTF-air mixtures were prepared by the method of partial pressures. That is, the system was first evacuated, then CTF vapor was let in to a predetermined pressure, and

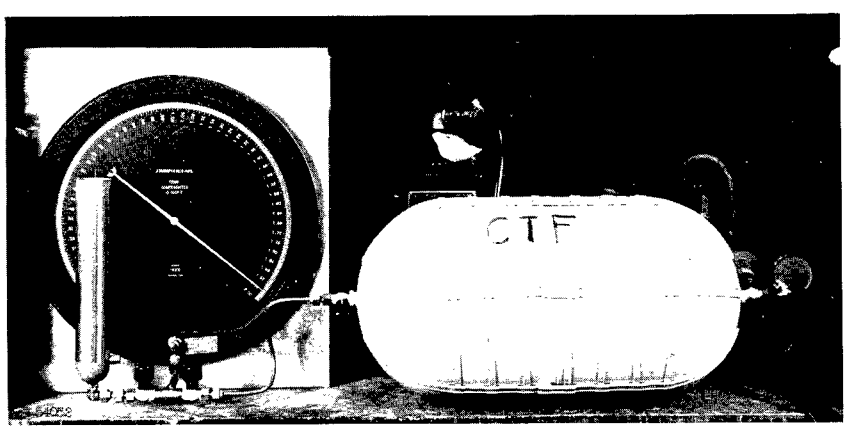

Fig. 16 - Apparatus for making CTF-air mixtures and for exposing samples to the dilute CTF

finally dry compressed air was admitted to the appropriate pressure between 1 and 2 atm absolute. The gases were allowed to stand for at least 1 hr to permit mixing by natural convection and diffusion. The volume concentration of CTF was taken as the ratio of CTF pressure to the total pressure.

In carrying out a test with a solid sample, a CTF-air mixture of the desired strength was prepared and the exposure chamber was connected to the reservoir and supported in a vertical position, except as noted for Armalon. When tests were made with water drops in contact with Armalon, it was necessary to turn the immersion chamber so that the test samples could be held horizontally. Otherwise, the water drops, which do not wet Armalon, would quickly slide off the samples. The CTF-air mixture was allowed to run through the chamber to flush out air and then a 3/4 by 2-1/2 in. strip of the material being tested was immersed in the still flowing gas mixture until ignition occurred, or for at least 1/2 min when there was no ignition. Liquid fuel samples were supported on glass wool wrapped around a glass rod. The samples were held well below the top of the exposure chamber to insure that they were in gas which had not been diluted by air currents at the mouth of the chamber.

Results of Tests

The reaction of the various materials with dilute CTF is given in Table 11 along with results found in earlier tests with undiluted CTF.

Table 11
Exposure of Various Materials to Gaseous CTF and Air Mixtures

Material	Reaction
Undiluted CTF	
Armalon, Uncoated	
Dry	No reaction in 1 min
With 0.1-cc drop of water	Water ignited in less than 2 sec in all tests; Armalon ignited at 5, 7, 9, 9, and 13 sec and continued to burn progressively
Armalon, Aluminum Coated	
Dry	No reaction
With 0.1-cc water drop on aluminum face	Water ignited in less than 2 sec; Armalon ignited in 6, 7, 8, 9, and 22 sec and continued to burn progressively
With 0.1-cc light lube oil on aluminum face near end of strip	Oil and Armalon both ignited immediately and Armalon continued to burn progressively
Aclar-Aluminum Foil Laminate	
Dry	No reaction in 2 min
With 0.1-cc light lube oil on aluminum face near end of strip	Oil and strip ignited immediately, and strip continued to burn progressively

(Table continues)

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Table 11 (Continued)

Material	Reaction
Undiluted CTF (Continued)	
Aclar-TFE Cloth Laminate	
Dry	No reaction in 2 min
With 0.1-cc light lube oil on Aclar face near end of strip	Oil and strip ignited immediately and strip continued to burn progressively
Aclar Impregnated TFE Cloth	
Dry	No reaction in 2 min
With 0.1-cc light lube oil near one end of strip	Oil and strip ignited immediately and strip continued to burn progressively
Neoprene	
Dry	No reaction in 1 min
Wet with 0.1 cc of water near end of sample strip	Wet portions ignited in 2, 3, 4, and 5 sec and samples continued to burn progressively
Butyl Rubber Impregnated Cloth	
Dry	Ignited in 2 sec and continued to burn rapidly
Wet with 0.1 cc of water near end of sample strip	Ignited immediately at one edge and continued to burn progressively
Vinyl Coated Glass Cloth	
Dry	Ignited immediately and continued to burn rapidly
Wet with 0.1 cc of water near end of sample strip	Ignited immediately and continued to burn rapidly
75% CTF	
Armalon, Aluminum Coated	
Dry	No reaction
With 0.1-cc drop of water	No reaction
Neoprene	
Dry	No reaction
Wet with 0.1-cc water near end of sample strip	Ignited and continued to burn progressively

(Table continues)

Table 11 (Continued)

Material	Reaction
50% CTF	
Armalon, Aluminum Coated	
Dry	No reaction in 1 min
With 0.1-cc drop of water	No reaction in 1 min
Face near end smeared with 1 drop of light lube oil	Ignited in 2 sec and continued to burn progressively
Neoprene	
Dry	No reaction
Wet with 0.1-cc drop of water near end of sample strip	Ignited in 6, 6, and 7 sec
Butyl Rubber Impregnated Cloth	
Dry	Ignited in 2 and 3 sec at edges of sample and continued to burn slowly
Vinyl Coated Glass Cloth	
Dry	Ignited in 1 and 2 sec at edges and continued to burn slowly
25% CTF	
Armalon, Aluminum Coated	
Dry	No reaction in 2 min
With 0.1 cc drop of water	No ignition in 4 min; back (Teflon) layer of the sample was partly bleached underneath the water drop
Smeared with 0.1-cc light lube oil near end of coated face	Oiled portion smoked lightly, but no other apparent reaction in 1 min
With scrap of paper in contact with aluminum face	Paper ignited in less than 1 sec, followed immediately by ignition of the Armalon, which burned progressively with a sooty flame
Aclar-Aluminum Foil Laminate	
Dry	No reaction in 2 min
With 0.1 cc of light lube oil on aluminum face near end of strip	Oil ignited with a slight "pop" after 4 sec. Aclar strip was sooty, but apparently undamaged.
Same, except oil was on Aclar face	Ignited in 5 sec. Aclar was almost completely burned away; foil was undamaged.

(Table continues)

Table 11 (Continued)

Material	Reaction
25% CTF (Continued)	
Aclar-TFE Cloth Laminate	
Dry	No reaction in 2 min
With 0.1-cc light lube oil on TFE face near end of strip	Ignited in 2 sec and burned slowly. Fire extinguished on removal to pure air, but reignited immediately when returned to 25% CTF.
Same, except oil on Aclar face	Same result as preceding test
Aclar Solution Impregnated TFE Cloth	
Dry	No reaction in 2 min
With 0.1-cc light lube oil near end of strip (oil soaked into cloth)	Ignited in 2 sec, and continued to burn progressively
Neoprene	
Dry	No reaction in 2 min
Wet with 0.1 cc of water near end of sample strip	One sample ignited in 11 sec; second sample dried, but showed no other reaction in 1 min
Butyl Rubber Impregnated Cloth	
Dry	No reaction
Wet	Ignited in 7 sec
Paper	
Dry	Ignited immediately
10% CTF	
Armalon, Aluminum Coated	
Dry	No reaction
With 0.1-cc drop of water	No reaction
Oily	No reaction
In contact with a piece of paper	Paper ignited; Armalon did not react
Neoprene	
Dry	No reaction
Wet with 0.1 cc of water near end of sample strip	No reaction
Face, near end, smeared with drop of lube oil	No reaction
In contact with a piece of paper	Paper ignited immediately, setting fire to the neoprene, which continued to burn rapidly

(Table continues)

Table 11 (Continued)

Material	Reaction
10% CTF (Continued)	
Butyl Rubber Impregnated Cloth	
Dry	No reaction
Wet	No reaction
Paper	
Dry	Ignited immediately
3% CTF	
Paper	
Dry	No reaction
Propellant Fuel	
MHF-3	Fumed; ignited in 4 sec
MHF-4	Fumed; ignited in 20 sec
UDMH	Fumed; ignited in 4 sec
Hydrazine	Fumed; ignited in 4 sec
2.5% CTF	
Propellant Fuel	
MHF-3	Fumed; ignited in 12 sec
MHF-4	Fumed; no ignition in 1 min
UDMH	Fumed; ignited in 6, 8 sec
Hydrazine	Fumed; ignited in 18 sec in 1 trial, failed to ignite in 2 trials lasting 30 sec
2% CTF	
Propellant Fuel	
MHF-3	Fumed lightly; no ignition in 30 sec
MHF-4	Fumed lightly; no ignition in 30 sec
UDMH	Fumed; ignited
Hydrazine	Fumed lightly; no ignition in 30 sec
1.5% CTF	
Propellant Fuel	
MHF-3	Fumed lightly; no ignition in 30 sec
MHF-4	Fumed lightly; no ignition in 30 sec
UDMH	Fumed; ignited in 7 and 15 sec
Hydrazine	Fumed lightly; no ignition in 30 sec
1% CTF	
Propellant Fuel	
UDMH	Heavy fumes were evolved for 90 sec, after which fuming decreased. The UDMH had disappeared in 120 sec without igniting

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REACTIVITY OF ARMALON AND ACLAR 33C TO UNDILUTED CTF VAPOR AT ELEVATED TEMPERATURES

Armalon and Aclar 33C appeared to have very similar resistances to attack by CTF vapor at ordinary ambient temperature. Since the outer layer of protective clothing is often exposed to sufficient heat, especially radiant heat, to substantially raise its temperature, it was deemed desirable to examine the behavior of Armalon and Aclar at elevated temperatures in an atmosphere of CTF vapor. None of the other materials examined in the previous tests approached these two in inertness, and only these two were carried through the test series. Neoprene was subjected to one relatively low temperature test.

Test Procedure

The 1-3/4 by 11-1/2 in. stainless steel exposure chamber used in the earlier tests was loosely wrapped with 3/16-in.-O.D. copper tubing which was connected to the bottom of the chamber. This in turn was surrounded by a cylindrical, electrically heated sleeve and a final layer of asbestos insulation. Temperature measurement and control was obtained by a thermocouple in a stainless steel well reaching nearly to the bottom of the chamber, and a temperature indicating controller for the heater sleeve. CTF was obtained through a direct connection between the copper helix and the stock tank.

Tests were made by bringing the temperature of the CTF flowing through the chamber to 150, 200, 250, or 300°C and then immersing a 3/4 by 2 in. sample strip of the material being tested in the CTF. The strips were held by an aluminum wire long enough to place the samples near the bottom of the chamber. All exposures were for a period of 2 min, unless ignition occurred sooner. Observations were made of any changes in appearance, texture, or flexibility of the samples.

Results of Tests

The results are given in Table 12.

As noted in the preceding tests, the Aclar layer of the laminates sometimes became brittle and was easily separated from the other layers. To determine whether this effect was due to heat alone, or due to reaction with the CTF, samples of the various Aclar combinations were heated in air, using the same apparatus, to temperatures as high as 350°C. No effects other than the appearance of incipient melting of the Aclar, and slight curling of the samples was observed. Obviously, the Aclar did react with CTF at elevated temperatures to the detriment of its physical properties.

DISCUSSION

Materials now used for protection against nitric acid or nitrogen tetroxide type missile propellants, as well as some other damage control gear, were shown to be unsuitable for protection against CTF. Butyl rubber impregnated cloth, vinyl polymer coated glass cloth, and parts of the Navy OBA (oxygen breathing apparatus) were self-igniting on contact with liquid CTF or CTF vapor. CTF vapor diluted to as little as 10% in air was incendiary with some of these materials in the presence of water or oily substances.

Neoprene, obtained as black, chemical resistant laboratory gloves, resisted liquid and gaseous CTF when the neoprene was dry and clean. However, a small amount of water or oil made the neoprene self-igniting on contact with 25% CTF vapor in air. Also, clean, dry neoprene was ignited by undiluted CTF vapor at 150°C.

Table 12
Effects of CTF Vapor on Armalon and Aclar 33C at Elevated Temperatures

Material	Effects at Temperature Indicated			
	150°C	200°C	250°C	300°C
Armalon, uncoated	Slight bleaching	Bleached; stiffened	Ignited in 1 sec in 2 trials; bleached but not ignited in 2 trials	Ignited immediately along edge, but fire was self-extinguished; remaining sample was bleached, stiffened and distorted
Armalon with aluminum coating	Bleached; aluminum easily rubbed off	Momentary ignition in 1 trial; no ignition in another; sample bleached in both trials; aluminum coating easily rubbed off	Bleached; aluminum easily rubbed off	One sample flashed along one edge, but did not otherwise burn; another sample did not ignite; both samples bleached; originally smooth aluminum side became pebbly
Aclar-aluminum laminate (5 mils thick)	Aclar easily peeled from aluminum foil	Laminate stiffened. Aclar easily peeled from aluminum foil.	Bubbles formed in Aclar; Aclar easily peeled from aluminum foil in 1 trial; Aclar ignited and continued to burn in 2nd trial	Aclar face ignited immediately near center, but fire did not spread in one trial; no ignition in 2nd trial; Aclar became brittle and flaky in both trials
Aclar-aluminum laminate (2 mils thick)	Laminate became stiffer; Aclar easily separated from foil	Laminate became stiffer; Aclar easily separated from foil	Bubbles formed in Aclar in 1 trial, but not in 2nd; Aclar easily peeled from foil in both trials	Aclar became brittle and easily flaked off of foil

(Table continues)

Table 12 (Continued)

Material	Effects at Temperature Indicated			
	150°C	200°C	250°C	300°C
Aclar-TFE laminate (5 mils thick)	Slightly bleached	Ignited immediately	Bleached; Aclar face nearly gone; remaining Aclar gritty and loose	Ignited and continued to burn briskly
Aclar-TFE laminate (2 mils thick)	Slightly bleached	Ignited immediately and continued to burn in 2 trials; bleached and became rough without igniting in 3rd trial	Ignited after 10-15 sec and continued to burn	Ignited immediately and continued to burn
Aclar solution impregnated, unannealed Teflon cloth	Bleached	Bleached; edges frayed	Ignited immediately and continued to burn	Ignited immediately and continued to burn in 2 trials; 3rd sample ignited in 10 sec and continued to burn
Aclar solution impregnated, annealed Teflon cloth	Bleached	Two samples ignited immediately and continued to burn. Third sample did not ignite, but bleached and frayed at edges	One sample ignited in 13 sec and continued to burn; 2nd bleached and Aclar disappeared without burning	One sample ignited immediately; 2nd ignited in 4 sec; both continued to burn

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Armalon (polyfluorethylene-propylene laminated with Teflon cloth) and various combinations of Aclar 33C (a polyfluorovinylidene) with aluminum foil or Teflon cloth showed much greater resistance to CTF liquid and vapor than any of the other materials tested. Both materials were unaffected by liquid CTF and undiluted CTF vapor at room temperature, when the samples were clean and dry. "Priming" with small amounts of water or oil or other combustibles made both materials more sensitive to CTF vapor. Both materials could ignite and burn slowly in 25% CTF in air initially at room temperature.

At elevated temperatures (200°C and higher) both Armalon and Aclar became more sensitive to undiluted CTF vapor, and there were occasional self ignitions of the samples at 200°C. At 250°C and above there was a strong probability of ignition. The Aclar, but not the Armalon, showed definite evidence of chemical reaction with the CTF with consequent deterioration of the material.

Although the foregoing tests demonstrate a wide range of CTF concentrations in which Armalon and Aclar will burn, it should be noted that the methods of ignition were extreme. The avoidance of easily ignitable material, such as grease or oil, on protective clothing is mandatory regardless of the kind of material of which it is made. Undoubtedly water may be present in damage control operations, but water does not wet Armalon and Aclar and droplets very easily move around, even on nearly horizontal surfaces. Thus, it appears unlikely that a drop would stay in place long enough to cause ignition. The neoprene, in contrast, was readily wetted, and, thus, is more likely to be ignited by CTF in the presence of water. One possible source of ignition is contamination with fuel which might be spilled from a damaged missile. It was found that as little as 1.5% CTF in air could cause self-ignition of UDMH and that 3% CTF would ignite any of the hydrazoid fuels or fuel components that were tested.

The results of the tests indicate that a reasonable amount of protection against CTF can be obtained from a gas-tight coverall made from Armalon or Aclar. Such a coverall would be designed to completely cover the damage control man and his oxygen breathing apparatus. It is anticipated that the wearer would be further protected by the cooling and cleansing effects of water spray from an L-11 fog nozzle or a Navy high velocity fog nozzle. Neoprene appeared useful for a coverall for protection against moderate concentrations of CTF but it was reactive, especially when wet, with liquid CTF and high concentrations of the vapor. Thus, coveralls made of neoprene would place much more dependence on a continuous, thorough washdown of the CTF with water spray than would Armalon or Aclar.

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CHAPTER 6

WATER SPRAY AS A DAMAGE CONTROL AGENT FOR CHLORINE TRIFLUORIDE

The use of water to convert liquid CTF to less hazardous compounds appears attractive as a method for disposing of accidentally released oxidizer. The principal products of the reaction between CTF and water are hydrogen fluoride, hydrogen chloride, and oxygen, accompanied by much smaller amounts of free chlorine and oxygen difluoride. Although the principal products, except for oxygen, are toxic and corrosive, they are highly soluble in water, and they should be readily trapped in water and washed away. It is well known that the bulk addition of water to liquid CTF results in an extremely vigorous or explosive reaction, but it appears feasible to apply water in a slow enough manner, such as a mist or spray, that the reaction proceeds smoothly. The tests reported in this section were made to show the effects on liquid CTF of water sprays ranging from a fine mist to a spray having coarse drops comparable to the spray produced by the Navy L-11 fog head. Additional tests were made to show the effectiveness of spray produced by the L-11 fog head in absorbing CTF vapor from a simulated slow leakage of this oxidizer.

WATER SPRAY APPLIED TO POOLS OF CTF

Test Procedure

Water spray was generated by one of three nozzles mounted with its axis vertical so that the spray was projected downward. The nozzles gave a choice of a fine, misty spray, a spray having an intermediate drop size, and a spray of relatively coarse drops. The nozzles are identified in this report by the manufacturers (Spray Engineering Company) model numbers J318D, 1B, and 4B. Water from the laboratory supply line was passed through a booster pump equipped for pressure regulation so that reproducible sprays were obtained from the nozzles. The sprays generated by these nozzles were the "full cone" type, i.e., a nearly uniform drop distribution in a transverse cross section of the spray. Liquid CTF was held in a 4.95 cm diameter by 1.35 cm deep dish placed under the nozzle. The water impingement rate was controlled by adjusting the distance between the nozzle and the CTF dish. A diagram of the apparatus is given in Fig. 17.

The drop size distributions of the sprays from the three nozzles used in the laboratory tests, and that of the L-11 fog head, were determined by trapping samples in melted petrolatum and measuring the drops with a calibrated microscope. The resultant data were arranged as cumulative percent of the number of drops in the sample versus drop diameter, and then plotted as logarithmic probability curves (Figs. 18 and 19).

In making a test, CTF was run into the dish and allowed to cool by evaporation until the loss was less than 0.2 gm/min. When the desired weight of cooled CTF was obtained, the dish was transferred to its position under the nozzle and the spray was started. (CTF:BPF was handled in the same way, except that its evaporation rate is low enough that self-cooling was not required.) The general appearance of the reaction, i.e., whether quiet, noisy, or explosive, was noted, as well as the appearance of any flames. The reaction time was taken from the start of the spray to the end of burning and

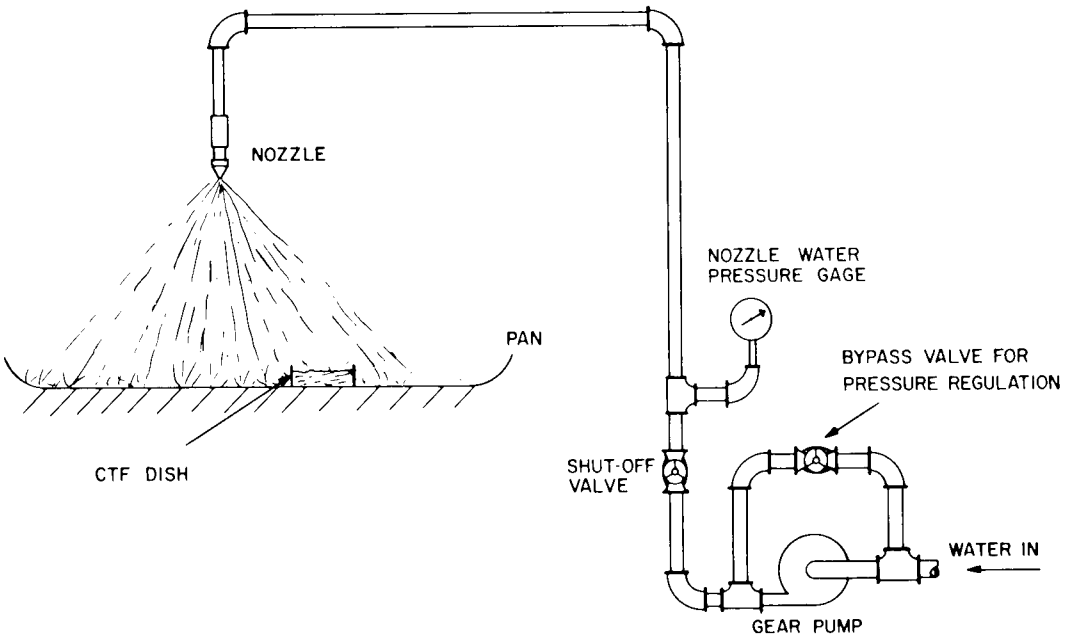

Fig. 17 - Apparatus for applying various water sprays to liquid CTF

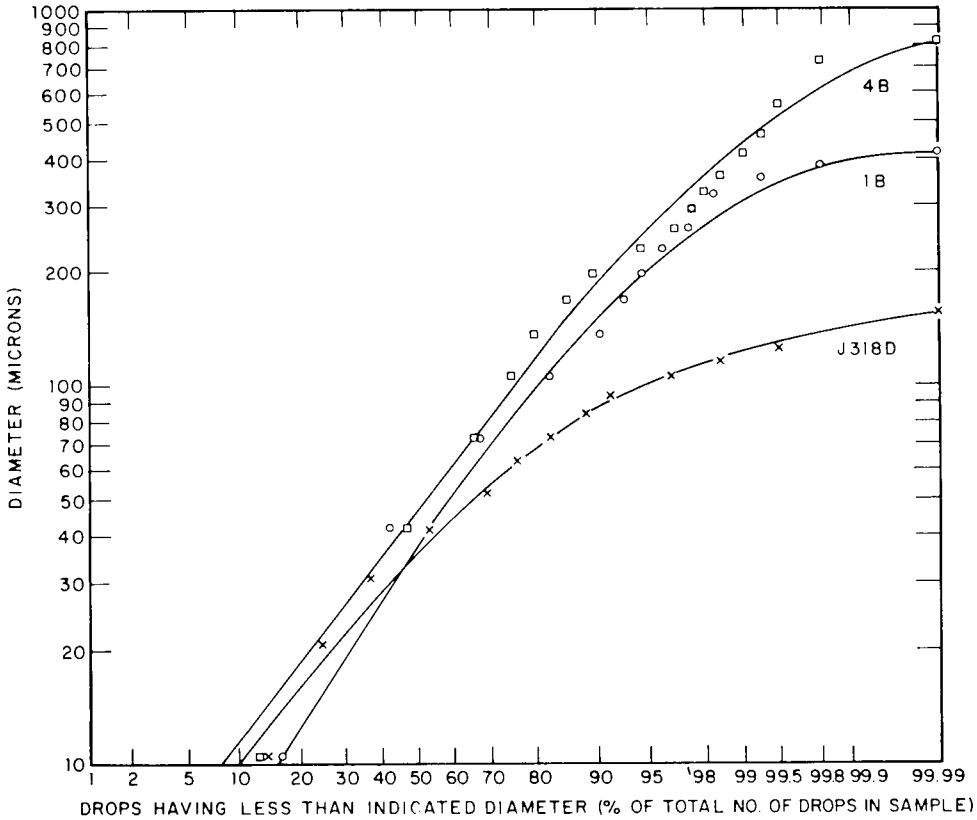

Fig. 18 - Drop size distribution of water sprays J318D, 1B and 4B

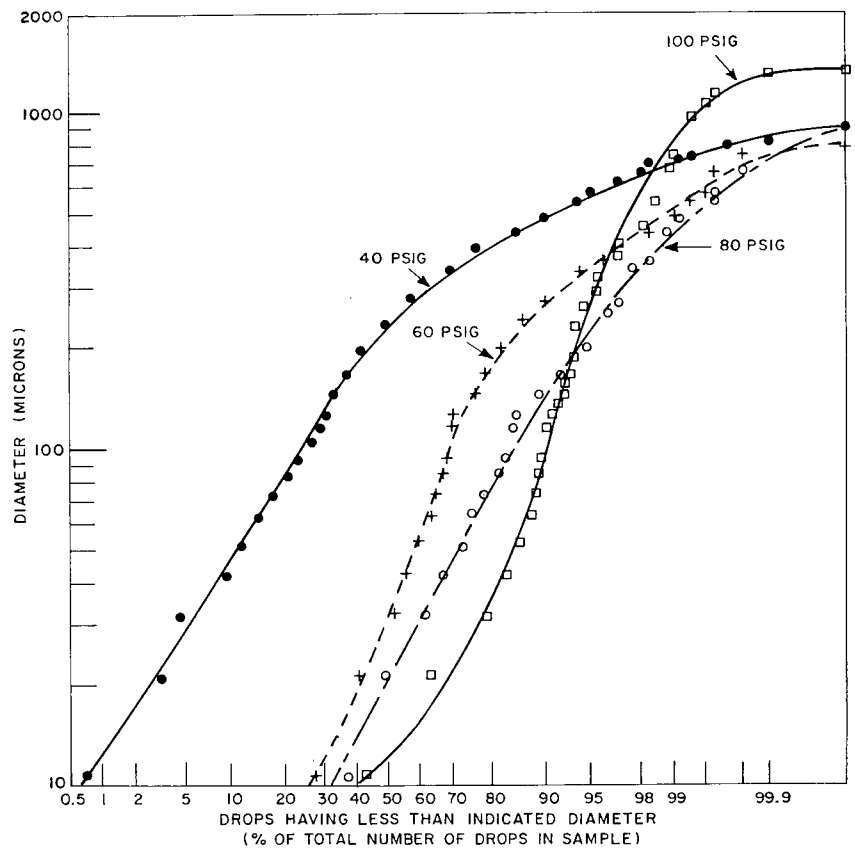

Fig. 19 – Drop size distribution in water spray generated by L-11 fog head at various pressures

evolution of fumes, provided the test was not terminated by an explosion. The spray was discontinued at the end of the reaction period and fluorine in the liquid residue was determined.

Results of Tests

The vigor of the reaction between oxidizer and water varied, as would be expected, with the size of the drops in the water sprays. The fine and intermediate sprays invariably produced flames above the oxidizers and showed little or no roughness in the reaction. The coarse spray produced steady flames in some tests with both oxidizers, and also caused explosions in some tests with CTF, but not with CTF:BPF. The CTF:BPF mixture produced noticeably more fumes with any of the sprays than the CTF alone, and generally reacted less vigorously than the CTF.

The data are summarized in Tables 13 and 14. The reaction time for CTF is the time lapse from the start of the water spray to the end of visible flames. There was no indication, such as fuming, that there was any reaction after flaming combustion ceased. The reaction time for CTF:BPF includes a period of fuming after flaming combustion ceased; this fuming was especially pronounced with the misty spray (J318D). The percent fluorine in the residue is the quotient of the weight of fluoride found in the residue

Table 13
Results of Applying Water Sprays to Pools of Liquid CTF

Spray Source	Water Rate* (gm/cm^2/min)	CTF Used		Reaction Time (min)	Fluorine in Residue (%)‡	Dissipation Rate (gm CTF/gm Water)	Appearance of Reaction
		(gm/cm^2)†	Depth (mm)				
J318D	0.52	0.48	2.7	1.00	6.7	0.92	Quiet, low flame
J318D	0.52	0.51	2.8	1.00	5.8	0.98	Quiet, low flame
J318D	0.52	1.02	5.7	1.58	1.9	1.24	Quiet, low flame
J318D	0.52	1.02	5.7	1.65	2.7	1.19	Quiet, low flame
J318D	0.48	1.53	8.5	2.42	1.9	1.32	Quiet, low flame
J318D	0.48	1.53	8.5	2.25	1.4	1.42	Quiet, low flame
1B	0.46	0.51	2.8	0.40	2.6	2.77	Mild crackling noise, steady flame
1B	0.46	0.51	2.8	0.40	2.8	2.77	Mild crackling noise, steady flame
1B	0.46	1.02	5.7	0.68	1.3	3.26	Mild crackling noise, with occasional ejection of sparks
1B	0.46	1.02	5.7	0.60	1.2	3.70	Same
1B	0.48	1.53	8.5	0.83	0.8	3.84	Same
1B	0.48	1.53	8.5	0.92	0.8	3.46	Same
4B	0.50	0.51	2.8	0.23	2.0	4.43	Vigorous crackling, with several loud pops
4B	0.50	0.51	2.8	0.23	1.4	4.43	Vigorous crackling noise
4B	0.49	1.02	5.7	Brief flare, followed by vigorous explosion which emptied CTF dish and produced numerous CTF-water fires in the test area.			
4B	0.50	1.02	5.7	0.42	0.8	4.86	Strong crackling sound, but no explosion
4B	0.50	1.02	5.7	0.40	0.8	5.10	Burned 5 sec, exploded, continued to burn
4B	0.50	1.02	5.7	0.38	---	---	Same
4B	0.50	1.53	8.5	Burned with crackling sound for a few sec, then exploded violently			

*To convert gm/cm^2 to gal/ft^2, multiply by 0.25.
†To convert gm/cm^2 to lb/ft^2, multiply by 0.049.
‡Based on weight of fluorine in CTF present at the start.

Table 14
Results of Applying Water Sprays to Pools of CTF:BPF Mixture

Spray Source	Water Rate* (gm/cm²/min)	CTF:BPF Used		Reaction Time (min)	Fluorine in Residue (%)‡	Dissipation Rate (gm CTF:BPF/gm Water)	Appearance of Reaction
		(gm/cm²)†	Depth (mm)				
J318D	0.50	0.61	2.8	0.50	5.6	2.44	Quiet, wavering, orange flame and fuming
J318D	0.50	0.61	2.8	0.56	2.3	2.18	Quiet, wavering, orange flame
1B	0.50	0.61	2.8	0.32	0.9	3.81	Yellow flame with steady, hissing sound and fuming
1B	0.50	0.61	2.8	0.27	0.8	4.52	Same
1B	0.49	1.20	5.6	0.56	0.5	4.38	Same
1B	0.49	1.20	5.6	0.60	0.4	4.08	Same
1B	0.49	1.20	5.6	0.60	0.3	4.08	Same
1B	0.49	1.82	8.5	0.81	0.3	4.58	Same
1B	0.49	1.82	8.5	0.77	0.2	4.83	Same
4B	0.50	0.60	2.8	0.27	0.6	4.44	Same
4B	0.50	0.60	2.8	0.27	0.7	4.44	Same
4B	0.49	1.20	5.6	0.45	0.3	5.43	Steady hissing accompanied by frequent snapping noise; yellow flame
4B	0.49	1.20	5.6	0.47	0.3	5.22	Steady hissing noise; yellow flame
4B	0.49	1.82	8.5	0.59	0.2	6.30	Steady hissing, accompanied by frequent snapping noise; yellow flame; very heavy fuming
4B	0.49	1.82	8.5	0.68	0.2	5.47	Same

*To convert gm/cm² to gal/ft², multiply by 0.25.
†To convert gm/cm² to lb/ft², multiply by 0.049.
‡Based on weight of fluorine in CTF:BPF present at the start.

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and the weight of fluoride calculated to be present in the oxidizer at the start. It is thus a measure of the effectiveness of the sprays in trapping pools of liquid CTF or CTF:BPF in situ. The dissipation rate was calculated by dividing the initial weight of oxidizer sample by the amount of water required to react with it or vaporize it, i.e.,

$$\frac{\text{gm oxidizer/cm}^2}{\text{reaction time x gm water/cm}^2\text{-min}}$$

Discussion

The foregoing tests demonstrated that pools of liquid CTF or a mixture of equal parts by weight of CTF and BPF can be safely dissipated by water sprays. A fine spray having a maximum drop size of 160μ reacts very quietly with either oxidizer, while a spray having a maximum drop diameter of 410μ reacts mildly with CTF:BPF and only slightly more vigorously with CTF. A spray having a maximum drop size of 840μ, reacted in much the same way with CTF:BPF, but showed a tendency to cause explosions and scattering of the oxidizer when applied to pools of CTF. This tendency toward violent reaction with CTF became more pronounced with increasing initial depth of the CTF pool.

The amount of oxidizer trapped in situ by the sprays was slightly higher for CTF:BPF than for CTF alone, but it amounted to only an inconsequential proportion of the amount of oxidizer present at the start of each test. This result is to be expected, since the accumulation of a substantial amount of water in bulk would certainly result in an explosive reaction and scattering of the liquids. The fluoride found undoubtedly was brought down by the sprays during the last few moments of the test when the amount of oxidizer present was slight.

The dissipation rate shows that, except for the J318D spray, a large proportion of the oxidizers were vaporized without reacting with the water at the test site. For the principal chemical reaction as given here:

$$ClF_3 + 2H_2O \rightarrow 3HF + HCl + O_2 + \text{heat}$$

and

$$BrF_5 + 3H_2O \rightarrow 5HF + HBr + \frac{3}{2} O_2 + \text{heat}$$

1 gm of water is capable of reacting with 2.57 gm of CTF or 2.91 gm of CTF:BPF. Only in the case of the J318D spray applied to CTF was there a substantial excess of water over that required for complete chemical reaction. The dissipation rate for the same spray applied to CTF:BPF showed a slight excess of water. In all other tests, the amount of oxidizer dissipated exceeded that which could react with the water. Manifestly, the heat of reaction resulted in vaporizing a portion of the oxidizer, which would then have to be scrubbed out of the atmosphere at a point more or less remote from the spill.

Comparison of the drop sizes found in the spray from a Navy L-11 fog head with those in the sprays used in the tests indicates that the L-11 spray should react relatively smoothly with CTF:BPF. A somewhat more vigorous reaction, probably accompanied by some spattering, would be expected if the L-11 spray were applied to pools of CTF. The L-11 spray was applied to about 2 lb of CTF:BPF held in a 1-ft-square pan. The reaction was mild, as expected, although a large amount of fumes was evolved. The pan of CTF may be seen (Fig. 20) on the ground just in front of the frame holding a Navy nozzle equipped with an L-11 fog head.

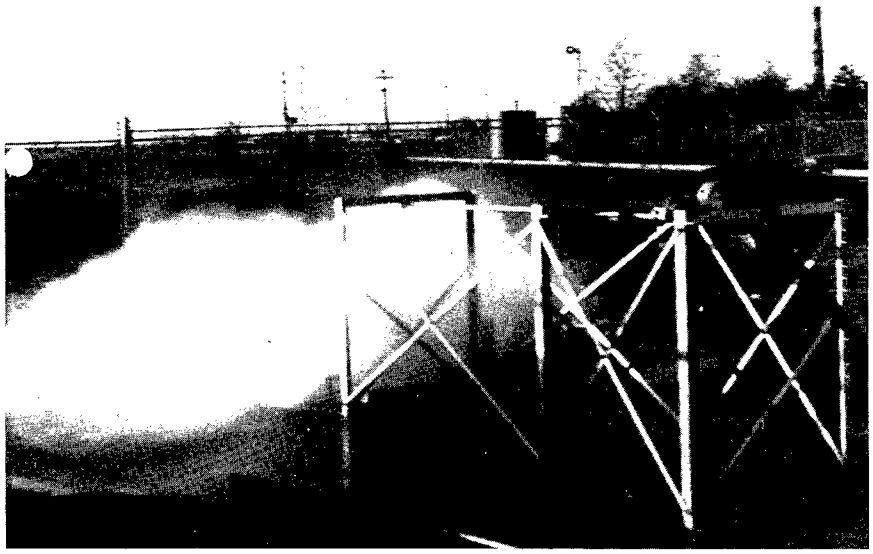

Fig. 20 - Application of L-11 spray to CTF:BPF

CTF VAPOR ABSORPTION BY WATER SPRAYS

There exists a possibility of leakage of CTF through "pin holes" which may be present in missiles due to faulty manufacture or corrosion. Where such a leak is above the liquid CTF in a missile, a jet of CTF vapor will be formed, thus producing both a toxic hazard and an ignition hazard. The following tests were made to outline, to some extent, the severity of these hazards, and to demonstrate the effectiveness of water sprays as a means of combatting them.

Small Scale Tests

Dilution of Vapor Leaks with Air — A CTF vapor leak was simulated by drilling a 0.054-in.-diameter hole in a tubing closure fitting which was then attached to a 500-cc tank of CTF. The nature of the jet of CTF vapor issuing under its own vapor pressure from this orifice was examined by the shadowgraph technique. The leak was placed so that it intercepted a beam of light projected onto a white screen. The difference in index of refraction of CTF and air produced shadows on the screen outlining the shape of the jet. It was found that a coherent stream of CTF was projected only about 1/2 in. from the orifice, after which there was turbulent mixing of CTF and air, resulting in a rapid increase in the diameter of the gas stream. The incendivity of this stream was explored by placing hydrazine, held on glass wool swabs, at various distances from the orifice. It was found that with the CTF supply at 70°F, the jet would ignite hydrazine 6 in. in front of the orifice, but would not cause ignition at 7 in. This test was repeated with the CTF heated to an initial temperature of 113°F to increase the vapor pressure. The jet again failed to ignite hydrazine at 7 in. when the gas was flowing at full pressure. Ignition did occur just as the CTF was cut off by closing the tank valve, but this may be attributed to the decrease in turbulence and consequent lessening of air entrainment. This assumption appears justified, since restarting the CTF stream at full pressure resulted in extinguishing the burning hydrazine.

Water Spray Applied to Simulated Leak—Test Procedure and Results — The effectiveness of a water spray in scrubbing CTF vapor from the atmosphere was explored on a small scale using the apparatus shown in Fig. 21. The simulated leak used in the preceding tests was mounted so that it discharged CTF vapor over the center of a 12 by 12 by 2 in. deep stainless steel pan. A water spray nozzle was mounted above the pan so that it projected a spray completely covering the pan at a rate of 0.8 gal water/min-ft^2. In carrying out a test, the water spray was turned on first, then the CTF was allowed to flow under its own pressure for approximately 15 sec, after which the spray was shut off. (All tests were started with the CTF at room temperature, approximately 70°F.) The amount of CTF released was determined by the weight loss of the reservoir cylinder, while the amount of CTF trapped by the spray was calculated from chemical analysis of the fluoride caught in the pan, and conversion of this result to the equivalent weight of CTF. The reaction of the water spray with the CTF vapor was quiet, and there was no flame, nor were fumes formed. The amount of CTF trapped by the spray is given in Table 15.

Table 15
CTF Vapor Caught by Water Spray Applied to a Simulated CTF Vapor Leak

CTF Vapor Released (gm)	Rate of CTF Vapor Leakage (lb CTF/hr)	CTF Trapped by Water Spray (Percent of CTF Released)
2.215	1.26	30
2.369	1.30	36
3.521	---	30

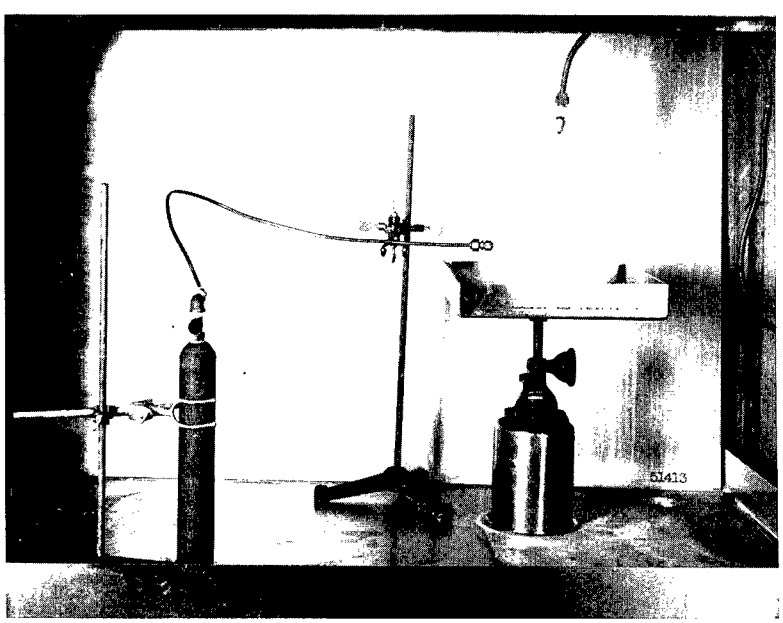

Fig. 21 - Small scale apparatus for trapping CTF vapor from a simulated leak

Discussion — Although only about one third of the CTF was trapped by the water spray in the foregoing tests, it was felt that water spray showed promise as a method for handling vapor leaks, and that larger scale tests would probably show an increase in effectiveness. Bench-scale tests were dropped at this point in favor of larger scale tests, using the Navy L-11 fog head as the water spray generator.

Absorption of CTF Vapor by Water Spray from Type L-11 Fog Head

Tests were made of the ability of water spray generated by the Navy type L-11 water fog nozzle (hereafter designated as "L-11 spray") to absorb CTF vapor from a vapor phase leak and convert it to less hazardous compounds.

Test Procedure — The apparatus comprised a 4 ft cubical steel tank, an L-11 fog head mounted centrally in the top plane of the tank, a simulated CTF vapor leak located 22 in. below the L-11 fog head, a source of CTF vapor, and appropriate auxiliary equipment to control water pressure and CTF vapor pressure. A drain valve was attached to the bottom edge of the tank through which the accumulated spray water from each test run was withdrawn for measurement and chemical analysis. In the first group of tests, the top of the box was open and the L-11 fog nozzle was mounted on a bar fastened across the top of the tank. In a second group of tests, a flat cover plate was used to close the top of the box in an effort to prevent loss of spray. When the cover was used, the nozzle was mounted centrally on the underside of the cover. A simulated leak was made by drilling a 0.027 in. diameter hole in a tubing closure fitting and attaching this by means of 1/4 in. copper tubing wrapped with waterproof insulation to a 500 cc cylinder of CTF mounted outside of the tank. The CTF cylinder was equipped with an electrical heating jacket to maintain the temperature, and consequently, the vapor pressure, of the CTF constant. Fresh water used for the spray was passed through a booster pump set to maintain the desired pressure at the nozzle. The apparatus is shown in Fig. 22.

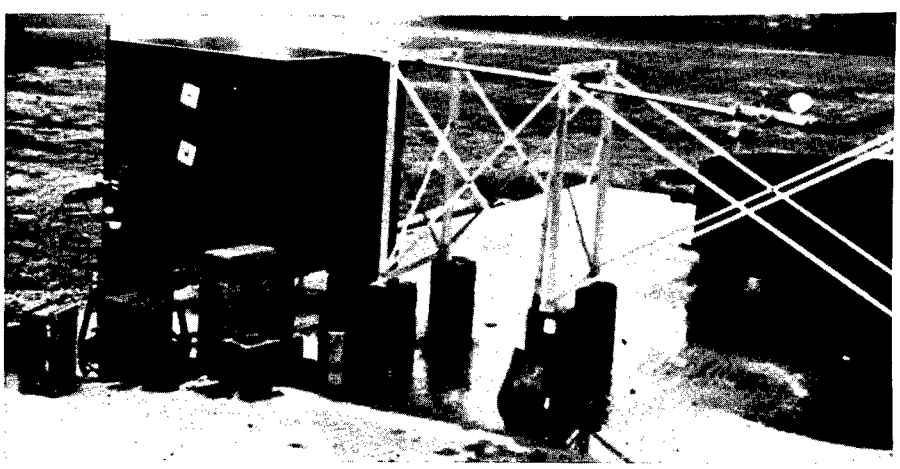

Fig. 22 - Apparatus used to test effectiveness of L-11 spray in trapping CTF vapor

Tests were made by adjusting the CTF reservoir temperature to produce a vapor pressure resulting in a discharge rate of 1 to 3 lb of CTF vapor per hour from the simulated leak. The water spray was started just before release of the CTF, and stopped immediately after shutdown of the CTF vapor flow. CTF flow was for a period of 0.25 min. (Test runs lasting much over 0.25 min often resulted in some liquification of CTF

in the vapor line, and erratic emission of CTF from the leak.) The contents of the tank were drawn off after each run and measured for total volume and the total fluoride content was determined by chemical analysis. The amount of CTF released during a test was noted as the weight loss of the CTF reservoir cylinder. All tests were made when the ambient temperature was well above the condensation temperature of CTF, and only a light breeze (not over 2 mph) was blowing.

Results of Tests — The CTF vapor and water spray reacted smoothly, without any sign of explosiveness or other roughness. No fumes or flames were observed, although a fine mist was continuously evolved from the tank. It should be noted that the L-11 nozzle produces spray by the impingement of a multiplicity of water jets, and that this type of spray entrains a large volume of air which eventually is forced back out of the tank, carrying some of the finer water drops with it. This spray is also observed in the absence of CTF. Observers standing downwind of the apparatus could detect only a faint trace of halogen odor in the mist when the CTF leak was in operation.

Some tests were run with a flat steel plate lid on the test tank in an effort to reduce the mist. This arrangement, however, did not produce much change in the amount of halogen recovered. The data are presented in Table 16, in terms of the rate of CTF release from the simulated leak and the proportion of this CTF brought down by the spray as calculated from the fluoride found in the accumulated spray.

Table 16
CTF Caught by L-11 Water Spray Applied to a Simulated CTF Vapor Leak

CTF Released (gm)	Rate of CTF Vapor Leakage (lb CTF/hr)	CTF Trapped by Water Spray (percent of CTF released)
Open top test apparatus. Ambient temperature 68-70°F		
1.999	1.06	92
2.802	1.48	83
1.987	1.05	88
2.745	1.45	85
Closed top test apparatus. Ambient temperature 84-90°F		
4.042	2.14	90
5.830	3.09	89
5.686	3.01	93

Discussion — The foregoing tests indicate that the Navy L-11 fog head supplies a spray that can rapidly and safely trap CTF from vapor phase leaks of considerable magnitude. The data indicate an efficiency of approximately 90% entrapment of the CTF where there is an opportunity for losses to the ambient atmosphere. In a relatively tightly closed ship's compartment, the L-11 spray should be even more effective. The data given were based on tests where the spray was flowing only while CTF vapor also was being released. Continued scrubbing of a ship's compartment atmosphere after a leaking missile is removed will result in rapid and complete decontamination.

CHAPTER 7

APPLICATION OF FIRE FIGHTING FOAM TO POOLS OF LIQUID CTF

The use of air-water foam as a means of bringing water into contact with liquid CTF to provide controlled destruction of the CTF has been proposed. There is also the possibility of foam being used for fire fighting purposes in the event of a missile mishap and this foam inadvertently coming in contact with the oxidizer. The following tests were made to show the results of covering liquid CTF with a blanket of mechanically generated fire extinguishing foam.

TEST PROCEDURE

A small-scale foam generator (Figs. 23 and 24) developed in the course of other programs at this Laboratory was set up. The outlet of the generator was provided with a Y-valve so that samples of the foam could be collected and tested in the operator's room of the test building or could be delivered through flexible tubing to the test cell. CTF was held in a 1 in. deep by 4-3/4 in. diameter stainless steel dish which was placed inside a 2 in. deep by 12 in. square pan. The outlet of the foam delivery tube was placed to deliver foam about 2 in. away from the dish, from where it flowed over the CTF. This arrangement allowed slugs of water, which occasionally formed in the foam line, to fall safely outside of the CTF container (Fig. 25)

In running a test, CTF was poured into the dish to form a pool 2 to 3 mm deep. In the meantime, the foam generator was started and adjusted to make foam of the desired "expansion"; i.e., ratio of foam volume to the volume of its liquid constituents. The foam first formed was run through the outlet in the operator's room where samples were collected for checking its quality by standard methods. When a satisfactory foam was obtained, the Y-valve was switched and foam was allowed to build up in the test pan and to flow over the CTF. The lowest expansion foam used (expansion 6) was fairly fluid, and promptly flowed over the CTF. As the expansion was increased in subsequent tests, the foam became increasingly stiff until, at expansion 16, the foam alternately built up a mound around the outlet and then collapsed so that the motion of the foam blanket over the CTF pool was slow and irregular. In some tests, water spray from an overhead nozzle was applied to the foam-covered CTF.

RESULTS

In general, the foams of various expansions at first reacted mildly with the CTF. The mild reactions were then terminated by more or less vigorous explosions which scattered the contents of the CTF dish. The individual tests are described in more detail.

Foam of expansion 6 was applied to CTF. The foam burned vigorously, but continued to flow over the CTF until it was completely covered. At this time there was a strong explosion, and the reaction apparently stopped due to depletion of the CTF, although foam remained in the dish. More CTF was added and the rapid burning was again observed for a short time, after which there was another vigorous explosion which scattered the contents of the dish.

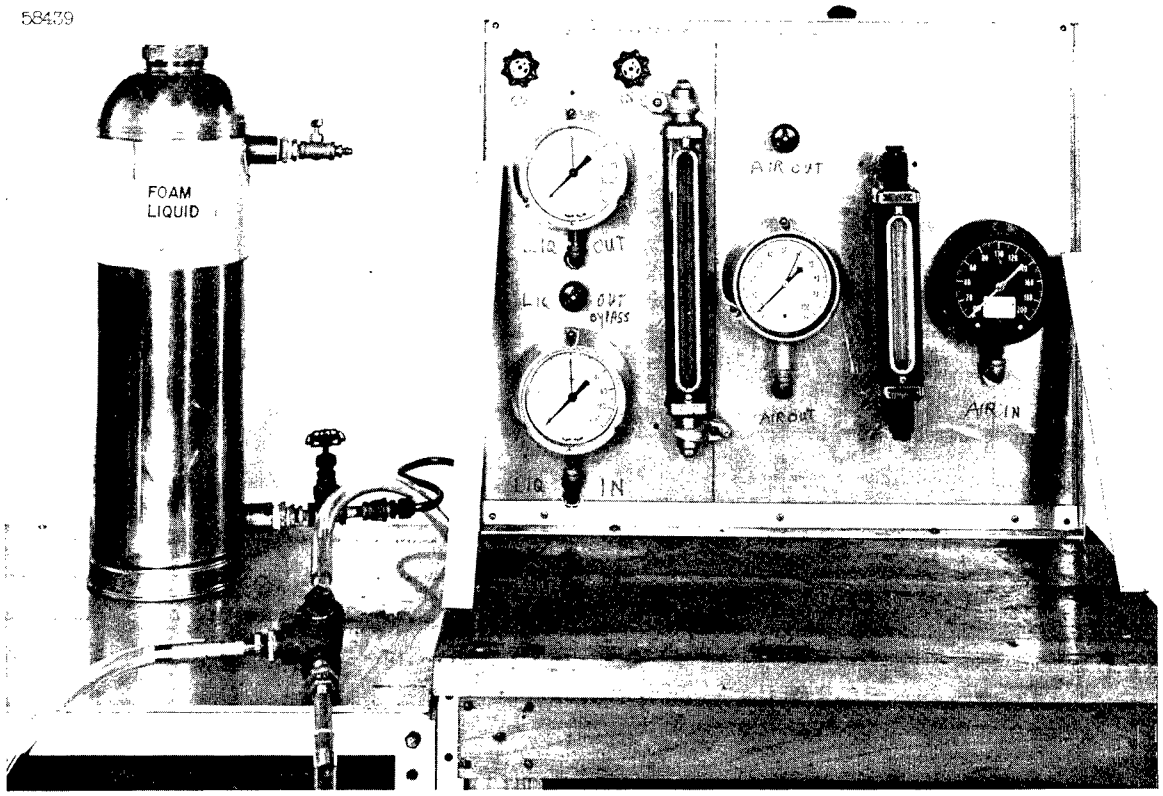

Fig. 23 - Foam generating apparatus

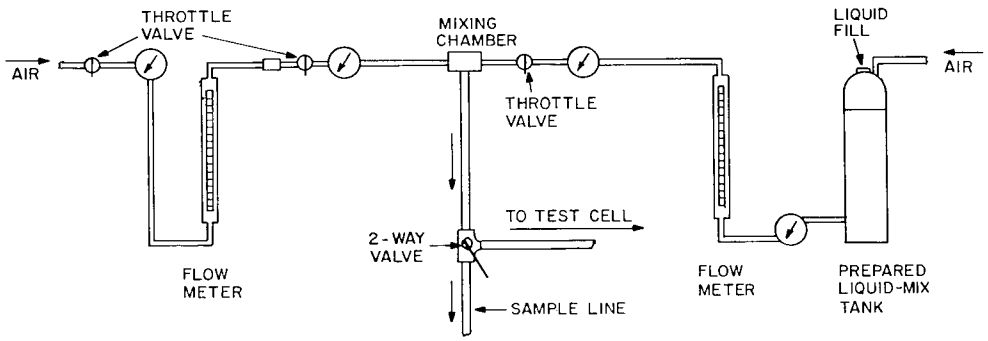

Fig. 24 - Diagram of foam generating apparatus

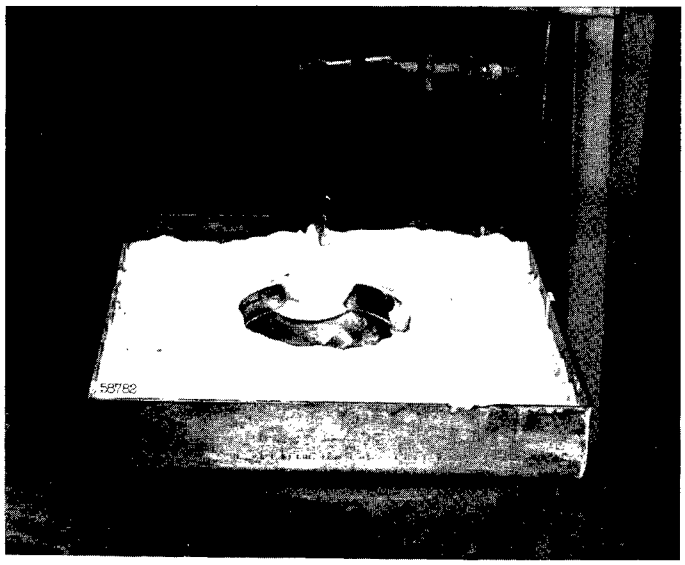

Fig. 25 - Apparatus for applying a foam blanket to a pool of CTF

Foam of expansion 6 again was applied to CTF. Vigorous reaction causing spattering of the foam started almost immediately on contact of the foam with the CTF, and continued until the dish was covered with foam. This test was repeated once more with the same results.

Foam of expansion 10 was applied to CTF. The foam flowed over the CTF with no apparent reaction other than a low flame at the leading edge of the foam blanket. When the CTF was completely covered, the water spray was actuated. There was a single loud explosion which scattered the contents of the dish.

Foam of expansion 13 was applied to CTF. The foam again showed no reaction other than quiet burning until the CTF was nearly covered. At this point there was a violent scattering of the contents of the dish.

Foam of expansion 16 was applied to CTF. This reacted smoothly with the CTF at the leading edge of the foam blanket, and flames were seen at scattered points throughout the foam after the CTF was completely covered. Water spray reduced the height of the flames and caused mild agitation of the foam, but there was no tendency toward vigorous reaction.

DISCUSSION

It is known that liquid starts accumulating at the base of a foam blanket as soon as agitation of the foam is stopped. Apparently the rate of accumulation of liquid at the interface of the foam and the CTF is slow enough to permit smooth reaction between the two when the foam is freshly formed. It is surmised that this drainage is not uniform throughout the foam blanket, and in time, globules of solution are formed and held up in the foam until they are heavy enough to break through to the CTF layer. This should produce a violent reaction, just as the bulk addition of water to liquid CTF does.

The intermittently vigorous reactions between foam and liquid CTF detract from its usefulness as a disposal agent for the oxidizer. However, the spattering does not appear vigorous enough to preclude using foam to extinguish fires in material adjacent to pools of CTF, even if such use results in casual contact between the foam and CTF.

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CHAPTER 8

EXTINGUISHMENT OF BURNING MHF FUELS

The constituents of the mixed hydrazines (MHF) series of propellant fuels are all readily soluble in water, hence, dilution of burning fuel is an obvious method of fire extinguishment. There will be occasions, however, when other extinguishants may be preferred. For example, portable dry powder extinguishers might be held in standby position to cover small spills of fuel. Again, mechanical foam may be used to combat an aircraft crash fire in which missile fuel constitutes only a small portion of the combustibles present. The following tests were made to compare the behavior of the MHF fuels with that of hydrocarbon fuels.

BURNING BEHAVIOR OF POOLS OF MHF-4

Five hundred cc of MHF-4 was placed in a 2 in. deep by 12 in. square pan and ignited. For about 1 min from the start, the MHF-4 burned very much like gasoline; i.e., there was a column of yellow flame about 3 ft high over the pool. After 1 min, the fuel began to froth, and toward the end of the burning period (5 min) the fuel appeared very viscous. During the latter part of the burning, bright orange colored tongues of flame were noted near the surface of the fuel. Immediately after the fire burned out, there was a syrupy residue which occasionally emitted sparks.

EXTINGUISHMENT OF BURNING MHF-4 WITH DRY CHEMICAL EXTINGUISHMENT POWDERS

Commercial Extinguishing Apparatus Used

A commercial 10-lb-capacity dry powder extinguisher was used for the initial tests of the extinguishing ability of bicarbonate base powders. This extinguisher used carbon dioxide from a small auxiliary tank to suspend and discharge the extinguishant powder, held in the main tank, through a short hose and nozzle. It was used without modification at first, but later it was changed to reduce the rate of application of powder to the burning fuels. Five hundred cc of MHF-4 were placed in the 2 by 12 by 12 in. pan and ignited. After a preburn of 15 sec, the extinguisher was operated from a distance of 10 ft, aimed so that the center of the powder cloud passed over the burning fuel. In two tests out of four, using sodium bicarbonate base powder, extinguishment was instantaneous. In the other two tests, flickering flames persisted for 2 or 3 sec in the lee of the pan wall. The tests were repeated, using PKP (potassium bicarbonate base) powder, with the same results. A similar set of tests was made with gasoline in place of the MHF-4. Again, the extinguishment was instantaneous, or only momentary burning occurred in the lee of the pan wall.

In an effort to increase the extinguishment time, and thereby make the test more definitive, the rate of powder application was decreased. The extinguisher nozzle supplied by the manufacturer had a 1/4-in.-diameter orifice. New nozzles having 3/16 in. and 1/8 in. orifices were substituted for the original. These changes in the powder delivery rate, however, did not make any apparent difference in the extinguishment time

and it became apparent that the commercial extinguisher expelled powder at much too high a rate to allow comparison of extinguishants or fuels.

Special Laboratory Extinguishing Apparatus Used

Another procedure was tried for measuring the relative effectiveness of dry powder extinguishants on MHF-4 and gasoline. An apparatus was set up (Fig. 26) in which a long tray of burning fuel was subjected to a cloud of extinguisher powder whose concentration varied according to distance from the source and adjustment of the generator pressure control. The 10-lb commercial extinguisher previously used was modified by substituting a pressure regulated supply of carbon dioxide for the original pressurizing cartridge. The discharge nozzle was a short, straight piece of 3/16-in.-I.D. tubing, rigidly mounted, and pointing horizontally, so that it projected a powder cloud enveloping the full length of the tray. The fuel tray was made of stainless steel, 1/2 in. deep by 3 in. wide by 36 in. long. The straight nozzle produced a rapidly expanding stream, so that the powder concentration was decreased by entrained air as it passed over the length of the tray. The powder concentration could further be controlled by regulating the carbon dioxide supply pressure.

In carrying out a test, 60 cc of fuel was placed in the tray and ignited. The powder discharge was initiated and the discharge pressure adjusted until flames over the fuel were driven back 2 ft from the end of the tray nearest the nozzle. In practice, there was some wavering back and forth of the flame front, but its position remained within ±2 in. of the 2-ft mark until the fuel was almost completely burned out.

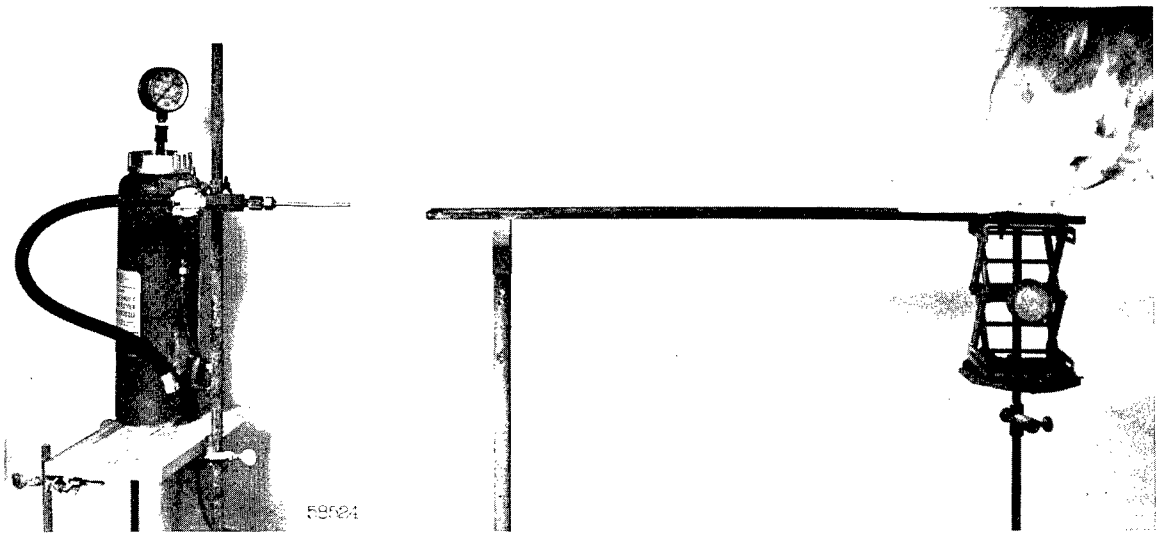

Fig. 26 - Apparatus for comparing relative ease of extinguishment for MHF and gasoline by dry powder extinguishants

The test was run several times with both MHF-4 and with gasoline. Both fuels required the same powder (PKP) discharge rate to hold their flame fronts at the 2-ft mark, and it appears that the dry powder extinguishant is as effective on the MHF fuel as it is on gasoline.

EXTINGUISHMENT OF BURNING MHF FUELS WITH MECHANICAL FOAM

Equipment for generating mechanical foam from Navy foam concentrate generally is available to damage control units for combatting gasoline fires. The use of this same type foam for missile fuel fires appears attractive. However, the solubility and chemical reactivity of the hydrazines, in contrast to hydrocarbons, should be expected to affect the fire extinguishing quality of the foam. The following tests were run to compare the relative effectiveness of type V protein base mechanical foam applied to missile fuel with the same type of foam applied to gasoline fires.

Test Procedure

The foam generator used in earlier tests was set up to deliver foam to a 2 by 12 by 12 in. pan containing burning MHF-3 or MHF-4 (Fig. 27). The foam was applied just inside the edge of the pan, at midlength, and it then flowed over the surface of fuel. The time required for the foam to form a complete blanket over the fuel and extinguish the flames was noted. The same test was made using gasoline for comparison.

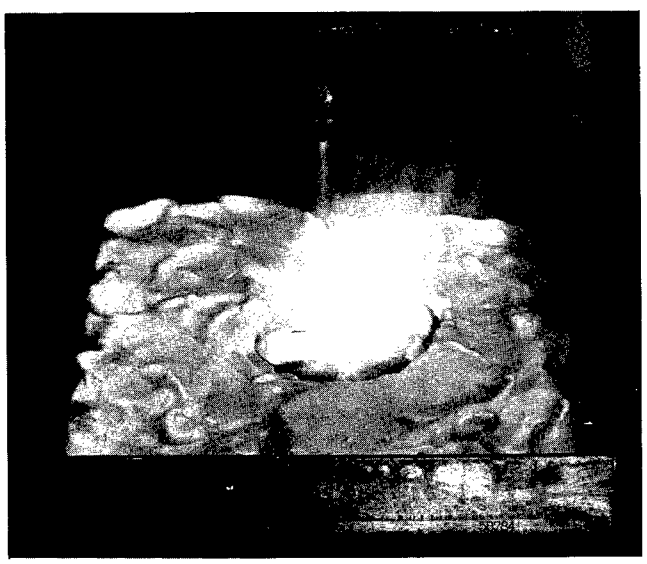

Fig. 27 - Application of foam to burning MHF fuels

Results

The time required for extinguishment of the burning fuels using foam of expansion* 4 and also using foam of expansion 9 is given in Table 17.

Table 17
Application of Foam to Burning MHF Fuels

Foam Expansion	Fuel	Extinguishment Time (sec)
4	MHF-3	51, 53
4	MHF-4	26, 30, 44
4	Gasoline	44
9	MHF-3	55, 70, 81, 84
9	MHF-4	43, 53, 73
9	Gasoline	44

Breakdown of the foam bubbles at the line of contact between the flowing foam blanket and the surface of the MHF fuels was much more noticeable than in the case of gasoline. However, the foam did form a seal over the fuel, effectively extinguishing the fire. A torch (kerosene soaked cloth) was passed back and forth over the test pan immediately after extinguishment to determine whether significant amounts of fuel vapor were escaping through the foam blanket. No reignition was produced in this manner. When a substantial area of the fuel was uncovered by pushing back the foam far enough that it did not promptly reseal, the fuel could be reignited. This produced "burnback" of the foam at a rate, judged by experienced observers, to be of the same order as the burnback over gasoline.

Discussion

Protein based, mechanically generated foam intended primarily for use in extinguishing hydrocarbon fires was found to be effective on MHF type fuels. When low-expansion foam (high proportion of water) was used, extinguishment time was approximately the same for MHF-3 and MHF-4 as for gasoline. With a high-expansion foam, extinguishment time was somewhat longer and more erratic for the hydrazines, especially MHF-3. The process of extinguishment appears to be a combination of cooling and air exclusion by the foam in addition to dilution of the fuel with water derived from the foam. The presence of MHF spills in case of an airplane crash should not significantly affect fighting aircraft fuel fires, and foam can be used to extinguish burning missile fuel alone.

*Ratio of the volume of the foam to the volume of its constituent liquids.

CHAPTER 9

SUMMARY AND GENERAL DISCUSSION

The desirability through improved performance of stored liquid propellant missiles for Naval use has been established. The concept of using liquid fuels and oxidizers stored in separate compartments of the missile propulsive system, in contrast to the single charge of solid propellant, has been accepted by the Navy. Currently, missiles using nitric acid as the oxidizer and mixtures of amines as fuel are aboard ship for evaluation tests. The substitution of interhalogens, particularly CTF (chlorine trifluoride), and mixtures of hydrazine and its derivatives, will provide an even more effective propulsion system. The foregoing tests were made to evaluate the hazards of accidental spills or leaks of either or both propellant components, and to point out methods of handling such mishaps. The use of materials and equipment now found aboard ship, or, where necessary, readily obtainable materials, has been emphasized.

The difference in safety hazards between fuming nitric acid and CTF is mostly one of degree rather than kind. CTF is more prone to form hypergolic pairs (self-igniting) with a variety of common materials than is nitric acid. Its lower boiling point also leads more readily to the formation of a hypergolic vapor. While the acid mixes readily with water in any manner to form less dangerous dilute solutions, CTF reacts vigorously to form other chemical compounds, and care must be used in applying water to avoid unacceptable, vigorous reactions. The toxicity of CTF is such that complete respiratory and body protection is required for personnel entering contaminated areas. This does not set CTF apart from other less active propellants, or even the products of combustion of ordinary combustibles, since all are substantially toxic and require protection. The only problem is the selection of suitable materials of construction.

The extinguishment of burning hydrazine fuels can be effected by any of the agents and techniques applicable to ordinary liquid combustibles. The hydrazoids, like the mixed amines, are soluble in water, and other investigations have shown that they can be extinguished by water applied as a cooling spray, or that they can be diluted to nonflammable solutions by bulk application of water. This investigation showed that they respond almost as readily as gasoline fires to protein base mechanical foam and to established dry chemical powder extinguishants. The fuels also are toxic and require personnel protective clothing. However, clothing which provides protection against the oxidizers should be far more than adequate for the hydrazoid fuels.

Chapters 2 and 3 of this report consider the use of powdered materials to absorb gross spills of liquid CTF to prevent spreading of the liquid, and to permit its removal by mechanical means to closed containers for subsequent disposal overboard. A wide variety of candidate absorbents were tested for compatibility with CTF. Only fully fluorinated inorganic salts were found suitable. The others were either spontaneously ignited, or they were easily ignited by minor amounts of contaminants or moisture. Calcium fluoride (fluorspar), cryolite, and technical sodium fluoride were applied to pools of CTF in sufficient quantities to soak up all of the liquid. At ambient temperatures, when the temperature of the powders was substantially higher than the boiling point of CTF (53°F), there was an initial rapid boiloff of 25 to 46% of the CTF. When the powder temperature was lower than the boiling point of CTF, there still was some initial boiloff in the amount of 13 to 22% of the original pool. Some initial boiloff was to be expected from the introduction of the warm powder, but the substantial loss from the introduction

of cold powder was surprising. It was later established (Chapter 4) that there is a reaction between each of the powders and CTF, resulting in the generation of noncondensable gaseous products. Calcium fluoride was the worst offender, while cryolite produced the least boiloff. In any event, the vaporized CTF must be removed by venting overboard, or by scrubbing the atmosphere with water spray.

The inorganic fluorides, in the degree of fineness of the powders tested, do not form compounds or gels having vapor pressures less than that of CTF alone (Chapter 4). Other investigators have had some success in gelling CTF with inorganic fluorides, but elaborate apparatus and techniques are required, and at this time it does not seem likely that gelling, in contrast to "soaking up," will be feasible in handling spilled CTF.

Various materials now used in the construction of propellant handlers protective clothing and other damage control gear were found deficient for protection against CTF (Chapter 5). However, two relatively new fluoropolymers, Armalon and Aclar, were shown to be far more resistant to CTF than any of the other materials tested. Although protective coveralls made of either of these two fabrics may react with liquid or strong gaseous CTF under some conditions, they should give reasonably reliable protection. It is anticipated that the wearer will keep back as far as practicable from pools of CTF, and that he will be additionally protected by a continuous washdown with water fog or spray. Both polymers are commercially available and methods of fabrication of finished products have been developed.

Incidental to the foregoing tests, the least concentration of CTF vapor in air capable of causing self-ignition of paper or of propellant fuel was measured. Paper was found to ignite in 10% CTF in air, while hydrazine fuels and fuel components could be ignited by 1-1/2 to 3% CTF in air.

Water spray was found to be effective both for dissipating pools of liquid CTF and for controlling leaks of CTF vapor (Chapter 6). Fine water spray reacts very quietly with liquid CTF, but requires considerably more time to dissipate the CTF than is required by coarse sprays. Laboratory tests showed that sprays having a maximum drop size up to about 800 μ in diameter reacted rapidly, but without excessive vigor. However, the data showed that the water required to just dissipate the pools of CTF was insufficient for complete chemical conversion of CTF to other compounds in situ. Hence, some of the CTF must have been vaporized unchanged and, in practice, it would have to be removed by ventilation or scrubbing of the atmosphere. Field tests showed that spray generated by the Navy L-11 fog head also could be applied to shallow pools of CTF without violent reaction and spattering of the oxidizer. Water spray from the L-11 nozzle was found very effective in trapping CTF from simulated vapor leaks. The tests show that with leakage rates up to 3 lb of CTF per hour, at least 83 to 93% of the CTF was converted to less hazardous compounds, and it may reasonably be assumed that a large part of the unaccounted for CTF also reacted with the spray.

The use of protein base mechanical foam also was tried as a means of controlled contact between liquid CTF and water. This means of applying water was prone to produce minor explosions and spattering of the CTF, and appears to be less appropriate than water spray. However, it is believed that accidental contact of foam used in fighting fires incident to CTF spillage will be tolerable.

The effectiveness of protein base mechanical foam, and of bicarbonate base dry chemical powder extinguishants, in extinguishing burning MHF fuels was determined by comparison with their effectiveness on burning gasoline (Chapter 8). It was found that the dry chemical extinguishant worked about as well on burning MHF as it did on gasoline. Foam of low expansion (low ratio of air to foam producing liquid) was nearly as effective on MHF fuel as it was on gasoline. High-expansion foam suffered from excessive breakdown of the bubbles in contact with the MHF. More high-expansion foam was required for extinguishment and its action was somewhat erratic.

The results of the tests reported here have pointed out materials and techniques for handling accidental spills of interhalogen-hydrazine missile propellants. It appears practicable to develop a decontamination procedure which, together with proper ventilation of the spaces in which missiles are handled, would permit handling of these propellants aboard ship. Further tests on a large scale should be made to evaluate the effects of released propellant components on nearby structural materials, and to establish the reliability of the decontamination procedures and the protective clothing materials.

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APPENDIX A

ADDITIONAL TESTS ON THE VAPOR PRESSURE OF CTF MIXED WITH CALCIUM FLUORIDE ABSORBENT

The pressure developed by mixing native calcium fluoride with CTF in a closed system, as reported in Table 10 of the text, was surprisingly high. The maximum pressure found was 34 psig higher than that of plain CTF at the same temperature. The reagent grade calcium fluoride produced 50 psig excess pressure. In contrast, none of the other materials produced more than 2.5 psig excess over the normal vapor pressure of the CTF (6.1 psig). Additional tests were made to determine whether the excessively high pressures were unique for the particular batches of calcium fluoride used in the earlier work, and to determine whether simple pretreatment of the samples, such as heating, would affect their behavior.

Native calcium fluoride from the same batch as that used earlier, a fresh batch of reagent calcium fluoride from the same source as before (source A) and reagent calcium fluoride from another manufacturer (source B) were obtained. Superficial moisture was determined as the weight loss on heating for 72 hr at 120°C. Samples also were heated at 500°C for two 24-hr periods. No weight was lost during the second period. The weight losses, expressed as percent of the original sample weight, are given in Table A1. (Determinations were made in duplicate.)

Table A1
Weight Loss of Calcium Fluoride on Heating

Type of Calcium Fluoride	Wt. Loss at 120°C (%)	Wt. Loss at 500°C (%)
Native mineral	0.012 0.013	0.145 0.145
Reagent, source A	0.845 0.847	1.99 2.03
Reagent, source B	0.415 0.428	1.17 1.13

Pressure rise in a closed system on mixing these powders, pretreated at 120°C or 500°C, with CTF was measured as described in Chapter 4. Pressure in the system was noted at numerous intervals up to 10 days after the sample holder was placed in a 20°C constant temperature bath. The results are plotted as pressure vs time curves in Figs. A1-A3. Since the CTF had been distilled into the sample holder cooled in dry ice, no 20°C pressure reading was available for the starting time; therefore, the curves were arbitrarily started at 6 psig (the vapor pressure of CTF at 20°) and zero time. In all of the tests either 20 or 5 gms of CTF were used with 100 gm of powder to give a powder/CTF ratio of 5:1 or 20:1. Pretreatment of the native calcium fluoride at 120°C was omitted, since this material has been shown to have essentially no moisture to be driven off at this temperature. No tests were made on untreated reagent grade powders because their relatively high proportion of superficial moisture would certainly result in the

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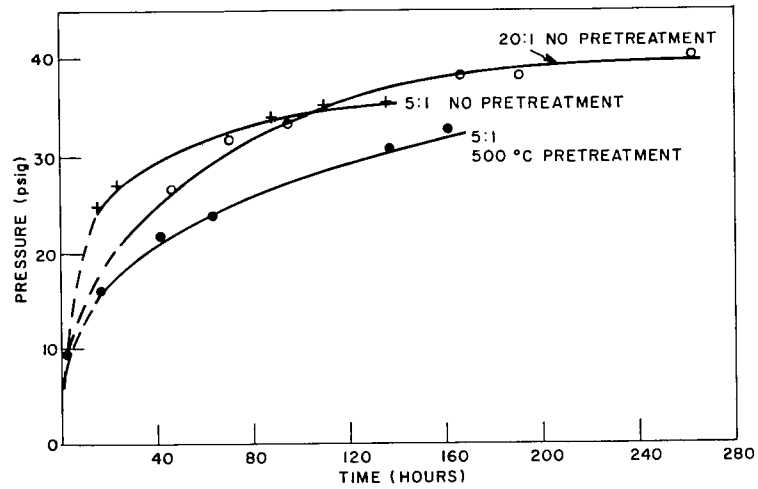


Fig. A1 - Native calcium fluoride, source A

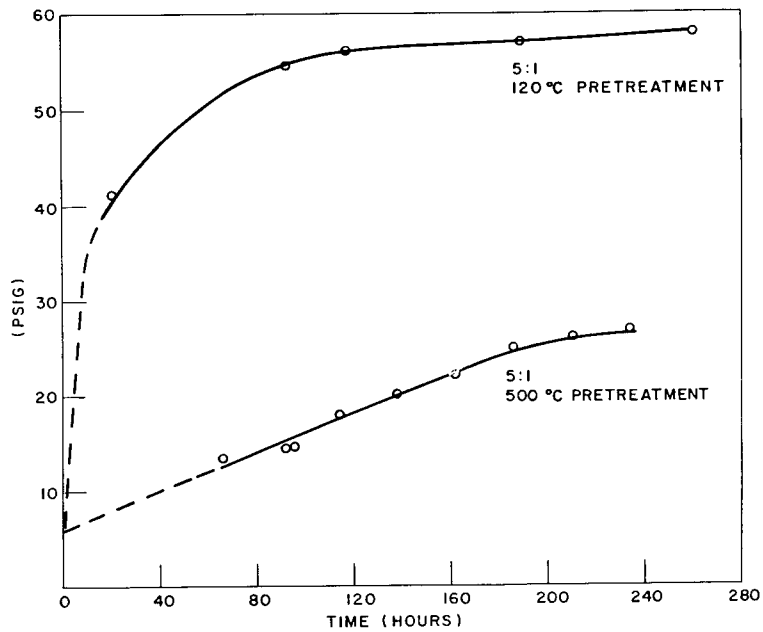
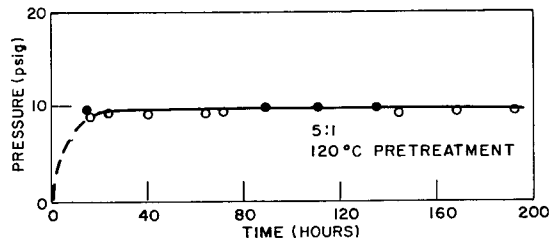


Fig. A2 - Reagent grade calcium fluoride, source A

Fig. A3 - Reagent grade calcium fluoride, source B



Figs. A1-A-3 - Pressures developed by mixing calcium fluoride with CTF in a closed system

formation of a substantial quantity of hydrogen fluoride and other gasses. The tests were discontinued after the trend of each curve was established. Presumably, the pressure would eventually become constant, as indeed it did with one powder, but the time involved was much too long to be of interest from the damage control point of view.

As shown in the curves, native calcium fluoride which had been pretreated by heating at 500°C gave a somewhat slower pressure rise than the untreated mineral. However, the eventual maximum pressure was of the same order — approximately 35 psig. Reagent grade calcium fluoride from source A, on the other hand, was greatly affected by the pretreatment. Powder heated to 120°C showed a sharp initial pressure rise followed by a leveling off in the vicinity of 58 psig, while the powder pretreated at 500°C showed a much slower, nearly linear rise to about 27 psig. Reagent calcium fluoride from source B behaved very differently from the others. The maximum or equilibrium pressure was rapidly attained and was identical for both pretreatments. The final pressure of 10 psig was only slightly more than that produced by the other absorbents tested.

Apparently, the natural mineral and the reagent calcium fluoride made by manufacturer A trapped a substantial amount of water within the crystals which was accessible to the CTF but which was not readily removed by the relatively vigorous heating. Calcium fluoride from source B apparently was prepared in a manner that its accompanying water was easily removed, even by mild treatment.

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APPENDIX B

DETONATION OF MHF-4 FUEL RESIDUE

Five-hundred-cc quantities of MHF-4 fuel were allowed to burn to self-extinction in a 2 by 12 by 12 in. stainless steel pan. (The pan was double walled, so that the inner part was supported only by its upper edges.) A substantial pool of syrupy residue remained in a corner of the pan after combustion stopped. Ten cc of liquid CTF was poured over the residue, and this produced an extremely violent explosion, which the authors believe was a detonation. The same result was obtained on three successive trials, except that the third explosion tore part of the pan bottom away from the sidewalls, as shown in Fig. B1. Another 2 by 12 by 12 in. pan having only single walls was obtained. Ten tests similar to those above were run, but no more strong explosions were noted. No further attempts were made to obtain detonations of the fuel or its residue. However, if this fuel, or one of similar composition, is adopted for missile use, the conditions for detonations should be found in order to determine whether they would influence damage control procedures.

Fig. B1 - View of test pan after detonation of residue from burning MHF-4 fuel. (Pan walls and bottom made of 1/8-in.-thick stainless steel.)

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Damage control procedures for spills of high energy missile propellants, especially CTF (chlorine trifluoride), have been examined. The usefulness of some shipboard firefighting equipment and protective clothing now available was evaluated, and some new methods and materials for handling spilled propellants are proposed.

Powdered inorganic fluorides may be used as absorbents to prevent spreading of pools of liquid CTF and to facilitate removal of the CTF for disposal. None of the fluorides tested showed any tendency to form compounds with CTF and thus lower the vapor pressure of CTF in a closed container. Water spray from the Navy L-11 fog head, as well as finer sprays, is effective in dissipating CTF by controlled chemical reaction. Sodium and potassium bicarbonate based dry chemical powder fire extinguishants produced enough heat of reaction that their principal effect was to cause rapid vaporization of pools of CTF.

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Materials now used in making propellant handlers' protective clothing as well as other damage control gear were found to be readily ignited by contact with liquid or gaseous CTF. Samples of two varieties of fabric formed from highly fluorinated polymers showed promise for making coveralls which could give reasonable protection from gaseous CTF and splashes of liquid CTF. MHF (mixed hydrazines) fuel fires were found to be comparable to gasoline fires in ease of extinguishment with dry chemical extinguishing powder. Protein base mechanical foam also was effective in extinguishing burning MHF fuel, but there was greater breakdown of the foam bubbles than occurs with similar foam in contact with gasoline.