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TREATMENT OF METAL SURFACES FOR USE WITH SPACE STORABLE PROPELLANTS: A CRITICAL SURVEY

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA 91103

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ABSTRACT

Stanford Research Institute, Menlo Park, California
TREATMENT OF METALLIC SURFACES FOR USE WITH SPACE STORABLE PROPELLANTS:
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SRI Special Report No. 951581-8
R. F. Muraca, J. S. Whittick, and J. A. Neff, June 30, 1968
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The survey reviews processes for treatments ("passivation") of metallic surfaces that are to come into contact with the space storable propellants OF_2, ClF_3, FLOX, CH_4, and B_2H_6. It is suggested that special treatment of metals that are to come into contact with oxidizers is not necessary as long as their surfaces are free of contaminants. In practice, however, preliminary exposure of metal surfaces to any of the fluorine oxidizers is recommended to ensure deactivation of contaminants which have resisted cleaning processes.

Details of a general procedure are given for pre-treatment of metal systems to be used with OF_2, ClF_3, and FLOX: (1) descale, degrease, dry, and (2) deactivate residual contaminants with a controlled fluorination treatment. The recommended fluorination treatment is merely a step in the cleaning procedure and not a deliberate attempt to provide "passivation." A detailed discussion of the formation and nature of protective fluoride films is included.

Available reports on the compatibilities and corrosion rates of metals and fluorine oxidizers are reviewed; guidelines for treatment of metal systems for use with methane and diborane are presented. Conclusions and recommendations for further work are included in a separate section.

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I. INTRODUCTION AND SUMMARY

The propellants which are currently under consideration for storage in space at temperatures ranging to as low as -200°F include fuels such as diborane and methane and highly-reactive oxidizers such as oxygen difluoride (OF_2), fluorine-oxygen mixtures (FLOX), and chlorine trifluoride (CTF). A series of investigations* have identified metals such as aluminum, nickel, copper, titanium, and stainless steel alloys as candidates for construction of hardware for storing and handling the semi-cryogenic propellants over periods of from 2 to 10 years; these metals appear to have satisfactory physical properties at low temperatures, resist corrosive attack, and do not induce propellant decomposition.

The semi-cryogenic propellants under consideration are highly reactive with a variety of materials; the occurrence of several serious explosions in metal-fluorine oxidizer propellant systems has been attributed to the violent fluorination of metal surfaces, and thus pre-treatment of metallic surfaces with fluorine and/or fluorine oxidizers has been employed to passivate them and to render them inert. However, there exists confusion as to whether one pre-treatment has merits over others, whether some pre-treatments yield surfaces which resist attack more than others, and even whether pre-treatment is required. In order to determine the efficacy and desirability of fluorine pre-treatments and whether passivation based on other principles can be effective, a comparison was made of cleaning procedures and passivation treatments; the findings are summarized in the following sub-sections.

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* "Advanced Valve Technology," Interim Report, Contract NAS7-436, TRW Systems report no. 06641-6004-R000, November 1, 1966;

"Advanced Valve Technology, Vol. II, Materials Compatibility and Liquid Propellant Study," Contract NAS7-436, TRW Systems report no. 06641-6014-R000, November 1967.

FLUORINE OXIDIZERS

There is some confusion as to why "passivation" is recommended for metal surfaces to be used with fluorine oxidizers, and particularly as to the implication and meaning of the term. Passivation is often regarded as the result of a special process which deactivates the surface of a metal by means of a protective film, and thus permits exposing the metal surface to an environment in which it ordinarily would be grossly corroded. Although this concept is correct, an examination of the results of compatibility and corrosion tests with fluorine oxidizers and metals revealed that passivation treatments did not lead to lower corrosion rates and that pretreatments did not prevent continued reaction between metal surfaces and the fluorine oxidizers. It was discerned that "passivation" processes are not needed, because protective and corrosion-limiting flims are formed whenever clean metal surfaces are brought into contact with fluorine or fluorine oxidizers; the processes are used to overcome the difficulties of obtaining cleanliness in a complicated system.

A review was made of the reactions of the oxidizers with clean metal surfaces, and it was found that a thin metal-fluoride film forms very quickly and achieves the major portion of its ultimate thickness on most metals within a few hours; the film limits the rate of attack, and for a given metal seems to have the same composition regardless of whether fluorine or a fluorine oxidizer was initially in contact with it. Although fluoride formation is highly exothermic, thin films are so effective in limiting attack that the ignition temperature of metals is not achieved. Studies have shown that the protective film is degraded by moisture, but is readily repaired without violent reaction on re-exposure to a fluorine oxidizer. Also, it has been shown the the film is tightly adherent in the oxidizer medium, is flexible, and reforms readily if damaged in any way.

The passivation of sensitive metal surfaces by application of nonfluoride proprietary coatings has been attempted; complete coating of intricate shapes is difficult, and most coatings are unstable and are readily converted to loose fluorine compounds which form sludges.

Furthermore, these coatings do not have the self-healing properties characteristic of fluoride passivating films.

The findings of the investigation also suggest that scrupulously clean metal systems need no prior treatment before exposure to fluorine oxidizers; however, because typical propulsion systems cannot be cleaned with certainty, some form of preliminary exposure to a fluorine oxidizer is recommended and, accordingly, there is outlined in Section III a procedure designed to deactivate those portions of a rocket propulsion system which may not have been subjected to thorough cleaning processes.

Compatible Metals

Almost all of the metals likely to be used in the construction of a propulsion system for use with fluorine oxidizers are in all ways compatible with the oxidizers with respect to low rates of corrosion, lack of stress corrosion, galvanic activity, embrittlement, and impact sensitivity. Typical metals include copper, nickel, aluminum, and stainless steel metals and alloys.

Corrosion rates of the metals in fluorine oxidizers are very low and characteristically of the order of a maximum of 0.1 mpy in the formative stages and typically of the order of 0.001 mpy over prolonged storage periods. Unfortunately, the tests were performed over short periods of time, typically less than 2 weeks, and therefore it is not possible to predict with assuredness that the low corrosion rates will be maintained over storage periods of 2, 5, or 10 years. On the other hand, since it is recognized that initial corrosion rates are usually much higher than final corrosion rates, it appears that the rate of attack of these metals by fluorine oxidizers is very low and probably will remain at low values for as long as 10 years.

The corrosion studies which have been performed have not taken into consideration the possibility that extended storage may lead to the formation of sludges which can clog orifices and invalidate valve actions; it is evident that even low corrosion rates will in time generate a sizable amount of sludge.

Titanium dissolves in chlorine trifluoride because its protective fluoride film is soluble and therefore cannot limit the rate of attack of the metal. On the other hand, various titanium alloys give indication of low corrosion rates in OF_2, FLOX, or F_2, but available data are insufficient to permit discerning whether instances of high corrosion rates are due to the inadvertent presence of impurities such as HF. Notwithstanding some indications that it is corrosion-resistant with these oxidizers, titanium cannot be recommended for use because in the presence of OF_2 or FLOX, it ignites upon impact. However, there exists the possibility that thin coatings of nickel on titanium may reduce the sensitivity of this metal to ignition by shock or impact; nickel-clad titanium has not been investigated for use with fluorine oxidizers.

FUELS

Liquid methane does not react with metals; thus, space propulsion systems based on methane as a fuel require no special treatment of metallic surfaces except for general cleanliness to remove dirt, metal dust, etc. which may lodge on valve seats or cause clogging of injectors.

Diborane is unreactive with most common metals; however, it is reactive with the contaminants likely to remain on fabricated metal surfaces, and it is emphasized that metal surfaces must be cleaned of impurities and scale oxide and thoroughly dried. The compatibility of diborane and titanium has not been investigated; it is not known whether titanium can extract hydrogen from diborane. The fuel can be handled only in closed systems which have been purged of air.

As indicated in Section II, attention must be given to the possible embrittlement of containers at the cryogenic temperatures required for storage of liquid methane or diborane.

II. TREATMENT OF METALLIC SURFACES FOR HANDLING AND STORING METHANE AND DIBORANE

Gaseous methane can be stored indefinitely in metal containers designed to provide acceptable burst-strength requirements for pressurized-gas vessels; no special treatment of metal surfaces is required, except for rigorous cleaning to remove dirt, metal dust, etc. which may lodge on valve seats or contribute to the clogging of injectors. On the other hand, storage of liquid methane imposes the additional requirement that storage-tank metals do not become excessively brittle at liquid-methane storage temperatures (-161° to -182°C). Metals found satisfactory for the oceanic transport of liquid methane (under LN_2 cooling) are 9% Ni steel, Invar (36% Ni steel), and annealed stainless steel 304L [24]; it is anticipated that these and similar alloys may be used in cryogenic space storage systems for methane.

Diborane is not reactive at room temperature with the usual metals of construction [7a] and has been found to be compatible with brass, lead, nickel, K Monel, low-carbon steel, and 18-8 steel (no data on titanium). It is shipped in chrome-moly steel cylinders fitted with brass outlet valves and dip-tubes. Stored in these cylinders at -20°C, diborane undergoes about 0.2% decomposition in one year; at warmer temperatures, decomposition pressures range from 0.14 atm at -18°C in 100 days to 52 atm at +25°C in 120 days [7b]. Thermal decomposition of diborane always involves the formation of hydrogen; other products may be volatile boron hydrides and quite often solid (BH_x) polymeric hydrides; the solid products are particularly undesirable in propellant systems because they may contribute to the clogging of injectors. The severity of problems posed by deposition of solids during long-term storage has not been evaluated. Storage below -80°C is not recommended because embrittlement of tank metals may lead to the rupture of storage vessels on impact, shock, or sudden pressurization.

Metallic surfaces in contact with diborane do not need to be passivated; however, it is stressed that all systems must be thoroughly cleaned to remove organic impurities and metal oxide scale, and that diborane may be used only in completely-enclosed systems which have been thoroughly purged with dry nitrogen or hydrogen [7]. Because it is a strong reducing agent, diborane may be quite reactive with the oxides present on metallic surfaces, and may be reactive with titanium. More importantly, the systems must be completely dry, for diborane is readily hydrolyzed to boric acid and hydrogen, and the boric acid sludge is particularly effective as a clogging agent in rocket propulsion systems. Metal embrittlement by hydrogen resulting from decomposition of diborane has not been noted.

A suitable procedure for preparing metal surfaces to be used with diborane has not been reported; however, procedures recommended for system components to be used with pentaborane [10] should be applicable. The rough (or welded) components are thoroughly descaled and then machined; after degreasing, residual oxides are removed as follows:

(1) System components fabricated of stainless steel:

- (a) Immersion in an aqueous solution containing from 45 to 55 wt-% nitric acid (technical grade) at room temperature for a minimum of 30 minutes,
- (b) Rinsing with water to remove all traces of acid (pH paper),
- (c) Drying with a stream of dry, hydrocarbon-free, filtered nitrogen gas, or by heating in an oven at 140-160°F.

(2) System components fabricated of aluminum or its alloys:

- (a) Immersion in an aqueous solution containing about 45 wt-% nitric acid (technical grade) at room temperature for a minimum of one hour,
- (b) Rinsing thoroughly with water to remove all traces of acid solution,
- (c) Drying by purging with dry, hydrocarbon-free, filtered nitrogen gas or by heating in an oven at 140-160°F.

After assembly of the treated components, the entire system must be thoroughly purged with dry nitrogen gas. If for any reason the system is vented to the atmosphere, it must again be purged with dry nitrogen gas prior to the introduction of diborane.

III. REVIEW OF PROCESSES TO CONDITION METALLIC SURFACES FOR USE WITH FLUORINE OXIDIZERS

A review of available literature indicates that fluorine oxidizers will react initially with the surface of nearly all solid materials and that the reaction at low temperatures (<400°C) quickly subsides because of the formation of an adherent, impervious fluoride film. It has been found that a wide variety of metals are compatible with fluorine oxidizers because of protective film formation and, in general, that the fluoride films are strong enough to withstand flexure and to resist direct impingement of rapidly flowing streams of the oxidizers.

Formation of protective fluoride films on metals involves the release of considerable heat of reaction, but since thick metal sections are ordinarily employed in the construction of fluorine oxidizer systems, and the amount of metal fluoride that is formed is very small, the heat of reaction is rapidly dissipated and ignition temperatures are not achieved. However, there are scattered reports of accidents with fluorine oxidizers in which metal systems have ignited, but it is now generally recognized that these deflagrations must have been initiated by rapid reaction of the oxidizer with organic substances, water, or with extremely finely-divided metals or metallic oxides of surface areas so large in proportion to mass that their vigorous reaction led to ignition of heavier metal sections. In fact, no ignition reactions were observed when metals in several sizes of subdivision, from bulk solids to powders finer than 300 mesh, were exposed to fluorine and the interhalogen gases at pressures in excess of one atmosphere [8].

Gross quantities of organic contaminants (which usually are found in systems because of carelessness) are not easily fluorinated and converted into volatile compounds which can be removed by purging or evacuation; moreover, the products of partial fluorination may be impact sensitive.

In a series of experiments seeking to probe the severity of the presence of large amounts of organic residua, from 1 to 60 milligrams of hexadecane were spread over 1-in^2 areas on the surfaces of metals and treated with 1 to 5 atmospheres of fluorine or chlorine trifluoride [19]. It was found that hexadecane was not entirely removed by fluorine and that finely-divided carbon often remained; reaction with chlorine trifluoride left an oily deposit of fluorocarbon (infrared analysis). About 50 mg/in^2 of petroleum jelly, Kel-F 90 grease, and Pydraul AC hydraulic fluid were treated with either 50 psig fluorine or 15 psia chlorine trifluoride for one hour at 77°F [9]. The results of these experiments conclusively demonstrated that relatively large quantities of contaminants do not disappear as volatile fluorides,* and that liquids may become semi-solid and slowly reactive. The carbonaceous residues which remained were found to be impact sensitive when in contact with liquid fluorine (modified ABMA tester); finely-divided carbon is ignited on contact with fluorine.

In view of the chemical reactivity of the fluorine oxidizers and the possibility that small amounts of organic matter and reactive scale or slags from welding operations may lead to destruction of metal systems by fire or explosion, it has become general practice to pre-treat assembled systems to remove reactive substances and to deactivate their sensitive surfaces before the systems are considered safe. All pre-treatment procedures described in the past involve the same general steps:

(1) Removal of scale, burrs, and visible contaminants by attrition or scrubbing with detergents or solvents.

(2) Thorough drying.

(3) Exposure to fluorine or fluorine oxidizers under conditions designed to limit rates of reaction so that deflagration does not take place.

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* The use of a system for detecting HF (an indication of the continuing attack of hydrocarbons by fluorine or its oxidizers) has been suggested as a method of following the progress of deactivation; in view of the incomplete reaction of contaminants with fluorine or its oxidizers, it is evident that HF detection can not be used to furnish reliable evidence.

Naturally, in contact with fluorine species, the metal surfaces become covered with a fluoride film which sharply limits further reaction, and so this step of the pre-treatment procedure has been called "passivation." Without a doubt, as is documented in Section V, the fluoride film establishes an impediment to further attack of metal surfaces and for this reason it can be correctly called an inhibiting or passivating layer, but it is to be noted that the formation of the fluoride film on the greater part of the surfaces of a metal system is incidental to the pre-treatment process--the primary intent of the pre-treatment is to ensure that inaccessible areas, insoluble substances, sharp edges, or crevices which resisted cleaning treatments are brought into contact with oxidizer in a controllable fashion and made to react quietly.

All available evidence indicates that the films produced by cautious treatment of metal surfaces with fluorine or any of the fluorine oxidants are identical with those produced when metals are brought into contact with these oxidants under a variety of other conditions; in fact (see Section V), the chemical structure of the fluoride film is essentially the same regardless of which fluorine species was used to produce it (at low temperatures).

It appears appropriate, therefore, to refer to pre-treatment processes as "conditioning" processes which consist of, actually, the following steps:

(1) Descaling, cleaning, degreasing, and drying.
(2) Deactivation with a fluorine oxidizer.

Although the deactivation step in principle is superfluous and can be omitted whenever metal surfaces are assured of immaculate cleanliness [15, 19, 29], it is recommended that conditioning pre-treatments be used on complex systems which characteristically include tortuous passages, close-fitting junctures, and the inevitable short-comings of unskilled or technically indigent labor.

The films covering the surfaces of metals deactivated by fluorine or fluorine oxidizers appear to be sensitive to moisture; their integrity is destroyed by water vapor (moist gases), and they may be substantially removed by contact with liquid water. However, most films are either repaired or replaced when contact with fluorine or a fluorine oxidant is resumed (gaseous or liquid phase), and it has been found that the rate of formation of a fluoride film on a metal is for all practical purposes independent of whether the action takes place on a clean metal surface or on a surface with a damaged film. Since the fluoride film on metal surfaces is at most of the order of 100 Å, regeneration of damaged films may lead to a nearly imperceptible production of particulate substances; copper, on the other hand, forms thick, regenerated films which have a tendency to slough off relatively large amounts of corrosion product.

As a result, a system which has been deactivated by contact with fluorine or fluorine oxidizers preferably should not be exposed to water in any form so as to minimize production of sludges of corrosion products. Note that there is concern that the introduction of moisture may have been concurrent with the introduction of other reactive materials as well as the possibility of formation of small amounts of sludge, but not that the metals of construction will be unduly corroded in service because of loss of "passivation;" passivity will be rapidly re-established when the metals are again brought into contact with fluorine or fluorine oxidizers (see Section V).

The remainder of this Section and Table 1 provide a summary of procedures for conditioning metal surfaces and systems to be used with fluorine oxidizers. The principles of the procedures appear sound except for one or two details.

A number of the procedures prescribe the use of vacuum for removal of water and solvent vapors; others prescribe the use of a purging gas, such as helium or nitrogen. Unfortunately, some propellant tanks cannot withstand vacuum and so there has been general tendency for the use of a purging gas; this may lead to difficulties since many systems are simply incapable of being adequately flushed with a slow stream of purging gas. It is recommended that heat and a purging gas be used over a sufficiently long period of time to permit the diffusion of solvent vapors from remote crevices into the main stream of purging gas.

It is to be noted that silicone greases and oils are relatively insoluble in most hydrocarbon or halogenated solvents; they cannot be removed by ordinary degreasing processes. Preferably, the use of such materials should be avoided in the manufacture of systems.

Although the practice of storing cleaned components in polyethylene bags is wide-spread in the aerospace industry and appears to present no major problems of contamination, it has been shown at SRI that metal specimens stored only for a day or so in polyethylene bags are covered with sufficient dioctylphthalate (polyethylene plasticizer) to be detectable by mass spectroscopy. In view of the reactivity of fluorine and fluorine oxidizers with organic compositions, it appears expedient simply to avoid this source of contamination. Cleaned components can be packaged in degreased glass vessels (aluminum cap-liners) or bags lined with aluminum foil (clean); aluminum foil may be used to protect cleaned components--provided it also is cleaned, since most foils are coated deliberately (or inadvertently) with organic films.

SYSTEM DESCALING AND CLEANING

Prior to assembly of systems for handling or storing fluorine oxidizers, component parts must be cleaned of surface dirt, grease, scale, and imbedded foreign material. A review of the procedures used in the aerospace industry for cleaning metal components [1] shows that the same general steps are used:

(1) Disassembly of components;

(2) Removal of scale, burrs, and surface contaminants by scrubbing, polishing, or degreasing in halocarbon solvents;

(3) Immersion in cleaning detergent, washing, and rinsing with clear water;

(4) Final rinsing with de-ionized water and drying in a vacuum oven.

If the components have reasonably clean surfaces, that is, only traces of oxide films, they may be dipped in a bath containing 10-25% nitric acid (short exposures for brass and copper), then washed thoroughly with deionized water and dried in a vacuum oven [10].

The cleaned components are handled carefully to avoid finger marks or other contamination and are stored in sealed containers until assembly.

TYPICAL CONDITIONING TREATMENTS FOR OXYGEN DIFLUORIDE (OF_2)

Storage tanks for OF_2 may be constructed from common metals such as stainless steel, copper, aluminum, Monel, and nickel, and will be serviceable from cryogenic temperatures to temperatures as high as 200°C [3].

Deactivation

After the thorough cleaning and assembly of component parts, the system is flushed with a drying solvent, such as carbon tetrachloride, trichloroethylene, or acetone and then purged thoroughly with dry nitrogen gas. This is followed by strong evacuation in order to assure the complete removal of solvents and moisture.

Nitrogen is introduced into the system at working pressure to permit leak testing; the pressure is released. The oxygen difluoride is admitted to the system and vented out through a suitable disposal system. When a strong reaction of OF_2 with ammonia vapor at the exit vent is noted, the system is considered to be ready for use. If the working pressure is to be greater than atmospheric, it is suggested that OF_2 be applied up to the working pressure in order to assure system compatibility [3]. The OF_2 is purged with dry nitrogen and the system is sealed at 0.5 psig until ready for service.

TYPICAL CONDITIONING TREATMENTS FOR FLOX (Fluorine-Oxygen)

The metals found to be satisfactory for storage vessels for fluorine [10] are apparently equally useful for FLOX [4, 26] and include stainless steels, aluminum alloys, and Monel. Copper or brass may be used for lines, fittings, and flanges [10].

Deactivation

Subsequent to absolutely thorough cleaning of component parts and to their assembly, the system is flushed with trichlorethylene or trichlorotrifluoroethylene, followed by a strong evacuation to remove all traces of solvents. It is suggested that prolonged contact of solvents with the polymeric materials used for gaskets, etc. be avoided [25].

After evacuation, dry nitrogen in introduced to scavenge residual moisture and solvents, and the system is again evacuated. Then FLOX, pure fluorine gas, or fluorine-helium mixtures are introduced into the system to a slight positive pressure which is held for a few minutes. The "fluorine" pressure is raised gradually, in increments, to 50 psig and maintained there for 30 minutes at room temperature (longer at low temperatures). Then the pressure is released and the system is maintained at a slight positive pressure of FLOX, fluorine, or helium to prevent inward leaks [25].

A system that cannot be evacuated is purged with dry nitrogen or helium (dew point less than $-100^{o}F$) until it is free of air and moisture. Gaseous fluorine is admitted to displace most of the nitrogen, then the vent is closed and system operating pressure is raised slowly, in increments, to 50 psig and maintained there for 30 minutes. The system is left with a slight positive pressure of fluorine or helium as above [25].

TYPICAL CONDITIONING TREATMENTS FOR CHLORINE TRIFLUORIDE (CTF, ClF_3)

The metals recommended for CTF storage are Monel, nickel, stainless steel, and aluminum [2]; copper, brass, and steel are also mentioned as suitable.

Deactivation

After all components are thoroughly cleaned, the system is assembled and flushed with a solvent such as carbon tetrachloride, acetone, or trichlorethylene. Then it is purged thoroughly with dry nitrogen gas and a CTF supply cylinder is connected. The exit vent is opened to the atmosphere, and nitrogen in the system is displaced by a gentle stream of CTF.

The flow of CTF is continued at about 1 atm pressure until a piece of dry filter paper or cotton cloth held at the exit vent (with long metal forceps) begins to burn. The exit valve is closed; CTF pressure in the system is increased to full cylinder pressure and maintained for about 15 minutes at room temperature.

If fluorine is used for passivation, pressure is gradually increased in 25-psig increments to about 350 psig. In this instance, pressure is maintained for 12 hours. In either case (CTF or F_2), system temperature may also be increased to working temperature. After pressurization, the system is vented and sealed (with the CTF cylinder in place) at atmospheric pressure [2].

Alternatively [10], the system is evacuated after solvent flushing for at least one hour to remove traces of solvents and moisture. Then CTF or fluorine is introduced at about 15 psig for 5 minutes and then raised to the vapor pressure of CTF (about 25 psig) or to 50 psig for F_2.

RECOMMENDED METAL CONDITIONING TREATMENT FOR USE WITH FLUORINE OXIDIZERS

As is evident from the data summarized in Table 1, a variety of deactivation procedures have been employed, but the exact details of the procedures are of little concern because the intent is to deactivate sensitive areas and to remove vestigial quantities of reactive materials by an initial exposure to reactive gas. Accordingly, it is possible to choose the best features of the metal conditioning treatments used thus far to establish a recommended procedure.

Recommended Procedure

(1) Disassemble the system into its individual components.

(2) Remove scale, burrs, and other visible surface contaminants by polishing or scrubbing, taking into account the nature of the metallic substances and the finish of the surfaces. Whenever possible, acid pickling should be used.

(3) Thoroughly dry and then degrease the components in a vapor degreaser or in successive rinses of clean solvent.

(4) Clean the components with detergent and water; when the water break is clean (check for presence of grease or silicone lubricant), rinse the components thoroughly in de-ionized water.

(5) Dry the components in warm air; finish the drying in a vacuum oven.

(6) Assemble the components as the finished system; do not use fluorocarbon greases or lubricants.

(7) If the final system must be welded, achieve attachment by electron beam welding; alternatively, weld in an atmosphere of inert gases (to reduce scale and residues, use no flux, if possible). If flux must be used, clean the system with detergent and water; allow long soaking periods for flux removal; dry thoroughly.

(8) Purge the system with dry nitrogen gas; if water may have entered the system, perform the purging over a prolonged period of time at a system temperature of $125^{\circ}C$.

(9) Cool, then displace the inert gas in the system with any of the fluorine oxidizers or gaseous fluorine itself. (The materials of construction must be compatible with fluorine or the fluorine oxidizer.) Check the effluent for richness of oxidizer with a cloth or other combustible substance; a chemical test may be more appropriate.

(10) When a positive test for the oxidizer is obtained, seal the vent and continue pressurization with the oxidizer to at least 25 psig and for a total of not less than two hours.

(11) Release excess pressure, capping the vent at about 0.5 to 1 psig.

Table 1

SUMMARY OF METAL CONDITIONING TREATMENTS FOR FLUORINE OXIDIZERS

METHOD[a] NO.	END USE	DRYING				DEACTIVATION				REF.
		N_2	He	Evac.	Oven	Inert Gas	Purge Gas[b]	Pressure	Time[c]	
1	OF_2	(1)		(2)		N_2	OF_2	working	-	3
2	OF_2	-		-	-	N_2	F_2	atm.	5-10 min	27
3	FLOX	X		X		N_2,He	FLOX	50 psig	30 min	25
4	FLOX	X		X		N_2,He	F_2	50 psig	30 min	25
5	FLOX	(1)		(2)		-	FLOX	0-15 psia	15 min @ 15 psia	26
6	CTF	X				N_2	CTF	25 psia	15 min	2
7	CTF	X				N_2	F_2	350 psig	12 hours	2
8	CTF			X		-	CTF	(1)15 psig (2)25 psig	5 min -	10
9	CTF			X		-	F_2	(1)15 psig (2)50 psig	5 min -	10
10	F_2	X				N_2	F_2	100% of working	10 min	13
11	F_2	X		X		-	F_2	50 psig	2 hours	9

[a] Metal system is free of scale, then degreased with a solvent and allowed to drain.

[b] The purge gas must be compatible with the materials of construction.

[c] At room temperature unless specified.

IV. REVIEW OF COMPATIBILITY STUDIES OF METALS WITH FLUORINE OXIDIZERS

There have been no comprehensive studies of the compatibilities of metals with oxygen difluoride, FLOX, and chlorine trifluoride; only scattered data are available for stressed and unstressed metallic specimens. Corrosion rate data are derived from the results of distressingly short-term storage periods of a few hours to a few hundred hours. In general, very low corrosion rates are reported for the metals which have been selected by preliminary checks for reactivity or shock sensitivity; in fact, experimental evidence suggests that corrosion essentially ceases after about one month. Neither stress corrosion nor significant differences in tensile properties were observed for specimens stored under stress in the various oxidizers. There are scattered reports where workers have tried to determine the corrosion rates of metals coated with proprietary substances. These kinds of systems are not considered practical for two reasons: (1) The difficulty of reliable coverage of intricate shapes and, more importantly, (2) The lack of the self-healing characteristics which make the fluoride films so valuable (see Section V).

OXYGEN DIFLUORIDE (OF_2)

Dawson, Lum and Schreib [12] selected metals for compatibility studies with OF_2 on the basis of high strength and suitability at cryogenic temperatures: steel alloys, aluminum alloys, nickel alloys, titanium alloy, and copper. The specimens (1/4" x 1-3/4") were thoroughly cleaned, degreased, and then sealed in glass ampoules (fitted with metal Bourdon gages); a pressure of 0.5 atm OF_2 was used for gas-phase tests and 1 cc liquid OF_2 for liquid-phase tests. During 2-week exposures at room temperature and at $-196^{0}C$, no pressure changes were detected. At the termination of the tests, most of the specimens were found to be coated with what was assumed to be a fluoride film; pitting was observed on some specimens stored in the liquid phase, but not on specimens stored in the gaseous phase. The weight changes shown in Table 2 were considered insignificant by the authors, and it was therefore concluded that the materials were compatible with OF_2. The authors also conducted impact tests on titanium 5Al-2.5Sn alloy (based on a system for LOX compatibility developed at NASA/Lewis); it was found that the alloy did not propagate combustion in contact with LOF_2 when impacted and penetrated by a nylon ball at a velocity of 5770 ft/sec.

Bleich and Hertz [4] selected type 301 stainless steel and K-Monel for tensile specimens (under stress) of butt-welded metals or resistance-spotwelded metals. The specimens were immersed in OF_2 at -196^oC in fluorine-passivated type 321 stainless steel containers for 200 hours. They concluded that these metals are compatible with OF_2, primarily on the basis of tensile data; there was only minor metallographic evidence of corrosion, and losses in strength at welded joints were attributed to inadequate preparation of specimens.

Tiner, English, and Toy [27] investigated the compatibility of stainless steels, aluminum alloys, nickel alloys, titanium alloys, and other metals with OF_2. Their preliminary work with impact tests (ABMA) indicated that stainless steels, aluminum, nickel, and copper alloys do not exhibit sensitivity with LOF_2 when tests are conducted under moisture-free conditions; titanium A110-AT and 6Al-4V exhibited faint sensitivity. (Ice and OF_2 mixtures can be detonated by impact.)

A series of preliminary immersion tests in OF_2 were conducted for 1-day and 21-day periods at -110^oF; metal samples (LOX-clean) were stored as tensile specimens in type 316 stainless steel bombs (several in each bomb according to alloy class). The tensile properties of a few selected specimens (welded and unwelded) indicated that immersion in OF_2 at -110^oF for 21 days does not lead to their deterioration. Preliminary corrosion data were also obtained from these storage tests.

On the basis of the results of impact testing, the preliminary corrosion data, and tensile properties after the immersion tests, several metals were excluded from further testing:

(1) Stainless steel type 410 because of low-temperature embrittlement.

(2) Titanium alloy A-110T and 6Al-4V, magnesium alloy HM-21-A, and tantalum, because of light-to-extreme sensitivity in the ABMA cup tests with OF_2.

(3) Excessive corrosion rates (apparently Al 2024-T3, Al 5456-H343, Al 7075-T6, and columbium-A).

The data of Tiner, English, and Toy [27] for the corrosion rates of metals in OF_2 (gas and liquid phases) are summarized in Tables 3 and 4. Apparently, passive films are established largely during the first few months of exposure at -110°F as suggested by high corrosion rates in the early phases of the tests; all of the materials examined appear to have excellent resistance to corrosion. It is possible that corrosion essentially ceases after the initial formation of a fluoride passivating layer (e.g., after one month).

In the preliminary experiments, it was suspected that water contamination in the OF_2 systems caused the formation of HF and led to spotting. A series of 1-day immersion tests in "OF_2 containing 1% water" was made [27]. Water was added to the sample containers and then frozen at LN_2 temperature prior to the introduction of OF_2, but since the authors found ice crystals on the lids and sides of the bombs at the conclusion of the tests, only a small fraction of the added water had reacted with OF_2. Thus, the data in Table 5 (corrosion rates in OF_2 with H_2O) indicate that water has little effect on the 1-day corrosion rate, except for isolated instances (cf. Table 3). It is of interest to note that the corrosion rate for titanium 6Al-4V appears to be quite low, but the alloy A110-AT-A appears to be excessively corroded. However, the nonequilibrium state existing in the test bombs (ice mixed with OF_2) prevents the drawing of firm conclusions. Additionally, the reported data on the appearance of specimens in Table 4 have obvious discrepancies (e.g., pitting in 20 days vs no change in 12 months); it must be concluded, therefore, that the storage tests were not conducted uniformly, that the OF_2 was not of uniform purity in the bombs, or that the systems were not moisture-free or absolutely clean. (It is recognized that the handling of OF_2 presents many problems, and that reproducible loading of bombs is particularly difficult.) In spite of discrepancies, the 12-month corrosion data of Tiner, English, and Toy in Table 3 and the appearance of the specimens (Table 4) indicate that most metals can be considered to be compatible with OF_2; the thin films of resistive fluorides which appear to be formed limit corrosion rates to very low values.

FLOX (Fluorine-Oxygen)

Compatibility tests with liquid FLOX-40 (40% fluorine-60% oxygen) of metals stressed to 80% of their room-temperature yield strength were conducted by Spicer [26]. The specimens, including stainless steels, aluminum alloys, Inconel and Monel, were cleaned in Alconox, rinsed with distilled water, and dried with acetone. Then the specimens, storage containers, and stress fixtures were vapor degreased with trichlorethylene; henceforth, all components were handled only by gloved (polyethylene) hands. The specimens were placed under restrained bends in simple double-L-shaped fixtures designed to accommodate 1-3 specimens each; 7 or 8 fixtures were located in each storage container made of 316 stainless steel. The fixtures were fabricated from 4340, 347, and 304 stainless steels or 2014-T6 aluminum alloy. No evidence of galvanic reaction was noted after storage tests; all combinations of test metals and fixtures were used.

The loaded containers were leak-checked with gaseous nitrogen at 200 psig and then vacuum-checked for 30 minutes, using a mercury manometer to indicate leakage. The containers and samples were passivated by releasing the vacuum with pre-mixed FLOX-40 and maintaining a pressure of 15 psia for 15 minutes. Then the containers were cooled to LN_2 temperature and FLOX-40 was distilled into them until the specimens were immersed; finally, container pressures were adjusted at 50-87 psig (at LN_2 temperature) with helium. The storage tests in FLOX-40 were conducted for periods of 16 to 19 hours at -196°C. Bomb pressures increased during storage (75 to 125 psig); the pressure increases were attributed to partial evaporation of the LN_2 baths. No changes in appearance of sample specimens were noted and weight changes (Table 6) were less than 0.1 mg/in^2. (Similar treatments and exposures of specimens to liquid fluorine resulted in weight changes of the same order of magnitude.) Unfortunately, the results of short-term tests cannot be used reliably for estimating long-term compatibility; however, they are of value for screening metals for longer-term storage tests.

Bleich and Hertz [4] have stored at -196°C welded and stressed 301 stainless steel and K-monel in FLOX-20, welded and stressed 321 stainless steel and Nickel-A in FLOX-30, and stressed 6061-T6 aluminum in FLOX-30; the stress fixtures used in the 200-hour tests were of simple double-L design. No mention is made of sample or container cleaning procedures, but it is noted that samples and containers (321 stainless steel) were passivated with fluorine prior to the tests. There was no apparent difference in the mechanical properties of stressed or unstressed specimens and specimens not exposed to the oxidizers. No metallographic evidence of corrosion was observed. The meager data suggest that fluorine and FLOX have the same action on metals, and that deactivation of metal surfaces can be accomplished either by FLOX or by fluorine.

CHLORINE TRIFLUORIDE (CTF, ClF_3)

Grigger and Miller [15] investigated the compatibility of a number of metals and alloys in liquid and gaseous CTF at 30°C. Preliminary tests were conducted with metals and alloys for which there was little or no background information on reactivity with CTF. Clean specimens were placed in a Kel-F trap attached to a vacuum system and cooled to -78° or -196°C; enough CTF was distilled into the traps to cover the specimens. Then the traps were sealed off and warmed to 30°C. Most of the metals were found to be unreactive with CTF, but the following selected results are particularly interesting and informative:

Columbium	Violent incendiary reaction at -78°C.

Titanium, Ti-100A	Vigorous reaction below 25°C until Ti dissolved; normal v.p. for CTF at end of reaction.
Titanium, pure	Same as Ti-100A
Titanium C-120AV-Ti	Same as Ti-100A, but 2 hours required for solution; normal v.p. for CTF at end of reaction.
Titanium A-110AT-Ti	Same as Ti-100A, but 2 hours required for solution; final system pressure at 60 psig; IR absorbance curve indicates metal hexafluorides.

Alloys of aluminum, copper, nickel, and stainless steels were selected for corrosion tests in liquid CTF [15]. Unstressed specimens were cleaned and placed (8 each) in steel containers with blow-out diaphragms. The containers were evacuated, loaded with CTF to immerse the specimens, sealed, and maintained for 21 days at 30°C. As the data summarized in Table 7 indicate, all corrosion rates are extremely low (< 0.2 mil/yr); the authors note that extension of 21-day rates to yearly rates is only within an accuracy of 0.1-0.2 mil/yr. The corrosion rates were determined from the differences in weights of specimens (initial minus final weight after removal of corrosion products), since computations based on weight gain would require positive identification of all corrosion products and assurance that products have not dissolved away, fallen off, or been lost in transfer.

Corrosion rates in gaseous CTF were determined in a separate series of tests. Containers with clean, unstressed specimens were evacuated and loaded to 5 psig with anhydrous CTF and maintained for 21 days at 30°C. The containers were evacuated and re-filled every 5 days to remove any gaseous products and to maintain CTF pressure. The values given in Table 7 show that corrosion rates in gaseous or liquid CTF are essentially the same and seldom more than 0.2 mpy.

Stressed specimens (U-bends secured with bolts) were also stored in liquid CTF for 21 days at 30°C. No evidence of stress corrosion could be ascertained by a dye penetrant or by visual inspection. In a separate series of tests, it was determined that the metals listed in Table 7 are not ignited by impact in CTF (19 ft-lbs to 140 ft-lbs) and do not enhance explosive shock.

Tests were performed to determine whether clean and dry metals need to be passivated for use with CTF [15]. Cleaned control specimens were exposed to liquid CTF for about one week; other cleaned specimens were exposed to liquid CTF for 40-60 hours, followed by exposure to the atmosphere for about 50 days, then re-exposed to liquid CTF for about one week. The results for duplicate specimens were in excellent agreement, so only one set of data for each metal was selected for illustration in Table 8. The authors concluded from the weight changes and the appearances of the specimens that there was little difference between the controls or the specimens which had prior CTF passivation, and that prior passivation for service with CTF was unnecessary. They, stress, however, the importance of cleanliness of the metal surfaces and suggest that systems be isolated after cleaning and perhaps flushed with dry nitrogen after standing. If contamination or excessive corrosion is suspected in fresh or passivated systems, it is recommended that the system be completely cleaned prior to introduction of CTF; for example: (1) alkaline or solvent degreasing, (2) acid pickling and mechanical abrasion if required, (3) water-rinsing, (4) mild alkali (Na_2CO_3) neutralizing, (5) water rinsing, (6) thorough drying above 100°C with dry nitrogen flushing.

Table 2

RESULTS OF TWO-WEEK COMPATIBILITY TESTS OF VARIOUS METALS WITH OF_2 [Ref. 12]

SAMPLE	GAS PHASE (ROOM TEMPERATURE)			LIQUID PHASE (-196°C)		
	Sample Wt., g	Weight Change, g	Visual Inspection	Sample Wt., g	Weight Change, g	Visual Inspection
Stainless Steel 301	1.4609	-0.0001	Coating	1.4625	-0.0008	Coating, minor pits
Stainless Steel 404	1.3767	-	No apparent change	1.3797	-0.0009	No apparent change
Stainless Maraging AM 367	3.1590	+0.0021	Coating	2.9429	+0.0005	Coating
Stainless Maraging AM 3551	0.2240	+0.0001	No apparent change	0.2155	+0.0013	Coating, minor pitting —more in area exposed to liquid
Aluminum 2024 T-3	0.3806	+0.0014	Coating	0.3777	+0.0001	Coating, minor pitting —more in area exposed to liquid; some deposits
Aluminum 2024 T-3 Alclad	0.4950	+0.0001	Coating	0.4347	+0.0007	Coating, minor pitting —more in area exposed to liquid; some deposits
Inconel X-750	1.5281	-0.0020	No apparent change	1.5053	+0.0007	No apparent change
Monel K-500	1.5101	-0.0004	Coating	1.5047	+0.0010	Coating
Monel 400	1.5507	-0.0004	Coating	1.5535	+0.0005	Coating
Titanium 5Al-2.5Sn	0.7993	-0.0012	Stained spots on surface	0.7935	+0.0001	Stained spots on surface
Magnesium AZ-31B, H-24	0.3113	-0.0019	Coating	0.3118	-0.0001	Coating, increased depth in gas phase
Beryllium Copper, 2% Be	1.4720	+0.0003	Coating, slight discoloration	1.4771	+0.0008	Coating and discoloration on surface, more so in area contacting liquid

Table 3

CORROSION RATES OF STRUCTURAL MATERIALS IN OF_2 [Ref. 27]

(Average of duplicate tests at -110°F and saturation
pressure of 450 psi in (G) gas and (L) liquid phases)

MATERIAL AND TREATMENT	OXIDIZER PHASE	CORROSION RATE - MPY			
		1-Day	21-Day	4-Month	12-Month
Aluminum Alloys					
Al 1100-0	L	1.2	0.04	0.004	0.001
	G	0.3	0.04	0.020	0.000
Al 2014-T6	L	0.4	--	0.000	0.002
	G	0.0	0.05	0.080	0.000
Al 2219-T81	L	1.8	--	0.000	0.002
	G	0.5	0.03	0.007	0.000
Al 6061-T6	L	0.4	0.02	0.004	0.000
	G	0.2	0.01	0.004	0.002
Al 7075-T6	L	0.4	0.09	--	--
	G	0.8	0.11	0.09	--
Al 7079-T6	L	0.4	0.06	0.007	0.009
	G	0.3	0.04	0.00	0.007
Stainless Steels					
SS301-FH	L	0.3	--	0.000	0.000
	G	0.8	0.01	0.005	0.001
SS316-A	L	0.2	--	0.002	0.000
	G	0.1	0.01	0.000	0.000
SS316-FH	L	0.3	--	0.001	0.000
	G	0.2	0.01	0.000	0.001
SS347-A	L	0.2	--	0.002	0.002
	G	0.2	0.01	0.001	0.003
SS347-FH	L	0.4	--	0.001	0.000
	G	0.3	0.01	0.000	0.000
AM350 (850SCT)	L	0.3	--	0.005	0.000
	G	0.4	0.00	0.002	0.004
PH-15-7Mo (TH 1050)	L	0.4	--	--	0.003
	G	0.1	0.01	--	0.003
Nickel and Copper Alloys					
Nickel 200-A	L	0.1	0.02	0.001	0.007
	G	0.2	0.01	0.002	0.007
Monel 400-A	L	0.2	0.02	0.003	0.000
	G	0.2	0.02	0.003	0.001
Inconel X (1300/20 hr)	L	0.0	--	0.002	0.001
	G	0.2	0.03	0.002	0.001
Rene 41/CMR (1400/16 hr)	L	0.0	--	0.001	0.001
	G	0.2	0.03	0.001	0.001
Copper-A	L	0.0	0.01	0.005	0.001
	G	0.2	0.02	0.005	0.001
Brass (70-30)-A	L	0.0	0.01	0.002	0.001
	G	0.4	0.00	0.004	0.001
Cufenloy 10-A	L	0.3	0.01	0.004	0.001
	G	0.3	0.02	0.004	0.000
Cufenloy 40-A	L	0.3	0.00	0.004	0.001
	G	0.3	0.01	0.003	0.001

Table 4

APPEARANCE OF METAL SPECIMENS STORED IN OF$_2$ AT -110°F [Ref. 27]

METAL	PHASE	1 DAY	21 DAYS	4 MONTHS	12 MONTHS
Al 1100-0	L	white deposit	-	iridescent film	film, cloudy patches
	G	no change	general pitting	iridescent film	cloudy patches
Al 2014-T6	L	white deposit	-	amber film, grey residue	no change, cloudy patches
	G	no change, stained	general pitting	amber film	amber film
Al 2219-T81	L	white deposit	-	iridescent film	no change
	G	no change	sl. blue stain	iridescent film	no change
Al 6061-T6	L	white deposit	white deposit, film	sl. stain	no change
	G	white deposit	sl. pitting	sl. stain	transparent film
Al 7079-T6	L	white film	film	sl. stain	no change
	G	no change	no change	sl. stain	cloudy film, no change
SS 301-FH	L	no change	-	iridescent film	-
	G	no change	no change	iridescent film	no change
SS 316-A*	L	no change	-	no change	no change
	G	no change	no change	no change	no change
SS 347-A	L	no change	-	spotty stain	lt. grey film
	G	no change	no change	spotty stain	lt. grey film
SS 347-FH	L	no change	-	iridescent film	no change
	G	no change	no change	no change	no change
PH15-7Mo (TH 1050)	L	no change	-	-	dk. grey film
	G	no change	no change	-	dk. grey film
AM350 (850SCT)	L	no change	rust particles	-	dk. grey film
	G	no change	possible pitting	-	dk. grey film
Nickel 200-A	L	blue-green residue, green stain	gold stain	amber film	cloudy film
	G	transparent film	general pitting	amber film	transparent film
Monel 400-A	L	no change	gold stain	amber film	no change
	G	stained	general pitting	amber film	no change
Rene 41 CMR (1400/16 hr)	L	grey film	black stripes	sl. stain	dk. grey film
	G	no change	no change	sl. stain	dk. grey film
Inconel-X (1400/16 hr)	L	no change	black stripes	amber stain	dk. grey film
	G	no change	possible pitting	sl. stain	dk. grey film
Cufenloy 10-A	L	spotty white deposits	stained	sl. darkening	pits and stains
	G	spotty white deposits	stained	sl. darkening	pits and stains
Cufenloy 40-A	L	stained	stained	dull irid. film	lt. grey film
	G	stained	stained	dull irid. film	lt. grey film
Copper-A	L	no change	stained	lt. amber film	thick film stains
	G	no change	stain, contact corrosion	lt. amber film	thick film stains
Brass (70-30)A	L	stained	stained	amber film	heavy stain
	G	no change, stained	sl. stain	lt. amber film	no change

* Construction material for storage containers.

Table 5

EFFECT OF 1% WATER ADDITION ON CORROSION OF STRUCTURAL METALS IN LIQUID OXYGEN DIFLUORIDE [Ref. 27]
(Immersion Tests Conducted at -110°F for One Day)

MATERIAL AND TREATMENT	WEIGHT CHANGE, g	CORROSION RATE		APPEARANCE
		mg/in^2	mpy	
Stainless Steels[a]				
SS301-FH	0.0002	0.0	0.0	No change
	-0.0001	0.0	0.0	No change
SS316-A	0.0000	0.0	0.0	No change
	-0.0071	2.3	6.5	No change
SS316-FH	-0.0024	0.8	2.2	No change
	0.0007	0.1	0.3	No change
SS347-A	-0.0002	0.0	0.0	Grey surface
	0.0003	0.1	0.3	Grey surface
SS347-H	-0.0002	0.1	0.3	Pitting
	0.0000	0.0	0.0	Pitting
PH15-7 Mo TH1050	-0.0002	0.1	0.3	Brownish corrosion deposit
	0.0004	0.1	0.3	Brownish corrosion deposit
AM350 850SCT	0.0001	0.0	0.0	Brownish corrosion deposit
	0.0000	0.0	0.0	Brownish corrosion deposit
AM355 850SCT	0.0004	0.0	0.0	Brownish corrosion deposit
	0.0001	0.0	0.0	Brownish corrosion deposit
Aluminum Alloys[b]				
Al 1100-0	-0.0002	0.1	0.8	Transparent film
	-0.0006	0.2	1.6	Transparent film
Al 2014-T6	0.0001	0.0	0.0	Blue film
	0.0002	0.1	0.8	Blue film
Al 2024-T6	-0.0001	0.2	1.64	Tarnish, pitting
	0.0000	0.0	0.0	Tarnish, pitting
Al 2219-T81	0.0001	0.0	0.0	Tarnish
	0.0000	0.0	0.0	Tarnish
Al 5456-H343	0.0001	0.0	0.0	Blue film
	0.0001	0.0	0.0	Blue film and pitting
Al 6061-T6	0.0000	0.0	0.0	Transparent film
	0.0000	0.0	0.0	Cloudy film
AL 7075-T6	0.0004	0.1	0.8	Tarnish
	0.0003	0.1	0.8	Tarnish
Al 7079-T6	0.0000	0.0	0.0	Film and pitting
	0.0002	0.1	0.8	Film and pitting

Table 5 (Concluded)

MATERIAL AND TREATMENT	WEIGHT CHANGE, g	CORROSION RATE		APPEARANCE
		mg/in^2	mpy	
Copper and Nickel Alloys[c]				
Copper-A	0.0007	0.2	0.5	Tarnish
	0.0004	0.1	0.3	Tarnish
Brass (70-30)-A	-0.0002	0.1	0.3	Pitting
	-0.0005	0.2	0.5	Pitting
Nickel 200-A	0.0000	0.0	0.0	Transp. film and nonhyd. spots
	0.0000	0.0	0.0	Transp. film and nonhyd. spots
Monel 400-A	-0.0005	0.2	0.5	Possible pits
	-0.0003	0.1	0.3	Possible pits
Rene' 41CMR (1400/16 hr)	-0.0002	0.1	0.3	No change and tarnish
	-0.0003	0.1	0.3	No change and tarnish
Inconel-X	-0.0004	0.1	0.3	Grey surface
	-0.0003	0.1	0.3	Grey surface
Cufenloy 10-A	-0.0005	0.1	0.03	Copper tarnish
	-0.0005	0.2	0.5	Copper tarnish
Cufenloy 40-A	-0.0002	0.1	0.3	Pitted and tarnished
	-0.0002	0.1	0.3	Pitted and tarnished
Other Metals				
Titanium, 6Al-4V[c]	0.0000	0.0	0.0	Tarnish
	0.0002	0.1	0.5	Tarnish
Titanium, A110-AT-A[c]	-0.1840	59.6	292.0	Grey surface
	-0.1000	32.4	158.0	Grey surface
Mg Alloy, HM21A-T8[b]	0.0008	0.2	2.6	Brownish coupon product
	0.0004	0.1	1.3	Brownish coupon product
Columbium-A[b]	-0.0001	0.0	0.0	Pitting, no change
	-0.0001	0.0	0.0	Pitting, no change
Tantalum-A[b]	0.0001	0.0	0.0	Pitting
	-0.0001	0.0	0.0	Pitting

[a] Test FOW-1, Bomb D2

[b] Test FOW-1, Bomb D11

[c] Test FOW-1, Bomb D2

Table 6

RESULTS OF LIQUID FLOX-40 IMMERSION TESTS: [Ref. 26]

(Samples stressed to 80% of normal yield strength)

SAMPLE	TEST NO.	IMMERSION PERIOD	HELIUM PRESSURE	SAMPLE WT., g	WT. GAIN[a] mg/in^2	REMARKS
Monel	Flox-1	16.0 hr	50 psig	21.2546	0.05	Pressure in the bomb increased to 80 psig after 16 hr due to partial evaporation of the LN_2 bath.
6061-T6				5.5407	0.03	
347 SS				17.6849	0.03	
Inconel-X				21.6801	0.06	
304 SS				16.7282	0.04	
2014-T6				5.8856	0.01	
301 SS				16.1817	0.02	
347 SS	Flox-2	18.0 hr	50 psig	15.5707	0.0	Pressure in bomb increased to 75 psig after 18 hr due to partial evaporation of the LN_2 bath.
5052-H34				5.6318	0.0	
Inconel-X				21.7765	0.06	
6061-T6				5.5311	0.06	
301 SS				16.1946	0.01	
Monel				21.4009	0.05	
347 SS				14.3420	0.01	
2014-T6				5.9329	0.01	
304 SS				16.1309	0.03	
6061-T6	Flox-3	17.0 hr	87 psig	5.5572	-0.05	Pressure in bomb increased to 125 psig after 17 hr due to partial evaporation of the LN_2 bath.
304 SS				16.4963	0.05	
301 SS				16.2654	0.0	
Monel				21.2558	0.11	
347 SS				15.6394	0.06	
6061-T6				5.3312	0.05	
5052-H34				5.2893	0.01	
2014-T6				5.7192	0.07	
2014-T6	Flox-4	19.0 hr	50 psig	5.9302	0.04	Pressure in bomb increased to 77 psig after 19 hr due to partial evaporation of LN_2 bath.
347 SS				17.7030	0.06	
Inconel-X				21.6590	0.07	
6061-T6				5.3199	0.0	
2014-T6				5.7406	0.02	
5052-H34				5.2079	0.03	
5052-H34				5.3913	0.03	
6061-T6				5.2985	0.01	

[a] All sample areas were of the order of 8 in^2.

Notes: (1) No detectable change in the appearance of the specimens after exposure to LF_2.
(2) No indications of galvanic dissimilar metal reactions in any of these tests.

Table 7

CORROSION RATES OF METALS IN CHLORINE TRIFLUORIDE (21-Day Exposure) AT 30°C [Ref. 15]

MATERIAL	AV CORROSION RATE, MPY	
	Liquid	Vapor
<u>Aluminum Alloys</u>		
AA 1061	0.01	-
AA 1100	0.01	0.02
AA 2024	0.01	-
AA 3003	0.01	-
AA 5052	0.01	-
AA 7079	0.01	-
<u>Copper Alloys</u>		
ETP Copper	0.11	0.11
DHP Copper	0.12	-
Beryllium Copper, 2% (Berylco 25)	0.11	-
Phosphor Bronze, 5%, Grade A	0.15	-
Aluminum Bronze, 8% (Ampco 8)	0.03	0.15
Yellow Brass	0.03	0.60
Rule Brass	0.07	-
Nickel Silver, 18% (Alloy A)	0.03	-
Cupro-Nickel, 30%	0.03	-
<u>Magnesium Alloys</u>		
AZ31B	0.03	0.20
HK31A	0.13	-
HM21A	0.05	-
<u>Nickel Alloys</u>		
"A" Nickel	0.00	0.06
Monel	0.01	0.02
Inconel	0.00	-
Incoloy	0.01	-
<u>Stainless Steels</u>		
AISI 304	0.02[a]	-
AISI 304	0.03[b]	-
AISI 316	0.03[a]	-
AISI 316	0.06[b]	0.09
AISI 347	0.05[a]	-
AISI 347	0.09[b]	-
AISI 403	0.04[a]	-
AISI 403	0.07[b]	0.13
Carpenter #20-Cb	0.02[a]	-
Carpenter #20-Cb	0.05[b]	-
PH 15-7 Mo (Cond. RH 950)	0.01	-
PH 15-7 Mo (Cond. TH 1050)	0.01	-
<u>Low-Carbon Steels</u>		
AISI 1010	0.01	0.07
AISI 1010 (Coated with Fosbond 40*)	0.04	-
AISI 1010 (Coated with Fosbond 27*)	0.01	-

[a] Rupture disc on test tank failed after 16 days; entire test repeated.

[b] Repeat test.

[c] *Trade Mark - Pennsalt Chemicals Corporation
(Fosbond 40 - a zinc phosphate-type coating)
(Fosbond 27 - an alkali phosphate-type coating).

Table 8

WEIGHT CHANGES IN PASSIVATION-PRESERVATION TESTS WITH LIQUID CHLORINE TRIFLUORIDE AT 30°C

[Typical Data from Ref. 15]

MATERIAL[a]	SUCCESSIVE EXPOSURES	EXPOSURE TIME	WT. CHANGE PER EXPOSURE, mg
Aluminum 1100	CTF Air CTF	64h 51d 164h	0.0 +0.1 +0.1
	Air CTF	51d 164h	+0.2 +0.1
Copper, ETP	CTF Air CTF	65h 51d 161h	+0.6 +0.1 +1.1
	Air CTF	51d 161h	+0.1 +1.0
Aluminum Bronze, 8% (Ampco 8)	CTF Air CTF	65h 51d 161h	+0.2 +0.2 +0.4
	Air CTF	51d 161h	+0.1 +0.5
Yellow Brass	CTF Air CTF	65h 51d 161h	+0.5 +0.2 +0.6
	Air CTF	51d 161h	+0.2 +0.7
Magnesium AZ31B	CTF Air CTF	65h 51d 164h	+0.1 +2.5 0.0
	Air CTF	51d 164h	+1.5 +0.2
"A" Nickel	CTF Air CTF	65h 51d 164h	+0.1 +0.2 +0.1
	Air CTF	51d 164h	+0.2 +0.1

Table 8 (Concluded)

MATERIAL[a]	SUCCESSIVE EXPOSURES	EXPOSURE TIME	WT. CHANGE PER EXPOSURE, mg
Monel	CTF	65h	+0.1
	Air	51d	+0.2
	CTF	163h	+0.3
	Air	51d	+0.3
	CTF	163h	+0.4
Stainless Steel 403	CTF	65h	-0.1
	Air	51d	+0.2
	CTF	163h	+0.2
	Air	51d	0.0
	CTF	163h	-0.1
Stainless Steel 316	CTF	65h	-0.1
	Air	51d	+0.1
	CTF	163h	+0.1
	Air	51d	0.0
	CTF	163h	0.0
Low Carbon Steel 1010	CTF	65h	+0.3
	Air	51d	+3.1
	CTF	163h	+1.1
	Air	51d	+2.2
	CTF	163h	+1.1
Low Carbon Steel 1010 with Fosbond 40* coating (zinc phosphate type)	CTF	20h	0.0
	Air	49d	-1.2
	CTF	163h	+0.6
	Air	49d	+0.4
	CTF	163h	+0.3
Low Carbon Steel 1010 with Fosbond 27* coating (alkali metal phosphate type)	CTF	20h	-0.4
	Air	49d	+1.8
	CTF	163h	0.0
	Air	49d	+0.5
	CTF	163h	+0.5

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* Trade Mark - Pennsalt Chemicals Corporation.

[a] Metal test pieces: exposed area in the range of 18-20 cm^2; weights in range of 4-24 g.

V. FORMATION AND NATURE OF FLUORIDE FILMS

The inhibition of fluorine-oxidizer attack on metal surfaces after a rapid formation of a coating of metal fluoride was mentioned briefly in Section III. The compatibility studies with fluorine oxidizers (Section IV) indicate that the corrosion layers on compatible metal surfaces are extremely thin. In the case of OF_2 where storage tests were conducted for periods up to one year, corrosive attack appears to cease in the first few weeks of exposure or is restricted to a fraction of the initial rate of attack.

The rate of formation of the fluoride film, its behavior on exposure to vacuum or the atmosphere, and its general structure are discussed in this Section. It is evident from the review of reports included in this Section and from classical references* that only metallic fluorides are formed by the complete interaction of metals or metal oxides with fluorine, halogenated fluorine compounds, or fluorine-oxygen compounds. The thickness of the primary film on metals ranges from 3-14 Å after the first minute of exposure to fluorine and is only 6-30 Å after one hour. Quoted rates of formation of a film on a given metal may appear to vary for a particular oxidizer, but these variations are likely to be due to contaminant HF and moisture in the oxidizers--as suggested by the results of compatibility studies noted in Section IV. Corrosion rates are very low.

REACTION OF FLUORINE WITH METALS IN DEACTIVATION PROCESSES

The thickness of the corrosion film formed by reaction of gaseous fluorine with a variety of metal powders at different temperatures was determined by Kleinberg and Tompkins [19]. A calibrated-volume system,

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* For example, Mellors Comprehensive Treatise on Inorganic and Theoretical Chemistry."

passivated with fluorine, was used to measure the drop in pressure of fluorine gas because of its reaction with metal powder surfaces. (No mention was made of special cleaning or reduction of metal powders.) Surface areas, determined by the BET method, ranged from about 36 to 3000 cm^2/g. The initial fluorine pressure was one atmosphere and temperatures of -113°, +83°, and +183°F were used in separate series of tests lasting as long as 100 hours. Consumption of fluorine with respect to available surface area of the metal powders was converted into film thickness of metal fluoride. It is noted that some inconsistencies in the results may be attributed to the uncertainty of surface areas at levels less than 1 m^2/g.

Data given by Kleinberg and Tompkins for the corrosion rates of a variety of metals in gaseous fluorine at 86°F have been re-plotted in Figure 1 with log time vs log film-thickness co-ordinates (instead of time vs film-thickness as in the original report). The linearities of the plots for the formation of films on aluminum, copper, and nickel are immediately apparent, and suggest that the curves published by the authors were of the form $y^n = kt$, because if the basic equation were to be expressed logarithmically, then: $\ell n\ y = k_1 + (1/n)\ \ell n\ t$. It is evident that a linear relationship will be found in a plot of $\ell n\ y$ (film thickness) vs $\ell n\ t$ if the original data are essentially of the power-law form.

Monel metal and stainless steel 316 corrosion rates also appear to be of the power law form, but the initial reactions proceed at different rates, as suggested by the change in slopes evident in Figure 1. This suggests that the initial stages of formation of fluoride films may have been involved with a reaction of surface oxides with fluorine while later stages represent the characteristic formation of film by reaction of fluorine and metal. Although other mechanisms may possibly be involved, the important point is that corrosion rates after about 10 hours seem to follow a power law for which n is between 2 and 3. For exponents greater than 2, it is assumed that retardation of diffusion is considerably greater than that determined by an increase in film thickness, such as may be realized by a decrease in diffusion coefficient of fluoride ion with film growth and age.

If the data of Kleinberg and Tompkins be plotted film-thickness vs log time, in order to test for compliance with a logarithmic rate of film growth [e.g., $y = k_1 \ell n (kt) + c$], the resultant plots (Figure 2) grossly depart from linearity; hence, the selection of a power law corrosion equation appears sufficient for the available data points. (Perhaps corrosion data will conform to a log decrement curve when data obtained from long-term tests are used.)

Extrapolation of rates obtained from Figure 1 suggest that nickel, aluminum, copper, and Monel will have fluoride film thicknesses of the order of 50 to 150 Å at the end of one year of attack, and that stainless steel 316 will have a film of no more than 1000 Å thick (4 micro-inches!).

A series of experiments performed by Kleinberg and Tompkins established that the fluoride films formed by interaction of metal surfaces and fluorine are affected by water vapor (in air); for example, metal surfaces which had been in contact with fluorine and then were exposed to air would take up additional quantities of fluorine. The authors found that anhydrous inorganic fluorides, e.g., MgF_2 and NiF_2, rapidly absorbed water (to form hydrates or an adsorbed film) and reacted with fluorine to an extent determined by their water content. Hence, the deterioriation of "passive" films by water was considered by them to be due (in part) to a mechanism involving hydration of inorganic fluoride compounds, and that when the hydrated films are again subjected to fluorine action, the water content of the film reacts and a protective film is re-established wherever exposed metal exists. Cannon et al. [8] also obtained data which demonstrated that fluoride films are destroyed by atmospheric moisture, and that the films are regenerated at rates comparable to the basic rates of formation of fluoride films on clean metals (with the exception of copper).

Cannon et al. carefully measured the rate of formation of films by fluorine gas on metal powders of aluminum alloys, copper, Monel, nickel, and stainless steel at $80^{\circ}F$ in a constant-volume system. Surface areas of 1000 to 7000 cm^2/g were determined by the BET technique. The consumption by the powders of fluorine initially at one atmosphere was measured at intervals from 1 to 800 minutes and converted to film thicknesses. The authors chose to interpret their measurements as indicative of a logarithmic corrosion rate, possible as suggested by the work of O'Donnell and Spakowski [21] in which the corrosion rate of iron in fluorine at 225°C appears to follow a logarithmic rate law. A characteristic semi-log plot of their data is reproduced in Figure 3 which suggests, within experimental error, that the initial rates of formation of fluoride films on copper, Monel, and nickel fulfill the logarithmic rate law. On the other hand, if the data in Figure 3 and data for other metals in their report be plotted in log-log form, straight lines also result and it can be assumed that the initial formation also appears to follow a power law (see Figure 4) as do the data of Kleinberg and Tompkins (cf. Figure 1) but the exponents are greatly different. Evidently, the mechanism of formation of the initial fluoride film is different than the mechanism of formation of thicker films, or the presence of HF or other contaminants has influenced the reaction rates as determined by the various authors. Nevertheless, the short-time measurement procedure adopted by Cannon et al. has been useful in demonstrating that the onset of corrosion of metal surfaces by fluoride is reproducible and that film formation takes place rapidly with nearly the entire thickness being generated in a matter of one or two hours. These findings are of importance in defining the time required for deactivation of metal surfaces by fluorine.

In an early study of the kinetics of reaction of reduced electrolytic copper powder (surface area about 400 cm^2/g) with fluorine between room temperature and 250°C, Brown, Crabtree, and Duncan [5] found that a fluoride film of about 10 Å is formed during 5 hours of exposure at room temperature. The reaction rate in the temperature range of 25° to 250°C was found to be logarithmic for the time duration of the experiments and independent of pressure variance from 6 to 60 torr at 100°C. On the other hand, more recent work by O'Donnell and Spakowski on the fluorination of copper [22] and related work on nickel indicate a pressure dependence for the reactions and that the lower temperature reactions follow a simple power law ($y^n = kt$).

FLUORINATION OF METALS AT ELEVATED TEMPERATURES

The mechanism of fluorine reaction with nickel at 600° to 700°C was examined by Jarry, Fischer, and Gunther [18] in metallographic and radio-autographic studies. They showed that fluorine, rather than nickel, migrates through the fluoride scales during the reaction by gross movement through pores and cracks or by some transport through the scale itself.

Reaction of fluorine with beryllium at temperatures of 125° to 775°C and pressures of 20 to 700 torr were studied by O'Donnell [20]. It was shown that the rate of reaction follows a power law and that beryllium is the diffusing specie. It also was shown by O'Donnell [21] that the reaction of iron with fluorine at temperatures of 225° to 525°C and pressures up to 200 torr proceeds according to a logarithmic rate law during test runs of about 5-6 hours. Thus, for the metals of interest to rocket engineers, it appears that the mechanism of film growth is ascribed to the movement of fluorine through defects in the fluoride film to the metal surface.

It has been shown by Cannon _et al_. [8] that the initial reaction of film formation can be enhanced by increased fluorine pressure at ambient temperatures (see Figure 5). Higher temperatures of fluorination might accelerate final film formation; however, it was found by O'Donnell and Spakowski [23] that fluorine consumption on reduced copper foils decreased with increased temperature in the range of 800° to 1200°F at fluorine pressures of about 200 torr in experiments of 2-3 hours each. It is assumed that the composition of the copper fluoride film is different at higher temperatures than at lower. The same authors [22] showed that the reaction at about 840°F was pressure dependent over the range of 10 to 130 torr and followed a logarithmic rate law; experiments were conducted for periods of 4-6 hours. The authors also noted the observation made by Brown _et al_. [5] that the passivity of specimens was lost upon heating in vacuum.

REACTIONS OF FLUORINE WITH METALLIC SURFACE OXIDES

Metal oxides and hydroxides as well as absorbed moisture are apt to be present on cleaned metal surfaces; water and the oxygenated compounds are consumptive of fluorine in deactivation processes and may lead to deflagration if their quantities are excessive. Fluorine reacts with cold, solid hydroxides to produce the fluoride of the metal, water, oxygen, or oxygen fluoride (OF_2); with cold water fluorine produces HF, O_2, and OF_2; with alkaline solutions a metal fluoride, water, oxygen, OF_2, and a peroxide [6] are formed.

Haendler _et al_. [17] demonstrated that fluorine reacts incompletely with copper oxide powder between 150° and 300°C to form CuF_2. Haendler, Patterson, and Bernard [16], working with nickel powder, reported that complete conversion to NiF_2 required a temperature of 550°C and three exposures to fluorine with grinding in-between; on the other hand, the reaction $NiO \rightarrow NiF_2$ was nearly complete at 325°C and totally complete at 375°C. The fluorination of NiO powders at temperatures of 25° to 180°C with gaseous chlorine trifluoride was studied by Farrar and Smith [14]; pressure differences from 0.3 to 0.1 atmosphere made only slight differences in the final interpretation of the mechanism of fluorination. It was concluded that subsequent to the formation of a critical thickness of NiF_2, a re-crystallization takes place which opens a pathway via grain boundaries for adsorbed fluorine to react with priorly unattacked oxide surfaces.

In summary, the results of available studies indicate that a temperature in excess of ambient may be required for the complete fluorination of metal surface oxides in a short time. However, other studies suggest that the greater portion of the reactions are completed to a sufficient extent (for safety considerations) after a nominal length of time at ambient temperatures (e.g., 1-24 hours).

STABILITY AND NATURE OF FLUORIDE FILMS

The general practice in fluorine-oxidizer deactivation is to expose cleaned systems for a short time to a reactive gas. In order to evaluate the effectiveness of this treatment, Cannon et al. [8] set up an experiment with metal powders to determine (1) the amount of oxidizer at one atmosphere and 77°F consumed as a function of time over periods of 60 to 120 minutes, (2) the amount of oxidizer consumed in a second treatment after room-temperature evacuation of the sample container, and (3) the amount of oxidizer consumed after exposure of an initially-reacted powder for 48 hours in air with 50% relative humidity. The experiments were performed with fluorine, ClF_3, ClF_5 and BrF_5. The results suggested that the initial reactions of the oxidizers with the metals were somewhat incomplete, for after evacuation and re-exposure to fluorine, some take-up was observed. The fluorine take-up was great for copper (and Monel) and nearly negligible for nickel. Similar behavior was observed when chlorine trifluoride was used for forming the initial fluoride film. Peculiarly, the authors did not ascribe a portion of the secondary take-up of fluorine to the probable loss of fluorine dissolved in the copper fluoride film matrix (also in the film on Monel). If a solution of halogen in the fluoride film is required to maintain integrity of the rate-controlling structure, when the halogen is removed by evacuation, the passivating nature of the film is destroyed. This mechanism perhaps is involved in the observations of O'Donnell [22] and of Brown et al. [5] that vacuum destroys the passivity of copper fluoride films.

The exposure of the fluorided powders by Cannon et al. to a humid atmosphere resulted in the consumption of fairly large amounts of oxidizer before a low rate of take-up was observed again; copper powder consumed more oxidizer after exposure initially. On the other hand, films on aluminum-2024 appeared to be quite stable in a humid atmosphere. It was concluded that passivation treatments of 15 to 30 minutes were sufficient to form a protective film (initial rapid consumption of oxidizer) and it was shown that the same kind of passivation could be achieved over a pressure range of 0.1 to 1.5 atmospheres. It was suggested that passivated aluminum could be used in systems after its exposure to the atmosphere, but that stainless steels and nickel should be re-passivated if the integrity and presence of a fluoride film is a necessary prerequisite to the success of a mission.

Reflection electron diffraction studies of fluoride films conducted by Cannon et al. [8] have shown the same features for films whether they be deposited on metal powders or bulk metals, thus validating the application of passivation studies made with powders to bulk metal systems. The diffraction patterns showed that the same general fluoride structures were present in films regardless of the mode of pre-treatment and the fluorine oxidizer and whether the films were exposed to humidity. Identified species were metal oxides and hydroxides, metal fluorides, hydroxy fluorides, and hydrated fluorides.

After exposure to CTF gas at 80°F for one hour, copper films contained both hydrated copper chloride and copper fluoride as well as other oxygenated fluorides. Exposure to a humid atmosphere caused the formation of blue crystals ($CuF_2 \cdot 2H_2O$); the primary film was CuF_2, easily removed by mechanical abrasion [8].

Studies with x-ray diffraction and electron diffraction techniques by Crabtree, Lees, and Little [11] showed that the fluorination of copper surfaces at about 300°C produced the same anhydrous cupric fluoride whether the original surface was reduced with hydrogen or left with the normal oxide film. Exposure to air for even a few minutes resulted in conversion to a green basic fluoride. Heating of the basic fluoride in low vacuum for two hours at 300°C changed the diffraction characteristics of the film, and suggested that copper was the migrating species.

INTEGRITY OF FLUORIDE FILMS

The fluoride films formed by contact of most metals with fluorine, the interhalogens, and other fluorine oxidizers not only are formed very rapidly but appear to be quite flexible, and thus remain as protective devices when the metals are flexed. A series of flexure tests on yellow brass, copper, aluminum, and Monel samples immersed in liquid fluorine has indicated that no increase in corrosion occurs when 5-mil strips of metal are gently flexed once per second for periods as long as 6 hours.

On the other hand, a more vigorous disruption of fluoride films, such as is afforded by the dropping of a weight on flat specimens, seems to result in localized activity between the fluorine oxidizer and the exposed metal surface. Experiments with various kinds of strikers at various impact levels indicate that titanium alloys undergo ignition in liquid fluorine as well as in liquid oxygen. Similar tests indicated that aluminum has a very small tendency to ignite in liquid fluorine. In other tests, tubes of copper, brass, nickel, Monel, aluminum-1100 and stainless steels 304, 316, 321, and 347 were filled with liquid fluorine and subjected to impact by pointed strikers and to the explosive shock of a No. 6 electric blasting cap. No apparent ignition or increase in corrosion was detected, and even vibration of samples at 30 cps for periods as long as 5 hours after impact produced no effects. Titanium, brass, copper, Monel, aluminum, mild steel, stainless steel, and Inconel-X were fractured in a liquid fluorine environment; only titanium exhibited a mild sensitivity [30].

Tests in liquid fluorine with copper and magnesium alloy AZ-31, in which the metal samples were continuously brushed with stainless steel bristles under a force considered sufficient to disrupt fluoride films, did not result in increased corrosion rates; it is suggested that film protection is not the controlling mechanism in corrosion resistance of metals to liquid fluorine (in spite of overwhelming evidence listed herebefore).

There is also a report that aluminum fluorine-pump housings and propellers have performed successfully even though the propeller occasionally rubs the housing [1].

Flex tests of metal bellows in liquid fluorine have also been performed to determine whether scuffing or stretching the fluoride films on metals is a factor in corrosion mechanisms. For the most part, these tests have been inconclusive, although it has been noted that metals appear to fatigue more easily in a fluorine environment [9, 13]. On the other hand, samples of AM350 stainless steel and titanium 6Al-4V which were deliberately fractured in high-velocity jets of gaseous fluorine (room temperature) gave no indication of ignition, and in other experiments, were found to have notch strengths in fluorine that compared favorably to their notch strengths in air [31]; related fracture tests in liquid fluorine with copper, brass, aluminum, Monel, and titanium resulted in minor ignition of titanium in at least one of 12 tests [30]. Clearly, none of the tests conducted with fluorine and designed to ascertain the efficacy of fluoride film protection and its resistance to abuse have been performed with sufficient care to permit drawing firm conclusions.

The corrosion of metals by OF_2 under cavitating flow conditions was determined in a special apparatus employing flow of the liquid propellant through an orifice at high pressure and impingement on the surface of metals, simulating operating conditions in typical propulsion systems considered for use in space [27]. Monel exhibited most resistance to flow and impingement attack, followed closely by stainless steel; in aluminum alloy samples, corrosion damage appeared to be a sharp function of flow and impingement conditions. It is suggested that the relative adherence of the fluoride films on the various metals are responsible for their dissimilar behavior. It is of interest to note that even though gross erosions of metal surfaces were evident, ignition did not occur; evidently, the rate of fluoride formation was rapid enough to keep up with the rate at which it was removed.

The results of various impact tests and ignitability tests have been presented in Section IV. It appears that violent disruption of protective films along with adiabatic temperature increases are often adequate to cause localized ignition of many metals and especially of the metals which form relatively volatile fluorides. Thus, tungsten and molybdenum, as well as titanium appear to be extremely susceptible to ignition on impact in fluorine or fluorine oxidizers and have correspondingly low ignition temperatures [25].

The fluoride films that are formed on most metals afford protection over a wide range of temperatures; notable exceptions are those which form relatively volatile fluorides. In liquid fluorine or fluorine oxidizers, some of these fluoride films are removed by dissolution with the result that the base metal is exposed to continued attack; for example, titanium and columbium dissolve readily in chlorine trifluoride.

In conclusion, available data suggest that the formation of tenacious, protective fluoride films appears to proceed with such rapidity that only the most severe scouring conditions can displace them to the point where deflagration or extremely rapid corrosion of the metals can take place. It is the remarkable tenacity and flexibility of fluoride films and their self-healing property that removes from consideration all schemes for thwarting the deleterious action of fluorine oxidizers on metals by the application of fragile coatings or the deposition of thin films of various substances. Fragmentary data suggest that metals which are flexed within their elastic range do not undergo accelerated corrosion rates in fluorine or the fluorine oxidizers (there may be some question about CTF). Fluoride films on metals seem to have properties similar to their oxide counterparts in respect to affording protection of the base metal, adherence, and flexibility.

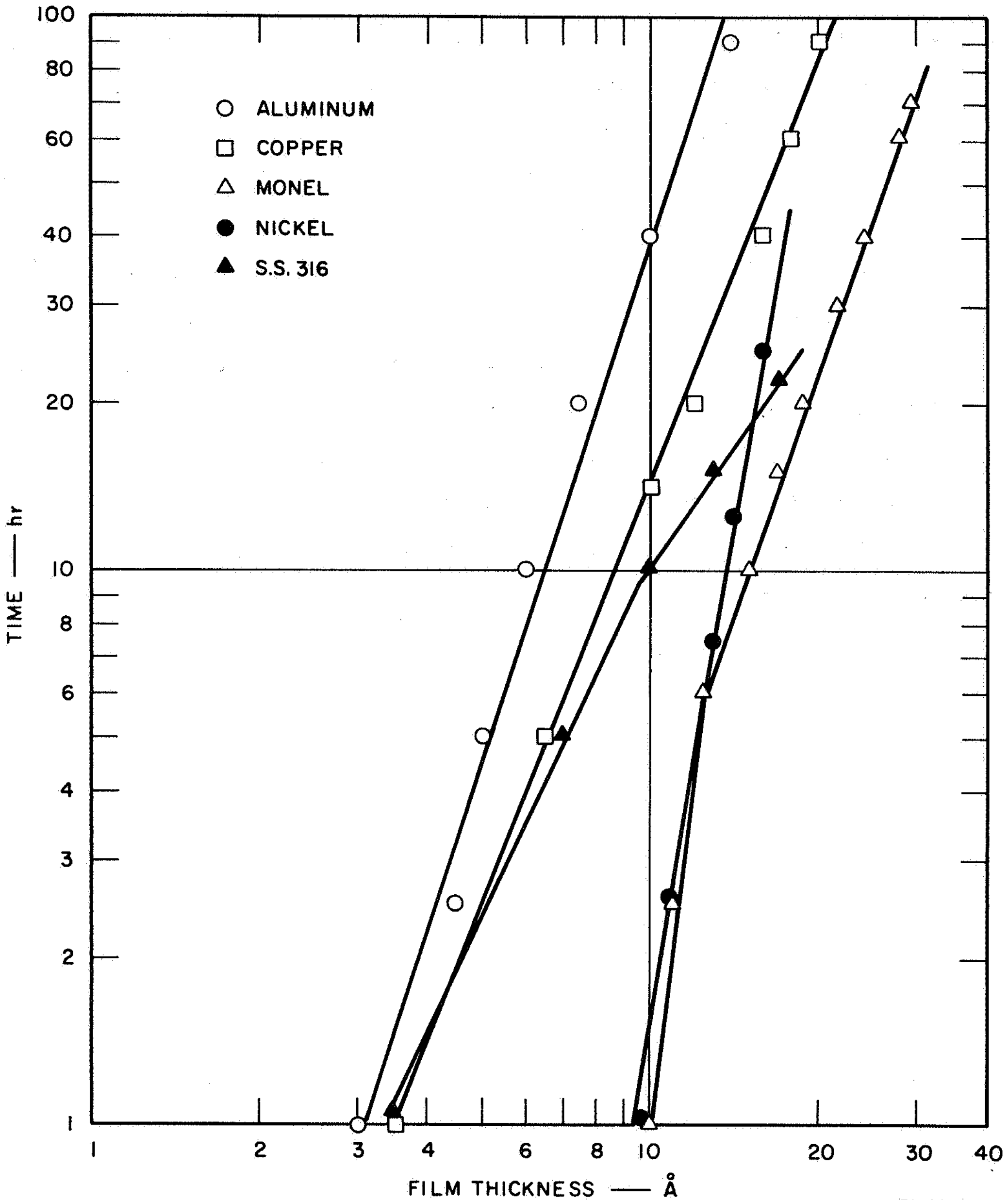

FIG. 1 LOG-LOG PLOT OF FLUORIDE FILM THICKNESS AS A FUNCTION OF TIME FOR VARIOUS METAL POWDERS EXPOSED TO ONE ATMOSPHERE OF FLUORINE AT 86°F. [DATA FROM REF. 19]

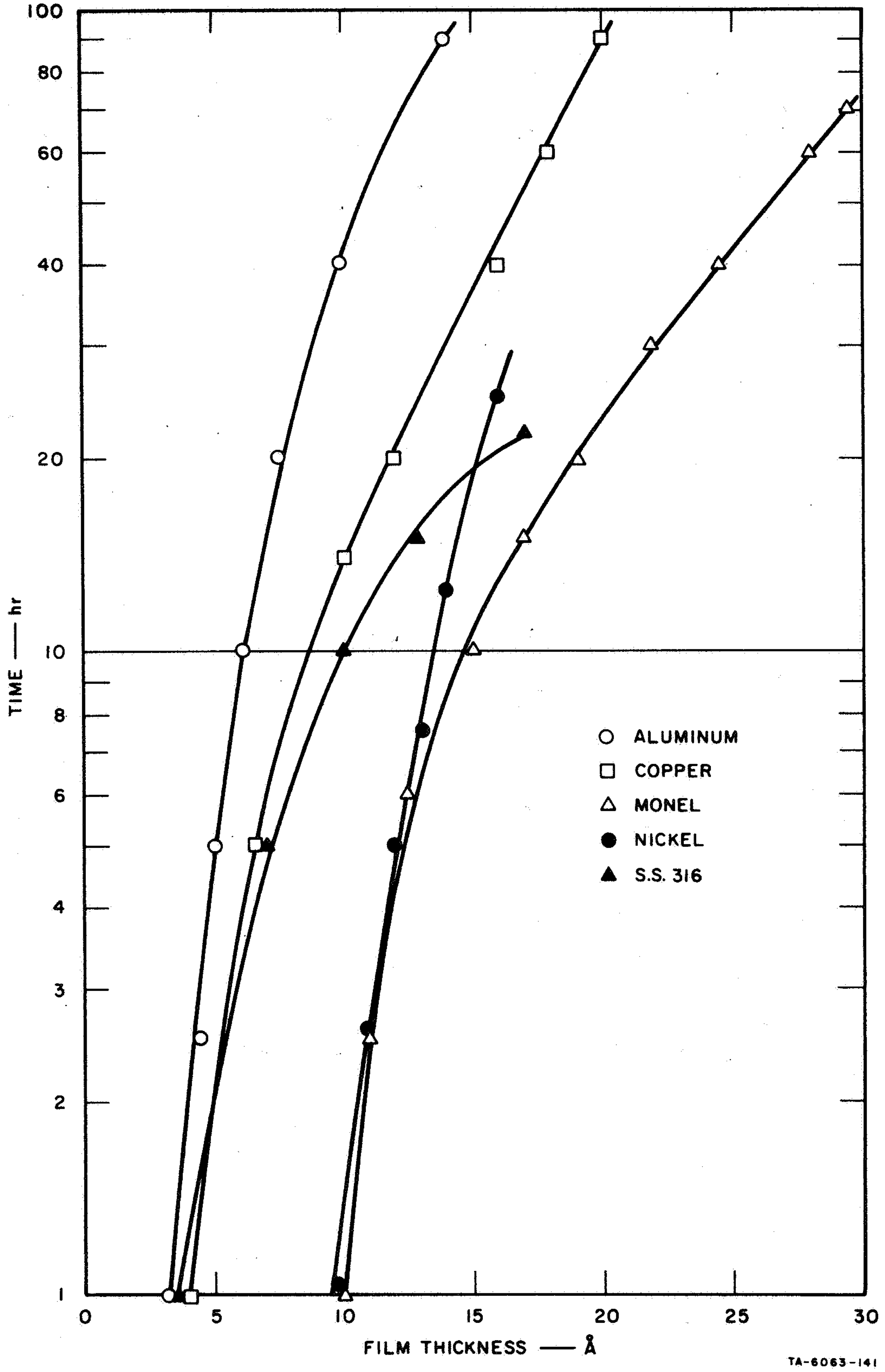

FIG. 2 FLUORIDE FILM THICKNESS vs LOGARITHM OF TIME FOR VARIOUS METAL POWDERS EXPOSED TO ONE ATMOSPHERE OF FLUORINE AT 86°F. [DATA FROM REF. 19]

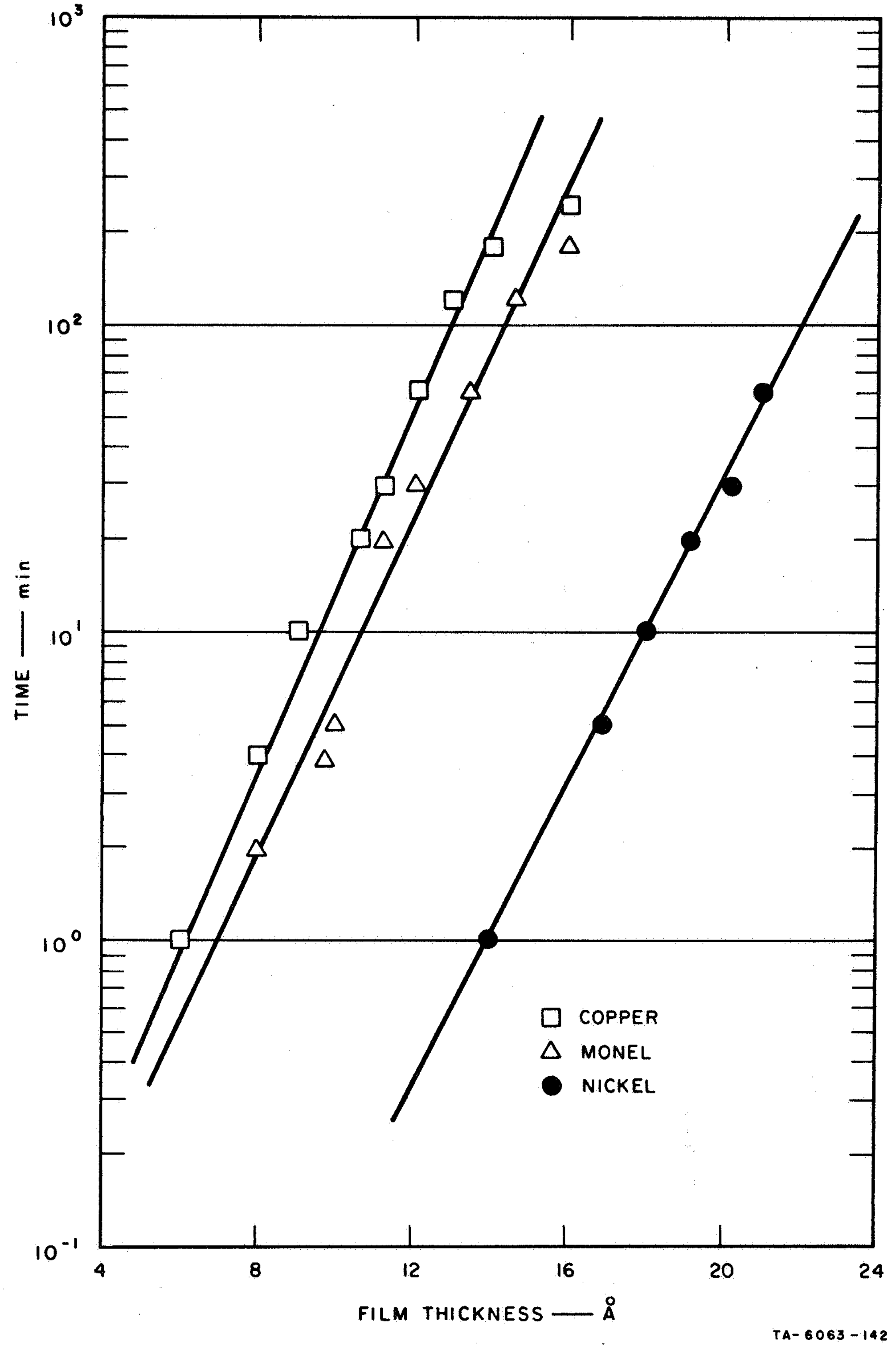

FIG. 3 FLUORIDE FILM THICKNESS vs LOGARITHM OF TIMᴌ COPPER, MONEL, NICKEL; ONE ATMOSPHERE OF FLUORINE AT 80°F. [REF. 8]

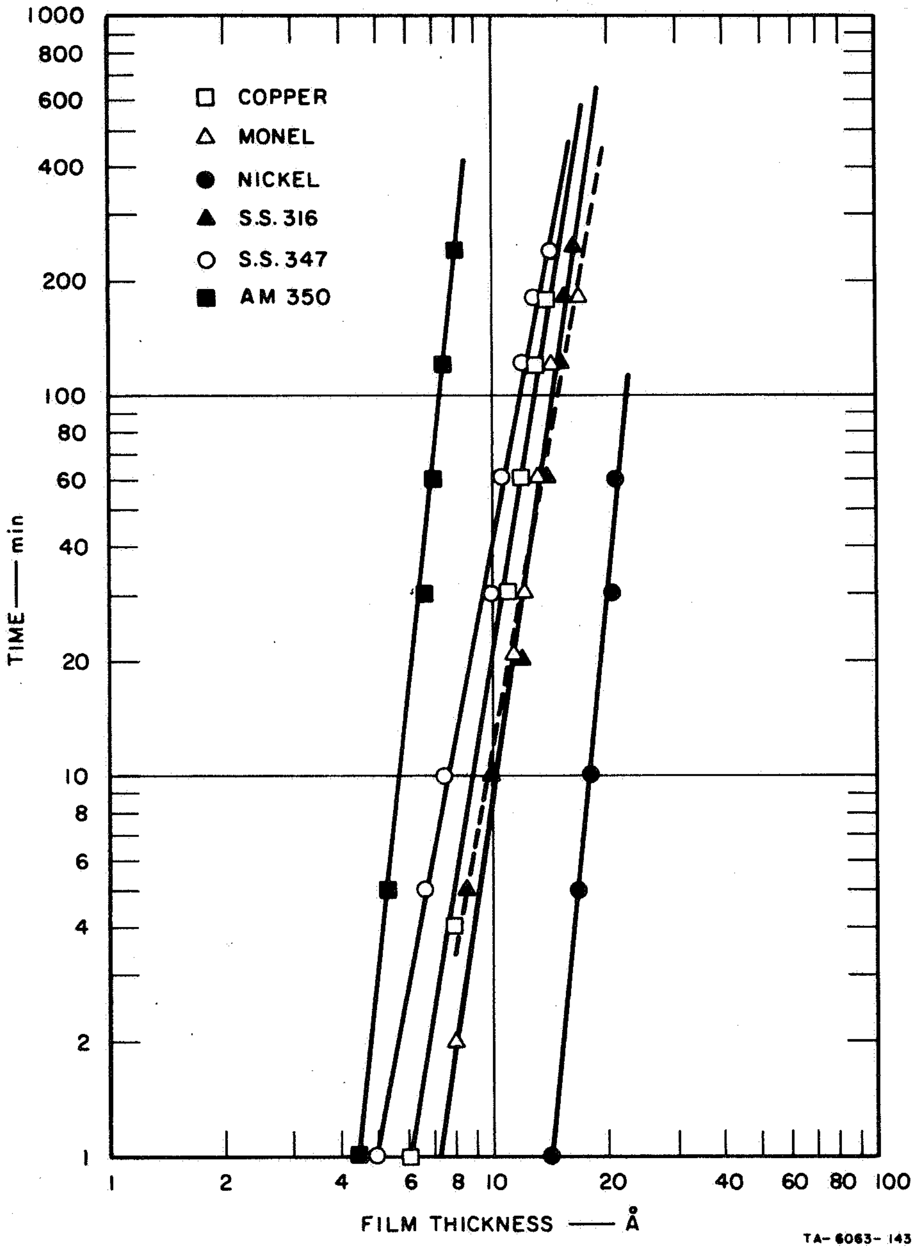

FIG. 4 RE-PLOTTED DATA OF CANNON et al. [8] TO SHOW CONFORMANCE WITH A POWER LAW OF RATE OF CORROSION.

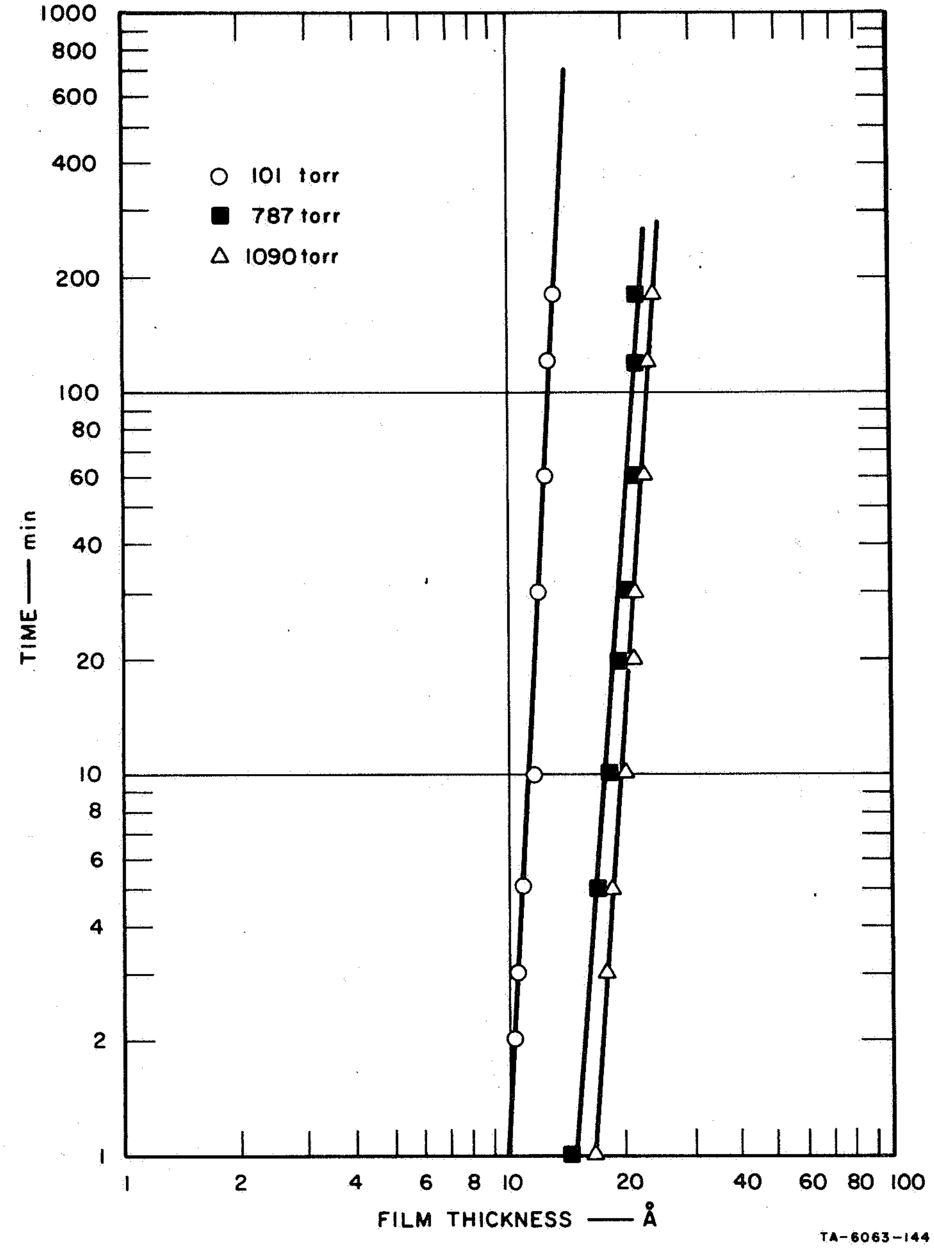

FIG. 5 EFFECT OF FLUORINE PRESSURE ON FILM FORMATION ON NICKEL POWDER AT 80°F. [DATA FROM REF. 8]

VI. CONCLUSIONS AND RECOMMENDATIONS

The primary conclusion resulting from a critical examination of available data on the storage and reactivity of liquid fuels and oxidizers with compatible metals is that "passivation" of metals is not a prerequisite, provided the metal surfaces are free of reactive contaminants. Fluoride films form almost instantly on most metals when brought into contact with fluorine or any of the fluorine oxidizers, and they appear to have the same structure and the same adherence, flexibility, and corrosion-inhibiting characteristics regardless of the way in which the fluorine or fluorine oxidant was brought into contact with metal. Thus, corrosion rates are not related to the way "passivation" is effected.

No pre-service treatment is required for metal systems to be used with methane or diborane (other than thorough cleaning). A conditioning requirement for diborane is that the system be completely purged of air by dry nitrogen prior to filling with the fuel simply because it reacts violently with oxygen.

Experiments have shown that there is a rapid initial reaction between the fluorine oxidizers and clean metal surfaces to produce a protective fluoride film that limits further attack of the metal; because the films are so thin, ignition cannot take place, and a clean system can be immediately put into service without pre-fluorination. However, since the surfaces of complicated systems are not readily accessible for thorough cleaning, a fluorination treatment, in which the oxidizer is allowed to react slowly with the systems, is recommended to deactivate residual contaminants and to purge the products of deactivation out of the system. Any fluorine oxidizer may be used for deactivation of metal systems prior to filling with any other fluorine oxidizer, as long as the metals are compatible with each oxidizer. A recommended general procedure for deactivation is summarized in Section III. It is further recommended that systems be deactivated just prior to use; if this is not always feasible, the deactivated system should be kept under a positive pressure of the oxidizer or dry helium or nitrogen.

The results of compatibility tests suggest that a number of alloys and metals are suitable for use with fluorine oxidizers since the observed initial corrosion rates (established within a few hours) are generally less than 0.1 mpy, and no shock or impact sensitivity is exhibited; these metals include copper, nickel, aluminum, and stainless steel alloys. The longest compatibility tests have been performed with OF_2 (1 year). Although the low corrosion rates observed in storage tests of 1-day to 12-month's duration with fluorine or the fluorine oxidizers imply compatibility, the possibility of accumulation of corrosion products during long periods of storage has not been explored; it is not certain whether corrosion essentially ceases after a time. Colloidal metal fluoride dispersions which floc upon cavitation may prove burdensome; no tests have been performed to evaluate the severity of the problem of sludge or floc.

The rate of corrosion of a metal under attack by fluorine or a fluorine oxidizer is initially (first hour) very high and gradually tapers off to some nearly constant rate (approaching zero). It is of interest to note that the corrosion rate of fluorine oxidizers with compatible metals are generally less than 0.1 mpy during the initial stages of corrosion. As a first approximation, one may use these rather high corrosion rates in order to estimate the extent to which corrosion may take place in a spacecraft propulsion system undergoing missions of 2, 5, or 10 years; the resulting corrosion will, of course, represent the maximum. However, it must be recognized that if the corrosion product sloughs off during the storage period, it may clog orifices, etc. in the propulsion system. For example, if a square foot of nickel were to be exposed to one of the fluorine oxidizers for 10 years, and the original corrosion rate is assumed to hold throughout the storage period (0.001 mpy), the weight of nickel fluoride corrosion product is computed to be 0.0122 ounces. It is unlikely that this amount of nickel fluoride will remain attached to the metal surface; consequently, sludge will develop if the corrosion rate remains unaltered over the 10-year period.

Some titanium alloys appear to have acceptable corrosion rates in short-term tests (weeks), but most are sensitive to impact in the fluorine-oxygen oxidizers and dissolve in chlorine trifluoride.

Studies of the formation and nature of fluoride films have revealed that protective films are extremely thin, adherent, and flexible, and limit corrosive attack to extremely low rates. The rapidity of formation of the protective films is such that self-healing occurs nearly instantaneously in an operating system should a small surface area of fresh metal be exposed by a sharp flexure.

RECOMMENDATIONS FOR FURTHER STUDY

The results of short-term tests for determining the compatiblity of the commoner metals of construction with diborane and the fluorine oxidizers indicate extremely low corrosion rates. However, if a metal is seriously considered for use with any of the propellants, storage tests should be conducted for periods of at least two years at the fixed or cycling temperatures expected during similar storage in space; particular attention must be given to the sludging-out of corrosion products.*
More specific recommendations are stated briefly as follows:

(1) As has been implied in the body of this report, absolutely clean metal surfaces can be brought into contact with semi-cryogenic propellants without fear of mishap; on the other hand, it has also been stressed that thorough cleaning of complicated hardware systems is difficult, and it has been implied that ordinary cleaning procedures and processes are inadequate. A comprehensive study should be undertaken in order to establish standardized procedures for cleaning specific metal surfaces. A subsequent study should be undertaken to define and demonstrate techniques based on the findings of the initial study for cleaning specific finished and assembled components.

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* Gel formation caused by contaminants in N_2O_4 has been examined in flowing and static systems [32]; continuing work is involved with clogging in flowing systems caused by contaminants in OF_2 and B_2H_6 [33].

(2) There are indications that titanium alloys are sensitive to impact and are ignitable when flexed severely in the presence of fluorine oxidizers; scattered information suggests that certain titanium alloys are unduly corroded by fluorine oxidizers. In view of the importance of titanium and its alloys as a structural material for spacecrafts, it is suggested that the impact sensitivity and flex resistance of titanium and its alloys in OF_2 and FLOX be determined in a sufficient number of experiments to permit statistical interpretation and the drawing of valid conclusions.

(3) Long-term corrosion tests should be performed only with the alloys of titanium shown to have satisfactory flex resistance and low levels of impact sensitivity.

(4) Nickel-clad titanium is suggested as a satisfactory material of construction for use in contact with OF_2 and FLOX; this composite material should behave like nickel with regard to impact sensitivity, inactivity under severe flex, and good corrosion resistance. The nickel can be deposited by catalytic reduction processes on exposed, intricately figured surfaces that are to come into contact with the oxidizers. The impact sensitivity of nickel-clad titanium alloys in OF_2 and FLOX should be investigated as soon as possible. The program of investigation should include a study of available nickel deposition processes as to their efficacy in producing ductile clads of reasonably uniform thickness. The study should also take into consideration the effect of pinholes in the cladding metal on impact sensitivity. It should include definitive observations whether pinholes or other discontinuities will induce high corrosion rates because of the galvanic couple Ni-Ti; rates of corrosion in OF_2 and FLOX should be determined over periods of at least two years with particular emphasis on the deposition of particulate matter.

(5) Scattered observations in the past have suggested that the presence of HF in fluorine oxidizers accelerates corrosion rates; other observations imply that HF is inactive. The effect of realistic quantities of HF and other impurities in fluorine oxidizers on sludging and on the rate of attack on metals needs to be established unambiguously.

(6) Titanium and its alloys become embrittled by hydrogen; and compatibility studies with diborane have not been performed; there is a possibility that titanium can react with hydrogen given off by the decomposition of diborane or that hydrogen can be extracted under impact. The compatibility of titanium alloys with diborane needs to be investigated under a variety of conditions including impact and severe flexure.

(7) The decomposition of diborane leads to the formation of solid polymeric hydrides which may be conducive to clogging of propulsion systems. Long-term storage tests should be initiated to determine whether sludges are formed and if they can clog propellant systems.

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