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AFRPL-TR-67-309

HALOGEN PASSIVATION PROCEDURAL GUIDE

Contract No. F04611-67-C-0033

S. K. Asunmaa, W. A. Cannon, W. D. English,
N. A. Tiner, and S. M. Toy

Astropower Laboratory, Missile & Space Systems Division
A Division of McDonnell Douglas Corporation

FINAL TECHNICAL REPORT AFRPL-TR-67-309

December 1967

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Air Force Rocket Propulsion Laboratory
Research and Technology Division
Air Force Systems Command
Edwards Air Force Base, California
United States Air Force

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FOREWORD

This report is a Final Summary Technical Report on Contract F04611-67-C-0033, covering the period 1 November 1966 to 1 November 1967, and it is also a Halogen Passivation Procedural Guide detailing methods to render a system safe for exposure to fluorine and other fluorinating agents, on that contract and on the previous Contract AF04(611)-10932. The work on these contracts was carried out at Astropower Laboratory, Advance Systems and Technology, Douglas Missile and Space Systems Division, McDonnell Douglas Corporation, under the supervision of Dr. N. A. Tiner, Head, Materials Department. Dr. W. D. English, Section Chief, Propellant Compatibility, was the Program Scientist, and experiments and analyses were conducted by Dr. S. K. Asunmaa, W. G. Black, W. A. Cannon, and S. M. Toy, with the technical assistance of C. R. Brown, A. Pinkul, D. R. Nelson, S. Miranda, S. Sanders, F. D. Kleist, and R. Ingersoll. The program was administered by the Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards Air Force Base, California, under the Technical Direction of Mr. Biggers as Project Engineer, succeeding Lt. Ralph Fargnoli.

This report was prepared by W. A. Cannon, with the assistance of S. K. Asunmaa, S. M. Toy, and W. D. English, under the supervision of N. A. Tiner.

This report has been reviewed and approved.

W. H. Ebelke, Colonel, USAF
Chief, Propellant Division

ABSTRACT

This final technical report summarizes the studies conducted on halogen passivation. In the body of the report, general reaction behavior of fluorine and halogens with metal surfaces and contaminants, and cleaning and passivation procedures for systems and components using fluorine-containing oxidizers are outlined. A test conducted to evaluate the effectiveness of the cleaning and passivation procedure applied to a valve assembly is described. The experimental details have been included in the five appendices. These cover: (1) reaction of fluorine system contaminants, (2) impact sensitivity of organic residues left from passivation, (3) corrosive behavior of passivated metal surfaces, (4) gases absorbed on passivated surfaces, and (5) mechanical stability of passivation fluoride films.

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SECTION I

SUMMARY AND CONCLUSIONS

A study of the effect of exposure of structural materials, impurities, and components to fluorine and to other fluorinating agents under typical "passivation" conditions has been carried out. The results obtained from the experiments are interpreted as follows:

a. Thin films of metal fluorides form very rapidly on structural metals.

b. The reaction generally ceases after the films are from 5 - 50 Angstrom units thick.

c. Exposure of clean unpassivated metals to high concentrations of fluorine causes formation of the films without further reactions.

d. Typical organic contaminants are NOT cleaned from systems by exposure to fluorinating agents.

e. Residues of organic contaminants remaining after "passivation" are violently reactive with fluorine, sometimes spontaneously, sometimes upon shock or impact.

f. Ice does not react completely with fluorine in mild "passivating" conditions and unreacted water is dangerously reactive when shocked or impacted.

g. Reactive metals, those which do not form metal fluoride films, such as tungsten, should not be introduced into systems for fluorine. Passivation reduces the reactivity of such metallic impurities, but there are not yet sufficient data to design adequate passivation procedures to assure complete removal of these impurities.

Studies of the metal fluoride "passive" films were also conducted. These included chemical analyses of the films and behavior of the films when exposed to mechanical and thermal shock, and to moisture. The results obtained from the experiments have been interpreted to mean —

a. The films obtained under mild passivation conditions consist of a metal fluoride layer lying on top of an unchanged metal oxide layer.

b. The passive films are hard and adherent. Repeated flexing, cryogenic thermal shock ($\Delta T = 400^{\circ}F$), or a combination of these procedures does not affect the mechanical stability of the films. There is no detectable cracking or flaking away of the film.

c. Exposure of the films to moisture causes alteration of the film and corrosion of the substrate metal. The surfaces can be repassivated, except for copper.

d. The films absorb an appreciable concentration of fluorine, halogen fluorides or hydrogen fluoride. These absorbed species are difficult to remove.

From the above interpretations it was concluded that –

a. Passivation of clean metal surfaces is not necessary prior to exposure to fluorine, but it does no harm.

b. Passivation can not be used to clean organic impurities, water, or reactive metals from systems or components; proper cleaning procedures and protection from recontamination are essential for safe systems.

c. Component passivation is less desirable than system passivation.

d. Passivated systems or components that have been exposed to moisture must be repassivated. Copper cannot be repassivated until the original fluoride film is removed.

ASSURANCE AND MAINTAINENCE OF SYSTEM CLEANLINESS, AND PROTECTION OF PASSIVE FILMS FROM MOISTURE-CAUSED DESTRUCTION ARE ESSENTIAL TO INSURE SAFE AND EFFICIENT OPERATION OF FLUORINE SYSTEMS.

The conclusions were tested by obtaining a typical fluorine system component, a solonoid valve, in a dirty condition, cleaning it, passivating it, and then filling it with liquid fluorine and operating it successfully.

SECTION II

GENERAL CONSIDERATIONS ON FLUORINE PASSIVATION

1. DEFINITION OF FLUORINE PASSIVATION (PASSIVATION STABILIZES SYSTEMS TO FLUORINE)

Passivation of a fluorine system, or of system components, is defined as pretreatment of the system or components with a fluorinating agent in order to stabilize the system or components so that they will not react catastrophically when fluorine is introduced under normal operating conditions. It is commonly done by exposing to gaseous fluorine under controlled conditions all surfaces of the system or components that can contact the fluid.

All metals and alloys react with fluorine, but they ordinarily react only to a limited extent by virtue of formation of an adherent, protective fluoride film. These protective films reach limiting thicknesses characteristic of the particular metals or alloys. The limiting film is generally known as a passive film.

2. REACTION OF FLUORINE WITH METALS (FLUORIDE FILMS FORM RAPIDLY)

The thicknesses and rates of formation of fluoride film on various metals and alloys have been investigated (References 1, 2). Powdered metals were used in these investigations in order to provide conveniently large surface to weight ratios. Experiments with coupons were also conducted for assurance that the state of subdivision did not affect the results. Some uncertainties exist concerning the method of calculating film thicknesses, because it is not known whether the fluorine reacts exclusively with the oxide film on the surface or whether part diffuses through the oxide film to react with the metal. The compositions of typical fluoride films on several metals and alloys have been investigated by the electron diffraction technique (Reference 2). Abundant evidence from the references cited above shows that the films formed consisted of metal fluorides and unchanged metal oxide hydrates and that the limiting film thicknesses formed on metals by exposure to fluorine, at pressures near one atmosphere and near room temperature, are in the range from about 5 to 50 Angstroms. The rate studies of fluoride film formation show that approximately 75% of the limiting film thickness is reached in 10 to 15 minutes exposure at one atmosphere. Some metals, notably copper and Monel 400, continue to react slowly with fluorine gas over an extended period of time and the apparent film growth continues at a very slow rate. However, most alloys, including 300 series stainless steels, appear to reach limiting film thickness.

Information available concerning the rates of reaction of the other potentially useful passivating agents chlorine trifluoride and chlorine pentafluoride is less conclusive. Techniques for reaction rate studies developed for fluorine are not applicable to these materials. It has been necessary, therefore, to employ less informative methods. On the basis of the studies, it has been tentatively concluded that metal reaction rates and film thickness for chlorine trifluoride and chlorine pentafluoride passivation are comparable to those for fluorine. Some differences in film composition and behavior toward moisture were observed, however (Reference 2). No definite advantage could be demonstrated for chlorine trifluoride or chlorine pentafluoride as passivating agents and they are less convenient to use and more difficult to purge from systems. Also, it was shown that the films from chlorine fluorides contained metal chlorides. Such residues are suspicious, since chlorides sensitize some metals to stress corrosion cracking.

No applicable reaction rate studies are known for bromine trifluoride and bromine pentafluoride although these interhalogens are known to be active fluorinating agents and undoubtedly form protective fluoride films on metals. The low vapor pressure of these compounds at room temperature practically precludes their use as passivating agents. In addition, passivation with BrF_5 was shown to leave a difficultly volatile, fluorine-containing residue, probably BrF_3.

The effect of pressure on the reaction rate of fluorine with metals has been investigated to a limited extent. Over a range of 100 to 1100 torr the reaction rate of fluorine with nickel at 77°F showed a cube root dependence on pressure (Reference 2). In a study of copper fluorination at 212°F and at pressures from 6 to 60 torr the reaction rate was found to be independent of pressure (Reference 3). Another investigation of the fluorination of iron above 400°F revealed a square root dependence on pressure (Reference 4). Obviously different mechanisms are operative in the different temperature regimes, however, the pressure effects are small enough to be ignored near room temperature.

3. EXPOSURE OF UNPASSIVATED METALS TO UNCONCENTRATED FLUORINE (CLEAN METALS ARE STABLE TO FLUORINE)

Metals in various states of subdivision from bulk to powders finer than 300 mesh have been abruptly exposed to fluorine gas at one atmosphere pressure and to liquid fluorine at -320°F. No ignition reactions were ever observed (Reference 2). The metals and alloys treated include 2014 aluminum, 2024 aluminum, 6061 aluminum, Monel 400, nickel 200, 304 stainless steel, 316 stainless steel, and 347 stainless steel. Similar exposure of finely divided nickel oxide and copper oxide to fluorine gas at one atmosphere failed to result in ignition. Minus 300 mesh 316 stainless steel powder was abruptly exposed to fluorine gas at 900 psig at room temperature without ignition. It appears that spontaneous ignition of metals of the compositions mentioned above is unlikely unless triggered by impurities.

Slow, stepwise, increase in fluorine concentration is unnecessary for passivation of thoroughly cleaned metal.

Metal powders as described above were also exposed abruptly to chlorine trifluoride and chlorine pentafluoride vapors at one atmosphere. No ignition reactions were observed.

The data collected indicate that, from the standpoint of the clean metal surface alone, passivation is relatively uncritical. Adequate protective films are readily formed at any pressure from 0.1 atmosphere to several atmospheres. An exposure time of 15 minutes is considered to be adequate for film formation. There is no experimental evidence that permits specification of an optimum time and temperature for passivation — a fairly broad range of conditions will result in adequate film formation. There are some indications that a relatively thin protective film is to be preferred. Thin films apparently absorb less moisture if exposed to the atmosphere and hence cause less secondary corrosion due to HF formation.

4. REACTION OF FLUORINE WITH ORGANIC MATERIALS (PASSIVATION DOES NOT CLEAN OUT CONTAMINANTS)

It is generally recognized that cleanliness is required during assembly operations in fluorine systems to ensure safe and reliable operation. Nevertheless, there is some opinion that passivation can be relied upon for final clean-up of residual organic contaminants. Some feel that this is the primary function of passivation. However, placing confidence in the capabilities of passivation to remove organic impurities is courting possible disaster. While it is possibly true that trace amounts of organic materials inevitably left behind by adequate cleaning procedures can be inerted by exposure to fluorine during passivation, we have found considerable evidence that even quite small amounts of contaminants are not effectively removed. It has been shown that typical system contaminants, i.e., hydrocarbon greases, organic polymers, and halocarbon oils in quantities on the order of 10 milligrams may leave reactive residues when exposed to passivation at pressures up to 200 psig at 200°F (see Appendix II). These are conditions that ordinarily cannot be reached in routine passivation of propulsion systems. Under milder conditions, say up to 50 psig at room temperature, many organic materials show a suprising reluctance to react significantly with fluorine. Also, residual unreacted or partially reacted materials are unstable and have been shown to react later due to initiation by shock or even by contact with liquid fluorine.

The net result of these observations is to put a severe burden upon cleaning and inspection to insure that no significant organic contamination finds its way into a system. We emphasize that in no case should passivation be considered a substitute for efficient cleaning, inspection, and assembly procedures. Slipshod or careless procedures should not be tolerated on the assumption that final passivation will take care of contamination left from cleaning or introduced during assembly.

Although fluorine may react rapidly or violently with all organic materials except carbon tetrafluoride, there are conditions under which slow reactions can take place. Conditions favorable for this are to be found where organic material is spread in a thin film on a thermally conductive substrate. This is a condition that may occur in a contaminated system. (See Appendix I.)

Numerous experiments have shown that slow reaction between fluorine and a contaminant deliberately added to a system invariably leads to a partially fluorinated material that is shock sensitive in liquid fluorine (see Appendix II). If the conditions of fluorination are vigorous enough to result in ignition of the organic material, a slight amount of residue may still be left, or under some conditions the high local temperature produced may lead to ignition of the metal substrate system. No exposure condition was found that could reliably lead to complete removal or inerting of the impurities short of complete destruction of the system.

The several processes occurring simultaneously when a reactive organic film is exposed to gaseous fluorine may be considered as follows: A spontaneous chemical reaction will take place at the solid-gas interface and the temperature at the interface will increase. The gaseous fluorine concentration on the interface decreases and mass transfer of fluorine to the surface takes place countercurrent to transfer of reaction products away from the surface. These are normal diffusion processes. At the same time, the heat generated in the reaction zone is dissipated by convection, radiation, conduction into the gas phase, and by conduction in the solid phase. If the heat generation rate exceeds the rate of heat loss from the reaction zone, the surface temperature will rise to the ignition temperature. Equations for the above processes can be written but their solutions are extremely complex.

Considering the processes described above, it is plain that for a selected fluorine gas pressure, the heat conduction away from the reaction zone through the solid phase is very important. For a relatively thick organic film of poor thermal conductivity, the heat generation at the interface will far exceed the heat loss and ignition will take place rapidly. For the same gas phase conditions, but with the organic film spread in a thin film on a metal base (a good heat conductor), the heat conduction through the solid phase is improved to the point where the ignition temperature is not reached. The thickness and conductivity of the film largely determine the maximum temperature gradient that can be obtained. Obviously there exists some critical film thickness below which ignition will not take place at a given fluorine pressure. Variations in the fluorine gas pressure will affect the rate of heat generation and will therefore influence ignition. Thus it is observed that high fluorine pressure is more likely to trigger ignition.

There is another factor not considered in the above analysis. While the usual course of reaction between fluorine and an organic is the complete fluorination to CF_4 and HF, if the conditions are such that ignition does not take place, partial fluorination reactions may occur. Instead of gaseous reaction products only, partially fluorinated solid reaction products are also formed. Further reactions then take place in the subsurface and diffusion of reactant and product must take place through the partially reacted surface film. This slows down mass transfer. It is believed that this is the reason that petroleum jelly, for example, seems to be almost completely unreactive in fluorine gas at one atmosphere: Under slightly higher pressure, a visible thin skin of perfluorinated halocarbon appears on the surface.

If the above reaction mechanism is correct and generally applicable to other organic materials, it presents an argument against slow, incremental pressure build-up in fluorine passivation. Such a procedure may allow time for formation of a perfluorinated diffusion barrier on the surface of a contaminant, which would leave largely unreacted organic material in the subsurface zone. An abrupt pressure application, on the other hand, could conceivably permit the desired complete fluorination reaction to take place, although it would not ensure such a reaction.

There is experimental evidence to show that with certain potential contaminants, chlorine trifluoride and chlorine pentafluoride render the system more passive than fluorine at equivalent pressures. These agents did, however, leave reactive residues in many cases. It is considered that the use of interhalogens for inerting organic contaminants is a promising area of further investigation.

5. REACTION OF FLUORINE WITH DYE PENETRANTS (AVOID DYE PENETRANTS IN F_2 SYSTEMS)

Cast A356 aluminum of controlled Grade III porosity was exposed to typical dye penetrant inspection (Shannon Glow P138A water washable penetrant). Specimens were then subjected to impact tests in liquid fluorine (see Appendix II). Specimens that received a bake-out at 220°F in vacuum for 18 hours after cleaning were apparently safe from reaction (no positive reactions in 20 impacts). There are so many variables, however, in porous materials, that organic dye penetrant inspection cannot be recommended without further investigation.

6. REACTION OF FLUORINE WITH WATER (FLUORINE-WATER REACTIONS ARE UNPREDICTABLE)

Although no detailed investigation has been published, reports indicate that water in vapor, liquid, or solid form can react explosively with fluorine and has been the cause of major system failure (Reference 5). Under some conditions high concentrations of water vapor can ignite and burn in fluorine. It is reported that in the form of ice, water shows no reactivity with gaseous fluorine. However, an explosive reaction occurs when ice is exposed to liquid fluorine. The reaction may be preceded by a variable and unpredictable induction period. Ice is extremely shock sensitive in fluorine.

Water contamination represents a hazard in fluorine systems comparable to organic contamination. Due consideration must be given to initial drying of all systems and special care must be exercised to avoid introducing water vapor through leaks or from purge gases.

In addition to the possible hazard of explosion, water is to be avoided because of enhanced corrosion due to reaction of water to produce HF. Metals vary in their susceptibility to corrosion in HF (see Appendix III), but in general they are attacked much more severely by HF than by fluorine.

7. REACTION OF FLUORINE WITH METALLIC IMPURITIES (AVOID TIG WELDING)

There is generally little likelihood of accidentally introducing incompatible metallic impurities into fluorine systems. Some concern has been expressed over introducing small pieces of tungsten during TIG welding. Tungsten has borderline compatibility in fluorine and its use is discouraged because of its failure to passivate and because of its low ignition temperature in fluorine.

Impact tests were made in liquid fluorine using simulated specimens contaminated with powdered tungsten (see Appendix II). The impact test data revealed that passivation reduced, but did not completely eliminate, the shock sensitivity of the tungsten contaminated specimens. Until additional investigations are made, TIG welding of fluorine systems cannot be given endorsement.

8. MECHANICAL STABILITY OF FLUORIDE FILMS (PASSIVE FILMS ARE NOT DESTROYED BY MECHANICAL FLEXING OR THERMAL SHOCK)

The mechanical stability of metal fluoride films formed on metal bellows by passivation in fluorine gas at one atmosphere and room temperature was tested. Bellows of 316 stainless steel (annealed), Inconel 625 (annealed), 6061-T6 aluminum (annealed), and copper (annealed) were subjected to various combinations of flexing to 75% of elastic limit, cryoshock, and liquid fluorine exposure without evidence of any loss of fluoride film from the surface (see Appendix V). Light and electron microscopy were used in conjunction with electron diffraction identification of particulate matter to ascertain that no significant amount of fluoride film was shed by the test specimens.

9. HYDROLYSIS BEHAVIOR OF FLUORIDE FILMS (MOISTURE DEGRADES PASSIVE FILMS)

Fluoride films exposed to atmospheric moisture became hydrated. This has been established by analysis of films in situ (Reference 2). Hydrolysis of fluoride films produces HF, which can cause corrosion of metals. The extent of corrosion may be limited to barely visible tarnish films, but under some conditions observed in the field, corrosion can be severe. It is worthwhile to take precautions to prevent exposure of fluoride films to atmosphere or other moisture. These precautions should include thorough purging of systems before opening them to the atmosphere and maintaining a blanket of inert gas in systems at slightly above atmosphere pressure so that inward leaks will not carry atmosphere moisture into the system.

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SECTION III

CLEANING PROCEDURES FOR FLUORINE SYSTEMS

1. GENERAL

Recommended materials and procedures for cleaning systems and components to be used in fluorine service are summarized here.

a. Components of a propellant system should be disassembled as much as possible for cleaning.

b. It is recommended that all final cleaning, inspection, assembly, and packaging of components be performed within a clean room meeting the requirements of Federal Standard 209, Class 100,000.

c. Components that require precleaning shall be processed first outside the clean room. Shop oil, marking dyes, dirt, scale, rust or other major contaminants shall be removed by appropriate solvents and hand scrubbing until the component is virtually free of contamination. The component should be dried before final cleaning.

2. MATERIALS

a. Trichloroethylene for vapor degreasing shall be per MIL-T-7003.

b. Trichlorotrifluoroethane shall be per MSFC-SPEC-237A.

c. Air used for drying shall be prefiltered to a 100 micron level (absolute), the hydrocarbon content shall not exceed 0.5 ppm by weight in terms of n-cetane, and the moisture content shall not exceed 23.6 ppm by weight (dew point -65°C).

d. Nitrogen used for drying or purging shall conform to MIL-P-27401B, Type 1 and also shall meet the other purity requirements of paragraph c above.

e. Acids shall be of ACS Reagent Grade.

f. Distilled, de-ionized, or clean tap water may be used but must be free of organic materials.

3. CLEANING STAINLESS STEEL, MONEL, INCONEL, NICKEL

a. Vapor degrease with trichlorotrifluoroethane or trichlorethylene.

b. Immerse in an alkaline steel cleaning solution.

The solution concentration, temperature, and the component immersion time is to be in accordance with the recommendations of the manufacturer of the alkaline cleaner used.

c. Rinse thoroughly with distilled water.

d. Immerse in a solution of 35% by volume nitric acid, maintained at 125°F, for twenty minutes.

e. Rinse thoroughly with clean tap or distilled water.

f. Blow dry with filtered, dry nitrogen.

4. CLEANING ALUMINUM ALLOYS

a. Vapor degrease with trichlorotrifluoroethane or trichlorethylene.

b. Immerse in an aluminum cleaning solution. The solution concentration and temperature, and the component immersion time shall be in accordance with the manufacturer of the aluminum cleaner used.

c. Rinse thoroughly with distilled water.

d. Immerse in a solution of 15% by volume nitric acid, maintained at 125°F for twenty minutes.

e. Rinse thoroughly with distilled water.

f. Blow dry with filtered, dry nitrogen.

5. CLEANING COPPER AND COPPER ALLOYS

a. Degrease with trichlorotrifluoroethane or trichlorethylene.

b. Immerse in an alkaline steel cleaner for two to five minutes.

c. Rinse thoroughly with distilled water.

d. Immerse in a solution of ten per cent (by volume) sulfuric acid at a temperature of 125°F until the surfaces are free of oxides.

e. Rinse thoroughly with distilled water.

f. Blow dry with filtered, dry nitrogen.

6. CLEANING NONMETALLIC SUBCOMPONENTS

a. When the fluorine system contains polymeric components used as valve stem packing or gaskets (ordinarily only fluorocarbon polymers are encountered in this service), they should be cleaned before installation. Polymers tend to absorb solvents and immersion or prolonged exposure is to be avoided. If necessary to use solvents for precleaning, only a brief flushing with acetone or trichlorotrifluoroethane should be used and this should be followed by through evacuation to remove all traces of solvents. If parts are extremely dirty or greasy it is better to replace them with new parts rather than attempt prolonged solvent cleaning. Glass and ceramic materials may also be cleaned by the following procedure which is expressly designed for polymeric materials:

(1) Flush all parts with a freshly prepared detergent solution. (Alconox or equivalent) Soft brushes or cloths may be used to assist detergent action but care should be taken to prevent scratching or distorting parts, or deposition of lint.

(2) Rinse thoroughly with distilled water.

(3) Place in vacuum oven or desiccator and heat under 1 torr vacuum at 220°F for eighteen hours. Vacuum drying may be omitted for glass and non-porous ceramics, in which case parts may be air dried or oven dried without vacuum.

b. Nonmetallic components or subcomponents that are not installed immediately should be packaged to prevent solvent absorption from air.

7. GENERAL PRECAUTIONS

a. After cleaning, but before packaging, all parts must be inspected in detail for any residual moisture, corrosion, oil, chips, dust, glass particles or any other foreign substance. The presence of any foreign material requires complete recleaning of the part. Slight discolorations at welds do not call for rejection of parts as long as foreign substances are absent. Inspection under short wave ultra violet light is recommended for a method of detecting many organic contaminant residues.

b. Dye-penetrant inspection is not recommended but in case parts have been so inspected during manufacture, such parts must be baked out in a vacuum oven or desiccator at 1 torr and 220°F for a minimum of eighteen hours after final cleaning.

c. All cast parts, porous parts such as filters, or parts containing welds of a porosity greater than Type IF, determined by X-ray inspection, must be baked out in a vacuum oven or desiccator at 1 torr and 220°F for a minimum of eighteen hours after final cleaning.

d. If not assembled into a system immediately, all parts should be packaged in a manner that will prevent damage or contamination. Note that all available packaging materials can result in residues that are dangerously reactive with F_2, so sharp edges on parts must be covered to prevent scraping. Plastic thread caps must NOT be used; cleaned aluminum thread caps are acceptable. If aluminum foil is used for packaging, a grade that is free of surface oil inclusions must be used.

8. SYSTEM CLEANING

After the system is assembled with the previously cleaned components, it is recommended that the assembled system be cleaned prior to initial operation. This procedure is to consist of flushing with trichlorotrifluoroethane or other similar halocarbon solvent, until the number of particles per 100 ml of recovered solvent reach the level of less than 1000 particles, 5 μ or larger. The flush is followed by system evacuation or purging with dry nitrogen or helium (dew point less than -100°F). Air and moisture must be excluded to avoid corrosion. If the design of the system does not permit evacuation or proper purging with inert gas it is better to omit the system flushing. In this case it is essential that all parts and components are scrupulously cleaned prior to assembly and that all assembly operations are carefully conducted under conditions of controlled cleanliness.

SECTION IV

PASSIVATION PROCEDURES FOR FLUORINE SYSTEMS

1. GENERAL

a. Nitrogen

A source of gaseous nitrogen in accordance with MIL-P-27401, type 1 and having a nominal dew point not over -100°F (1.53 ppm moisture) should be available. Gaseous nitrogen evaporated from the liquid is suitable and will meet the dew point requirement.

b. Helium

MSFC-SPEC-364B gaseous helium may be used as a purge gas in place of nitrogen. The dew point must be below -100°F.

c. Fluorine

Gaseous fluorine meeting the following requirements should be used for passivation:

F_2	98.5% minimum
O_2, N_2, and inerts	1.0% maximum
CO_2, HF, and other gases	0.5% maximum

d. Vacuum Pumps

If used, vacuum pumps must be capable of producing a system vacuum of one torr or less. If vacuum pumps are not capable of producing this low a pressure, then during the pumping operation, the system must be backfilled at least twice with dry nitrogen or helium to one atmosphere pressure with the pumps valved off followed by pumping between fills.

2. VACUUM PROCESSING

If the system will tolerate a vacuum, it is pumped thoroughly. Dry nitrogen or helium is introduced and pumped out again to assist in removing residual water or solvent vapors. While the system is under vacuum, pure fluorine gas is introduced at a rate of pressurization not to exceed 15 psi per minute to a final pressure of 50 psig. The system shall be statically maintained at this pressure at room temperature for a minimum of 30 minutes. The fluorine gas is vented from the system to a pressure of 0. 5 psig. A portion of the gas may be condensed for HF analysis as described in Section V below. If desired the system may be purged with dry helium or nitrogen, in which case a minimum pressure of 0. 5 psig should be left in the system after pumping.

3. NONVACUUM PROCESSING

If the system will not tolerate evacuation, it should first be purged thoroughly at room temperature with dry nitrogen or helium until it is free of traces of moisture and solvent vapors. Due consideration must be given to diffusion from dead ends of the system, etc. Provision should be made for parallel flow paths if feasible to avoid dead ends in the system. This is important and each system presents its own design problem. The inert gas purge is then turned off and a gas fluorine purge started until most of the nitrogen is displaced. The vent should be closed and the fluorine pressure increased at a rate of not more than 15 psi per minute until a pressure of 50 psig is reached. This pressure should be maintained until all blind portions have been exposed to fluorine (75%) for a minimum of thirty minutes at room temperature.

As a first approximation which can be used for short stubs and bellows convolutions, the following considerations apply. The initial purge of the system with fluorine will replace all inert gas in the portions of the system which are open to free flow of gas. Thus only the blind portions retain inert gas. This gas is at a pressure of 0 psig or 15 psia. When the system is pressurized with gas fluorine to 50 psig (65 psia), the average fluorine concentration in the blind portions is 50/65 = 77%. Sufficiently rapid mixing of the fluorine and inert gas will occur so that one can assume that the concentration of fluorine is at least 75% for the total exposure period. If, however, the l/d ratio is greater than four, when pressurization with the fluorine occurs, the fluorine will tend to compress the inert gas ahead of it with minimal mixing into the blind portions. Thus there will be a volume of inert gas relatively free of fluorine at the end of the blind lead farthest from the main system volume. Mixing of nitrogen into this will depend upon diffusion processes. Relative diffusion rates vary with the reciprocal of the square root of the molecular weight of the gases involved.

The fluorine is vented from the system to a minimum pressure of 0. 5 psig. A portion of this fluorine may be taken at this time for HF analysis (see Section V). The system should then be purged with dry helium or nitrogen to a minimum pressure of 0. 5 psig to be left in the system after purging.

If any leaks are found during these tests, the system should be shut down and corrective action taken.

4. SHUTDOWN AND REUSE

If a system must be shut down after assembly but before passivation, a slight positive pressure of inert gas should be kept on the system. If operations are confined to tightening fittings, flanges, or packings to correct leaks no contamination will be incurred and no further cleaning is required. If partial disassembly of the system is required to correct faults, and the necessary operations may in any way lead to contamination, then complete recleaning of the parts involved is necessary. Portions of the system not involved should be capped off without delay after disassembly and maintained under a slight positive pressure with inert gas.

If a system must be shut down after passivation but before operation, thorough purging with dry, inert gas must be carried out before opening the system. After thorough purging to remove most residual fluorine, the system may be opened. Portions of the system not involved in any disassembly must be capped and left under a positive pressure of inert gas. If operations on any part of the system in any way lead to possible contamination, then complete recleaning of that part involved is necessary followed by purging and passivation after reinstallation in the system. The important consideration to keep in mind is that exposure of passivated surfaces to atmospheric moisutre leads to excessive corrosion in a fairly short time. If passivated systems are thoroughly purged with dry inert gas before exposing them to atmospheric moisture, the extent of secondary corrosion is somewhat reduced.

5. PREPASSIVATION OF SYSTEM COMPONENTS

Prepassivation of system components before installation is not recommended. The passivated surfaces may absorb atmosphere moisture during assembly of the system and lead to added corrosion problems. It is better and safer to assemble clean components and passivate the entire system at once. If valid reasons require prepassivation, careful exclusion of moisture during final assembly is advisable.

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SECTION V

EVALUATING A SYSTEM FOR PRESENCE OF CONTAMINANTS

Experience in handling fluorine systems has shown that most failures resulting in burnout are traceable to initiation of reaction by organic contamination. Any system analysis capable of demonstrating that a given system is free of significant quantities of organic contaminants is of potential value. Such a system analysis may be used in two ways. First, it can be used as a basis for establishing that cleaning processes are reducing organic contamination to safe levels, and secondly, it may find application as a test procedure to establish that passivated systems are free of gross contamination which might have been inadvertently introduced during assembly or checkout. Such a system test becomes doubly important in view of our findings that many typical system contaminants are not rendered inert by conventional passivation techniques even at fluorine pressures up to 200 psig.

After passivation of a system with fluorine gas at 50 psig, any hydrogen-containing contaminants, such as hydrocarbon oils or greases and water, will react sufficiently to increase the HF content of the fluorine gas. If the surface to volume ratio of the system is favorable, the following procedure becomes particularly useful: After passivation, and while still under full fluorine pressure, a quantity of fluorine (recommended sample size of about 10 ml) is condensed to a liquid at liquid nitrogen temperature in a glass tube using a suitable sampling line and valve attached to the system. If visual inspection of the condensed fluorine indicates a substantial amount of flocculent, white solids (solid HF), severe contamination of the system by water or H-containing organics may be suspected. The applications of this procedure requires that the fluorine used for passivation be substantially freed of HF before introduction into the system. A quantitative analysis of the HF content of the fluorine before use and after introduction to the system will give a more accurate estimate of contamination.

The sensitivity of an inspection method based on HF analysis of the gas phase, or the minimum amount of contaminant that can be detected, depends on a number of interrelated factors that are too difficult to define without preliminary experimental data. The extent of reaction varies with time, temperature, and pressure, as well as with the composition of the organic material. In the case of perfluorinated organics containing no hydrogen, the proposed analysis method would be useless. The degree of contaminant dispersion is likely to have considerable effect on the extent of reaction. As a first approximation, a well dispersed organic material is likely to undergo more reaction in a given time due to the greater gas-solid interface presented. On the other hand, a quantity of organic contaminant in the form of a lump or thick smear may be in poorer thermal contact with the metal walls of the system and hence the reaction will proceed at an accelerated rate due to a higher temperature at the gas-solid interface. The situation is obviously extremely complicated. In the final analysis the volume of the system is extremely important. A given amount of organic material will produce a concentration of HF inversely proportional to the volume of a system.

A key requirement for practical application of the inspection procedure is a sensitive method for analysing HF in fluorine gas. A standard procedure is near infrared spectrophotometry in which the absorbance due to HF at 2535 millimicrons is measured. A high resolution infrared spectrophotometer is required as well as an elaborate sampling system and such a method is not well suited for field analysis. Mass spectroscopy was investigated, however reaction of fluorine with traces of organic materials and moisture in the sampling system produced a significant HF background which obscured analysis for low concentrations of HF.

1. TEST METHOD AND PROCEDURE

Astropower Laboratory has developed a method of analyzing for HF content of fluorine. The method is comparatively rapid and requires only simple equipment. A quantity of gaseous fluorine to be analyzed is condensed at LN_2 temperature in a tared, calibrated glass tube. About 10 ml of sample are required for samples low in HF while 5 ml are sufficient if the HF content is over 0.2% by weight. The liquid volume of the sample is noted and the fluorine is pumped off while the tube is maintained at liquid nitrogen temperature. The receiver is valved off and the liquid nitrogen bath is removed. The tube is allowed to warm to room temperature and stand 30 minutes. Finally the tube is warmed in hot water an additional 15 minutes. The tube is then evacuated, dried, and weighed. The loss in weight of the glass is due to volatilization of SiF_4 produced through reaction of the HF with the silica in the glass.

The per cent HF in the fluorine is calculated as follows:

$$\%\ \text{HF by wt} = \frac{\text{wt loss} \times 1.33 \times 100}{\text{vol } LF_2 \times 1.56}$$

Thus a weight loss of 1 mg attendant upon the analysis of a liquid sample of 10 ml is

$$\%\ \text{HF by wt} = \frac{0.001 \times 1.33 \times 100}{10 \times 1.56} = 0.009$$

or roughly 0.01%. This is about the sensitivity of the method and is approximately the concentration of HF to be found in gaseous fluorine which has been passed through a tower of sodium fluoride pellets to remove excess HF. Cylinder fluorine, depending on the source, will contain variable quantities of HF up to 0.25% by weight, hence it is advisable to routinely pass the gas through an efficient sodium fluoride tower if the HF content is of concern at all.

The test apparatus shown schematically in Figure 1 was constructed. A stainless steel bomb — nominally of 1.1 liter capacity — is connected to a manifold having a pressure gage and appropriate valving to evacuate the system and admit purified fluorine gas. The calibrated glass receiver is attached to the manifold as shown on Figure 1. This apparatus simulates on a small scale a typical fluorine storage or feed system. Weighed quantities of organic impurities are inserted in the bomb and the system subjected to an appropriate passivation cycle. While pressurized with fluorine, a sample of gas is taken from the bomb, condensed in the glass receiver, and the HF content determined as outlined above. The increase in HF content of the gas phase is correlated to the extent of the reaction of the organic contaminant.

To conduct an experiment the system was first thoroughly cleaned and after final assembly was subjected to prolonged evacuation to remove the last traces of water vapor. The contaminant used for the majority of experiments was USP petroleum jelly: A weighed quantity was placed as a uniform thin film on a 3/4" x 3" x 0.025" 316 stainless steel coupon and inserted in the bomb. After resealing the bomb it was again evacuated and finally filled with fluorine at the appropriate pressure. With the 1.1 liter system, the minimum fluorine pressure used was 50 psig because a lower pressure would not permit condensation of a sufficient volume of LF_2 for analysis. Accordingly, the apparatus was modified for later work by replacing the bomb with a larger one increasing the total volume of the system to 7.5 liters. All experiments were conducted at ambient temperature which averaged 77°F. The initial HF content of the fluorine gas was reduced to the lowest practical value by passing the fluorine over sodium fluoride pellets before introducing it to the system. This reduced the HF content to about 0.01% by weight.

After the simulated passivation of the system in the presence of the known quantity of hydrocarbon, a-LN_2 bath is placed around the evacuated glass receiver, which has been weighed to the nearest 0.1 mg, the valve connecting it to the system is opened, and a sample of appropriate volume collected. After noting the volume of sample, the fluorine in the tube is pumped out at -320°F. The valve is closed, the LN_2 bath removed, and the tube allowed to warm to room temperature where it is held for 30 minutes. Finally the tube is warmed in hot water for an additional 15 minutes. The operator must take precautions in case the tube should burst from excessive pressure during the analysis. Next, the tube is evacuated, removed from the manifold and dried in a vacuum oven at 220°F. After cooling, the tube is weighed on the analytical balance. The loss in weight of the tube multiplied by 1.33 represents the weight of HF condensed along with the GF_2 in the tube.

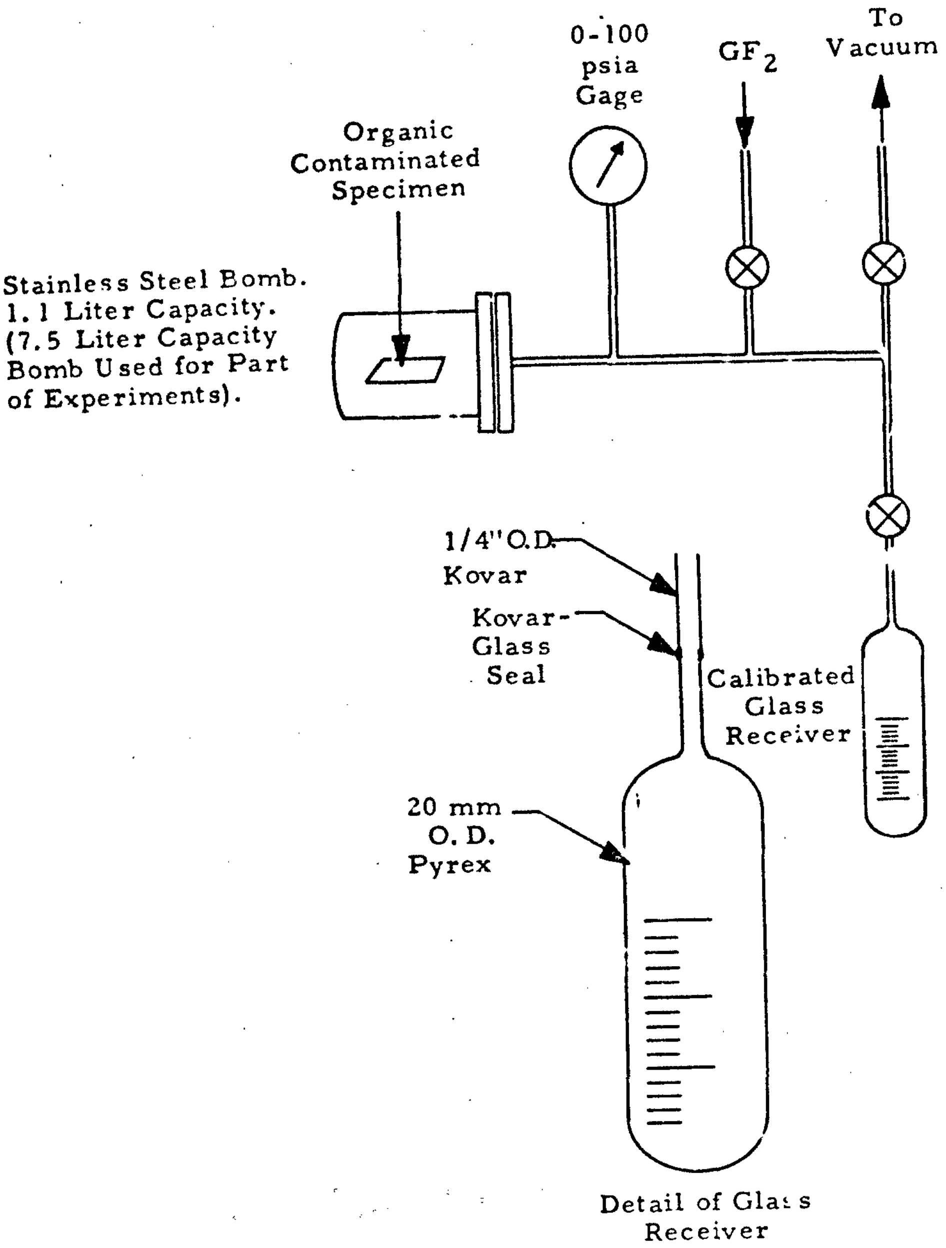

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Figure 1. Apparatus for HF Analysis

2. EXPERIMENTAL RESULTS

The results of tests conducted in the 1.1 liter system are given in Table I. Trial 1 established that in the absence of added contaminant the amount of HF found by analysis is in agreement with the anticipated HF content of the purified fluorine. In Trial 2 (Table I) 100 mg of USP petroleum jelly was exposed at 50 psig for 1 hour. During exposure, the contaminant gained 17.7 mg weight and the calculated HF content in the system was 21.2 mg, based on the analysis of the 5.0 ml LF_2 condensed from the bomb. This calculation takes into account the conversion factor of 1.33 for converting the weight loss of glass to HF according to the postulated reaction as follows:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

An additional factor takes into account that only about 90% of the fluorine in the bomb can be condensed at LN_2 temperature.

The USP petroleum jelly is assumed to consist of chains of repeating $-CH_2$ groups. The attack by fluorine may be assumed to replace hydrogen as follows:

$$\underset{MW=14}{-CH_2-} + 2F_2 \rightarrow \underset{MW=50}{-CF_2-} + \underset{MW=40}{2HF}$$

For each mole of CH_2 reacting as above, a molecular weight increase of 36 should be obtained and two moles of HF are produced. Thus the weight of HF produced should be in the ratio of 40/36 = 1.11 to the weight increase of the petroleum jelly.

In some of the trials this ratio is approached. For example in Trial 2 the ratio of total HF to weight gain is 21.2/17.1 or 1.20 compared to the theoretical 40/36. Most of the ratios run considerably higher. The worst agreement is in Trial 3, wherein the ratio of HF produced to weight gain is 42.4/24.9 or 1.70. There is a general tendency for the quantity of HF produced to be greater than that calculated on the basis of the weight gain of the petroleum jelly. There is visible evidence that the fluorination causes some degradation of the hydrocarbon to form volatile fluorocarbons which end up in the receiver with the condensed sample of fluorine. These are eventually volatilized and do not interfere with the HF analysis but the weight increase of the hydrocarbon is correspondingly less. The extent of this degradation varies from run to run depending on the experimental conditions.

Trial 3 shows that doubling the time of exposure nearly doubles the amount of HF produced from a given quantity of hydrocarbon but the weight increase of the hydrocarbon was only about 50% greater. Reducing the amount of hydrocarbon from 100 mg to 10 mg with a corresponding decrease

TABLE I. SUMMARIZATION OF EXPERIMENTAL DATA - 1.1 LITER SYSTEM VOLUME. ALL EXPERIMENTS AT AMBIENT TEMPERATURE WHICH AVERAGED 77°F.

Trial	Contaminant	GF_2 Passivation		Vol. LF_2 Condensed For Analysis	Wt. Change Of Contaminant (g)	Wt. Change Of Receiver (g)	Calculated Wt. HF In System (g)	Remarks
		Pressure	Time					
1	None	50 psig	1 hr	5.0 ml	———	−0.0005	0.0008	Blank Test
2	100 mg Petroleum Jelly	50 psig	1 hr	5.0 ml	+0.0177	−0.0145	.0212	
3	100 mg Petroleum Jelly	50 psig	2 hr	5.0 ml	+0.0249	−0.0290	0.0424	
4	10.2 mg Petroleum Jelly	50 psig	2 hr	4.8 ml	+0.0103	−0.0077	0.0113	
5	100 mg Petroleum Jelly. Slow pressure build up (See Text)	50 psig Final	2 hr Total	4.5 ml	+0.0173	−0.0140	0.0204	
6	10 mg Petroleum Jelly	50 psig	2 hr	5.0 ml	?	−0.0081	0.0119	Final Wt. could not be determined due to accident.
7	100 mg KEL-F 90	50 psig	2 hr	4.5 ml	−0.0010	−0.0022	0.0032	

in film thickness (Trial 4), resulted in a greater proportional weight gain, the hydrocarbon roughly doubling in weight; thus, the thinner the film, the greater the apparent extent of reaction. Trial 5 involved the gradual buildup of fluorine pressure in small increments, starting at 0.1 atmosphere absolute, to determine if such a procedure results in less reaction than that of a fairly fast pressurization. There appears to be a slight effect in this direction. The pressure was increased incrementally over a period of one hour to a pressure of 50 psig and this pressure was held for one additional hour. This resulted in about the same total reaction produced in one hour at 50 psig in Trial 2. Trial 6 is a repeat of Trial 4 to determine reproducibility. Due to accidental loss of material from the stainless steel coupon, the weight change of the petroleum jelly could not be determined, but the calculated total HF produced agrees very well with that obtained in Trial 4. In Trial 7, 100 mg of KEL-F90 was exposed to fluorine in the system. As expected, no significant weight change or increase in HF was noted.

Table II is a summary of data obtained in experiments conducted in a system of 7.5 liters total volume. The table is largely self-explanatory. In general, the quantity of HF produced for a given time and temperature of exposure is greater in the 7.5 liter system than in the 1.1 liter system. If this is a real trend and not due to experimental error, it can probably be attributed to the inhibiting effect of HF at the higher corresponding concentration in the small bomb.

For passivation at 50 psig for 2 hours, the foregoing data would indicate that at least 2 or 3 mg of HF are produced for each mg of petroleum jelly present in the system at the 10 mg level when the hydrocarbon is dispersed in a more or less uniform film covering about 2.5 to 5 square inches of metal surface. From this it is estimated that, under favorable circumstances, one could detect as little as one milligram of similarly dispersed hydrocarbon material by the HF produced in a system of about 7.5 liters volume.

If a system is contaminated to such an extent that a concentration of HF greater than 0.1% by weight is produced in the system by passivation upon condensation of the liquid fluorine sample, the solubility of HF in fluorine is exceeded. The presence of HF will be revealed as a flocculent, white precipitate in the liquid fluorine. Thus, the technique is potentially capable of detecting fairly low concentration of organic contaminants by the appearance alone of fluorine condensed from the system. About 15 mg of HF will saturate 10 ml of liquid fluorine at -320°F. Any HF in excess of this amount forms a readily visible flocculent precipitate which is quite distinctive in appearance.

TABLE II. SUMMARIZATION OF EXPERIMENTAL DATA - 7.5 LITER SYSTEM VOLUME
ALL EXPERIMENTS AT AMBIENT TEMPERATURE, WHICH AVERAGED 77°F.

Trial	Contaminant	GF_2 Passivation Pressure	GF_2 Passivation Time	Vol. LF_2 Condensed For Analysis	Wt. Change Of Contaminant (g)	Wt. Change Of Receiver (g)	Calculated Wt. HF In System (g)	Remarks
1	None	15 psig	1 hr	13.0 ml	—	−0.0106	0.0163	Blank Test - Amt. HF seems too high.
2	None	10 psig	1 hr	7.5 ml	—	−0.0034	0.0075	Blank Test repeated.
3 (a)	100 mg Petroleum Jelly	6 psig	2 hr	8.0 ml	Not Weighed	−0.0168	0.0298	
3 (b)	Same Sample - bomb not opened	25 psig	2 hr	15.0 ml	+0.0435	−0.0400	0.0764	
4	100 mg Petroleum Jelly	15 psia (1 atm)	2 hr	5.2 ml	+0.0119	−0.0143	0.0237	
5	100 mg Petroleum Jelly	50 psig	2 hr	12.2 ml	+0.0232	−0.0107	0.0378	0.0034" mean film thickness
6	10 mg Petroleum Jelly	50 psig	2 hr	16.0 ml	+0.0137	−0.0237	0.0628	0.00034" mean film thickness
7	10 mg Petroleum Jelly	50 psig	2 hr	16.0 ml	+0.0178	−0.0118	0.0313	0.00017" mean film thickness

SECTION VI

CLEANING AND PASSIVATION PROCEDURE EVALUATION

1. GENERAL SUMMARY

A solenoid-operated cryogenic valve was selected for the procedure evaluation program. After due consideration, a valve assembly consisting of the Marotta Valve Corporation, Model MV510TX, part No. 806239, with suitable modifications, was selected. This is a two-way, two-position, magnetically operated valve with a variety of components such as bellows, metal seals, and metal gaskets. In addition it permits remote operation, convenient disassembly, and has limited clearance between moving parts which provides a good test for operation in a potentially corrosive environment. The valve assembly included an MS27851-08 straight threaded tubing fitting on the inlet port.

The valve was purchased in an industrially clean condition — specifically NOT LOX-clean.

This valve was subjected to the recommended disassembly, cleaning, reassembly and passivation in a flow system. It was then subjected to a cycle of operations in which liquid fluorine at -320°F and up to 100 psig pressure was pumped through it at an average flow rate of 1. 7 gallons per minute. The cycle of operation also included periodically closing the valve during pumping. Following the program of operation, during which time a total of 19. 2 gallons of liquid fluorine were pumped, the valve was brought to room temperature, purged, disassembled and inspected.

The objective of the evaluation was to demonstrate that typical fluorine system components, subjected to the recommended cleaning and passivation procedures can be used without deterioration or excessive corrosion.

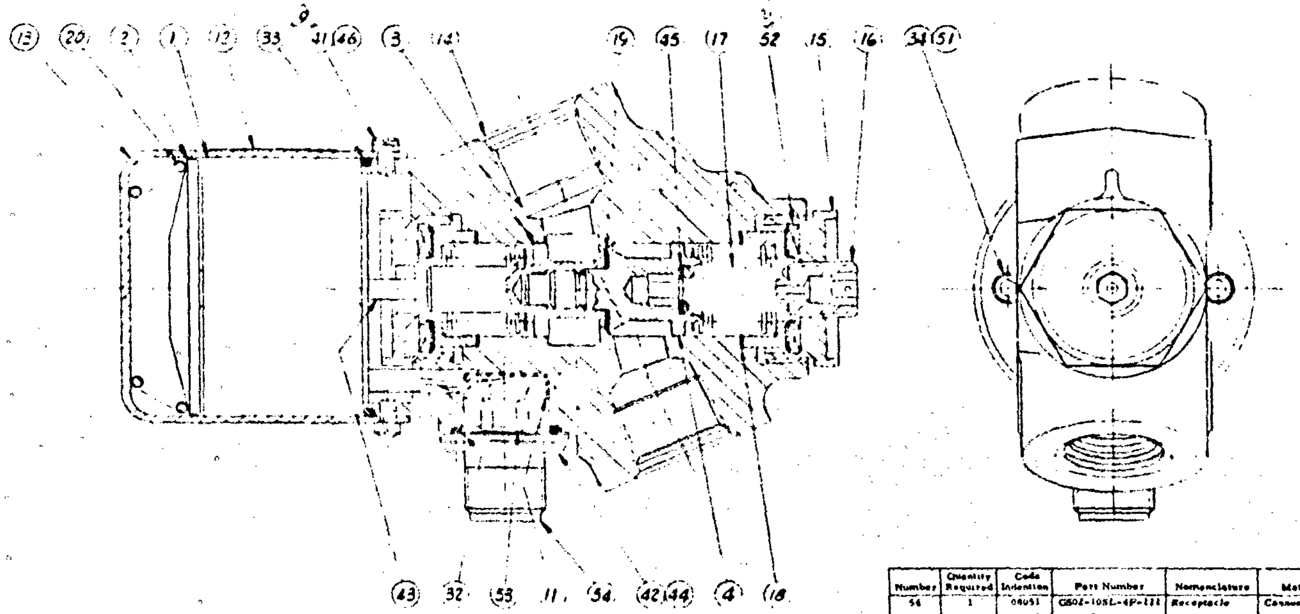
2. DESCRIPTION OF VALVE ASSEMBLY

The Marotta valve is shown in Figure 2. In addition to changes given in Figure 2 (EO 10530), the following additional modifications or changes were observed in construction of the valve:

a. No Zyglo or other dye penetrants was used on any fabricated part.

b. No lube or thread compound was used in internal threads of poppet assembly. Part SK5808 and 815766 Figure 2.

c. Female poppet assembly was constructed of 316-SS.



1. Do not use lubrication of any type in Assembly of Poppet Halves.
2. Stamp Nameplate Rev. 10530.
3. Valve Service: F_2
   Operating Pressure: 0-700 PSIG
4. Lubricate the threads of the two nuts 734972 prior to assembly to the valve body and the armature adjusting screw AN565AC832H24 with a light film of Bray Oil Co. number 631 lube.

Number	Quantity Required	Code Indention	Part Number	Nomenclature	Material	Specification	Finish
54	1	06051	GS02-10SL-4P-121	Receptacle	Cannon Electric Company		
53	AR	70331	51T-275-16	Tubing	Alpha Wire Corporation		
52	2	60380	NTA-916	Bearing	The Torrington Company		
51	2	86579	110-6	Dynaseal	Precision Rubber Prod. Corporation		
46	AR		MS20995C20	Lockwire			
45	4		AN960C4	Washer			
44	4		AN936A4	Washer			
43	1		AN565AC832H24	Screw			
42	4		AN515C4-5	Screw			
41	2		AN500AD6-3	Screw			
34	2		5100C832-0625	Screw			
33	1		J200AF33	O-Ring	Synthetic Rub	MIL-P-25732	None
32	1		J200AF18	O-Ring	Synthetic Rub	MIL-P-25732	None
21	2		735099	Race Brg	Carbon Stl		
20	1		108031	Spring	302 Hd Stl	QQ-W-423	Pass
19	1		734979	Seat	Copper	–	None
18	2		734978-1	Seal	Copper	–	None
17	1		734974	Spring	302 SSt	QQ-W-423	Passivate
16	1		734973	Screw	300 Ser SSt	QQ-S-763	Passivate
15	2		734972	Nut	316 SSt	QQ-S-763	Passivate
14	1		SK5805	Body	316 SSt	QQ-S-763	Passivate
13	1		730632	Cover	1100 Al Aly	QQ-A-561	Anodize
12	1		729151	Nameplate	Al Aly	Photo-Foil	Anodize
11	1		107311	Insulator	Glass Melamine		None
4	1		SK5508	Poppet Assy			
3	1		815766	Poppet Assy.			
2	1		815761	Armature Assy.			
1	1		217312-1112	Coil Assy.			

Figure 2. Valve Assembly - 1/2" T.S., 2 Way, 2 Pos., Magnetic Bellows. (From Marotta Valve Corp. Drawing No. 806239)

d. Male poppet assembly was constructed of K-Monel. (This was necessary to avoid possible thread galling if both parts were 316-SS. No thread lubricant could be used.)

e. Bellows were constructed of 321-SS.

f. Only Heliarc welding was used for joining, except for electrical parts, which are not in the fluid-contact zone.

g. All welds were leak checked.

h. Seat (part No. 734979) was made of OFHC copper, 16 microinch AA finish, heat treated to dead soft after finishing machining.

i. Body seals (part No. 734978-1) were made of OFHC copper, 16 microinch AA finish, heat treated to dead soft after finish machining.

j. Sealing surfaces in poppet assembly for copper seat were 16 microinch AA finish.

k. Sealing surfaces in valve body for copper seat and mating surfaces for body seals were 16 microinch AA finish.

l. Outlet port was 1/2" AN male fitting, V-groove butt welded to valve body with 100% penetration.

m. An MS27851-08 straight-threaded tubing-to-tubing fitting was used at the inlet side of the valve for test purposes. This assembly consisted of an MS27854-08 threaded flange, an MS27855-08 seal, and an MS27853-08 plain flange and MS27852-08 nut. The MS27853-08 plain flange was Heliarc welded to a 1/2" male AN fitting. The MS27851 assembly is shown in Figure 3. The MS27855 seal is shown in Figure 4. Figure 5 is a photograph of the complete valve assembly.

3. VALVE ASSEMBLY CLEANING PROCEDURE

Upon receipt of the valve from the manufacturer, it was disassembled and subjected to the cleaning procedures recommended earlier for the particular alloy compositions. The disassembled poppet, with copper seal, is shown in the center of Figure 6, and the end caps are shown at the bottom.

After cleaning, the valve was reassembled and leak checked. It showed zero external seal and zero seat leakage at 500 psig nitrogen pressure.

4. INSTALLATION OF VALVE ASSEMBLY USED IN FLOW SYSTEM

The valve was installed in a fluorine flow apparatus for passivation and flow testing. The flow apparatus consists of a pair of expulsion pumps connected in a double flow loop having check valves arranged so that as liquid is pumped alternately back and forth between

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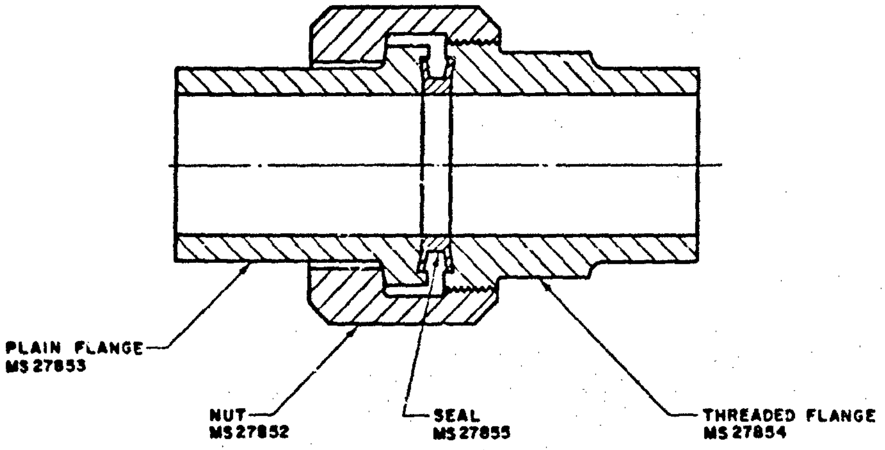

MS ASSEMBLY NO.	TUBE O.D.	NUT	PLAIN FLANGE	THREADED FLANGE	SEAL
MS 27851-02	1/8	MS 27852-02	MS 27853-02	MS 27854-02	MS 27855-02
MS 27851-04	1/4	MS 27852-04	MS 27853-04	MS 27854-04	MS 27855-04
MS 27851-06	3/8	MS 27852-06	MS 27853-06	MS 27854-06	MS 27855-06
MS 27851-08	1/2	MS 27852-08	MS 27853-08	MS 27854-08	MS 27855-08
MS 27851-12	3/4	MS 27852-12	MS 27853-12	MS 27854-12	MS 27855-12
MS 27851-16	1	MS 27852-16	MS 27853-16	MS 27854-16	MS 27855-16

1. DO NOT USE UNASSIGNED PART NUMBERS.
2. REFER TO MS 27850 FOR INSTALLATION INSTRUCTIONS.

FOR DESIGN FEATURE PURPOSES, THIS STANDARD TAKES PRECEDENCE OVER PROCUREMENT DOCUMENTS REFERENCED HEREIN.

REFERENCED DOCUMENTS SHALL BE OF THE ISSUE IN EFFECT ON DATE OF INVITATIONS FOR BID.

Review activities: 11, 14, 19, 69, 85 & NAS

This standard has been approved by the Department of the AIR FORCE and is mandatory for use by that activity. All other military activities are required to employ this standard where suitable.

APPROVED 14 JULY 1967 REVISED

P.A. USAF 12 Other Cust	Figure 3. Fitting Assembly, Straight Threaded, Fluid Connection, 4000 psi	MILITARY STANDARD MS 27851 (USAF)
PROCUREMENT SPECIFICATION MIL-F-27417	SUPERSEDES	SHEET 1 OF 1

DD FORM 1 SEP 57 672-1 (Limited coordination)

PREVIOUS EDITIONS OF THIS FORM ARE OBSOLETE.

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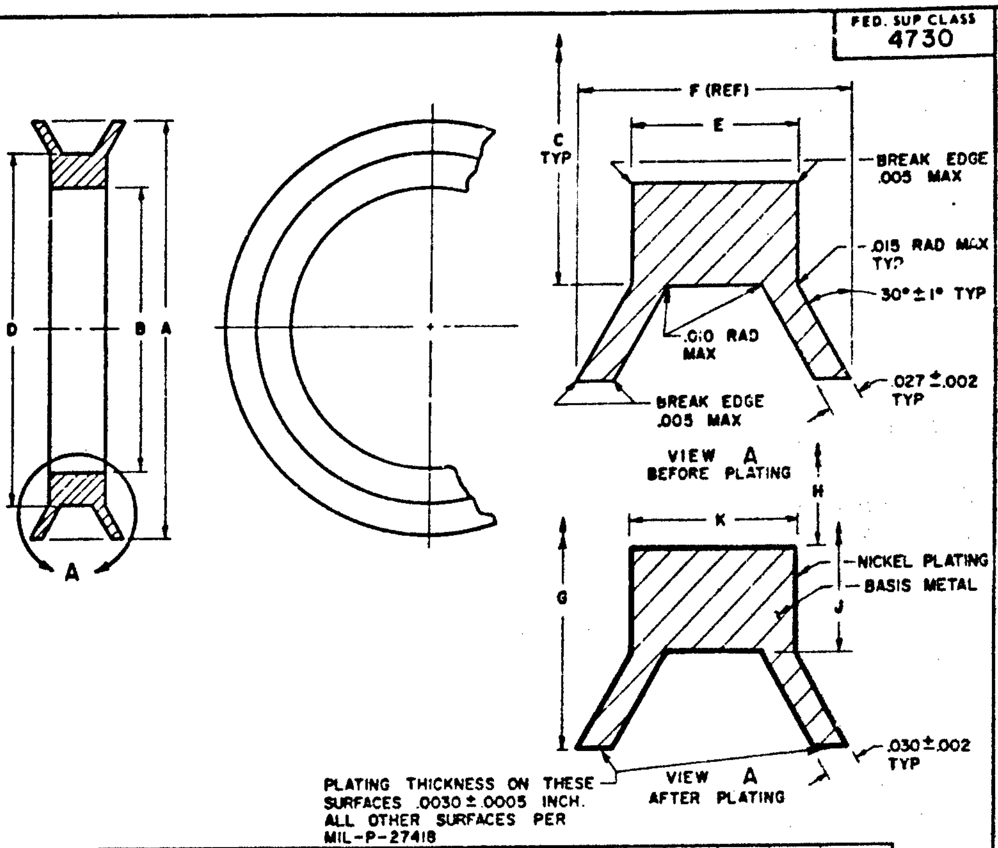

MS PART NO	TUBE O D	A DIA +.000 −.002	B DIA +.002 −.000	C DIA +.010 −.000	D DIA +.000 −.005	E ±.004	F REF	G DIA +.001 −.003	H DIA +.002 −.000	J DIA +.000 −.005	K ±.004	APPROX. WEIGHT LB/100
MS27855-02	1/8	.342	.100	.172	.174	.095	.193	.348	.096	.178	.099	
MS27855-04	1/4	.444	190	.274	.276	.120	.218	.450	.186	.280	.124	.220
MS27855-06	3/8	.556	.290	.386	.389	.150	.248	.562	.286	.393	.154	.440
MS27855-08	1/2	.653	.382	.488	.491	.150	.248	.664	.378	.495	.154	.500
MS27855-12	3/4	.880	.572	.710	.713	.150	.248	.886	.566	.717	.154	.990
MS27855-16	1	1.092	.744	.922	.925	.150	.248	1.098	.740	.929	.154	1.550

1. ALL DIAMETERS SHALL BE CONCENTRIC WITHIN .002 FIR.
2. MATERIAL: CORROSION-RESISTANT STEEL, AMS 5639, AMS 5650 OR AMS 5651.
3. FINISH: NICKEL PLATING PER MIL-P-27418.
4. CLEANING: FINISHED PARTS SHALL BE CLEANED PER MIL-F-27417.
5. SURFACE TEXTURE IN ACCORDANCE WITH USAS B46.1, UNLESS OTHERWISE SPECIFIED, SURFACES TO BE 32 MICROINCHES BEFORE PLATING.
6. BREAK SHARP EDGES .003-.015 UNLESS OTHERWISE SPECIFIED
7. DIMENSIONS IN INCHES. UNLESS OTHERWISE SPECIFIED, TOLERANCES: LINEAR DIMENSIONS ±.010, ANGULAR DIMENSIONS ± 5°.
8. RUBBER STAMP P/N AND MFR IDENT ON CONTAINER OR PACKAGING PER AS 478-30.
9. DO NOT USE UNASSIGNED PART NUMBERS.
10. REFER TO MS27851 FOR ASSEMBLY.

FOR DESIGN FEATURE PURPOSES, THIS STANDARD TAKES PRECEDENCE OVER PROCURMENT DOCUMENTS REFERENCED HEREIN.
REFERENCED DOCUMENTS SHALL BE OF THE ISSUE IN EFFECT ON DATE OF INVITATIONS FOR BID.

APPROVED 14 JULY 1967 REVISED

Review activities: 11, 14, 19, 69, 85, & NAS

This standard has been approved by the Department of the AIR FORCE and is mandatory for use by that activity. All other military activities are requested to employ this standard where suitable.

P.A. USAF 12 Other Cust	Figure 4. Seal, Cres, Nickel Plated, Fluid Connection Fitting, High Pressure	MILITARY STANDARD MS27855 (USAF)
PROCUREMENT SPECIFICATION MIL-F-27417	SUPERSEDES	SHEET 1 OF 1

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Figure 5. Complete Valve Assembly, Marotta Valve Model MV510TX Part No. 806239-E010530 And MS27851-08 Tubing To Tubing Fitting

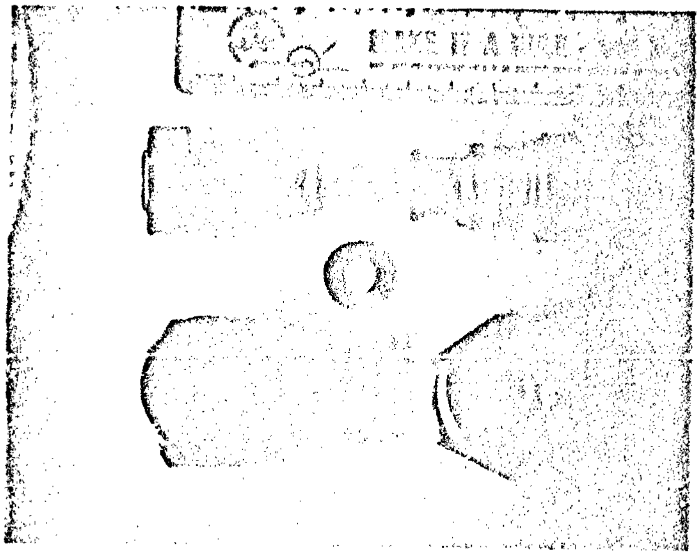

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Figure 6. Disassembled Poppet Assembly. Copper Seal In Center

the expulsion pumps, a unidirectional liquid flow passes through the test specimen. The expulsion pumps use helium gas as driver, with metal bellows separating the driving gas and liquid being expelled. The flow system schematic is shown in Figure 7 and Figure 8 is a photograph of the system with valve assembly installed.

A calculated mean flow rate can be obtained by multiplying the number of pump cycles per minute by the volume displaced per pump cycle. This quantity usually exceeds the actual measured flow rate due to slight check valve leakage. At higher pressures the check valves seat better and calculated and measured flow rates are more nearly the same.

5. SYSTEM PASSIVATION AND FILL

After installing in system and leak checking it, the system was evacuated and fluorine gas admitted to 50 psig at room temperature with the valve open. After one hour the fluorine gas was vented and pumped out. The system was cooled to LN_2 temperature and filled with liquid fluorine by condensing from a cylinder bank. Approximately nine pounds of fluorine were required to fill the system with liquid at -320°F.

6. FLOW TEST

The valve was operated for a total time of 11.4 minutes with a total measured flow of 19.2 gallons liquid fluorine at -320°F. The test conditions and mean flow rates are given in the data sheet, Table III.

At the conclusion of the flow test, the liquid nitrogen bath was allowed to boil off and the fluorine vented from the system. Approximately eighteen hours were required for all the liquid fluorine to evaporate, therefore after the flow test, the valve was in contact with liquid or gaseous fluorine for an additional eighteen hours as the system warmed to room temperature. At the end of this time the system was purged with dry nitrogen at room temperature (valve open) for three hours. The valve was then removed from the system and capped.

7. TEST EVALUATION

After removing the valve from the system it was leak checked with nitrogen at 500 psi. There was zero external leak and a 75 cc/min leak through the seat. This leak rate dropped to 17 cc/min when the valve was cycled three times. The leakage was due to fine particulate matter lodged in the copper seat as explained below.

The valve was disassembled and the various subcomponents inspected visually with the aid of a low power binocular microscope. Immediately after disassembly, all parts of the valve body, inlet and outlet parts, and poppet assembly had a bright appearance. The male end of the poppet assembly became perceptibly tarnished after exposure to the laboratory air (40% RH at 75°F) for several minutes. The fluid-contacting part of the

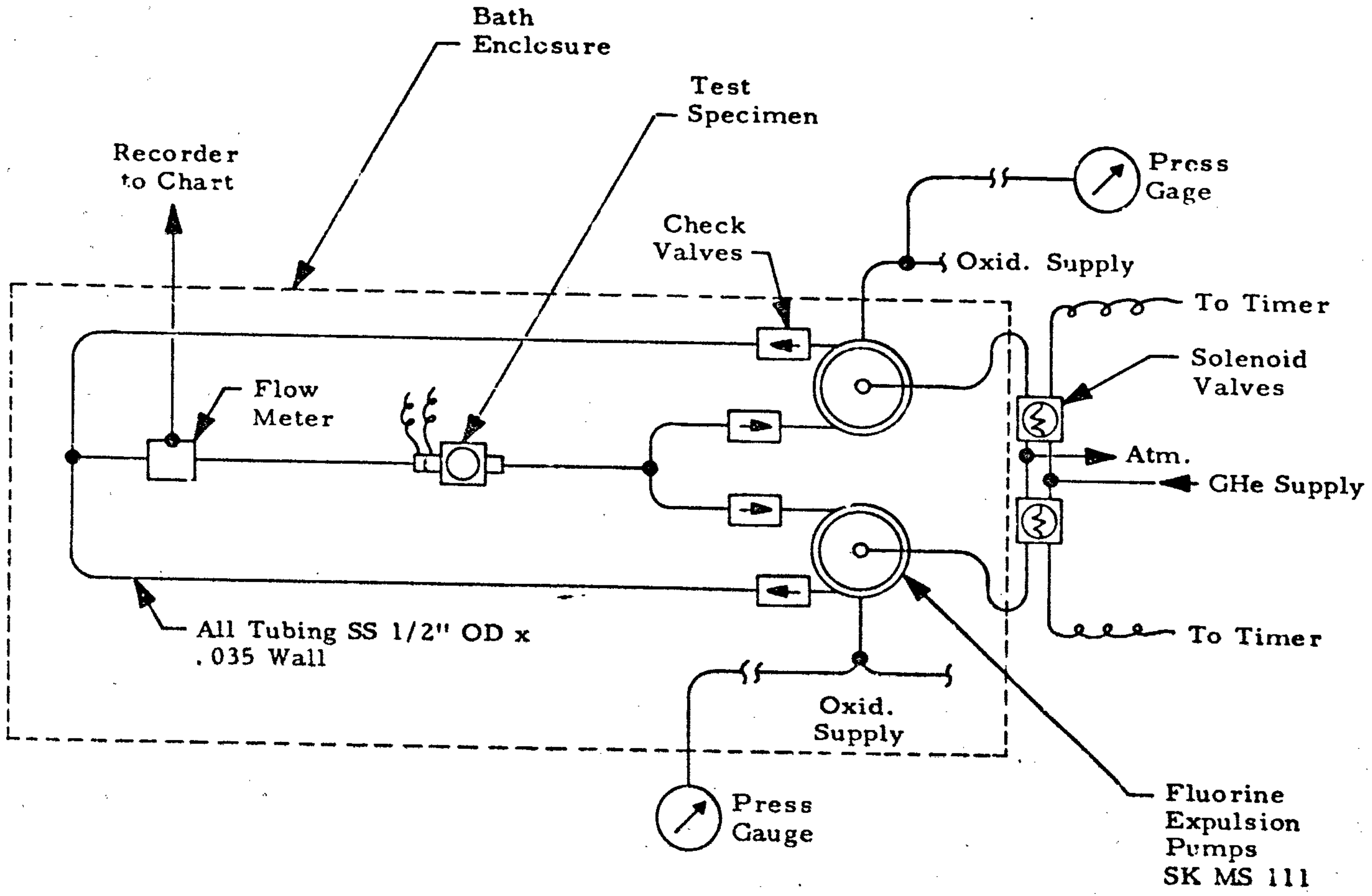

Figure 7. Bellows Pump Flow System

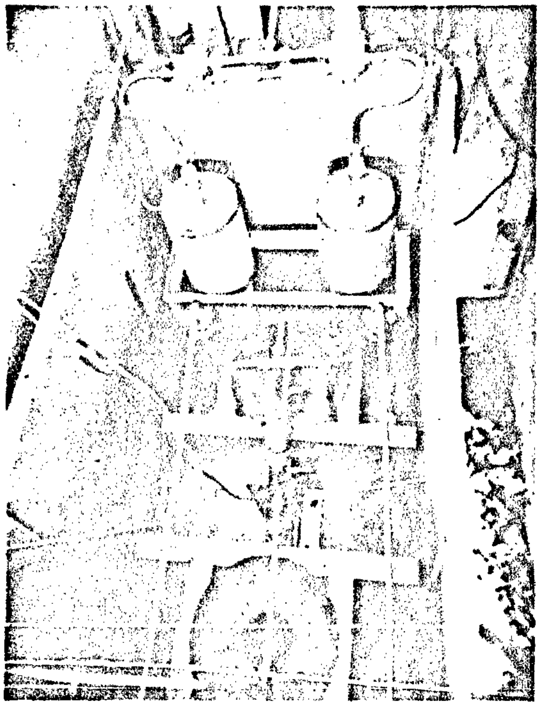

Figure 8. Bellows Pump Flow System With Marotta Valve Installed (Center Foreground)

TABLE III. MAROTTA VALVE FLOW TEST OPERATIONAL DATA
TEST TEMPERATURE -320°F

Test Condition	Gas He Driving Pressure (psi)	Strokes per min	Flow Time (min)	GPM (Calc.)	Mean Gal/min (measured)	Total Flow (gal) (measured)	Remarks
1	70	60	1.17	2.89	1.98	2.31	Valve closed for 8 sec. after cycle
2	70	60	0.25	2.89	1.98	0.50	Valve closed for 22 sec. after cycle
3	70	60	0.79	2.89	1.98	1.56	
4	70	40	0.38	1.93	1.55	0.59	
5	70	60	0.60	2.89	1.97	1.18	Valve closed for 10 sec. after cycle
6	100	60	0.45	2.89	2.25	1.01	
7	100	40	0.12	1.93	1.80	0.21	
8	100	40	1.07	1.93	1.53	1.63	Pumping stopped 30 sec. to adjust pressure
9	100	40	1.08	1.93	1.91	2.07	
10	150	30	0.45	1.44	1.67	0.75	
11	200	30	0.50	1.44	1.67	0.83	
12	—	30	0.78	1.44	1.10	0.86	Driving pressure decreased. Pumping stopped 36 sec. to adjust pressure
13	50	30	1.74	1.44	1.40	2.42	
14	50	40	0.78	1.93	1.62	1.27	
15	—	60	1.25	2.89	1.62	2.02	Driving Pressure Decreasing
			Total Time = 11.41			Total Flow = 19.21 gallons	

copper seat and body seals were very slightly tarnished. Numerous white irregular particles which appeared to be metal fluorides were found lodged in the valve body in locations where the flow was stagnant. These particles were approximately 10 to 100 microns in size. The source could not be located but they obviously originated in parts of the system other than the valve. One of the smaller particles, near the microscope's limit of resolution, could be seen imbedded in the sealing surface of the copper valve seat. This was possibly responsible for the increased leakage through the seat following the flow test. The poppet assembly and copper seals are shown in Figure 9 after the flow test. Aside from slight tarnishing of the Monel and copper parts, no significant corrosion could be detected visually. The MS27851 assembly and MS27855 seal were taken apart and inspected. No corrosion could be seen on any of the parts. The MS27855 seal is shown in Figure 10. It was unchanged in appearance during the test. It has a satiny nickel-plate finish and so does not have the bright appearance of the stainless steel portion of the poppet assembly.

The various parts including the poppet assembly, copper seat, copper seals, and MS27855 seal were weighed then exposed in air for an additional eighteen hours at 77°F and 50% relative humidity. The parts were weighed again and examined for signs of further corrosion. All weight changes were less than 0. 1 milligram except the Monel part of the poppet assembly which gained 1. 1 milligrams. No change in appearance of any of the parts was detected. Figure 11 is photographs of the poppet assembly before and after the eighteen-hour exposure at 50% RH.

8. CONCLUSIONS

A valve component (Marotta Valve, Model MV510TX) containing a variety of subcomponents and having 316 SS, 321 SS, Monel, copper, and nickel (MS27855 seal is nickel plated) was cleaned, assembled, passivated and subjected to and operated while containing flowing liquid fluorine at -320°F. This was followed by slow evaporation of the fluorine as the temperature was raised to room temperature over a period of about eighteen hours. Finally the valve was purged by flowing dry nitrogen for three hours.

After disassembly of the valve, there was no visible corrosion of any of the stainless steel or nickel parts immediately after opening the valve or after additional exposure to humid air.

Monel and copper parts were apparently slightly tarnished by exposure although the tarnish was not perceptible on Monel until it had been exposed to the laboratory air for several minutes. Observations on the copper parts were not conclusive because these parts could not be examined in detail immediately after opening the valve.

Exposure to air at 77°F and 50% RH for an additional eighteen hours did not result in any further visible corrosion. During this exposure the Monel part of the poppet assembly gained 1. 1 milligrams in weight. All the other parts were unchanged in weight.

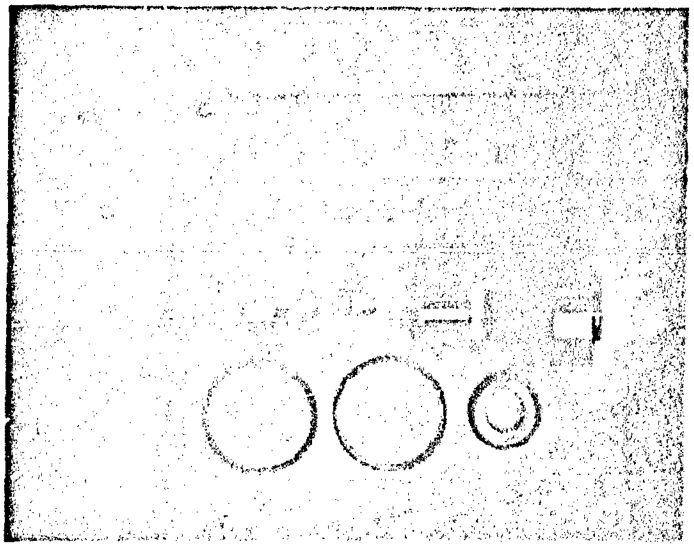

Figure 9. Poppet Assembly and Copper Seats After Flow Test

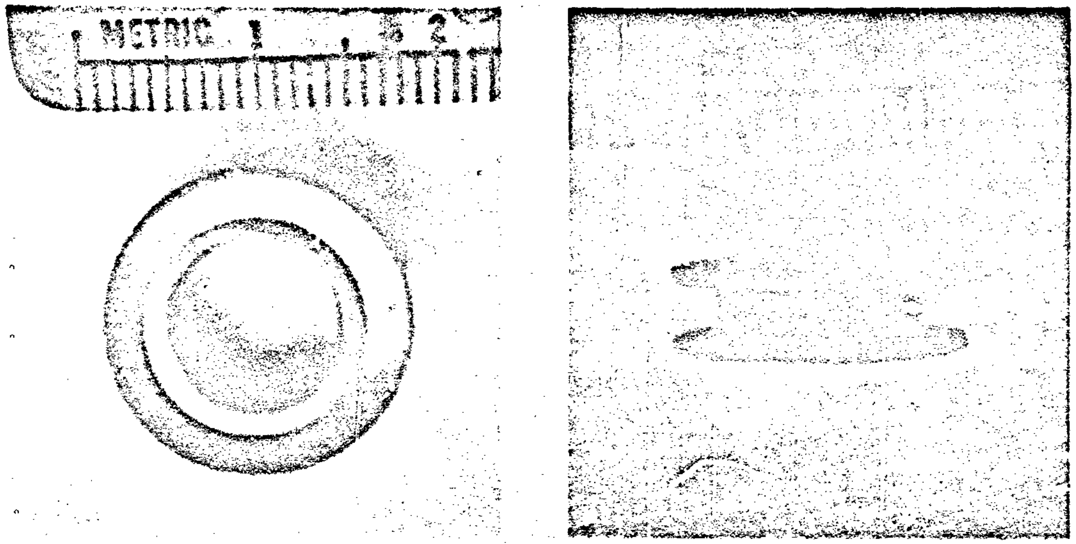

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Figure 10. MS27855 Seal After Flow Test

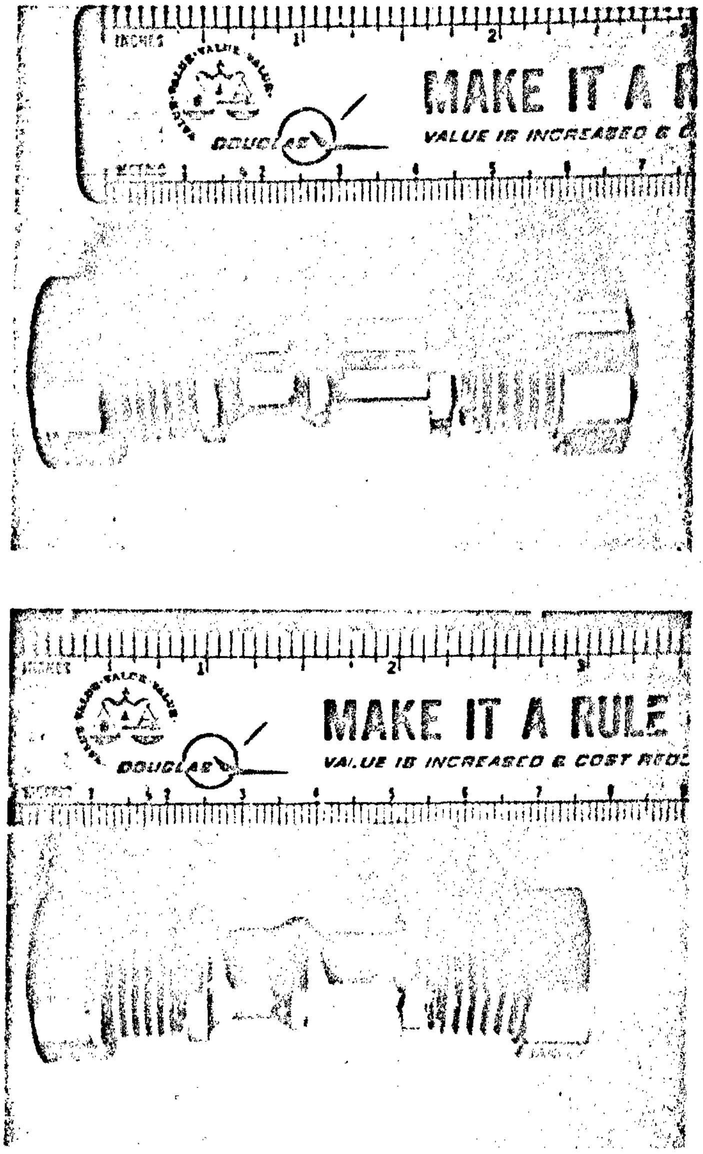

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Figure 11. Top — Poppet Assembly After Flow Test. Photographed After About One Hour Exposure To Laboratory Atmosphere

Bottom — Additional Eighteen Hours Exposure At 77°F And 50% Relative Humidity

In the absence of any possibility of organic contamination, the stainless steel and nickel parts could be returned to service with or without additional passivation. It would appear advisable to subject the Monel and copper parts to cleaning before reuse in view of the perceptible tarnish.

The cleaning and passivation procedures followed were adequate to prepare the valve for liquid fluorine service.

Marotta Valve Model MV510TY is suitable for service in liquid fluorine when properly cleaned and passivated.

APPENDIX I

REACTION OF GASEOUS FLUORINE WITH POTENTIAL SYSTEM CONTAMINANTS

1. APPARATUS AND PROCEDURES

The reactions of gaseous fluorine with typical system contaminants were investigated under a variety of conditions including flow and static exposure and pressures ranging from one atmosphere to 200 psig. Contaminants were smeared as thin films on one side of metal coupons 0.5" x 2.0" x approximately 0.025" thick.

Experiments in which contaminants were exposed at one atmosphere pressure were conducted in glass vessels so that reactions could be observed. The glass systems used for these exposures are shown in Figure 12. The detailed procedures used are described below.

a. Static System – Incremental Pressure Buildup

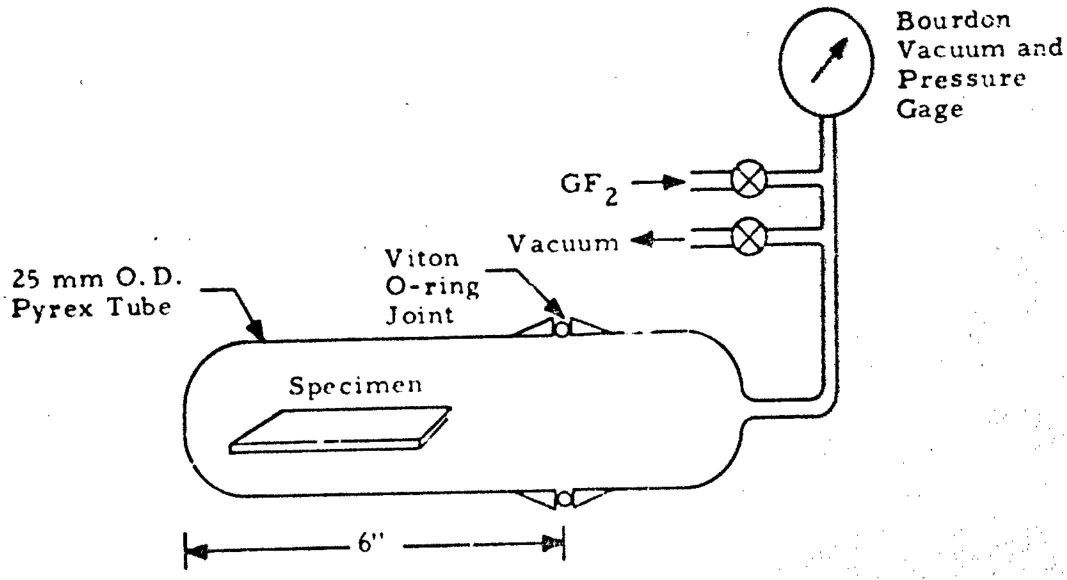
With the specimen in place in the Pyrex tube, the system is first evacuated. Gaseous fluorine is admitted to a pressure of one psia for five minutes, then the tube is again evacuated. The alternate five-minute pressurizations with gaseous fluorine and evacuations are continued at pressure levels of 2, 4, 8, and 15 psia. The specimen is kept under continuous observation from behind a safety shield during the exposure. Neglecting the time required to bring the pressures to the desired levels and for pumping out the fluorine between exposures, the specimens are exposed for a total of 25 minutes at gradually increasing fluorine pressure.

b. Static System – Sudden Pressure Buildup

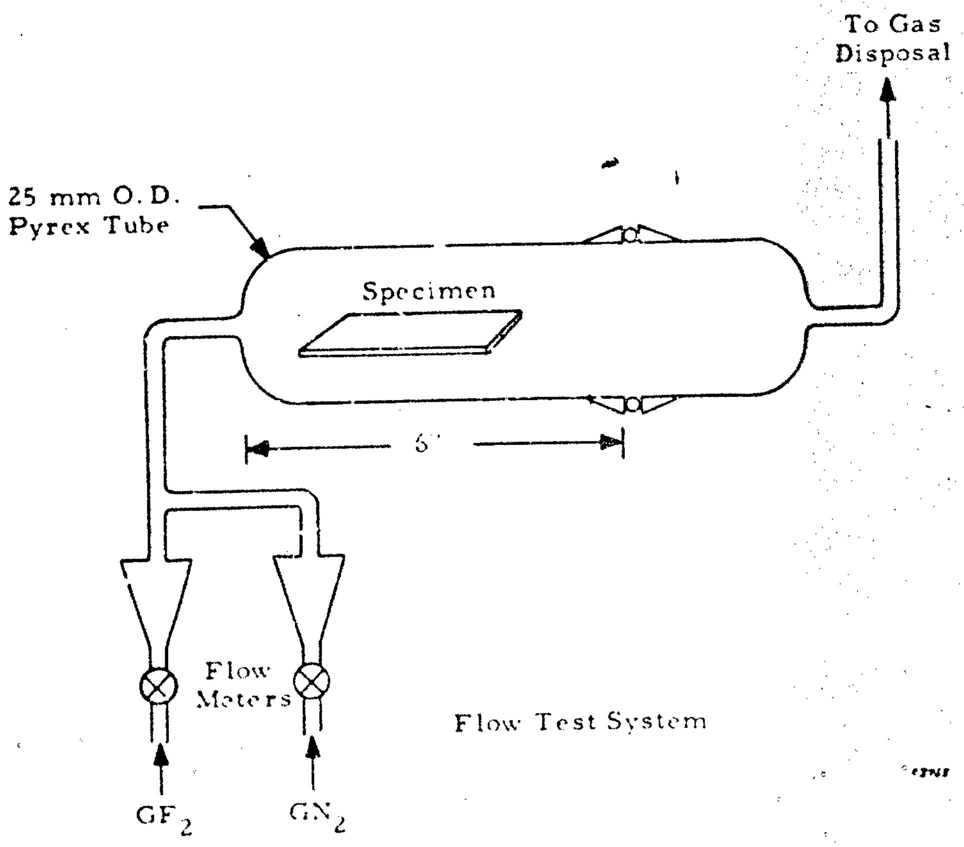
The contaminated specimen is first evacuated, then the system is abruptly pressurized to 15 psia with fluorine gas. After five minutes, the tube is pumped out. The specimen is kept under continuous observation.

c. Flow System – Incremental Concentration Buildup

With the specimen in place in the Pyrex tube, a flow of gaseous nitrogen at a rate of 100 ml per minute is established through the tube. Gaseous fluorine is then added to the stream in flow increments of 10 ml/minute with five-minute intervals between increases until the flow rate of gaseous fluorine is 50 ml/minute. The flow rate of gaseous nitrogen is then decreased in increments of 10 ml/minute until only pure fluorine is flowing in the system. After five minutes in pure fluorine, the flow is shut off and the tube is purged with pure nitrogen. The specimen is observed frequently during the test. The total exposure time following this procedure is



Static Test System



Flow Test System

Figure 12. Static and Flow Systems for Exposure of Typical Contaminants to Fluorine Gas

approximately 75 minutes with a gradually increasing partial pressure of fluorine.

d. Flow System — Sudden Concentration Buildup

With the specimen in place in the tube, a nitrogen flow rate of 100 ml/minute is established. The flow of gaseous fluorine is abruptly increased to 50 ml/minute while the nitrogen flow rate is simultaneously decreased to zero. After five minutes the fluorine flow is stopped and the tube purged with pure nitrogen.

e. Static System — High Pressure

For static test exposures of contaminated specimens at higher pressures, an all metal system was used. This was similar to the static system shown in Figure 12 except that the Pyrex tube was replaced with an equivalent section of one inch O. D. stainless steel tubing closed at one end and having an AN closure at the other end for connection to the gas manifold.

2. CONTAMINANTS

The following representative contaminants have been used in this phase of the investigation.

Petroleum Jelly U. S. P.

KEL-F 90 — Halocarbon Stopcock Grease

Pydraul AC — Phosphate Type Industrial Hydraulic Fluid

Polyurethane — Polyurethane Foam Insulation

Acrylic Lacquer — Commercial Clear Lacquer in Aerosol Dispenser

Coupons 0.5" x 2" were cut from 0.025" nickel 200 sheet stock. A limited number of similar coupons of 2014 aluminum, 316 stainless steel, and Monel 400 were also used in this phase of the investigation. The edges of the coupons were filed to remove burrs. All coupons were acid etched and LOX cleaned to remove corrosion products and traces of oil and grease. Thin, uniform films of contaminants were applied individually to one side of separate coupons. Petroleum jelly and KEL-F 90 were smoothed on with glass rods. The Pydraul AC was applied as a small droplet from a glass rod. It did not spread uniformly on the surface substrate, however. The polyurethane foam was mixed and cured in place on the coupon. It does not foam uniformly due apparently to low temperature during cure. The acrylic lacquer was applied as a single wet coat from the aerosol dispenser. After final weighing the specimens were stored in a dust-free environment until ready for exposure.

Due to the difference in film application, the loading varied considerably among the various contaminants. In later experiments an effort was made to maintain the loading at a level near 50 mg per coupon. The calculated film thickness for petroleum jelly at this loading is 4.5 mils.

3 OBSERVATIONS

Table IV gives the data for a series of tests of contaminated nickel coupons exposed to fluorine gas in the static system at a maximum pressure of one atmosphere and at room temperature. Except for the KEL-F 90 specimens and one of the polyurethane-coated specimens, small weight gains were observed. None of the films ignited. Minor changes in appearance were observed only for petroleum jelly and Pydraul AC while the others were unchanged.

Table V gives data for a similar series of experiments with the flow system. Similar results were obtained. Generally either weight gains or small weight losses were observed.

Different alloys were used for coupons in the series of static system experiments in Table VI. Only petroleum jelly was used as the contaminant. All specimens except one lost weight, but the weight changes were small compared with the total amount of contaminant present.

In view of the minor reaction that took place for exposure at one atmosphere, an additional series of tests was conducted at fluorine gas pressures of 50 psig. The data for exposure of petroleum jelly UPS and KEL-F 90 on nickel 200 coupons are presented in Table VII for one hour exposure at room temperature. There was no ignition of the contaminants but relative weight gains of the petrolatum films were appreciably greater than at one atmosphere pressure. KEL-F 90 lost weight.

Some additional exposures were carried out at 50 psig fluorine pressure for 1-hour and 24-hour periods. The data and conditions of exposure are given in Table VIII. In this set of experiments one of the petroleum jelly samples ignited and was almost completely consumed. The other sample exposed under apparently identical conditions did not ignite. It would appear that the conditions are on the borderline for igniting a petroleum jelly film. Both polyurethane specimens ignited and left carbonaceous residues.

4 INFRARED ANALYSIS OF ORGANIC RESIDUES

Infrared spectra were made of residues from reaction of gaseous fluorine with petroleum jelly USP and Pydraul AC. Spectra from exposure time of one hour at one atmosphere are shown in Figure 13(a) and (b). These spectra are identical with the materials before exposure, however it is concluded that there is no reaction with fluorine leading to any products that can be detected by this infrared analysis. The samples exposed to fluorine at 50 psig show evidence of considerable C-F bond formation as shown in the spectra of Figure 14(a) and (b) for one hour exposure of Pydraul AC and 24 hours exposure of petroleum jelly USP. (The one hour exposure sample of petroleum jelly USP was not available for analysis because it ignited during the test.) The C-F bond is indicated by the broad absorption band between 7.7 and 9 microns.

TABLE IV. EXPOSURE OF CONTAMINATED SPECIMENS (0.5" x 2") TO FLUORINE GAS — STATIC SYSTEM

Specimen Number	Contaminant	Uncoated Specimen Weight	Weight of Contaminant	Wt. Change During Exposure	Remarks
		A. Incremental Pressure Buildup			
Nickel N8	Petroleum Jelly	3.2158 g	0.0061 g	+ 0.0008 g	Film became partly opaque
Nickel N11	KEL-F 90	3.2290 g	0.0227 g	- 0.0008 g	No visible change
Nickel N41	Pydraul AC	3.2842 g	0.0058 g	+ 0.0001 g	Droplets became cloudy
Nickel N36	Polyurethane	3.1942 g	0.0679 g	+ 0.0015 g	No visible change
Nickel N34	Acrylic Lacquer	3.2799 g	0.0029 g	+ 0.0004 g	No visible change
		B. Sudden Pressure Buildup			
Nickel N11	Petroleum Jelly	3.0917 g	0.0092 g	+ 0.0006 g	Film became partly opaque
Nickel N18	KEL-F 90	3.2616 g	0.0242 g	- 0.0014 g	No visible change
Nickel N12	Pydraul AC	3.1195 g	0.0049 g	+ 0.0005 g	Droplets became cloudy
Nickel N30	Polyurethane	3.1933 g	0.0394 g	- 0.0008 g	No visible change
Nickel N24	Acrylic Lacquer	3.2678 g	0.0029 g	+ 0.0002 g	No visible change

TABLE V. EXPOSURE OF CONTAMINATED NICKEL SPECIMENS (0.5" x 2") TO FLUORINE GAS – FLOW SYSTEM

Specimen Number	Contaminant	Uncoated Specimen Weight	Wt. of Contaminant	Wt. Change During Exposure	Remarks
A. Incremental Concentration Buildup					
Nickel N33	Petroleum Jelly	3.3205 g	0.0394 g	+ 0.0033 g	Film became cloudy
Nickel N26	KEL-F 90	3.1580 g	0.0187 g	0.0000	No visible change
Nickel N28	Pydraul AC	3.1623 g	0.0287 g	+ 0.0048 g	Liquid appeared to partially solidify
Nickel N1	Polyurethane	3.0573 g	0.0490 g	+ 0.0031 g	No visible change
Nickel N21	Acrylic Lacquer	3.4236 g	0.0236 g	+ 0.0035 g	No visible change
B. Sudden Concentration Buildup					
Nickel N15	Petroleum Jelly	3.2041 g	0.0581 g	- 0.0033 g	Film became cloudy
Nickel N29	KEL-F 90	3.1705 g	0.0153 g	- 0.0001 g	No visible change
Nickel N38	Pydraul AC	3.0686 g	0.0504 g	- 0.0002 g	Liquid partially solidified
Nickel N31	Polyurethane	3.0872 g	0.0367 g	+ 0.0004 g	Duller appearance
Nickel N21	Acrylic Lacquer	3.1427 g	0.0220 g	+ 0.0006 g	No visible change

TABLE VI. EXPOSURE OF CONTAMINATED SPECIMENS (0.5" x 2") TO FLUORINE GAS – STATIC SYSTEM – CONTAMINANT PETROLEUM JELLY USP

Specimen Composition and No.		Uncoated Specimen Weight	Weight Contaminant	Weight Change During Exposure	Remarks
A. Incremental Pressure Buildup					
2014 Aluminum	(B1)	1.7398	0.0537	-0.0014	Turned cloudy and small bubbles formed.
316 S.S.	(J1)	0.0536	0.0536	+0.0004	Turned cloudy
Monel 400	(Q1)	0.0493	0.0493	-0.0020	Turned cloudy
B. Sudden Pressure Buildup					
2014 Aluminum	(B2)	1.7440	0.0501	-0.0019	Turned cloudy
316 S.S.	(J2)	2.2275	0.0564	-0.0009	Turned cloudy
Monel 400	(Q2)	3.5313	0.0498	-0.0025	Turned cloudy

TABLE VII. EXPOSURE OF CONTAMINATED NICKEL SPECIMENS (0.5" x 2") 50 PSIG FLUORINE GAS — ONE HOUR — STATIC SYSTEM

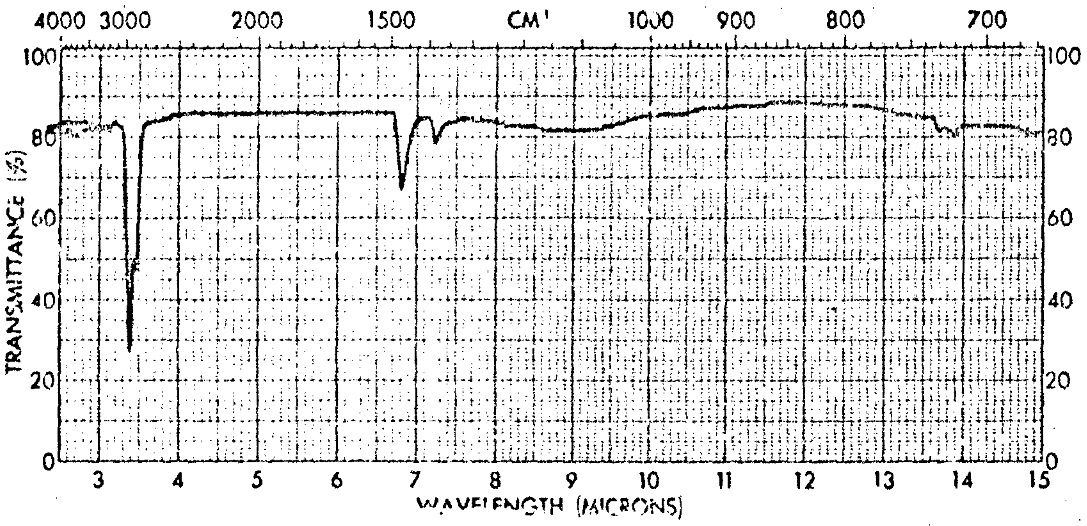
Specimen Number	Contaminant	Uncoated Specimen Weight	Weight of Contaminant	Weight Change During Exposure
Nickel N3	Petroleum Jelly	3.2352	0.0490	+ 0.0085
Nickel N4	Petroleum Jelly	3.1825	0.0511	+ 0.0094
Nickel N5	KEL-F 90	3.1368	0.0484	- 0.0019
Nickel N7	KEL-F 90	3.1613	0.0587	- 0.0004

TABLE VIII. EXPOSURE OF ORGANICS TO HIGH PRESSURE FLUORINE

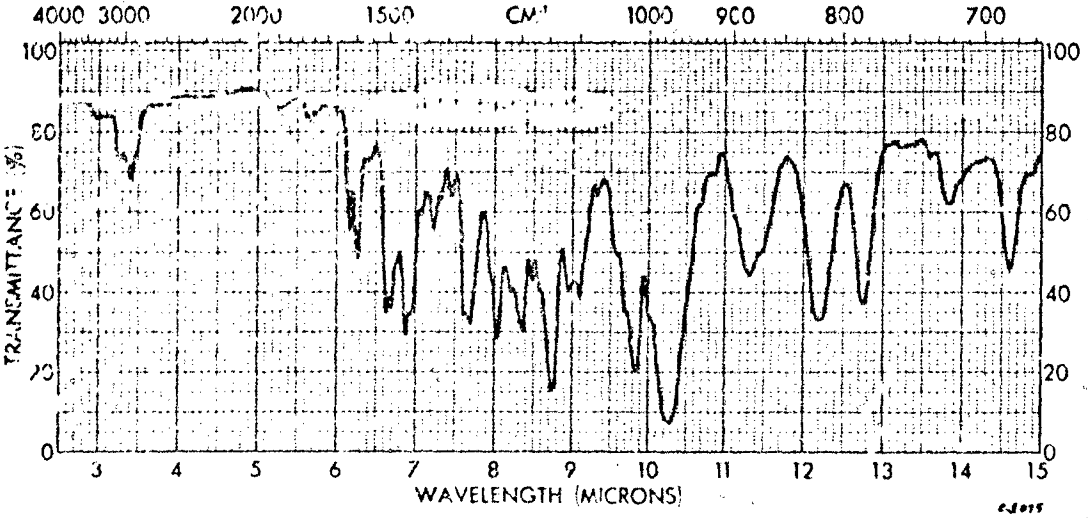
(50 psig, 77°F)

1-Hour Exposure	Initial Sample Weight	Weight Change	%	Observation
Petroleum Jelly USP	0.0575	-0.0548	-95	Carbon residue
KEL F-90	0.0503	-0.0009	-2	—
Pydraul AC	0.0497	+0.0123	+25	Semi-solid residue
Polyurethane	0.0496	-0.0353	-71	Carbon residue
24-Hour Exposure				
Petroleum Jelly USP	0.0484	+0.0237	+49	Solid film residue
KEL F-90	0.0427	-0.0113	-26	Oily residue
Pydraul AC	0.0528	+0.0243	+46	Brown solid residue
Polyurethane	0.0537	-0.0410	-76	Carbon residue

Petroleum jelly USP and KEL F-90 grease spread on 0.5" x 2" 304 stainless steel panels. Pydraul AC and polyurethane foam contained in ABMA aluminum impact cups (1" dia x 3/4" high).

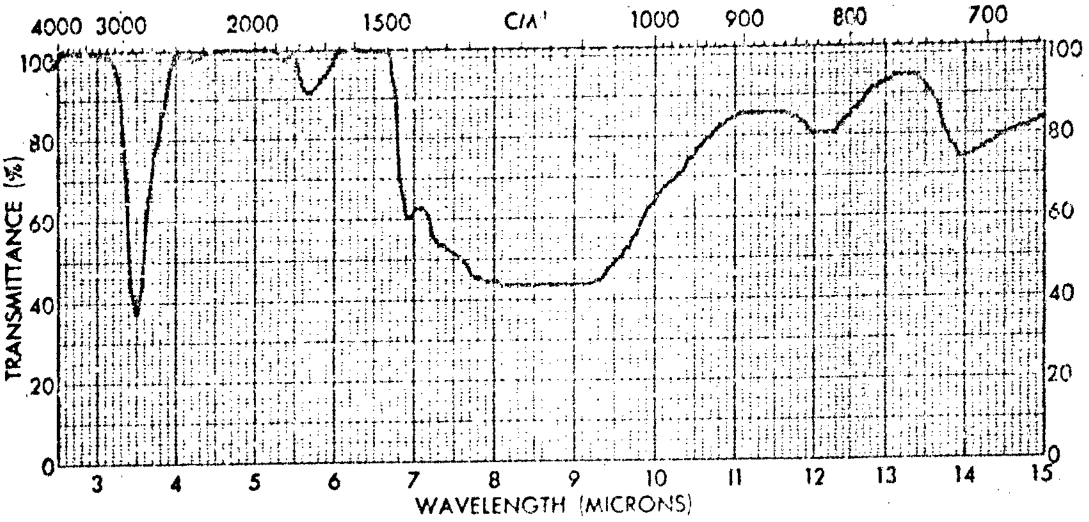


(a) Petroleum Jelly USP Exposed to GF_2 for 1 Hour at One Atmosphere Pressure at 25°C (77°F)

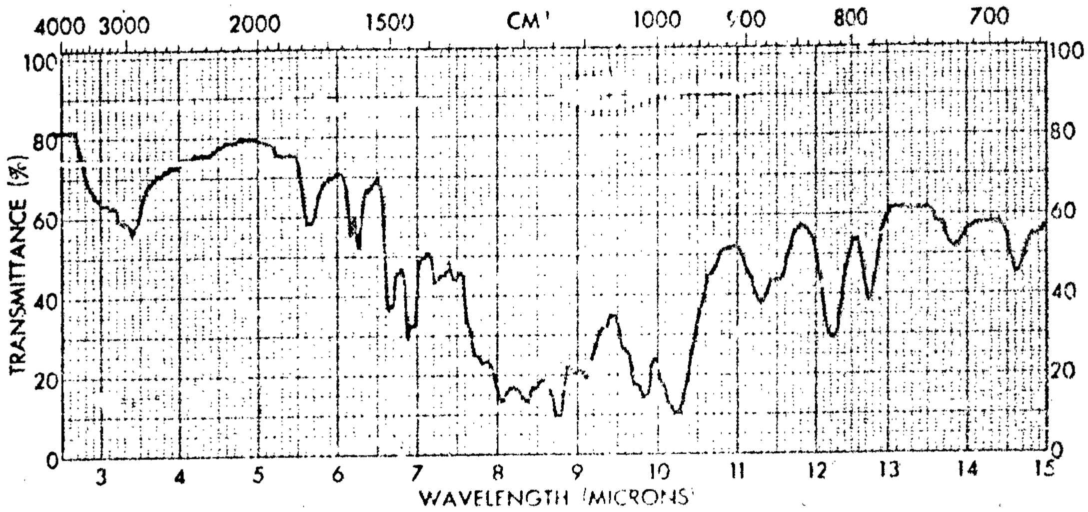


(b) Pydraul AC Exposed to GF_2 for 1 Hour at One Atmosphere Pressure at 25°C (77°F)

Figure 13. Infrared Spectra



(a) Petroleum Jelly USP Exposed to 50 psig Fluorine for 24 Hours at 25°C (77°F)



(b) Pydraul AC Exposed to 50 psig Fluorine for 1 Hour at 25°C (77°F)

Figure 14. Infrared Spectra

5. EXPOSURE OF ORGANICS IN CONTROLLED ENVIRONMENTAL BALANCE

The controlled environment balance provides for continuously following the weight change of a specimen while it is exposed to flowing fluorine gas. It consists of an Ainsworth single pan analytical balance with a platinum chain hang-down extending through a vertical tube into a cylindrical reaction chamber. The chain terminates in the chamber and supports a specimen pan. Fluorine gas is fed into the chamber at the bottom and is exhausted at the top through a side arm in the vertical tube through which the platinum chain hangs This arrangement insures that relatively little fluorine gas escapes from the chamber into the room; what does escape is exhausted through the fume hood enclosing the balance assembly. A system of baffles inside the chamber prevents direct impingement of flowing gas on the balance pan Samples are placed on or removed from the pan through a gasketed closure on the front of the chamber.

Figure 15 gives results for exposing separate samples of petroleum jelly, Pydraul AC, and polyurethane foam to flowing gaseous fluorine in the apparatus at 25°C (77°F); With a flow of fluorine into the chamber of 50 ml/min and with a total chamber volume of 400 ml, several minutes are required for the fluorine concentration to build up to a high level as air is displaced This probably accounts for the delay in the weight increase shown for the polyurethane specimen. After the initial delay, the specimen showed a continuous gain in weight but at a decreasing rate for the period of exposure. A total weight increase of approximately 13 mg for a specimen of initial weight of 49 mg was observed.

Pydraul AC, 350 mg, was exposed in an aluminum cup (1 inch diameter). After approximately 45 minutes during which a shallow minimum in the weight was observed, the specimen gradually increased in weight during the 150-minute exposure time. At this time the total weight gain was about 7 milligrams

Petroleum jelly USP, spread as a uniform 50 mg film on a one-inch square 304 stainless steel coupon, did not change weight during 150-minute exposure, as shown in Figure 15

6 HIGH TEMPERATURE HIGH PRESSURE EXPOSURE OF ORGANICS

In view of the incomplete combustion of typical system contaminants at fluorine pressures to 50 psig, additional exposures were carried out at temperatures to 200°F and pressures to 200 psig The organic contaminants were spread as films on 0 016" x 0 5" x 2" 304 stainless steel coupons. Each coupon was dished slightly with a rectangular punch to help retain the organic material while the coupon lies flat in the bomb Liquefication of some of the organic contaminants at the elevated temperature would otherwise result in loss of material by creeping over the edges of the coupons. Loading the organic material was maintained as near as practicable to 50 mg per coupon

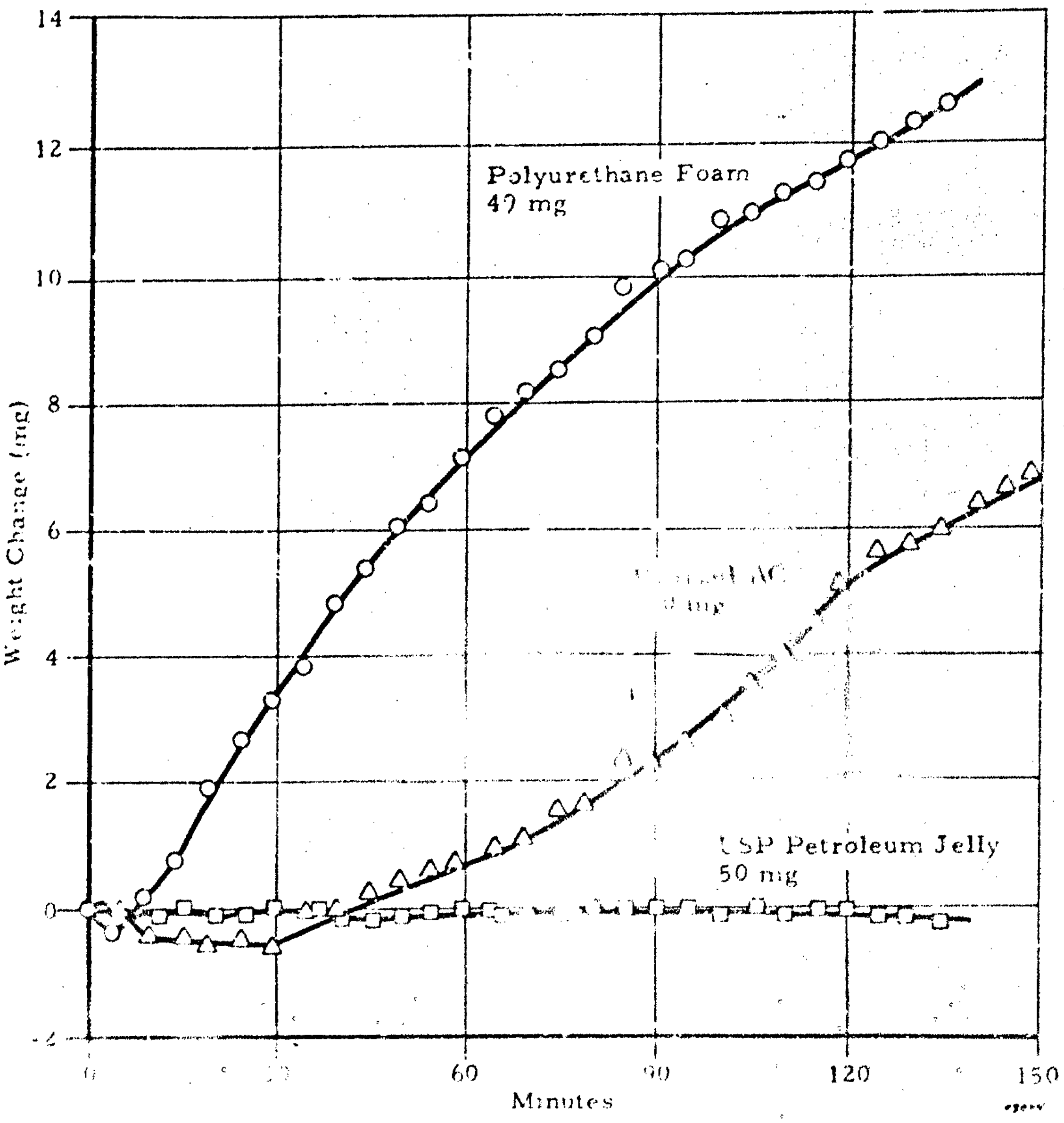


Figure 15. Weight Change as a Function of Time for Some Typical Contaminants. Flowing OF_2; 25°C (77°F); One Atmosphere.

Weighed test specimens were exposed individually to fluorine gas in stainless steel bombs 1" ID and 6" long. For exposures at elevated temperatures the bomb was inserted in an oven thermostated at 200°F. Exposures of each of four organic contaminants were carried out at three different temperature-pressure conditions as follows: (a) 200 psig fluorine pressure at room temperature; (b) one atmosphere fluorine pressure at 200°F; and (c) 200 psig fluorine pressure at 200°F. All exposures were for periods of one hour.

In these exposures, all materials reacted extensively except KEL-F 90 grease under conditions (a) and (b) above. The data are summarized in Table IX. Appreciable residues are left for all materials under conditions (a) and (b). Based on previous experience, it is considered that such residues would be impact sensitive in liquid fluorine. Under condition (c) only minor residues are left as evidenced by the weight loss data of Table IX. Visible carbonaceous reaction products were left from KEL-F 90 and Pydraul AC. No evidence of any organic residue was found in the petroleum jelly specimen. The failure to show a weight loss of 100% is probably due to the increase in weight of the metal coupon by reacting with fluorine. Discoloration of the coupon is evidence of very high local temperature during exposure. Photos of the coupons following exposure are shown in Figure 16. The polyurethane foam specimen ignited during pressurization destroying both bomb and coupon.

7. REACTION OF CHLORINE TRIFLUORIDE WITH SYSTEM CONTAMINANTS

a. Apparatus and Procedure

The static system (Figure 12) was used and chlorine trifluoride vapor was introduced abruptly to the evacuated system containing the contaminated coupon. A maximum pressure of one atmosphere was used with the system initially at room temperature.

b. Observations

The results for petroleum jelly and KEL-F 90 contaminated nickel 200 coupons are given in Table X. The petroleum jelly film ignited in chlorine trifluoride proving that this medium is more reactive than fluorine at equivalent pressure. However, the residue left weighed approximately 50 percent more than the original petroleum jelly film. The KEL-F 90 film liquefied and bubbled This behavior is attributed to the reaction of the chlorine trifluoride with the finely-divided silica used as a thickener in the grease, to form silicon tetrafluoride.

8. REACTION OF GASEOUS FLUORINE WITH CONTAMINATED POROUS STAINLESS STEEL

TABLE IX. EXPOSURE OF TYPICAL SYSTEM CONTAMINANTS TO FLUORINE GAS

(a) 200 psig GF_2; room temperature; one hour

Spec No.	Contaminant	Wt Contaminant (mg)	Wt change (mg)	% Loss
J-22	Pet. Jelly USP	50.5	-43.1	85
J-12	KEL-F 90	51.1	- 2.8	5.5
J-7	Pydraul AC	49.9	-33.9	68
J-1	Polyurethane Foam	48.5	-44.4	92
(b) 1 atm. GF_2; 200°F; one hour				
J-17	Pet. Jelly USP	51.8	-11.7	23
J-10	KEL-F 90	56.1	- 5.8	10
J-14	Pydraul AC	48.4	-37.3	77
J-18	Polyurethane Foam	44.9	-20.4	45
(c) 200 psig GF_2; 200°F; one hour				
J-24	Pet. Jelly USP	51.4	-47.2	92
J-16	KEL-F 90	49.6	-48.7	98
J-21	Pydraul AC	49.8	-48.4	97
J-6	Polyurethane Foam	52.5	—Specimen Destroyed—*	

---

* Specimen ignited during pressurization with fluorine gas and destroyed bomb.

a.
200 psig; R. T.

top - Petroleum jelly USP
2nd - KEL-F 90
3rd - Pydraul AC
bottom - Polyurethane

b.
1 atm.; 200°F

top - Petroleum jelly USP
2nd - KEL-F 90
3rd - Pydraul AC
bottom - Polyurethane

c.
200 psig; 200°F

top - Petroleum jelly USP
2nd - KEL-F 90
3rd - Pydraul AC

c3335

Figure 16. Exposure of Contaminants to Fluorine at High Temperature and/or High Pressure.

TABLE X. EXPOSURE OF CONTAMINATED NICKEL SPECIMENS TO CHLORINE TRIFLUORIDE VAPOR – ONE ATMOSPHERE – STATIC SYSTEM

Substrate	Contaminant	Uncoated Specimen Weight	Weight of Contaminant	Wt. Change During Experiment	Remarks
Nickel N10	Petroleum Jelly	3.1675 g	0.0567 g	+ 0.0263 g	Sample ignited in 30 seconds. Flame died out and exposure continued for one hour. Black, waxy residue left on specimen.
Nickel N6	KEL-F 90	3.0466 g	0.0495 g	- 0.0015 g	Grease liquified and small bubbles appeared in film after three minutes. Exposure continued for one hour.

a. Apparatus and Procedures

Stainless steel (type 316) filter elements in disc form 1/16" thick and 1/2" diameter were impregnated with Halocarbon oil and dye penetrant fluid. Samples covering a range of porosities from about 30 to 50 percent were used. Mean pore sizes were on the order of 30 microns.

Impregnation was carried out by immersing the discs in the respective fluid, heating under vacuum to about 50° - 60°C to remove air from pores, then releasing the vacuum and cooling the specimens under the impregnating fluid. Finally the specimens were removed from the fluid and the surfaces superficially dried by blotting with absorbent paper. The impregnated specimens were tested for reaction with fluorine by exposure in the static test system to fluorine gas at one atmosphere for one hour at room temperature.

b. Contaminant Fluids

Halocarbon Oil – Series 13-21 Halocarbon Products Corporation.

Dye Penetrant Fluid – Contrast Dye Penetrant-MIL-L-25135, Group 1. This material partially volatilized during the vacuum impregnation of the porous stainless steel discs.

c. Observations

The results of the exposure of the contaminated specimens to fluorine gas are given in Table XI. The Halocarbon impregnated specimens were unchanged in weight or appearance. The Dye Penetrant-impregnated specimens burst into flame upon initial pressurization with fluorine. The flame subsided after a few seconds after which pressurization with fluorine was resumed and exposure continued for one hour. The weight losses of the specimens ranged from 10 to nearly 50 percent of the original weight of contaminant.

9. REACTION OF GASEOUS FLUORINE WITH DYE PENETRANT FLUID IN GLASS CAPILLARIES

a. Apparatus and Procedure

Two Pyrex glass capillaries, one 100 micron and the other 30 micron inside diameter were filled with Dye Penetrant fluid. One inch sections of each capillary were broken out and the filled capillaries exposed individually in flowing fluorine gas in the flow system (see Figure 12). The tubes were kept under continuous observation with a binocular microscope during the exposure.

b. Contaminant

Dye Penetrant Solution – Contrast Dye Penetrant-MIL-L-25135, Group 1.

TABLE XI. EXPOSURE OF POROUS STAINLESS STEEL SPECIMENS TO FLUORINE – ONE ATMOSPHERE – ONE HOUR – STATIC SYSTEM

Specimen	Contaminant	Weight Specimen	Weight Contaminant	Weight Change	Remarks
31655 - 32% porosity	Halocarbon Oil	1.1415 g	0.1159 g	+ 0.0002 g	No visible reaction
31655 - 41% porosity	Halocarbon Oil	0.9711 g	0.1280 g	+ 0.0006 g	No visible reaction
31655 - 50% porosity	Halocarbon Oil	0.8556 g	0.1638 g	- 0.0002 g	No visible reaction
31655 - 32% porosity	Dye Penetrant	1.1206 g	0.0536 g	- 0.0190 g	Burst into flame on initial exposure. After flame died out exposure continued for one hour total.
31655 - 41% porosity	Dye Penetrant	0.9745 g	0.0712 g	- 0.0071 g	
31655 - 50% porosity	Dye Penetrant	0.7877 g	0.0792 g	- 0.0347 g	

c. Observations

After about five minutes exposure the dye penetrant fluid in the 100 micron capillary turned black or dark blue at the meniscus. This change from the initial red color penetrated further into the fluid in the capillary to a depth of about 400 microns after one hour. The meniscus was originally 700 microns inside the capillary and did not recede further during the exposure of one hour. In view of these observations it seems that only a very slow reaction takes place due to slow diffusion into and out of the capillary.

The observations with the 30 micron capillary were similar except the depth of discoloration in the fluid was only about 100 microns.

APPENDIX II

IMPACT SENSITIVITY

1. IMPACT SENSITIVITY OF ORGANIC RESIDUES FOLLOWING PASSIVATION

Type 316 stainless steel impact specimens (discs, 5/8" diameter by 0.016" thick) were individually coated on one side with the following organic contaminants.

a. Petroleum jelly, USP
b. KEL-F 90 halocarbon grease
c. Acrylic lacquer
d. Polyurethane foam insulation

Contaminant coating was held as nearly as possible to 50 mg per square inch (15 mg per specimen). After applying organic contaminants, the specimens were exposed to a simulated passivation cycle of one-hour exposure to gaseous fluorine at one atmosphere at 25°C (77°F). Following passivation, specimens were impact tested in the modified ABMA tester in liquid fluorine at -195°C (-320°F) at 72 ft-lb energy level (Reference 6). All impacts yielded reactions ranging from moderate to extreme, indicating that all organic residues were impact sensitive. The data are summarized in Table XII.

One of the two petroleum jelly coated specimens and one of the two acrylic lacquer coated specimens reacted violently in the liquid fluorine before actual impact. Reactions occurred spontaneously after about 5 seconds contact with liquid fluorine. Neither the KEL-F 90 nor the polyurethane foam contaminated specimens reacted prior to impact. It should be mentioned that the specimens are cooled to -320°F (LN_2 temperature) before the LF_2 is added.

2. IMPACT SENSITIVITY OF DYE PENETRANT RESIDUES

Cast aluminum impact specimens (discs, 0.040" thick by 5/8" diameter) were machined from an A356 aluminum billet of grade III porosity. Specimens were exposed to dye penetrant inspection using Shannon Glow P138A water-washable penetrant. A normal rinse with water was used for removing dye penetrant. After drying, all specimens were vapor degreased in Genesolve D. Fluorescent residues were still present on all specimens after vapor degreasing. These could be detected under low power magnification with ultraviolet illumination. Some of the samples were exposed to a vacuum bakeout at 105°C (220°F) for 18 hours after vapor degreasing.

TABLE XII. IMPACT SENSITIVITY TESTS PASSIVATED ORGANIC CONTAMINANTS

Oxidizer – LF_2
Samples – Coatings on 316 Stainless Steel
Ambient Temperature; $54^{\circ}F$: Test Temperature; $320^{\circ}F$
Atmosphere – Dry GN_2
Impact Energy – 72 ft-lb

Drop No.	Sample	Type of Reaction Extreme	 Moderate	 Faint	 None	Remarks
1	Blank				x	
2	KEL-F 90		x			
3	KEL-F 90		x			
4	Petroleum Jelly	x				
5	Petroleum Jelly		x			Reacted before impact
6	Acrylic Lacquer	x				
7	Acrylic Lacquer		x			Reacted before impact
8	Polyurethane		x			
9	Polyurethane		x			
10	Blank				x	

Fluorescent residues could still be detected after vacuum bakeout but the number of fluorescent spots was reduced.

Previous work in this laboratory (Reference 7) has shown that A356 cast aluminum with grade III porosity fails to pass impact tests in liquid fluorine at -320°F when subjected to Penetrex ZL-22 dye penetrant inspection followed by the cleaning and bakeout procedure described in the preceding paragraph. (Shannon Glow P138A used in the current investigation is the equivalent of Penetrex ZL-22. The latter was no longer available for use.) The bare metal, unexposed to dye penetrants, is stable in LF_2 impacts.

In the current investigation, after passivation in gaseous fluorine for 1 hour at one atmosphere pressure at 25°C (77°F), no reactions were obtained in 20 impact specimens in liquid fluorine at -195°C (-320°F) using the modified ABMA test at 72 ft-lb energy (Reference 6). One out of six specimens passivated in gaseous CTF for 1 hour at one atmosphere pressure at 25°C (77°F) reacted on impact and one out of six passivated in gaseous fluorine after normal cleaning, but without the vacuum bake out, also reacted. The results indicate that if the cleaning cycle includes a vacuum bake out at 105°C (220°F) for at least 18 hours the impact sensitivity is materially reduced if not eliminated.

3. IMPACT SENSITIVITY OF TUNGSTEN-CONTAMINATED SPECIMENS

Inclusions such as those that might be introduced by electrode sputtering in TIG welding were simulated by plasma spraying a mixed aluminum and tungsten powder onto A356 cast aluminum impact specimens. Layers of slightly less than 0.002-inch mean thickness were produced. Three different concentrations of tungsten powder (1%, 3%, and 10% by weight) were studied.

Examination of the specimens by means of a stereo microscope (30X) showed that tungsten grains were definitely present and identifiable in the aluminum coating matrix. The tungsten appeared darker in color, and the crystal grains had much sharper angles than the aluminum, which had partially melted.

The specimens were divided; half were passivated in gaseous fluorine at one atmosphere pressure for 1 hour at 25°C (77°F). Five of twelve unpassivated specimens reacted on impact in the ABMA tester in liquid fluorine at -195°C (-320°F). Only one of eighteen passivated specimens reacted on impact. The data are summarized in Table XIII.

The results indicate that tungsten particles are impact sensitive in LF_2 and that they become materially less so after passivation. More tests will be required to establish if passivation alone can render tungsten contamination safe.

TABLE XIII. IMPACT SENSITIVITY TESTS
TUNGSTEN-CONTAMINATED CAST ALUMINUM

Oxidizer – LF_2
Samples – A356 Al (Tungsten Contaminated)
Ambient Temperature: 55°F: Test Temperature; -320°F
Impact Energy -- 72 ft-lb
Atmosphere – Dry GN_2

Drop No.	Sample	Type of Reaction Extreme	 Moderate	 Faint	 None	Remarks
1	A2				x	
2	A2		x			
3	A2			x		
4	B2				x	
5	B2				x	
6	B2				x	
7	B2				x	
8	B2			x		
9	B2				x	
10	C2				x	
11	C2			x		
12	C2			x		
13	A1				x	
14	A1				x	
15	A1				x	
16	A1				x	
17	A1				x	
18	A1				x	
19	B1				x	
20	B1				x	
21	B1		x			Flash, no sound
22	B1				x	
23	B1				x	
24	B1				x	
25	C1				x	
26	C1				x	
27	C1				x	
28	C1				x	
29	C1				x	
30	C1				x	

A1 – 1% W – passivated
B1 – 3% W – passivated
C1 – 10% W – passivated
A2 – 1% W – as deposited
B2 – 3% W – as deposited
C2 – 10% W – as deposited

4. IMPACT SENSITIVITY OF ORGANIC RESIDUES FOLLOWING PASSIVATION IN GF_2 AT 50 PSIG AND IN ClF_5 AT ONE ATMOSPHERE

Type 316 stainless steel impact specimens, in the form of discs, 5/8" diameter and 0.016" thick, were individually coated on one side with the organic contaminants tabulated below. The loading in each case was 15 mg of contaminant per specimen (equivalent to 50 mg per square inch).

	Contaminant	Average Thickness
a.	Petroleum jelly, USP	0.0038"
b.	KEL-F 90 halocarbon grease	0.0017
c.	Pydraul AC hydraulic fluid	0.0021
d.	Polyurethane foam insulation	~ 0.010

The estimated film thicknesses in the tabulation is calculated from the densities of the materials if uniform thickness of film is assumed. The polyurethane films were foamed in place and the densities are much higher than typical for such foams. When spread in such a thin film the dissipation of heat from the polyurethane during curing is so great that relatively little foaming takes place. Under the circumstances the material is likely to be less reactive with fluorine than if it were fully foamed, however the simulation to accidental spillage is appropriate.

After application of contaminant, specimens were exposed to simulated passivation cycles as follows: (1) gaseous fluorine at 50 psig for one hour at 25°C (77°F), or (2) gaseous chlorine pentafluoride at one atmosphere (15 psia) for one hour at 25°C (77°F). Specimens were exposed in stainless steel bombs in sets of three samples which included only one type of contaminant in the bomb at a time.

The appearance of the specimens shown in Figure 17 following the simulated passivation treatments gives some indications concerning the relative reactivities of the various contaminants. Petroleum jelly USP, partially burned in chlorine pentafluoride as shown in Figure 17a leaving variable amounts of a carbonaceous residue on the impact specimens. In gaseous fluorine at 50 psig, the petroleum jelly reacted to form a semisolid skin on the surface of the film having a wrinkled appearance. This is in agreement with previous observations with petroleum jelly wherein chlorine pentafluoride was found to be more reactive than fluorine, even with the relatively large pressure difference.

KEL-F ([illegible] Figure 17b), except for partial liquefaction, is relatively unaffected by either chlorine pentafluoride or gaseous fluorine under the exposure conditions used. Conversion from a grease-like consistency to a viscous fluid is a normal consequence of the exposure, but there is no evidence of any extensive reaction or dimunition in amount of material

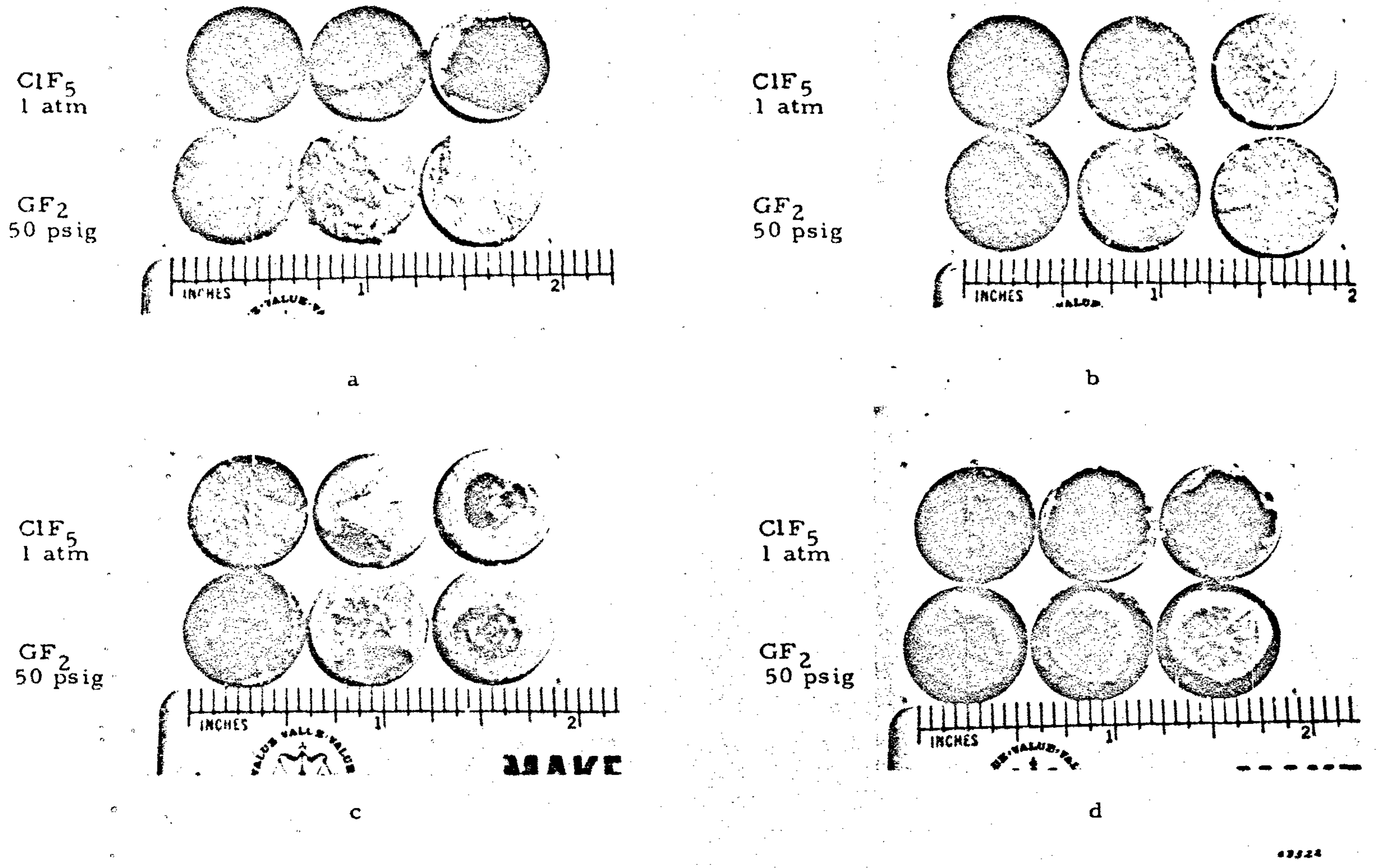


Figure 17. Impact Specimens After Passivation.

Pydraul AC hydraulic fluid (Figure 17c) is converted to a semisolid during exposure to chlorine pentafluoride and fluorine. The residues following exposure to chlorine pentafluoride are darker in color possibly signifying more reaction than in fluorine; however this observation is only of qualitative significance. Although the Pydraul as applied to the discs originally covered substantially the entire surfaces, after exposure the residues are drawn up in samll globules, which implies that moderately high local temperatures were produced during part of the exposure.

Polyurethane foam reacts extensively both in chlorine pentafluoride and gaseous fluorine. Less residue was left from exposure to the latter, which implies the reverse order of reactivity observed for petroleum jelly. Figure 17d clearly shows the extensive carbonaceous residues left distributed all over the coupons exposed to chlorine pentafluorine while only a minor carbonaceous residue is left around the rim of the coupons exposed to gaseous fluorine at 50 psig. The central parts of the latter are apparently completely free of any organic residue although the surface is very slightly discolored due to fluorination of the 316 stainless steel.

Following the exposures to oxidizer the specimens with organic residues were impact tested in the modified ABMA tester in liquid fluorine at -195°C (-320°F) at 72 ft-lb energy levels (Reference 6). All organic residues were impact sensitive. The data are summarized in Table XIV. Samples were run in triplicate except in cases where the violence of reaction dictated limiting the test to two specimens to lessen the chance that flying specimens and holders would interfere with subsequent tests. Blank tests are conducted at the beginning of the test program and after every 10 or 12 tests to ensure that the system is free of moisture or contamination which might lead to false reactions.

Reactions generally ranged from moderate to extreme except for the polyurethane coated specimens which had been exposed to gaseous fluorine at 50 psig. The reactions with these were faint, probably because only a very small reactive residue was left. Two specimens reacted in liquid fluorine before impact. One was a petroleum jelly residue and the other a polyurethane residue both from exposure to chlorine pentafluoride. These reactions were classed as extreme but the evaluation by the operator may be influenced by the premature ignition. Type of reaction is judged by the operator according to the size and intensity of the flash produced, but the presence or absence of the striker pin and drop weight will readily affect the visibility of the reaction flash.

5. IMPACT SENSITIVITY OF ORGANIC RESIDUES FOLLOWING HIGH PRESSURE PASSIVATION-200 PSIG

To determine the impact sensitivity of the organic residues, 5/8" diameter stainless steel discs were coated on one side with 15 mg of each of the following: (1) petroleum jelly USP; (2) KEL-F 90; and (3) Pydraul AC. Polyurethane foam was omitted from this series of tests because of the possibility of ignition of the coupon at the high fluorine pressure. Specimens,

TABLE XIV. IMPACT SENSITIVITY OF ORGANIC RESIDUES.

Oxidizer: Liquid Fluorine
Samples: Organic Residues on 316 Stainless Steel
Test Temperature: -320°F
Atmosphere: Dry Gaseous Nitrogen
Impact Energy: 72 ft - lb.

Drop No.	Contaminant	Exposed to	Type of Reaction				Remarks
			Extreme	Moderate	Faint	None	
1	None	———				X	Blank Test
2	Petroleum Jelly	GF_2 - 50 psig		X			
3	Petroleum Jelly	GF_2 - 50 psig		X			
4	Petroleum Jelly	ClF_5 - 1 atm.		X			
5	Petroleum Jelly	ClF_5 - 1 atm.	X				Reacted before impact
6	KEL-F 90	GF_2-50 psig		X			
7	KEL-F 90	GF_2-50 psig		X			
8	KEL-F 90	GF_2-50 psig		X			
9	KEL-F 90	ClF_5-1 atm.		X			
10	KEL-F 90	ClF_5-1 atm.		X			
11	None	———				X	Blank Test
12	Pydraul AC	GF_2-50 psig		X			
13	Pydraul AC	GF_2-50 psig		X			
14	Pydraul AC	ClF_5-1 atm.			X		
15	Pydraul AC	ClF_5-1 atm.			X		
16	Pydraul AC	ClF_5-1 atm.			X		
17	Polyurethane	GF_2- 50 psig			X		
18	Polyurethane	GF_2- 50 psig			X		
19	Polyurethane	GF_2- 50 psig			X		
20	Polyurethane	ClF_5-1 atm.	X				Reacted before impact
21	Polyurethane	ClF_5-1 atm.		X			
22	None	———				X	Blank Test

in sets of three, contained in aluminum impact cups, were exposed to fluorine gas at 200 psig at room temperature for one hour. Separate specimens, again in triplicate were exposed to fluorine gas at 200 psig for one hour at 200°F. Extensive reactions occurred with all materials, generally of the degree indicated in Appendix I, Figure 16 and Table IX, involving the 0.5" x 2" test coupons.

Specimens, with residues intact, were subjected to impact sensitivity tests in the modified ABMA tester in liquid fluorine at -195°C (-320°F) at the 72 ft-lb energy level (Reference 6). All residues from the exposure at 200 psig at room temperature were impact sensitive. Of the nine specimens exposed at 200 psig and 200°F, five yielded positive results on impact test. The data are presented in Table XV. Therefore under extreme exposure conditions, reaction residues are left even though partial burning of the contaminant has occurred.

TABLE XV. IMPACT SENSITIVITY OF RESIDUES FROM HIGH PRESSURE (200 psig) EXPOSURE.

Oxidizer: Liquid Fluorine
Samples: Organic Residues on 304 Stainless Steel
Test Temp.: -320°F
Atmosphere: Dry Nitrogen
Impact Energy: 72 ft - lb.

			Type of Reaction				
Drop No.	Contaminant	Exposed to	Extreme	Moderate	Faint	None	Research
1	None	—				X	Blank Test
2	Petr. Jelly USP	GF_2, R. T. 200 psig		X			
3	Petr. Jelly USP	↓		X			
4	KEL-F 90				X		
5	KEL-F 90				X		
6	Pydraul AC			X			
7	Pydraul AC			X			
8	None	—				X	Blank Test
9	Petr. Jelly USP	GF_2, -200°F 200 psig				X	
10	Petr. Jelly USP	↓				X	Small reaction before impact - none on impact
11	Petr. Jelly USP			X			
12	KEL-F 90				X		
13	KEL-F 90					X	
14	KEL-F 90				X		
15	Pydraul AC			X			
16	Pydraul AC					X	
17	Pydraul AC			X			
18	None	—				X	Blank Test

APPENDIX III

CORROSION OF PASSIVATED SURFACES

1. TEST METHOD

In work described before (Reference 8) corrosion test coupons (1" x 3") of 2014 aluminum, Monel 400, nickel 200, 316 stainless steel, and copper were passivated by various techniques, then exposed to 90-95% relative humidity at 160°F to determine relative corrosion rates. Weight changes of specimens in one week were generally less than 2 mg per specimen and in many cases no weight changes could be detected at all. Therefore, the extent of corrosion was too small to discriminate among various passivation methods.

A more rigorous accelerated corrosion test was devised to induce greater corrosion; this could then be used as a basis of comparison for passivation methods. At the same time it was desirable that the accelerated corrosion test simulate to a degree the corrosion conditions that might be encountered in actual practice. The accelerated test procedure initially developed involved exposure of passivated test coupons and unpassivated controls to the vapor of 10% aqueous HF solution in a closed system at 100°F. Exposure times of 24 hours were used. The detailed procedure has been described previously (Reference 8).

2. RESULTS AND DISCUSSION

Sets of test coupons (3/4" x 3") of the five alloys were given various passivation treatments then subjected to the accelerated corrosion test. For each set of specimens a set of unpassivated controls was exposed at the same time. The relative corrosion rates are based on the increase in weight of specimens during exposure to the accelerated corrosion test.

The passivation procedures investigated are tabulated below together with reference to the corresponding figure which presents the results of the test.

a. Passivation in gaseous fluorine at one atmosphere at room temperature for 24 hours. Evacuated for 30 minutes at pressure of approximately 1 torr at room temperature. Refer to Figure 18.

b. Passivation in gaseous fluorine at one atmosphere at room temperature for one hour. Evacuated for 30 minutes in vacuum oven at pressure of 1.5 torr at 200°F. Refer to Figure 19.

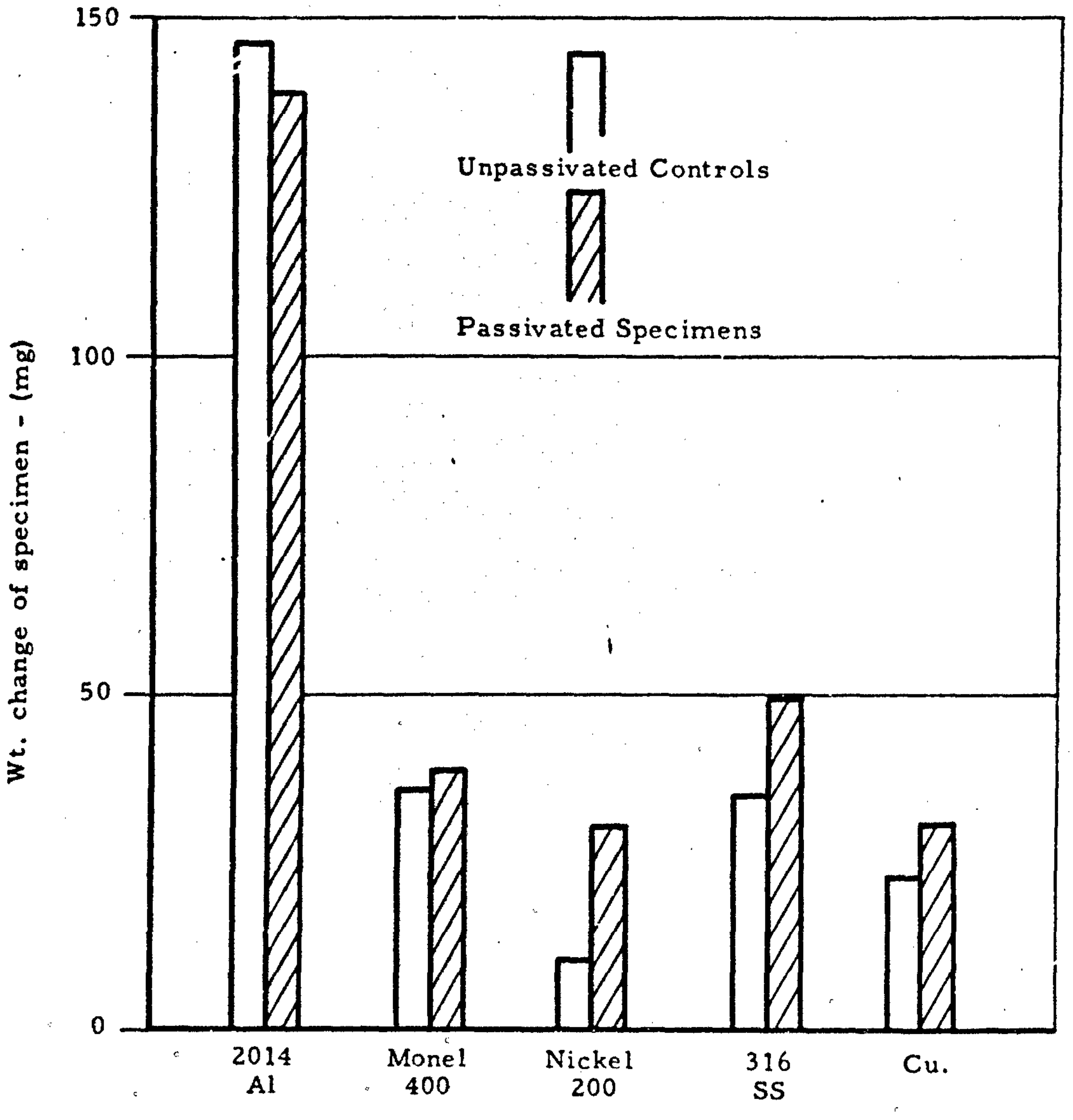


Figure 18. Relative Corrosion of Passivated and Unpassivated Coupons. Fluorine Passivation.

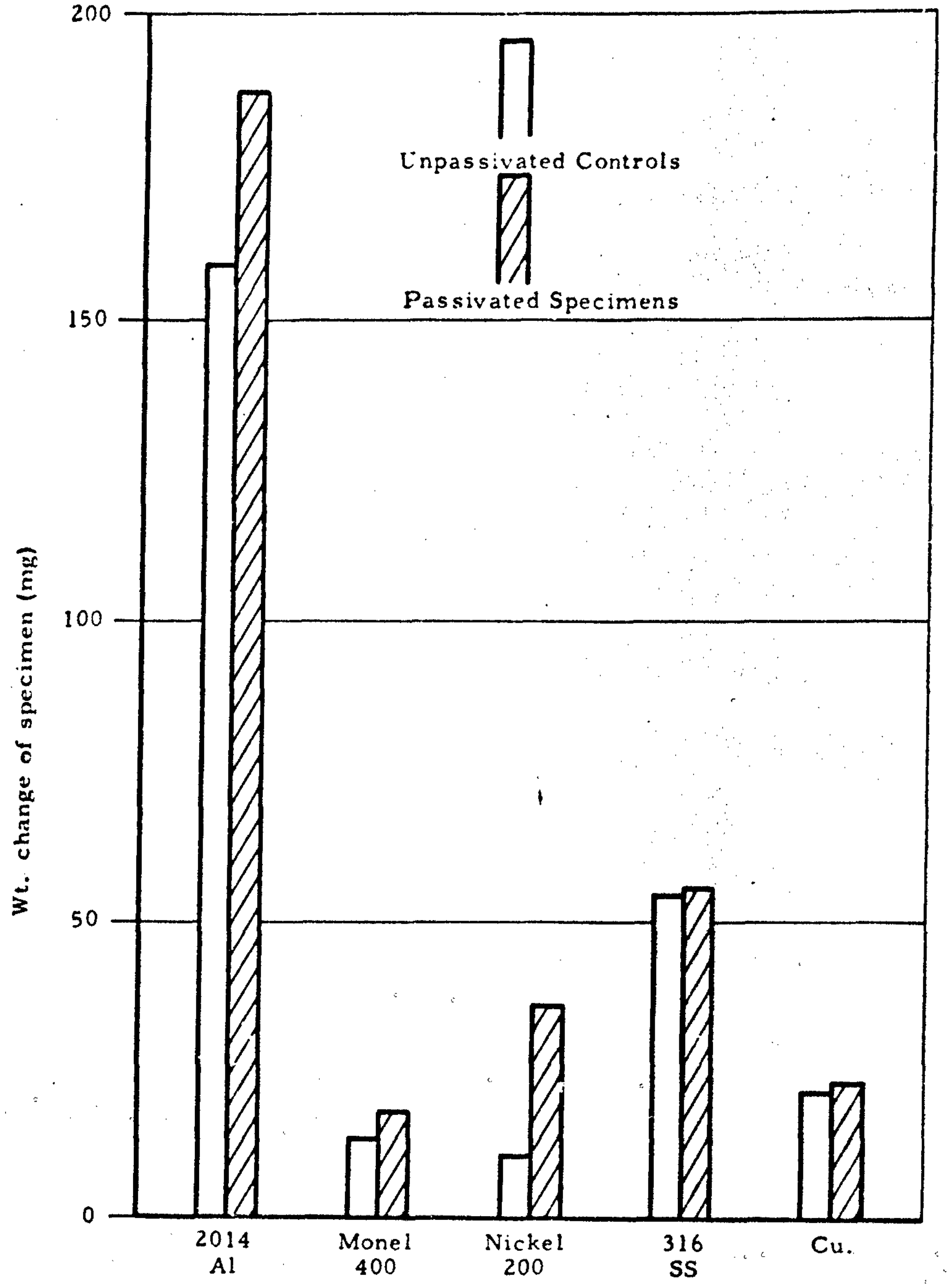


Figure 19. Relative Corrosion of Passivated and Unpassivated Coupons. Evacuation at 200°F following passivation.

c. Passivation in gaseous chlorine pentafluoride at one atmosphere pressure at room temperature for one hour. Evacuated for 30 minutes at pressure of approximately 1 torr at room temperature. Refer to Figure 20.

d. Passivation in gaseous chlorine pentafluoride at one atmosphere pressure at room temperature for one hour followed by evacuation in vacuum oven for 30 minutes at pressure of 1.5 torr at 200°F. Refer to Figure 21.

e. Passivation in gaseous chlorine pentafluoride at one atmosphere pressure at room temperature for one hour. After evacuation for 15 minutes, liquid nitrogen was condensed in the system at -195°C (-320°F) to completely cover passivated coupons. Concurrently liquid nitrogen was condensed on unpassivated control coupons in a separate system. The liquid nitrogen was allowed to boil off and the gas vented from the system. After the specimens warmed to room temperature they were evacuated for 15 minutes at about 1 torr pressure. Refer to Figure 22.

f. The passivation and post treatment of test specimens and controls were identical to those outlined in (e.) above except that carbon tetrafluoride was used instead of liquid nitrogen for rinsing and purging. For data refer to Figure 23.

Although the data produced during this general survey outlined above, indicate certain interesting trends, it is apparent that the variation from run to run is too large to permit definite conclusions. This is particularly true of the 2014 aluminum specimens where the corrosion film is so thick that some flaking off may have occurred during the exposure. The other alloys apparently have thin adherent films, but considering only the corrosion of the control specimen, there is great variation from one exposure test to another. Copper gave the most consistent results; all weight gains for control specimens fell in the range from 21 to 28 mg. The weight gains for the nickel controls, on the other hand, ranged from 11 to 49 mg. In view of these results it became necessary to devote further study to the corrosion test in an effort to eliminate factors contributing to scatter of the data.

The data presented in this section indicate that in most cases coupons which have been prepassivated in fluorine or chlorine pentafluoride suffer greater corrosion during the accelerated test than unpassivated controls. The use of liquid nitrogen and liquid carbon tetrafluoride to rinse and purge specimens appeared to reduce the secondary corrosion more nearly to that of unpassivated controls. Baking out specimens at 200°F in vacuum following passivation does not have a significant effect on secondary corrosion. These results must be viewed in light of additional data to be presented in subsequent sections. The data for aluminum may be completely unreliable

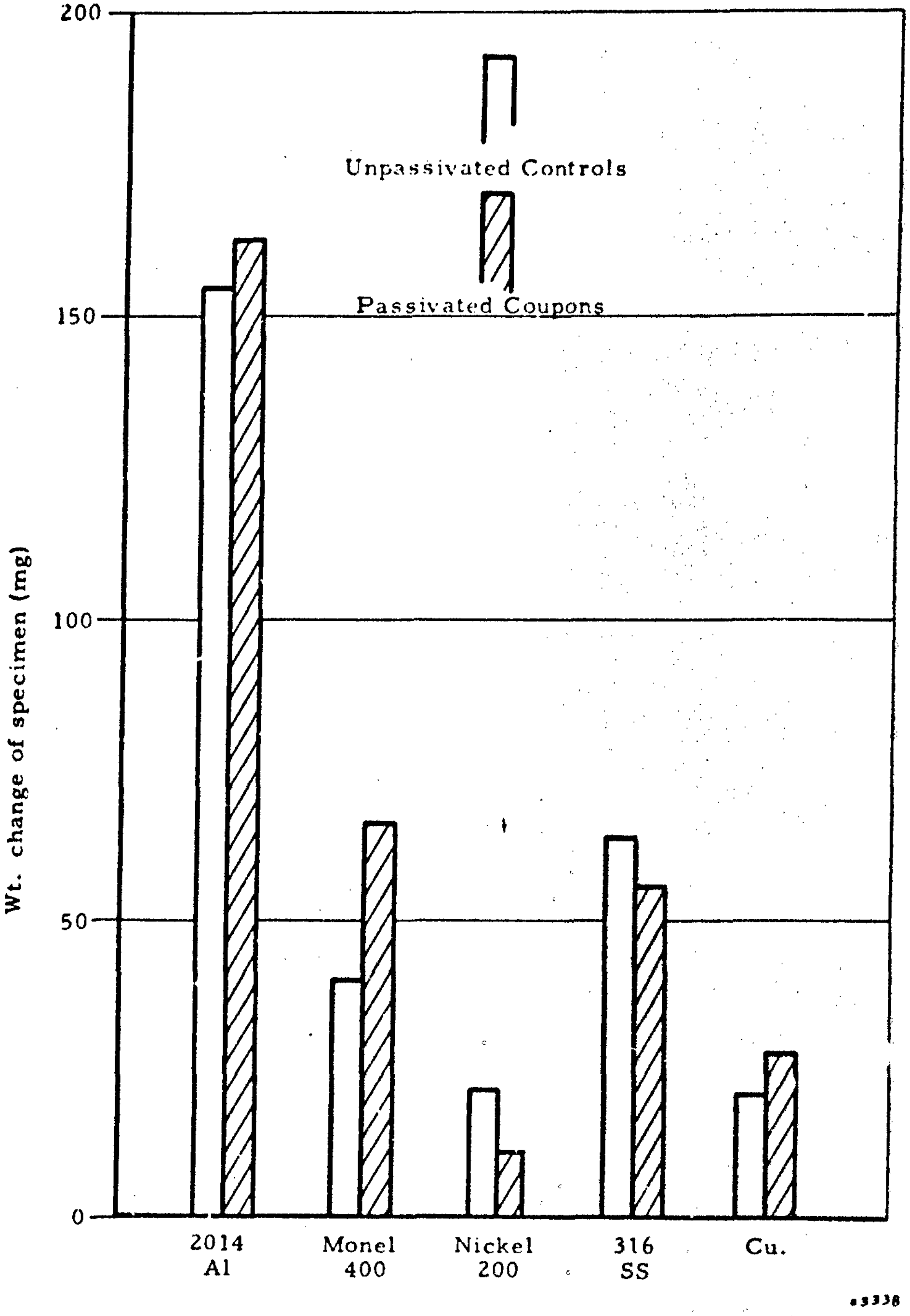


Figure 20. Relative Corrosion of Passivated and Unpassivated Specimen. ClF_5 Passivation

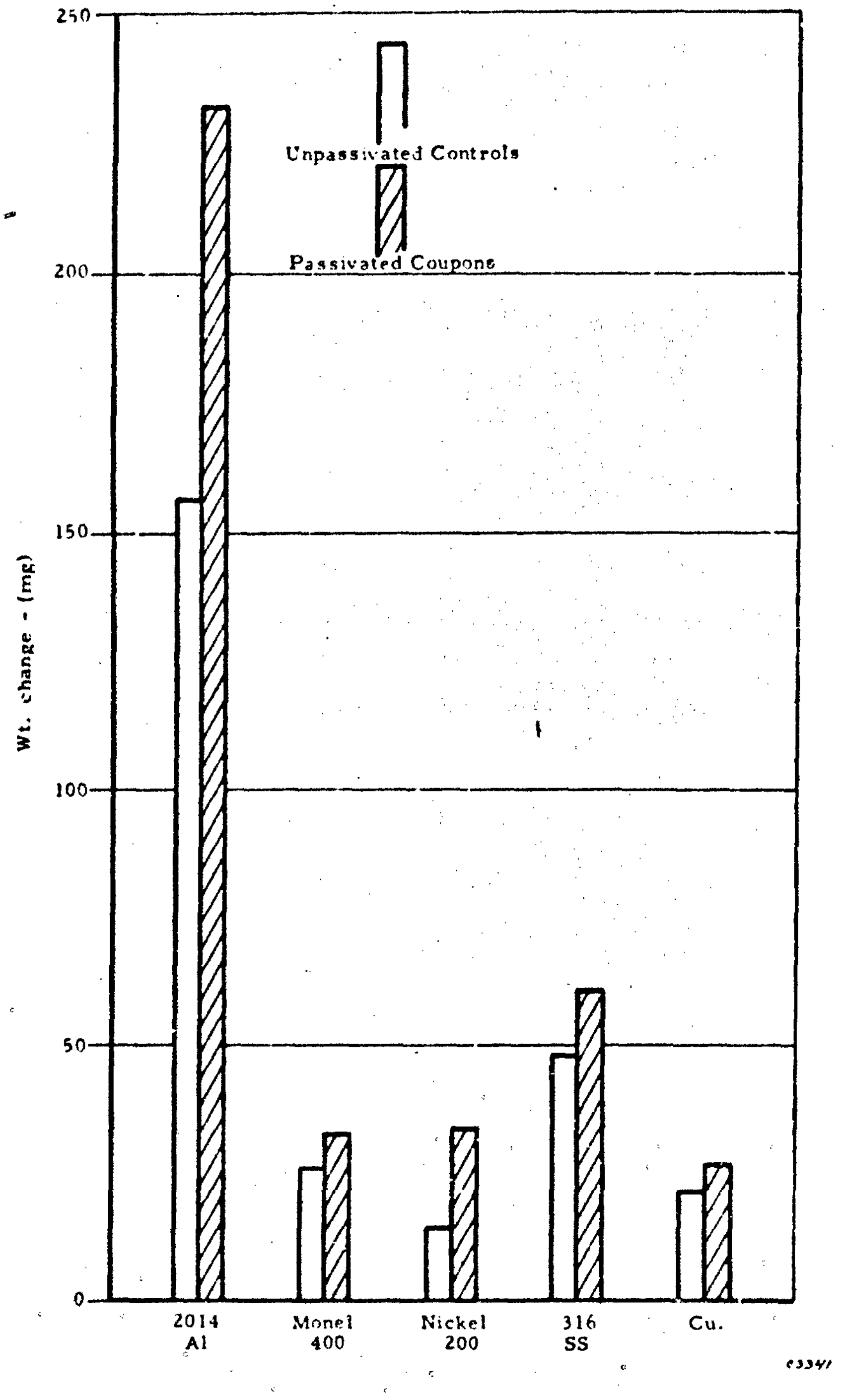


Figure 21. Relative Corrosion of Passivated and Unpassivated Coupons. ClF_5 Passivation with vacuum bakeout at 200°F

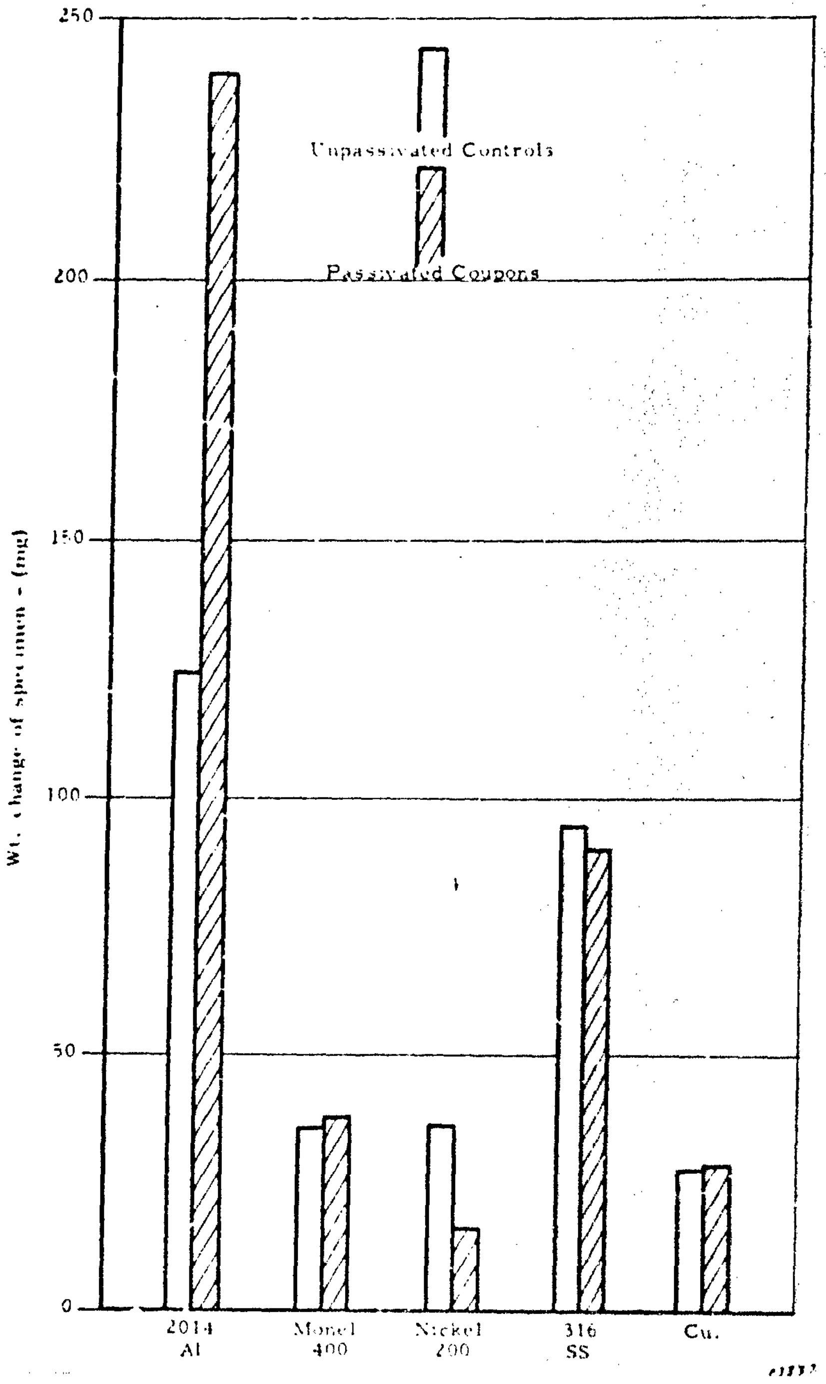


Figure 22. Relative Corrosion of Passivated and Unpassivated Coupons. ClF_5 Passivation, LN_2 Rinse

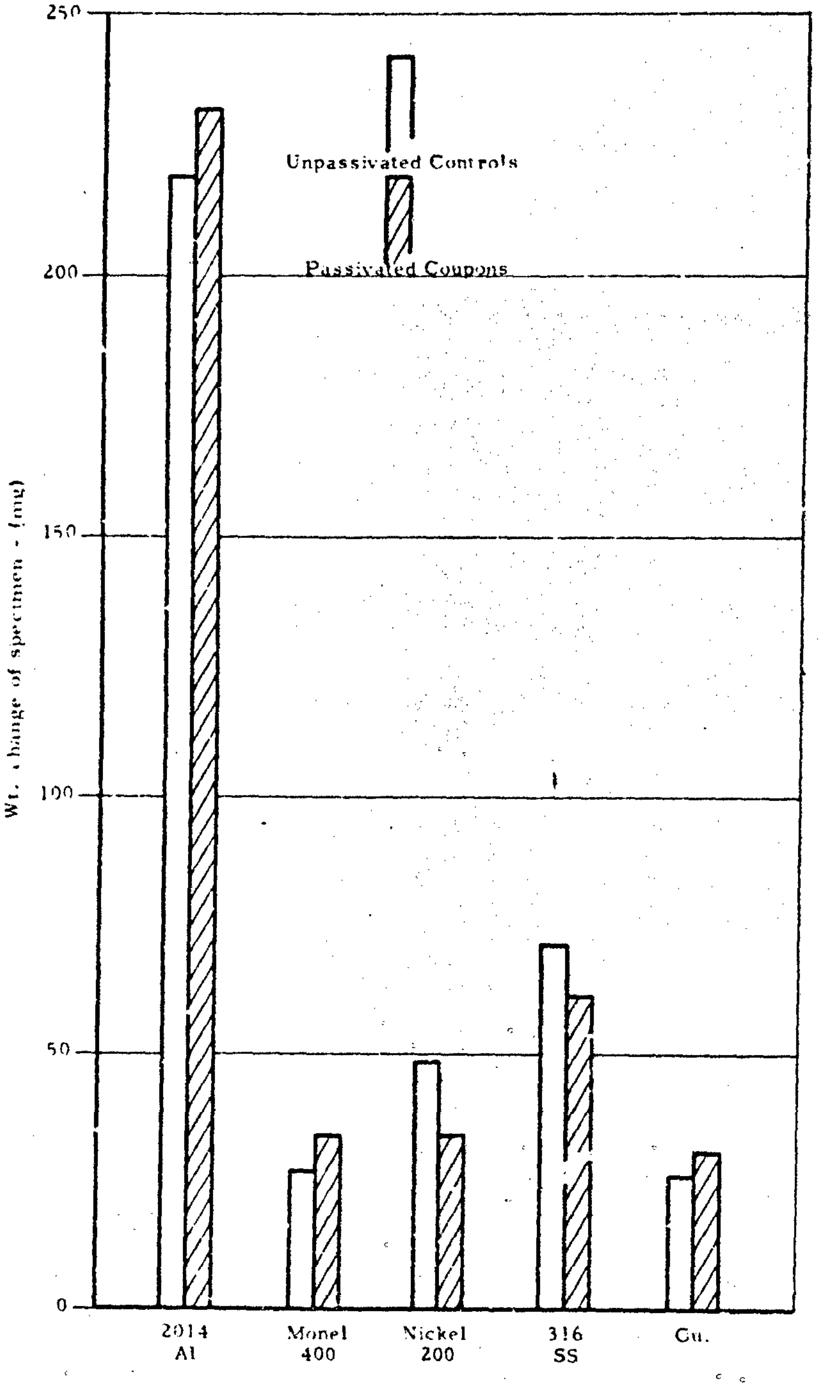


Figure 23. Relative Corrosion of Passivated and Unpassivated Coupons. ClF_5 Passivation, CF_4 Rinse

due to the very thick corrosion scale and the probability of flaking during handling.

3. INVESTIGATION OF HF CORROSION OF ALLOYS

The scatter of corrosion test data cited above prompted additional study of HF corrosion. A review of test data and procedures revealed several possible sources of error. Some of them were: (1) lack of temperature control in environmental chamber; (2) potential dripping of condensate on specimens during exposure; (3) inefficient circulation of vapor in environmental chamber; and (4) loss of HF solution via evaporation during the relatively long (viz. 24 hour) exposure. Also, no information was available concerning the extent of corrosion as a function of time.

The accelerated corrosion test was modified as follows: (1) the chamber was modified to prevent dripping of condensate on specimen; (2) a more efficient fan for circulation of vapor was employed· (3) better temperature control was achieved by placing a thermocouple in a protective well directly inside the chamber; and (4) the duration of the test was shortened to produce somewhat thinner corrosion films. To compensate for the shorter time of exposure, the test temperature was increased to 130°F.

Five metal corrosion coupons (3/4" x 3") were subjected to the modified corrosion test described. Time of exposure was 4 hours and the weight change data are presented in Table XVI. Corrosion films were observed to be more uniform and adherent than those obtained previously.

Attack of the metal by HF in the presence of water vapor results in formation of a hydrated metal fluoride film with corresponding weight increase. The fluoride films are water soluble and can readily be removed by treatment of the specimens with hot water. This was done for the specimens listed in Table XVI and after drying the specimens the weight losses compared to the original specimen weights were obtained. The arithmetic difference between the weight gain due to film formation and the weight loss due to metal present in the fluoride film represents the weight of metal fluoride produced during the corrosion test. These weights are listed in Table XVII and are compared with the theoretical weights of metal fluoride based on the weight loss of metal and the assumed metal fluoride composition. The fairly good agreement between observed and theoretical weights indicates that the assumptions concerning the composition of corrosion products are substantially correct. Data on penetration are presented in Table XVII to show that corrosion rates for 2014 aluminum are roughly ten times that for the other alloys. Monel, nickel, and copper are most resistant to HF attack.

Another significant factor is the rate of attack as a function of time for the individual alloys. This was determined for the five alloys by continuously weighing 3/4" x 3" coupons while suspended by a platinum wire in the environmental chamber containing vapor of 10% aqueous HF at 120°F.

TABLE XVI. MODIFIED ACCELERATED CORROSION TEST - VAPOR OF 10% AQUEOUS HF SOLUTION; 130°F; 4 HOURS.

Metal Or Alloy	Initial Wt. (g)	Final Wt. (g)	Δw (mg)	Wt. After Dissolving Corrosion Film (g)	Δw From Initial Wt. (mg)
2014 Al	3.9064	3.9883	+81.9	3.8838	-22.6
Monel 400	7.8884	7.9012	+12.8	7.8818	- 6.6
Nickel 200	8.3776	8.3895	+11.9	8.3711	- 6.5
316 SS	7.2369	7.2539	+17.0	7.2274	- 9.5
Copper	8.0694	8.0799	+10.5	8.0611	- 8.3

TABLE XVII. THEORETICAL AND ACTUAL WEIGHTS OF METAL FLUORIDE CORROSION FILMS AND CALCULATED PENETRATIONS

Metal or Alloy	Wt. Metal Loss of Coupon (mg)	Assumed Composition Of Metal Fluoride	Theoretical Wt. Metal Fluoride (mg)	Actual Wt. Metal Fluoride (mg)	Penetration Mils/Year*
2014 Al	22.6	$AlF_3 \cdot 3H_2O$	115	104.5	172
Monel 400	6.6	$CuF_2 \cdot 2H_2O + NiF_2 \cdot 4H_2O$	17.1	19.4	16.4
Nickel 200	6.5	$NiF_2 \cdot 4H_2O$	18.7	18.4	16.0
316 SS	9.5	$FeF_3 \cdot 3H_2O$	28.8	26.5	26.0
Copper	8.3	$CuF_2 \cdot 2H_2O$	18.0	18.8	20.4

*Calculated from:

$$\text{Penetration (mils/Year)} = 5.27 \times 10^5 \times \frac{\text{Wt. Loss (g)}}{\text{area (in}^2\text{)} \times \text{density (g/cc)} \times \text{time (hr)}}$$

The weight gain data are presented in Figures 24-28. Each curve has an induction period at the start during which time the vapor concentration and temperature are building up. With the exception of aluminum, none of the alloys reaches a limiting film thickness in 5 or 6 hours. The metal reaction rate of aluminum is very rapid and slows down rather abruptly after 2 hours exposure. This could be due to a change in mechanism or flaking off of the film. Some of the other alloys — notably copper — show inflection points which may or may not be due to errors in weighing or inadvertent changes of environment during a particular run.

The degree of reproducibility of the accelerated corrosion test was investigated by exposing five samples each of 316 stainless steel and Monel 400 simultaneously. The observed weight changes are recorded in Table XVIII. There still exists an undesirably large scatter in weight increases for supposedly identical coupons. These variations are probably related to factors such as surface treatment, position in the chamber, and possibly alloy composition. Further evaluation appeared unprofitable and it was considered that any inferences to be drawn from corrosion data should be based on statistical analysis of a number of replicate samples.

4. APPLICATIONS OF MODIFIED CORROSION TEST

Five 3/4" x 3" 316 stainless steel corrosion test specimens were passivated in gaseous fluorine at one atmosphere pressure for 24 hours at room temperature. The fluorine was pumped off and the samples were evacuated at less than 1 torr pressure for 30 minutes. The five passivated coupons together with five unpassivated control specimens were subjected to the modified corrosion test in the vapor of 10% aqueous HF at 130°F for 6 hours.

The observed weight changes for the passivated coupons and the unpassivated controls are shown graphically in Figure 29. The question of whether there exists a significant difference between the sets is best answered by a statistical analysis of the data. Such an analysis is presented in Table XIX. The results of the analysis show that there is a significant difference and that the passivated samples undergo slightly greater corrosion than the unpassivated controls.

A set of five 316 stainless steel coupons (3/4" x 3") were cleaned and passivated in gaseous fluorine at one atmosphere pressure for one hour at room temperature. Following the passivation the samples were pumped down to less than 1 torr and left under continuous vacuum for 72 hours. After this time they were corrosion tested in aqueous HF vapor and the weight gains compared with a set of five unpassivated control coupons. The weight gains are presented graphically in Figure 30 and the statistical data in Table XX. Inasmuch as the means fall very close together it is obvious even without completing the statistical analysis, that there is no significant difference in corrosion of the passivated samples and unpassivated controls. Therefore, the lengthy evacuation has reduced the propensity of the

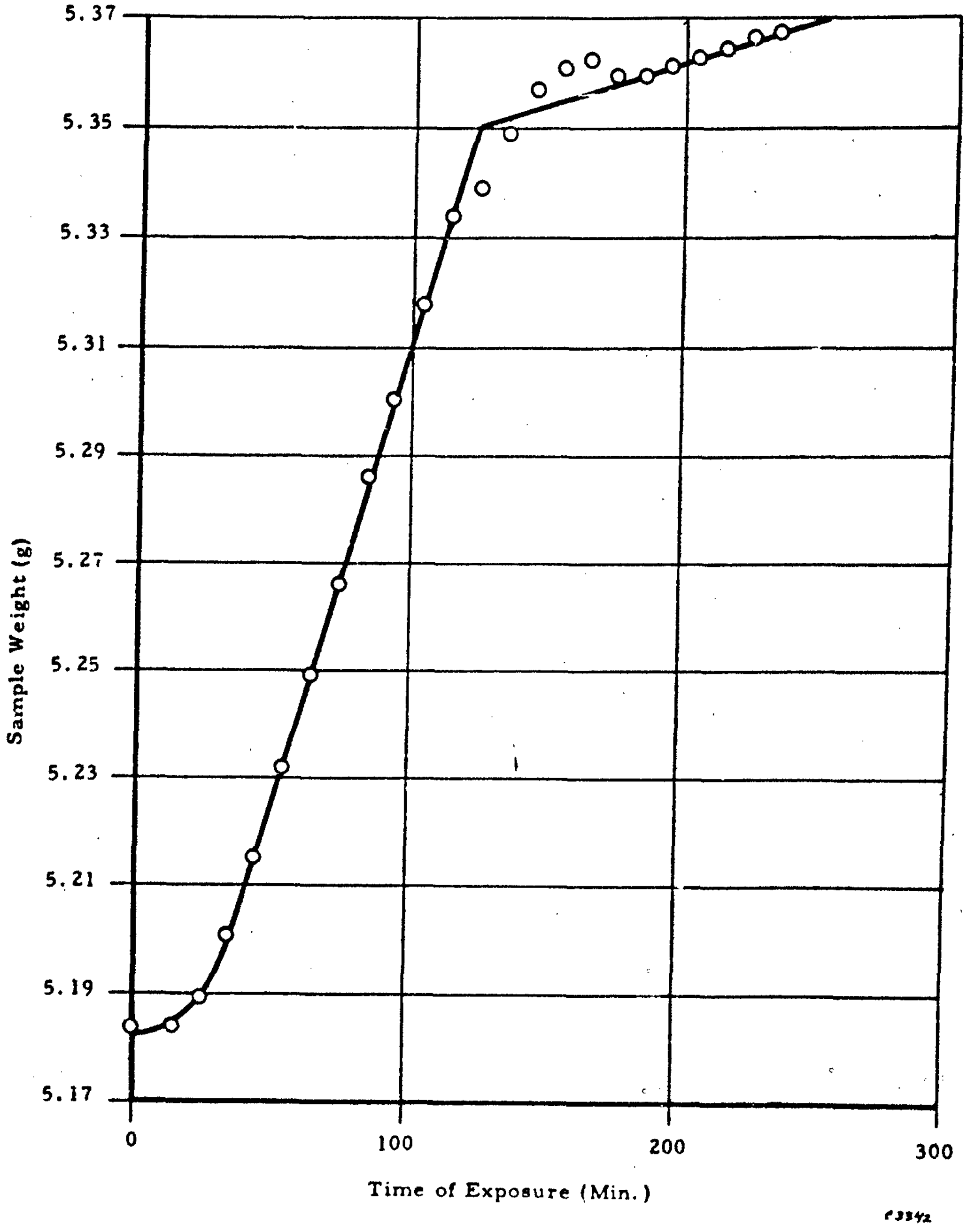


Figure 24. Corrosion of 2014 Al Coupon (3/4" x 3") in Vapor of 10% HF Solution at 120°F

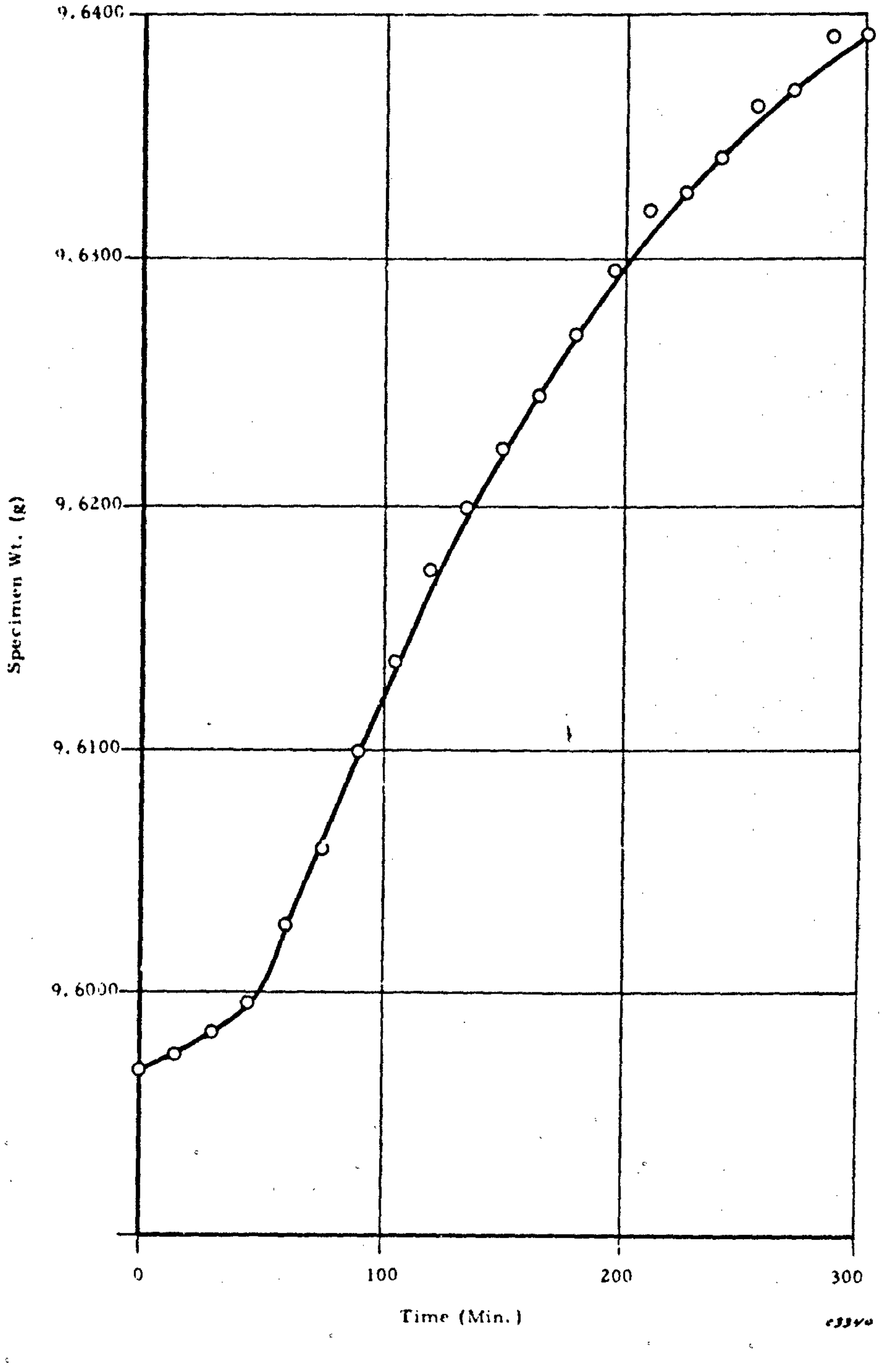


Figure 25. Corrosion of Monel in Vapor of 10% HF at 120°F (3/4" x 3")

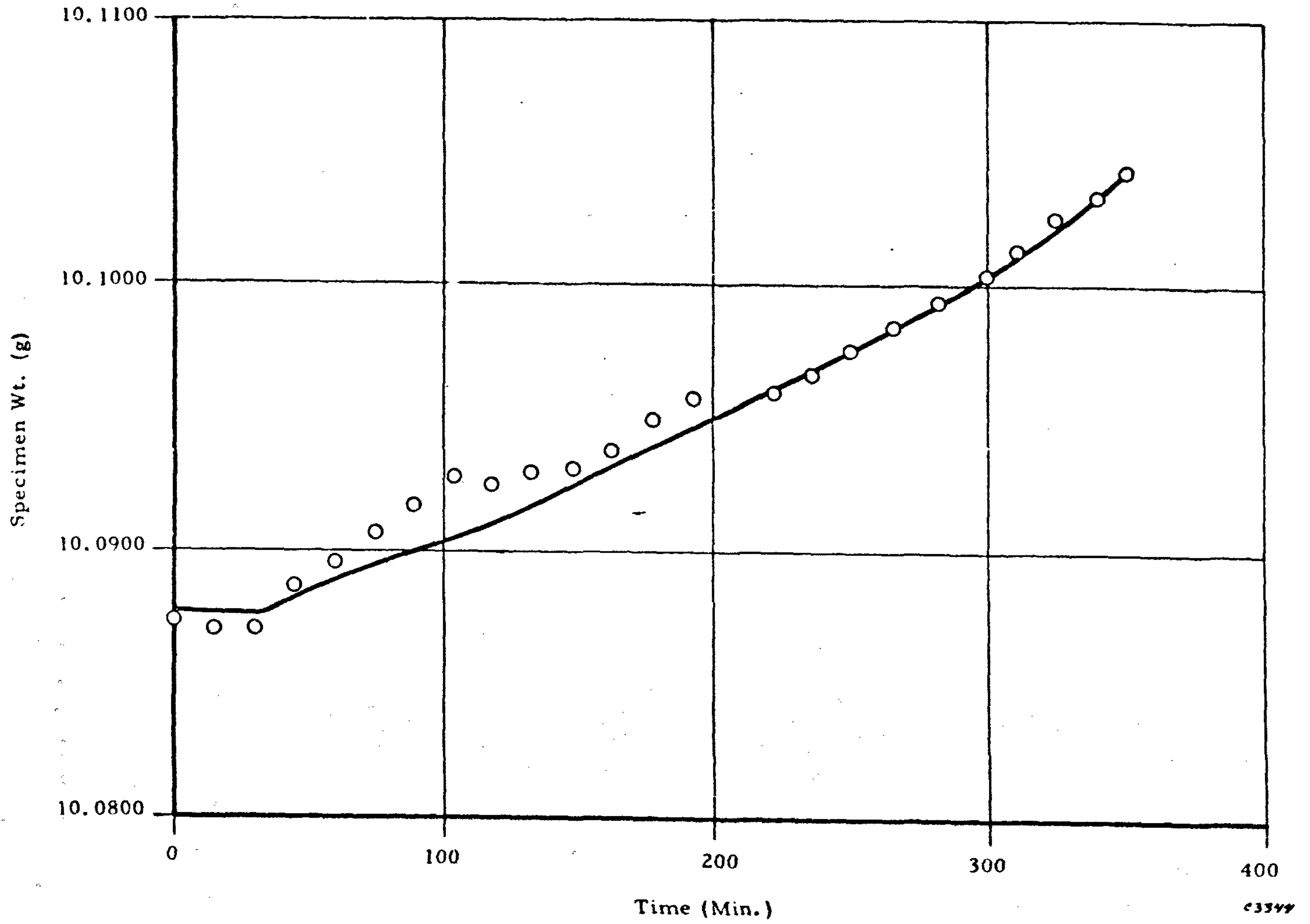


Figure 26. Corrosion of Nickel in Vapor of 10% Aqueous HF at 120°F (3/4" x 3" Coupon)

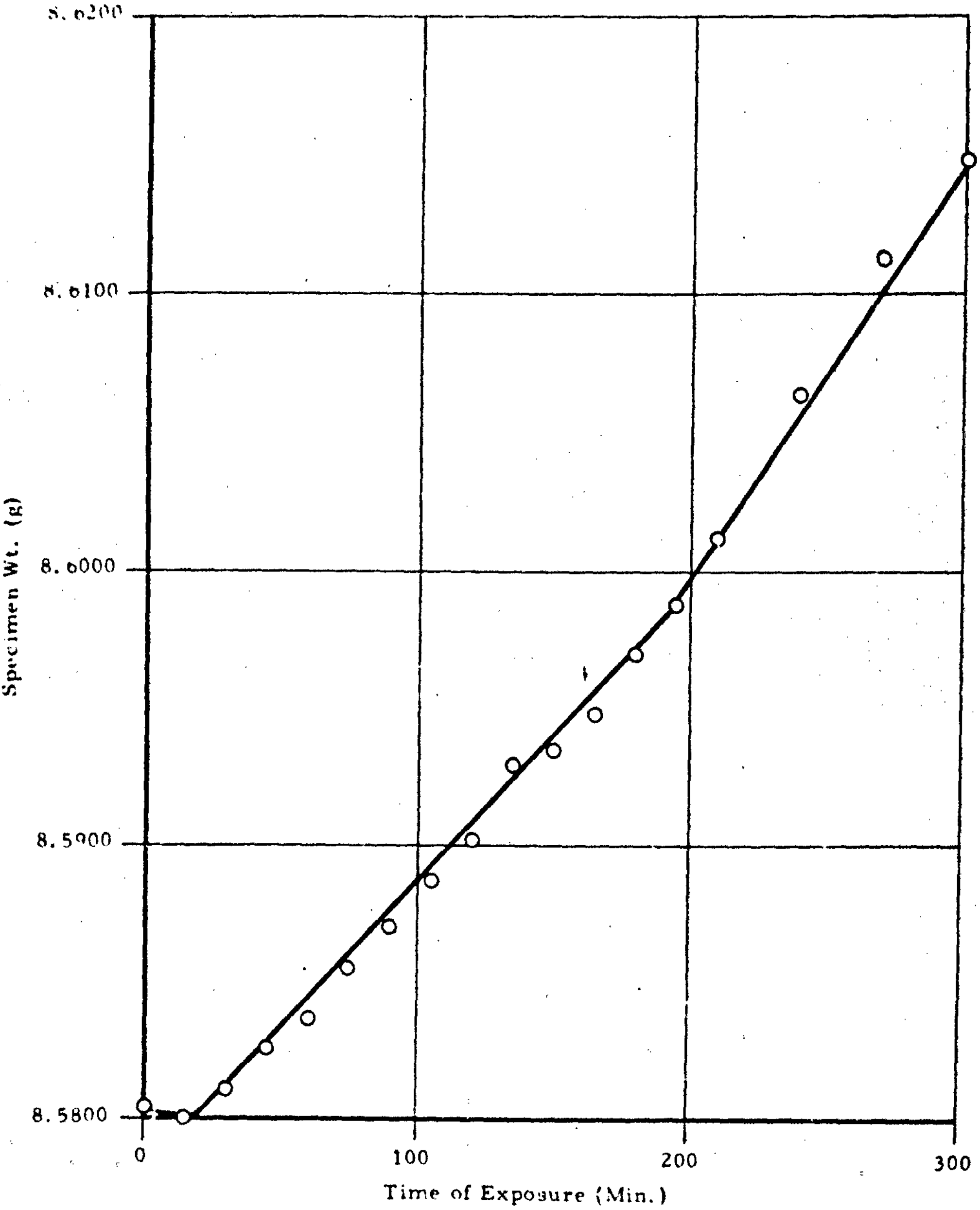


Figure 27. Corrosion of 316 Stainless Coupon (3/4" x 3") in Vapor of 10% HF Solution at 120°F

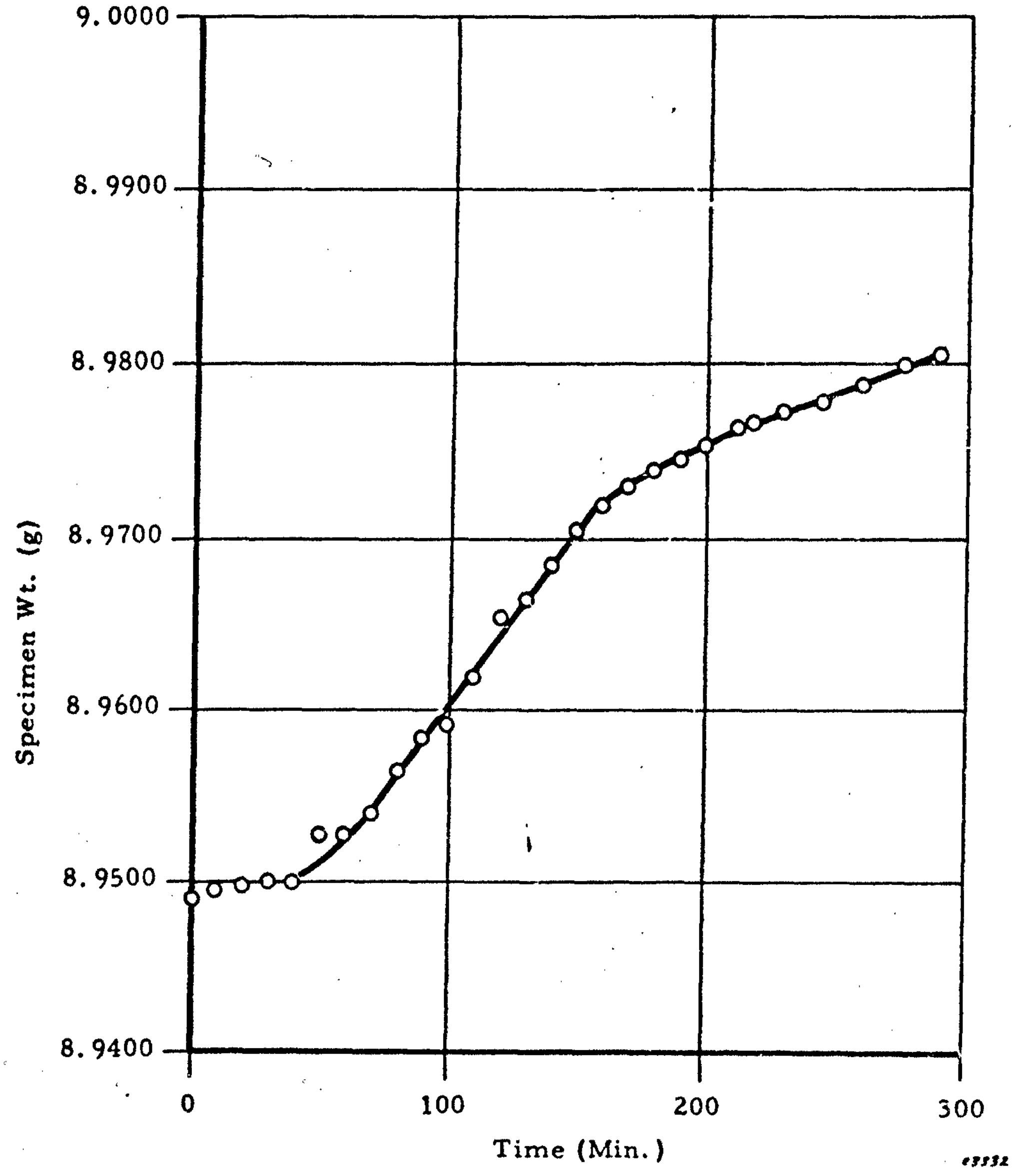


Figure 28. Corrosion of Copper (3/4" X 3") in Vapor of 10% HF at 120°F

TABLE XVIII. REPRODUCIBILITY OF ACCELERATED CORROSION TEST.
10% AQUEOUS HF VAPOR; 6 HOUR EXPOSURE TIME; 130°F.

Spec.	Initial Wt. (g)	Final Wt. (g)	Δw (mg)	
316 SS	6.4317	6.4541	+22.4	
316 SS	6.7853	6.8061	+20.8	
316 SS	7.2176	7.2395	+21.9	
316 SS	7.1204	7.1384	+18.0	
316 SS	6.7127	6.7390	+26.3	
			Mean	+21.9 mg
Monel 400	6.9553	6.9675	+12.2	
Monel 400	6.9119	6.9226	+10.7	
Monel 400	7.2081	7.2200	+11.9	
Monel 400	6.9248	6.9361	+11.3	
Monel 400	7.0255	7.0415	+16.0	
			Mean	+12.4 mg

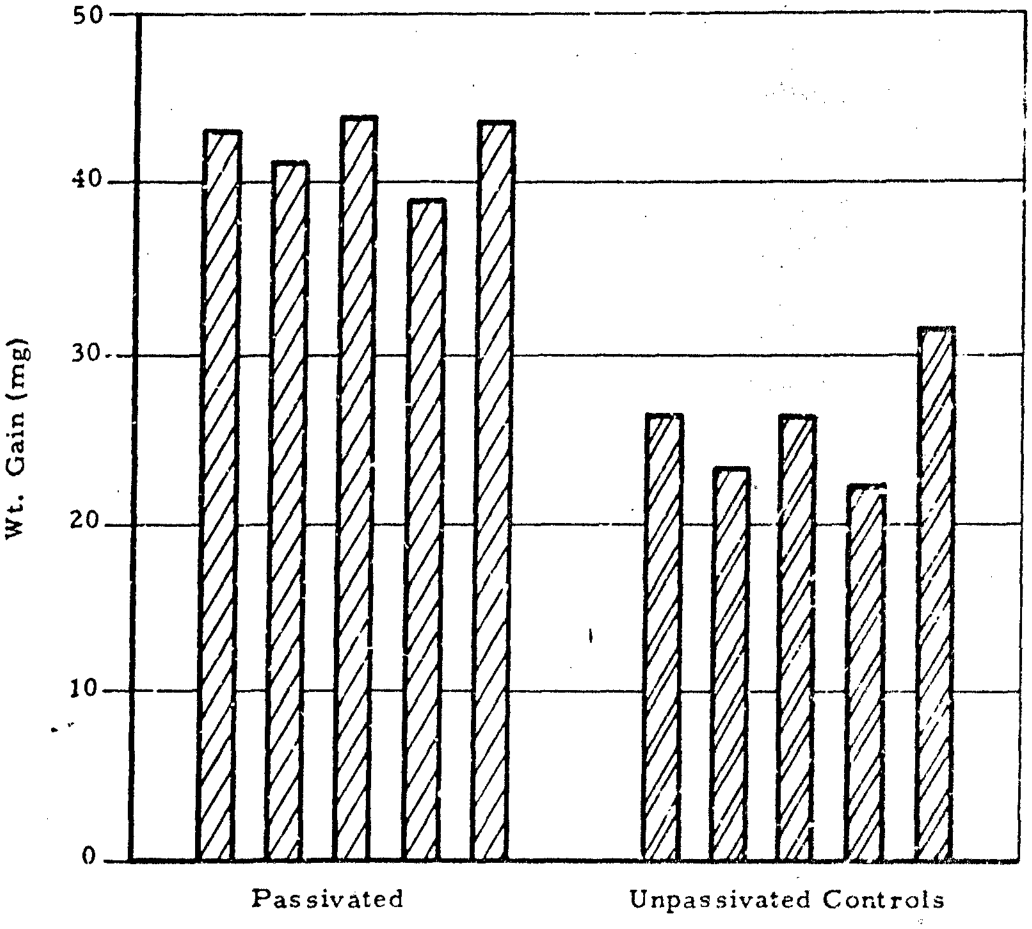


Figure 29. Relative Corrosion - 316 Stainless Steel Coupons 3/4 "x 3" Passivation in GF_2 at 1 Atm. for 24 Hr., Followed by 30 Minute Pump Down

TABLE XIX. ANALYSIS OF CORROSION DATA.

Passivated Samples

Sample	Δw (mg)	Deviation From Mean - χ	χ^2
1	43.2	1.0	1.0
2	41.3	0.9	0.8
3	43.9	1.7	2.9
4	38.8	3.4	11.6
5	43.7	1.5	2.2
			18.5

Mean ($M\chi$) = 42.2

$$\text{Variance} = \nu = \sigma_x^2 = \frac{18.5}{N-1} = \frac{18.5}{4} = 4.63$$

Standard Deviation $= \sigma_x = 2.15$ ←

Unpassivated Controls

Sample	Δw (mg)	Deviation From Mean - y	y^2
1	26.4	0.1	0.0
2	23.5	3.0	9.0
3	26.4	0.1	0.0
4	22.7	3.8	14.4
5	33.5	7.0	49.0
			72.4

Mean (M_y) = 26.5

$$\text{Variance} = \nu = \sigma_y^2 = \frac{72.4}{4} = 18.1$$

Standard Deviation $= \sigma_y = 4.25$ ←

(Continued)

TABLE XIX. ANALYSIS OF CORROSION DATA. (Continued)

"t" Test

Passivated Samples	Unpassivated Controls
$N_x = 5$	$N_y = 5$
$M_x = 42.2$	$M_y = 26.5$
$\sigma_x = 2.15$	$\sigma_y = 4.25$

$$\sigma_{M_x} = \frac{\sigma_x}{\sqrt{N}} = 0.96 \qquad \sigma_{M_y} = \frac{\sigma_y}{\sqrt{N}} = 1.90$$

$$\sigma_{M_x - M_y} = \sqrt{\sigma_{M_x}^{2} + \sigma_{M_y}^{2}} = \sqrt{.92 + 3.62} = 2.14$$

$$t = \frac{M_x - M_y}{\sigma_{M_x - M_y}} = \frac{15.7}{2.14} = 7.33$$

t is greater than 3 therefore the difference in means is certainly significant.

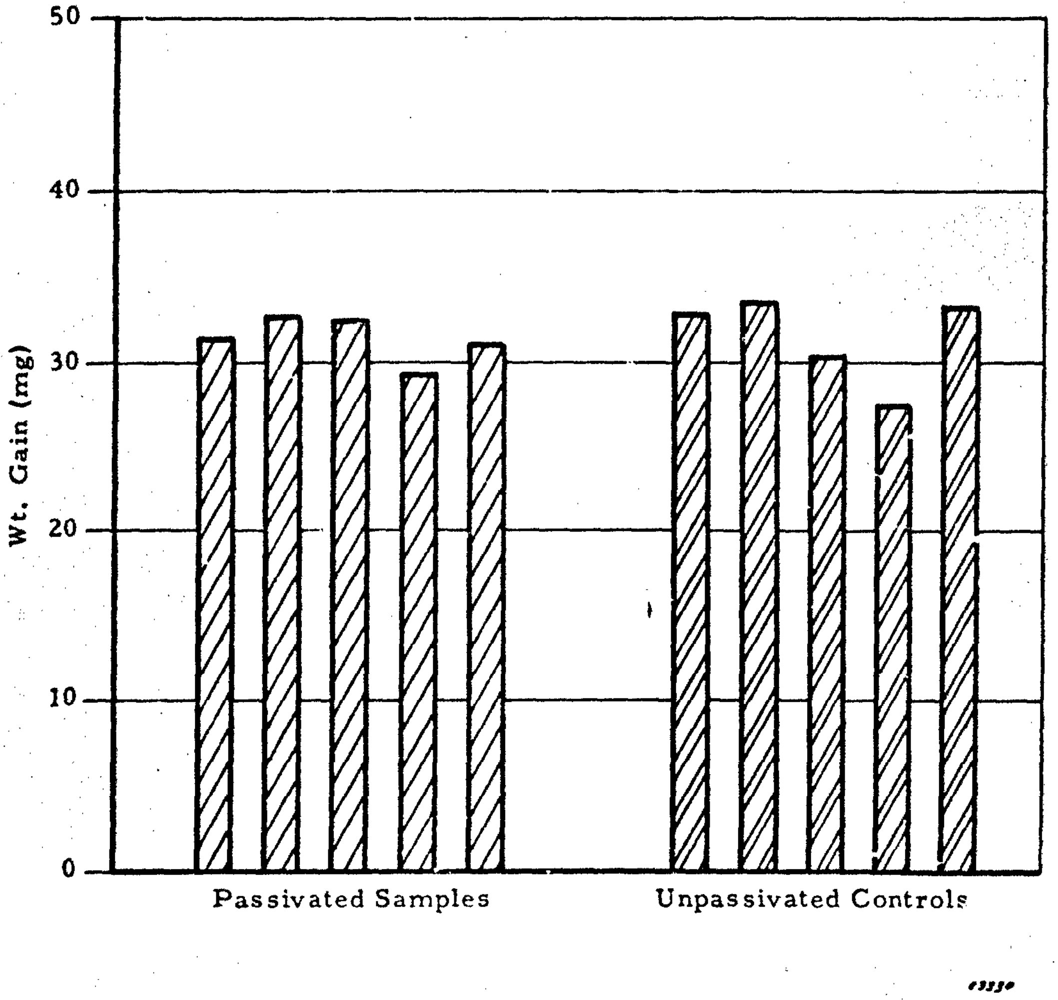


Figure 30. Relative Corrosion. Passivation in GF_2 for 1 Hr. at One Atmosphere Pressure at Room Temperature Followed by Pumpdown and Storage of Specimen Under Vacuum for 3 Days

TABLE XX. ANALYSIS OF CORROSION DATA.

Passivated Samples

Sample No.	Δw (mg)	Deviation from Mean - χ	χ^2
1	31.2	0.1	0.0
2	32.6	1.3	1.7
3	32.5	1.2	1.4
4	29.4	1.9	3.6
5	31.0	0.3	0.1

Mean (M_X) = 31.3 Σ_X^2 = 6.8

Variance = $\sigma_x^2 = \frac{6.8}{4} = 1.70$

S. D. = σ_x = 1.3

Unpassivated Controls

Sample No.	Δw (hy)	Deviation from Mean - y	y^2
1	32.6	1.2	1.4
2	33.3	1.9	3.6
3	30.1	1.3	1.7
4	27.8	2.6	6.7
5	33.1	1.7	2.9

Mean (M_y) = 31.4 Σ_y^2 = 16.3

Variance = $\sigma_y^2 = \frac{16.3}{4} = 4.08$

S. D. = σ_y = 2.0

passivated materials to corrode in the environment. The results of the two foregoing experiments serve to confirm observations that systems or components which have been poorly purged or incompletely pumped down following exposure to fluorine, frequently suffer excessive corrosion when exposed to warm, humid air. Conversely, systems which have been carefully purged need not suffer adverse corrosion.

5. EFFECT OF SOLVENT RINSING ON SECONDARY CORROSION

A few experiments were described previously in this section in which rinsing of metal specimens with LN_2 and carbon tetrafluoride appeared to reduce the extent of secondary corrosion following passivation. Definite conclusions could not be made because of scatter of data and the limited number of samples.

The following experiment was designed to permit a better statistical average of results. A total of ten 3/4" x 3" 316 stainless steel coupons were passivated — five specimens in each of two glass vessels connected to a common manifold. The passivation treatment consisted of exposure to gaseous fluorine for 24 hours at one atmosphere and at room temperature. Following the passivation, the fluorine gas was pumped off and liquid nitrogen condensed in one of the tubes in amount sufficient to completely immerse the specimens. The liquid nitrogen was then rapidly evaporated. Both sets of specimens were finally evacuated and the total pumping time for both was 30 minutes. Both sets were then subjected to the accelerated corrosion test. The data are presented graphically in Figure 31 and the statistical data in Table XXI.

The mean of the weight increases for the liquid nitrogen — rinsed specimens is higher than the untreated specimens but application of the "t" test reveals that the difference is probably not significant. Thus it is concluded that the liquid nitrogen treatment as imposed in this experiment is not effective in reducing secondary corrosion.

A similar experiment was carried out to test the efficiency of carbon tetrafluoride as a rinsing and purging agent of the passivated surfaces. The experiment was identical to the one described immediately before except carbon tetrafluoride was condensed on the specimens instead of liquid nitrogen. The weight gain data for the samples are given in Figure 32 and Table XXII. Again, on the basis of the statistical analysis, no significant difference can be established between passivated specimens and passivated and rinsed samples.

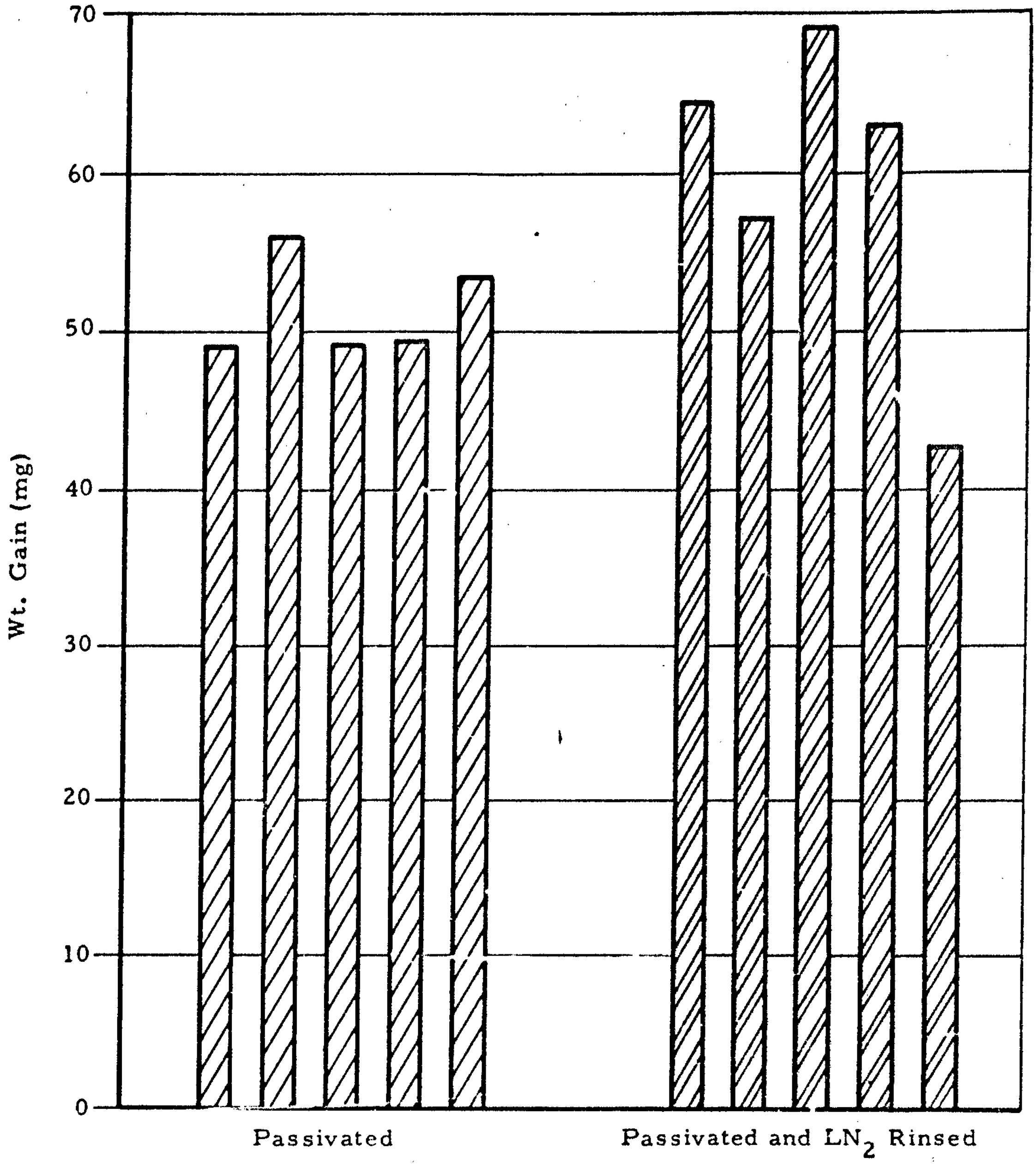


Figure 31. Relative Corrosion - Passivated Samples of 316 SS With and Without LN_2 Rinsing.

TABLE XXI. ANALYSIS OF CORROSION DATA - LN_2 RINSED SPECIMENS

Passivated Samples

Sample No.	Δw (mg)	Deviation from Mean - χ	χ^2
1	49.3	2.0	4.0
2	56.0	4.7	22.1
3	49.4	1.9	3.6
4	49.4	1.9	3.6
5	53.5	2.2	4.8

Mean $(M_\chi) = 51.3$ $\Sigma_\chi^2 = 38.1$

Variance $= \sigma_\chi^2 = \frac{38.1}{4} = 9.52$

S. D. $= \sigma_\chi = 3.1$

Passivated and LN_2 Rinsed Samples

Sample No.	Δw (my)	Deviation from Mean - y	y^2
1	64.3	5.1	26.0
2	57.1	2.1	4.4
3	69.4	10.2	104.0
4	62.9	3.7	13.7
5	42.5	16.7	279.0

Mean $(M_y) = 59.2$ $\Sigma_y{}^2 = 427.1$

Variance $= \sigma_y{}^2 = \frac{427.1}{4} = 106.8$

S. D. $= \sigma_y = 10.3$

(Continued)

TABLE XXI. ANALYSIS OF CORROSION DATA - LN_2 RINSED SPECIMENS (Continued)

"t" Test

Passivated Samples	Passivated and LN_2 Rinsed
$N_X = 5$	$N_y = 5$
$M_X = 51.3$	$M_y = 59.2$
$\sigma_X = 3.1$	$\sigma_y = 10.3$

$$\sigma_{M_X} = \frac{3.1}{\sqrt{5}} = 1.38 \qquad \sigma_{M_y} = \frac{10.3}{\sqrt{5}} = 4.60$$

$$\sigma_{M_X - M_y} = \sqrt{\sigma_{M_X}^2 + \sigma_{M_y}^2} = \sqrt{1.90 + 21.2} = 4.80$$

$$t = \frac{M_X - M_y}{\sigma_{M_X - M_y}} = \frac{51.3 - 59.2}{4.80} = -1.65$$

With a value of t less than 2 the difference of means is probably not significant.

TABLE XXII. ANALYSIS OF CORROSION DATA - CARBON TETROFLUORIDE-RINSED SPECIMENS.

Passivated Samples

Sample No.	Δw (mg)	Deviation from Mean - X	X^2
1	26.9	3.0	9.0
2	24.6	5.3	28.0
3	39.6	9.7	93.7
4	29.7	0.2	0.0
5	28.6	1.3	1.7
Mean (M_X) =	29.9	Σ_X^2 =	142.4

Variance = $\sigma_X^2 = \frac{142.4}{4} = 35.6$

S. D. = σ_X = 6.0

Passivated and LF4 - Rinsed

Sample No.	Δw (hy)	Deviation from Mean - y	y^2
1	24.2	3.6	12.9
2	28.5	0.7	0.5
3	32.0	4.2	17.6
4	24.0	3.8	14.4
5	30.3	2.5	6.2
Mean (M_y) =	27.8	Σ_y^2 =	51.6

Variance = $\sigma_y^2 = \frac{51.6}{4} = 12.9$

S. D. = σ_y = 3.6

(Continued)

TABLE XXII. ANALYSIS OF CORROSION DATA - CARBON TETROFLUORIDE-RINSED SPECIMENS. (Continued)

"t" Test

Passivated Samples	Passivated and LF4 Rinsed
$N_x = 5$	$N_y = 5$
$M_x = 29.9$	$M_y = 27.8$
$\sigma_x = 6.0$	$\sigma_y = 3.6$

$$\sigma_{M_x} = \frac{6.0}{\sqrt{5}} = 2.68 \qquad \sigma_{M_y} = \frac{3.6}{\sqrt{5}} = 1.60$$

$$\sigma_{M_x - M_y} = \sqrt{\sigma_{M_x}{}^2 + \sigma_{M_y}{}^2} = \sqrt{7.18 + 2.56} = 3.10$$

$$t = \frac{M_x - M_y}{\sigma_{M_x - M_y}} = \frac{29.9 - 27.8}{3.10} = 0.68$$

t being less than 1 the difference in the means is not significant.

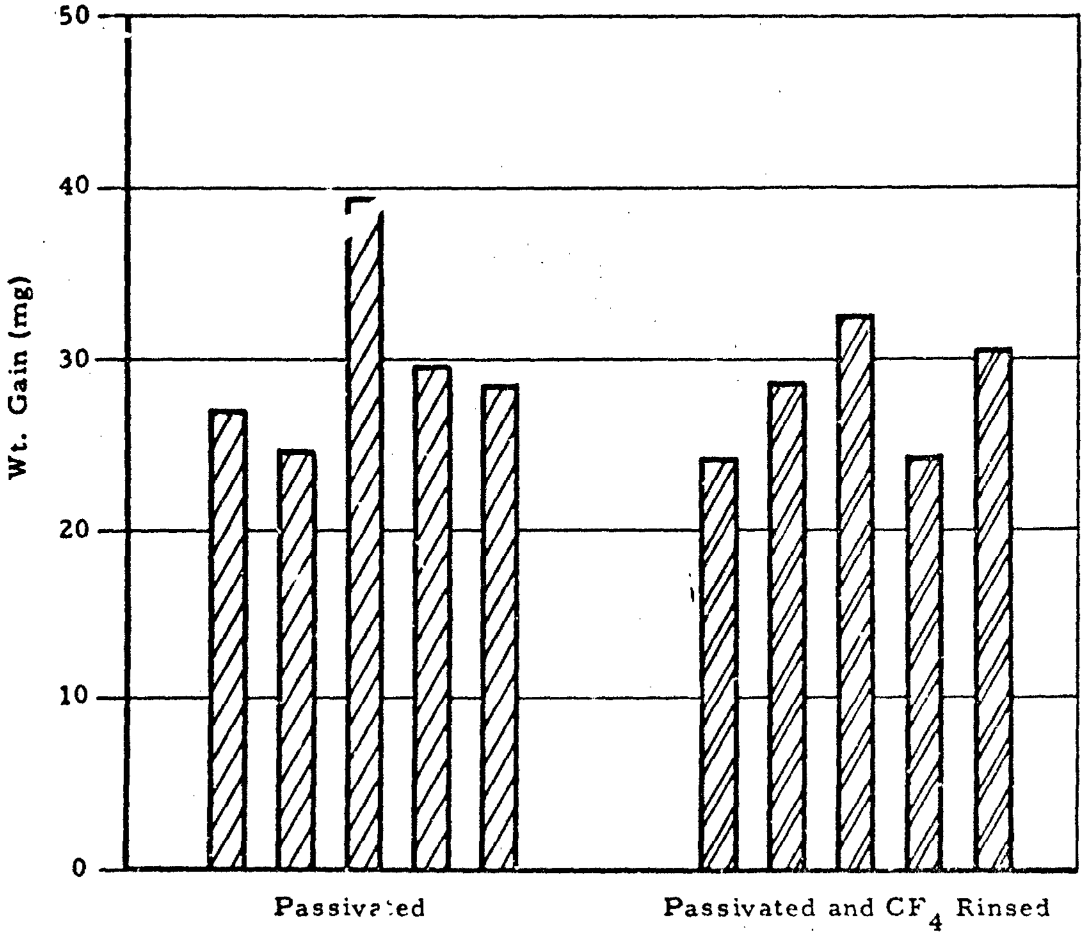


Figure 32. Relative Corrosion - Passivated 316 SS With and Without CF_4 Rinsing.

APPENDIX IV

DESORPTION FROM PASSIVATED SURFACES

1. PROCEDURE

Eighty grams of 304 stainless steel powder were placed in a bomb, evacuated, and passivated by exposure to fluorine gas at one atmosphere pressure for 1 hour at 25°C (77°F). The surface area of the powder was 1010 cm^2/gram as measured by the krypton gas B.E.T. method. Therefore, the total metal surface area was roughly eight square meters.

Following the passivation cycle, the bomb was evacuated to the best vacuum obtainable with the mechanical oil pump used in the system — roughly 0.5 torr. The evacuation was continued for 15 minutes at room temperature.

The bomb was valved off under vacuum and attached to the inlet system of an Aerovac AVA1 mass spectrometer. The residual gas in the bomb was leaked into the analyzer at a total pressure of 5×10^{-5} torr and the mass spectrum scanned from AMU 12 through 70.

The bomb was again pumped with the mechanical pump for an additional 15 minutes and reattached to the mass spectrometer and an additional scan made over the same mass range. Finally, the bomb was heated to approximately 100°C (212°F) while attached to the mass spectrometer and a third scan made.

2. RESULTS AND DISCUSSION

The relative peak heights obtained in the mass analysis for the separate samples are shown in Table XXIII. The relative peak heights are not directly related to concentration because of the variable response of the instrument to each molecular species. The results are therefore most useful from a qualitative standpoint.

The most prominent peaks in the spectra are due to oxygen, nitrogen, fluorine, HF, and an unknown constituent with AMU of 46. This has been identified in gaseous fluorine from some sources and is evidently strongly adsorbed in the metal powder because it shows up more strongly after heating. Water vapor — AMU 17 and 18 — is not prominent. It is almost absent after the first evacuation of the bomb.

TABLE XXIII. MASS SPECTRA OF RESIDUAL GASES FROM PASSIVATED SURFACES

AMU	Probable Ion	Relative Peak Heights Above Background (1) After Initial Evacuation	(2) After Second Evacuation	(3) Bomb Heated
14	N^+	0	0.05	0.05
16	O^+	0.10	0.20	0.20
17	OH^+	0.05	0.10	0.0
18	H_2O^+	0.35	0.0	0.0
19	F^+	0.07	0.2	0.15
20	HF^+	1.6	2.4	2.4
28	N_2^+, CO^+	1.7	1.9	1.9
32	O_2^+	0.25	0.5	0.6
34	-	0.05	0.1	0.1
44	CO_2^+	0.02	0.0	0.0
46	-	0.25	0.4	0.5
50	-	0.02	0.05	0.1

APPENDIX V

MECHANICAL STABILITY OF METAL FLUORIDE FILMS

The degree of mechanical stability of fluoride films formed on metal structural components used in fluorine rocket propulsion systems is not well known. A mechanically stable passive fluoride film acts as a protective coating against corrosion attack by the fluorine. However, loose hard, grainy metal fluoride particles can scratch or erode the sealing surfaces, i.e. valves, resulting in poor seal leakage performance for the sealing component. Accumulation of such particulates can also plug orifices or other restrictive channels.

Mechanical stability tests were designed to evaluate the metal fluoride stability on metal bellows of 316SS, Inconel 625, Al6061-T6, and copper when exposed to various combinations of flexing, cryoshock, gaseous fluorine and liquid fluorine conditions. The test data seem to indicate that the mechanical stability of metal fluorides formed are excellent and that for all practical purposes very little (max. 0.007%) of the exposed metal fluoride surface is depleted.

Precleaning of the test system introduces a high background of particulate contamination as evidence by residue on 0.45 micron filter prior to the mechanical stability test. Flakes as large as 1000 Å have been collected. The evidence suggests that most of the different kinds of particles arise during the assembly and servicing of the test. Once the structural components are assembled, the test assembly must be flushed a sufficient number of times to minimize the background contaminant.

1. TEST APPARATUS AND MATERIALS

The Rapid Screening Tester with fixtures for testing metal bellows specimens under repeated bending by alternate compression is illustrated in Figure 33.

The basic apparatus consists of a double walled stainless steel test container, a specimen mount attached to the lid (to allow translational reciprocating motion of the specimens), a metal bellows seal on the reciprocating shaft, a variable eccentric cam drive to change the axial displacement of the shaft, and an electrically driven, variable speed rotary motion power unit.

The jacket of the test container contains no direct plumbing connections with the interior of the container. It is used as a temperature control bath by flowing H_2O or LN_2 through it during different tests.

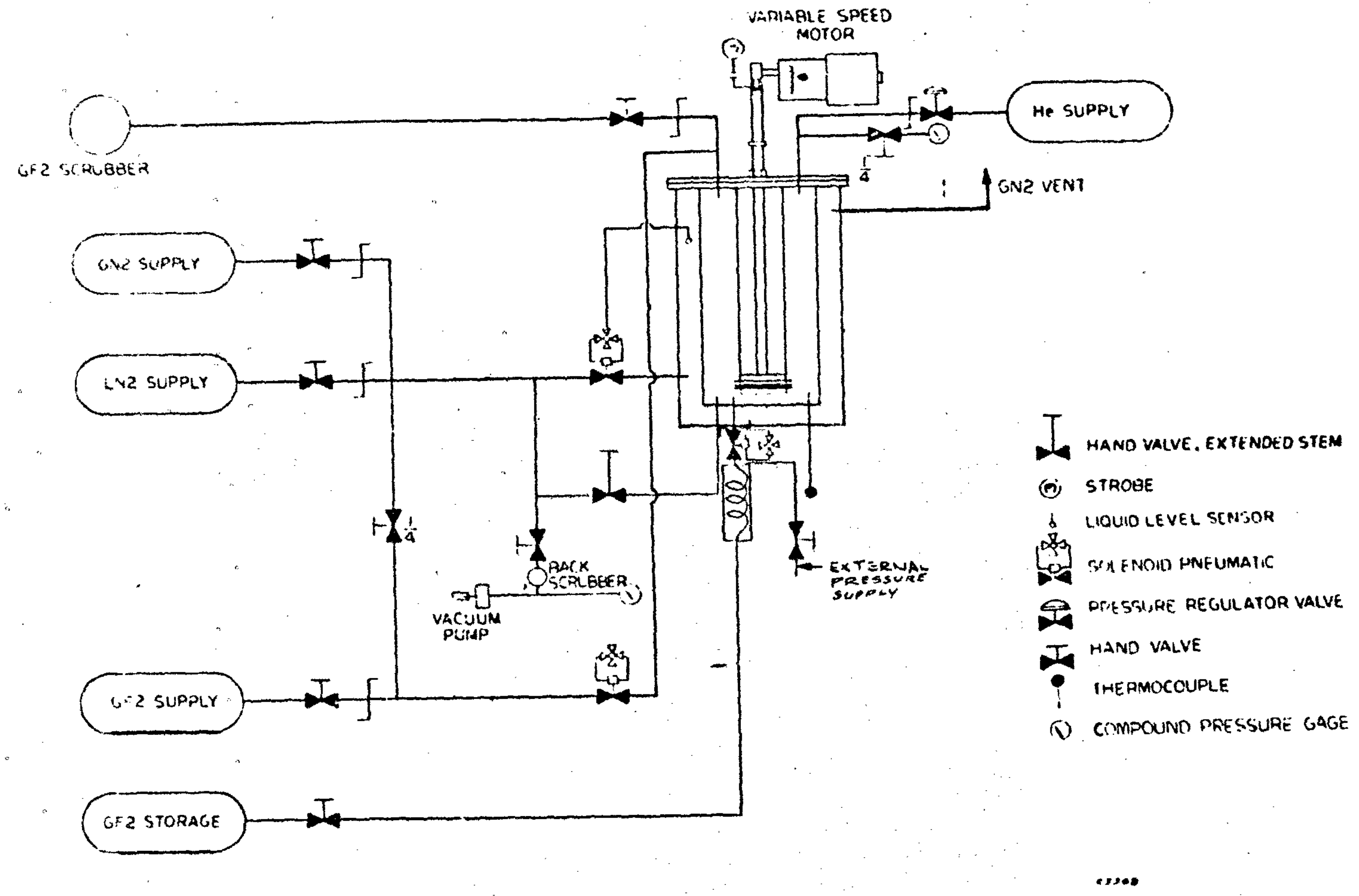


Figure 33. Schematic, Fluorine Bellows Test Apparatus

The apparatus is connected to supplies of GN_2, LN_2, vacuum, GHe, GF_2, to instruments and to a venting system by means of stainless steel lines. A particle collector is connected at the bottom of the test chamber and is immersed in LN_2 to maintain it at -320°F when necessary. The instruments used with the tester include two Bourdon pressure gages (compound, 60 psig), a strobe lighting unit, and a revolution counter.

Materials tested were in the form of Bellows specimens. They were formed from cold rolled mill annealed (dead soft) sheet. The sheets were rolled into a tube, butt welded and hydroformed to contain three typical bellows outside convolutions. Figure 34 is a drawing of the specimens.

The bellows test coupons were prepared from four alloys, aluminum 6061-0, mill annealed 316 stainless steel, annealed Inconel 625, and annealed copper. During fabrication of the bellows, the weld is work hardened (1/8 to 1/4 full hard). Al 6061 was heat treated to the T6 condition after forming operation, the others are annealed. Convolution heights, h, were different in each alloy. Table XXIV also contains a listing of the selected parameters of the bellows coupons.

The calculation of axial displacement of bellows from the rest position (α_e) is based on the maximum stress (σ_m) at the root of convolution being equal to 75% yield stress. On the basis of elastic theory, using experimentally derived correction factors, it can be shown that (Reference 9, 10)

For stainless steel type 316

$$\sigma_m = \frac{41.4 \times 10^6\, t\, \alpha_e}{N_c h^2}$$

For Nickel alloy Inconel 625

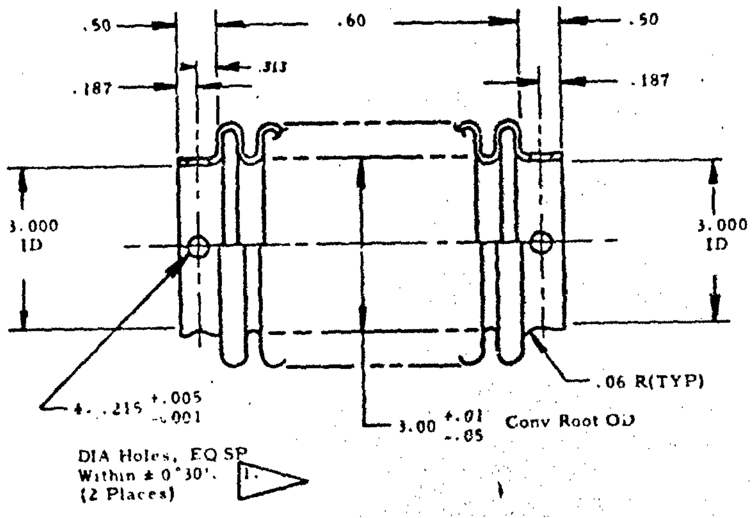
$$\sigma_m = \frac{42.7 \times 10^6\, t\, \alpha_e}{N_c h^2}$$

For aluminum alloys

$$\sigma_m = \frac{17.6 \times 10^6\, t\, \alpha_e}{N_c h^2}$$

For copper

$$\sigma_m = \frac{26.3 \times 10^6\, t\, \alpha_e}{N_c h^2}$$



Number of Convolutions: 3

Convolution Height: 0.41 ± 0.01

Pitch (REF): 0.233

Number of Plies: 1

Weld Per: MIL-W-8604

One Longitudinal Butt Weld Per Ply.

Figure 34. Typical Convoluted Bellows Specimens

TABLE XXIV. SELECTED MECHANICAL PROPERTIES; HEAT TREATMENT AND DIMENSIONS OF HYDROFORMED METAL BELLOWS

Materials	Yield Strength, ksi RT	Yield Strength, ksi 320°F	t in.	h in.	Heat Treatment After Hydroforming Bellows
Inconel 625 (annealed)	100	160	0.008	0.31	1900°F for 5 min.
316 SS (annealed)	65	60	0.009	0.31	1400°F for 5 min.
A16061-T6	35	45	0.016	0.33	T-6
Copper (annealed)	8	14	0.010	0.45	800°F for 10 min.

where t is thickness of ply

N_c is number of outside convolutions

h is mean convolution height

Application of these formulae resulted in calculation of cam displacement values for the metal bellows as detailed in Table XXV. The cam displacement is set by a micrometer dial gage. The following cleaning procedure was used on the metal bellows before assembly for testing:

a. 316SS and Inconel 625 bellows were soaked in HNO_3 + HF at 180°F, rinsed in distilled water, rinsed in acetone, dried with GN_2, ultrasonically cleaned in Freon bath, dried with GN_2 and wire brushed to remove ink stains.

b. Copper bellows were rinsed in acetone, dried with GN_2, soaked in Oakite No. 33, rinsed in distilled water, rinsed with acetone, GN_2 dried, ultrasonically cleaned in Freon bath, dried with GN_2, dipped two minutes in HCl, rinsed in water, GN_2 dried, rinsed in acetone and GN_2 dried.

c. Aluminum 6061-T6 was soaked in aluminum cleaner No. 980 at 80°F per 5 minutes, rinsed in water, rinsed in acetone, GN_2 dried, ultrasonically cleaned in Freon for 5 minutes and dried in GN_2. A prior precleaning cycle consisting of soak in Oakite No. 33 for ten minutes, rinse in water, ultrasonic cleaning in Freon for five minutes, and wire brushed to remove ink stains was found to be inadequate.

2. TEST PROCEDURE

The mechanical stability of fluoride films was evaluated by the low cycle fatigue test, 5 cps, in the rapid screening tester according to the following four test sequences:

Test 1 — The metal bellows is fluorinated in gaseous fluorine, GF_2, at 1 atmosphere for 1 hour, flexed for 500 cycles, and then thermally shocked by flowing liquid nitrogen during an additional 1500 cycles. Total chill down time is 3 minutes. The LN_2 is then turned off. The LN_2 containing any spalled off metal fluoride particles is drained into the particle collector below the test chamber. The particle collector is kep in a LN_2 bath to maintain it at -320°F.

The test chamber is reheated to room temperature by circulating water through the chamber jacket for at least 30 minutes. The low cycle fatigue and thermal shock treatment is repeated four more times on the metal bellows. The particle collector is warmed up after the last test cycle.

TABLE XXV. CAM DISPLACEMENT SETTING FOR METAL BELLOWS IN ONE DIRECTION FROM REST POSITION.

	Axial Displacement		Cycle in one Direction	
Material	RT	LN_2	RT	LN_2
Inconel 625 (annealed)	0.031"	0.047"	±0.031"	±0.047"
316 SS (annealed)	0.018"	0.017"	±0.018"	±0.017"
Al6061-T6	0.015"	0.019"	±0.015"	±0.019"
Copper (annealed)	0.007"	0.012"	±0.007"	+0.012"

RT - Room Temperature
LN_2 - Liquid Nitrogen Temperature

The particle collector is warmed up after the last test cycle. The test chamber and particle collector are evacuated and the particle collector valve closed. The test chamber is flushed by 500 cc of filtered Freon TF by sucking it in under vacuum. Next, the test chamber is pressurized with GN_2 to 20 psig. The collector valve is open for the Freon to enter and the GN_2 is vented through the collector exhaust valve.

The particle collector is disconnected from the rapid screening tester and a 0.45 micron millipore filter unit connected to one entrance port. The other entrance port is pressurized with 15 psig GN_2. The Freon filtrate is collected in a plastic bottle for reuse. The millipore filter unit is capped off and opened in a dry box. The 0.45 micron filter paper is removed and immediately placed in a small jar filled with Freon TF to a 1/8" depth. The sample is subjected to metallurgical examination and analyses. If no significant amount of metal fluoride particulate are found on the filter paper, skip Test 2 and proceed to Test 3. If metal fluoride on filter paper is above the background amount go to Test 2.

Test 2 — Test 1 procedure is repeated with same metal bellows specimen without flexing. Metal bellows and filter paper sample are subjected to metallurgical examination and analysis.

Test 3 — A new metal bellows is passivated, tested for 2000 cycles in 1 atm GF_2. The fluorine is flushed out with GN_2, and particulate matter is collected into particle collector with Freon TF. The filter paper and metal bellows are subjected to metallurgical examination and analysis.

Test 4 — A new metal bellows specimen is cooled to -320°F. LF_2 is condensed into the test chamber. The immersed bellows is flexed for 2000 cycles and then is drained into particle collector. The test apparatus is purged with GN_2 and flushed with Freon TF into particle collector. The filter paper sample and metal bellows are subjected to metallurgical examination and analysis.

3. TEST RESULTS

a. Stainless Steel Specimens

The first series of low cycle fatigue tests was conducted on a 316SS hydroformed metal bellows No. 1. It was run through Test 1.

Examination of the millipore filter unit revealed a large amount of particulate on the 0.45 micron filter paper and support screen (Figure 35).

Microscopic observations revealed flakes of copper, brass, Teflon, 100-500 Å thick flakes of a crystalline material (interference colors), microdroplets of a resin type material (other than Teflon) and some metal other than copper were observed both in a filter paper used for wiping the screen and on the millipore filter. Square shape particles were more frequent than elongated flakes or polymer ribbons with

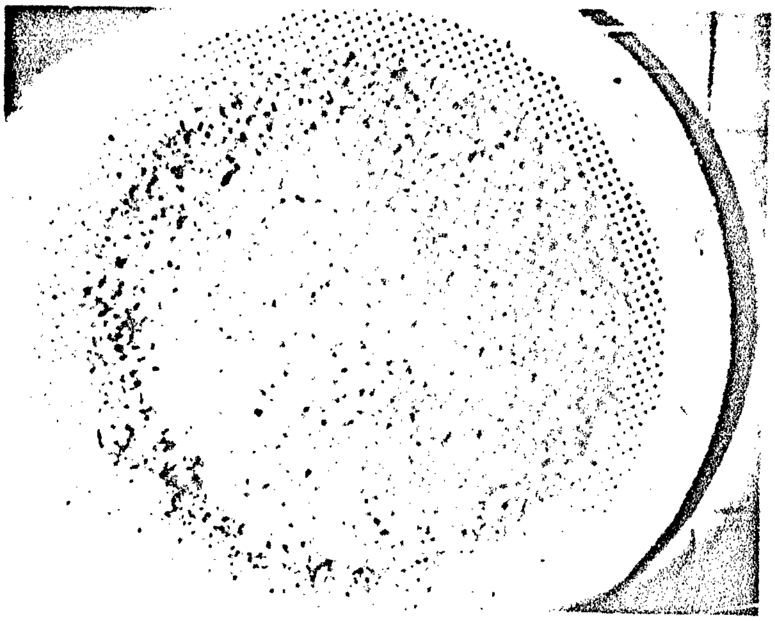


Figure 35. Particulate Trapped On 0.45 Micron Millipore Filter

dimensions varying from 0.5-0.6 millimeter to 40-50 microns. The smallest particle size approximates the microscope resolution limit of 0.5 micron. Brown polymeric material with high porosity and large pore size appeared to indicate material other than Teflon.

The great majority of collected particles consists of the thin crystalline flakes (500-1000 Å) with some larger structures. The particles are reminiscent of mica fragments, but may indicate a surface coating on the test sample or on the bellow surfaces.

The heavy amount of particulate material collected leads one to suspect the background particulate was too high during this test. Therefore, the test system was Freon cleaned six times before the first test was repeated.

Decreasing amount of particulate matter was observed on the millipore filters from the consecutive cleaning tests. Polymer flakes, metal fragments, mica type flakes and small amounts of amorphous substance penetrating into the millipore structure were noted. In sample 5 some oil-type substance partly covered the filter pores giving it a translucent appearance. The oil-type liquid did not evaporate during storage at ambient temperature in a desiccator for several days. In the sample 6 from the final cleaning stage, no amorphous background material was noted, but a few mica type laminated flakes about 400 μ diameter were observed. For details see Table XXVI.

After establishing the background particulate by these cleaning tests, the same 316SS Bellows No. 1 was rerun through Test I, an examination of the particulate collected for this test revealed (1) three mica type flakes, (2) very small fragments of polymer, and (3) "structureless" coating covering the entire millipore surface. Specimens one and three were examined by selected area electron diffraction.

The sample one flake (1), pressed between two electron microscope grids was sufficiently thin at flake borders for transmission analysis. Computed diffraction patterns indicated muscovite type material. The origin of this material cannot be explained, unless material of this type was used for packing of Freon containers or was introduced from the liquid nitrogen system.

Specimen 3 was transferred from the millipore filter surface to a nitrocellulose film for selected area diffraction. Computed diffraction patterns are given in Table XXVII columns 1 and 4. Iron fluoride in addition to Fe oxides were identified. The major fraction appears to consist of iron oxides rather than iron fluorides. $Fe_3F_5 \cdot 3H_2O$, $Fe_3F_5 \cdot 7H_2O$, and FeF_2 were indicated by the principal lines and a series of additional lines in rather good agreement with the ASTM tabulated data.

The same 316SS bellows No. 1 was subsequently run through Test 2. The particulate matter from this test revealed more polymer flakes

TABLE XXVI. PARTICULATES COLLECTED FROM THE CLOSED SYSTEM CLEANING, STEPS 2 THROUGH 6.

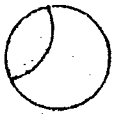
	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6
(1)	Thin transparent (mica type) flakes (interference colors) with adhered metal residue flake size 100 μ dia.	Heavy small particle contamination; penetrates filter pores. Complete coverage.	No obvious amount of contamination of type 3 (1).	More amorphous type 3 (1) material than in 4.	Minimum amount of particulate matter. Light brown discoloration does not contain particles but "residual oil."
(2)	Metal flakes with high reflectance 2 polygonal flakes 200 μ long. 14 similar flakes, 10-20 μ long clusters of 50 particles 1 μ dia. and less, metal luster.	10 μ and smaller flakes with interference colors of 2.	A few 50 μ metal fragments.	Very few metal fragments.	Some metal type flakes, 50 μ dia., and dark particles, 2 μ dia., no metal reflectance.
(3)	10 μ Teflon flakes very thin; some 10 times less than in Av1 (1).	One 20 μ flake of green "fluoride."	Numerous 400-200 μ Teflon flakes, folded interference colors; distances about 1 millimeter.	4-5 plastic flakes	4 plastic flakes 50 μ dia.
(4)	————	Insect hairs of cilia type.	————	Oil partly penetrating millipore filter pores, observed as follows: 	Center of filter very clean, except some fine powder.

TABLE XXVII. COMPUTED ELECTRON DIFFRACTION PATTERNS FOR PARTICULATES 1 TO 5 COLLECTED IN SS316 BELLOWS TEST NO. 1 (FLEXING, LN_2 THERMAL SHOCK, 2000 CYCLES REPEATED FIVE TIMES) AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (THE PRINCIPAL LINES ARE UNDERSCORED)

Specimen					$Fe_2F_5 \cdot 7H_2O$	$Fe_2F_5 \cdot 3H_2O$	FeF_2	Fe_2O_3
1	2	3	4	5				
5.00		6.28				$\underline{5.49}$		
							$\underline{4.81}$	
		4.54			4.51	4.69		
		4.24			$\underline{4.25}$		$\underline{4.18}$	
				3.98			3.81	
		3.56				3.71		3.68
		3.28			3.22	3.22		
						3.16		
	2.92					$\underline{3.09}$		
	2.86					$\underline{2.97}$		
				2.70	2.74	2.67		
2.66-63		2.63	2.68		2.60		2.63	
2.55	2.42			2.54	2.51			$\underline{2.53}$
	2.30		2.30			2.34		
2.21		2.19					2.24	
	2.02	1.99			2.05	2.08		2.07
	1.96				1.92		1.91	
				1.86	1.82	1.83	1.86	1.83
1.75		1.77	1.76	1.78			1.81	
						1.74	1.77	
	1.69					1.68	1.66	$\underline{1.69}$
			1.60			1.61	1.60	1.63
1.53	1.52	1.51	1.53	1.55			1.57	
							1.49	1.48
				1.40		1.45		1.45
						1.42		
1.31		1.35	1.31				1.38	1.34
1.29	1.26	1.27	1.27	1.29			1.33	1.31
				1.20			1.22	1.25
			1.16	1.16			1.15	
	1.10	1.12	1.09	1.09			1.10	
1.05		1.07		1.05				
1.03		1.01						
0.99			0.99					
0.93	0.91	0.93	0.89	0.91				

than in Test 1. The interference colors noted indicate that the flake thicknesses approximate 600 to 1000 Å. Gray and dark material adhered to the polymer flakes appears to be the main particulate matter collected. Electron diffraction indicated mainly Fe_2O_3 and NiO with minor amount of iron and nickel fluorides. Note Table XXVIII columns 1 through 6. FeF_2 and Fe_3F_5 with 7 and $3H_2O$ are indicated. The total amount of fluorides appears to be very low and represents a thin surface layer. Some extracted surface material is shown in Figure 36.

The fluorinated bellows surfaces were examined under a binocular microscope, at a magnification of about 30X and under a metallographic microscope at a magnification of about 100X.

Local removal of the surface layer due to mechanical damage was observed close to the regions exposed to handling. Minor areas of attack were noted on the bellows edges under maximum tension.

The material — collecting area of the millipore filter approximates 3.14 cm^2. Consider that one per cent of this area or 0.03 cm^2 be covered by fluoride carrier oxides. The surface area of the bellows proper (inside and outside surfaces) approximates 396 cm^2. The extracted fluoride coated material thus may be estimated as 0.007%. Other fluorinated surfaces exposed to the same treatment as the bellows except flexing. constitute about 95% of the entire surface that contributes to the collected particulate matter. Consequently only 0.0003% or 3 ppm of the actual surface may be depleted of its fluoride coating.

b. Copper Specimens

The second series of low cycle fatigue tests was conducted on copper bellows. Cu bellows No. 4 was run through Test No. 1 procedure. Copper bellows No. 3 was run through Test No. 3 procedure, except that two atmospheres of GF_2 was used. Copper bellows No. 5 was run through Test 4 procedure. No visual damage of bellows was seen.

The computed electron diffraction patterns indicate copper, copper oxide CuO and copper hydroxide $Cu(OH)_2$ which were recorded from surface protuberances and at the thin edges of extracted surface flakes of the particulates collected from bellows flexing. Only the crystalline fractions are identified by means of this method. An identification made on the basis of the d-values using the ASTM X-ray standards indicated CuF_2 in one diffraction pattern only. It was recorded from a selected area, about one micron diameter. The observations suggest that a minimum amount of the passivating CuF_2 coating has been removed from the bellows under flexing. The trace amount found was detected at the edges of a copper flake which may originate from the machined parts where apparently some mechanical damage resulted from handling. It should be noted that the copper fluoride was identified as CuF_2 rather than as $CuF_2 \cdot nH_2O$ or CuOHF. It is thus concluded that any contact with atmospheric humidity and its decomposing action have been prevented in

TABLE XXVIII. COMPUTED ELECTRON DIFFRACTION PATTERNS OF PARTICULATES 1 TO 6 COLLECTED IN SS316 BELLOWS TEST NO. 2 (FLEXING, LN_2 THERMAL SHOCK, 2000 CYCLES REPEATED FIVE TIMES) AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (THE PRINCIPAL LINES ARE UNDERSCORED)

Specimen						$Fe_2F_5 \cdot 7H_2O$	$Fe_2F_5 \cdot 3H_2O$	FeF_2	Fe_2O_3	NiF_2	NiO
1	2	3	4	5	6						
						8.80					
						5.40	5.49	4.81			
						4.69	4.69			4.85	
4.38	4.40	4.40	4.40			4.51					
4.25						4.25		4.18		4.10	
3.89	3.83	3.85	3.85			3.81	3.71	3.81		3.78	
		3.56	3.66						3.68		
3.38				3.55	3.46						
3.20	3.29	3.20	3.29	3.27 3.20	3.29	3.22	3.22				
		3.14					3.16			3.11	
3.06							3.09				
2.86			2.92				2.77			2.98	
	2.69		2.74			2.74	2.67			2.75	
						2.60		2.63			
		2.53		2.54		2.51			2.51	2.53	
2.44	2.44										2.41
2.39	2.30	2.36	2.36	2.39-6			2.34				
2.31			2.27					2.24		2.22	
2.16		2.16	2.19 2.16								
			2.12	2.12			2.08				2.09
2.02	2.03		2.03	2.03	2.02	2.05			2.07	2.00	
1.98	1.93	1.96	1.93	1.92	1.93	1.92		1.91			
1.83	1.86		1.88			1.82	1.83	1.86 1.81	1.83	1.88	
1.75	1.76	1.78	1.78-1.76	1.76			1.74	1.77		1.72	
	1.71	1.69					1.68	1.66	1.69	1.69	
1.60	1.66	1.66		1.60	1.63		1.61	1.60	1.63		
1.55	1.57		1.53	1.50				1.49	1.48	1.49	1.48
	1.51	1.50	1.46		1.46		1.45		1.45		
1.42	1.43	1.36	1.38	1.36	1.38		1.42	1.38		1.37	
1.34		1.34						1.33	1.34		
1.29	1.30	1.30	1.28	1.31					1.31	1.31	
1.23	1.25	1.24 1.22	1.23	1.29	1.22			1.22	1.25	1.17	1.26

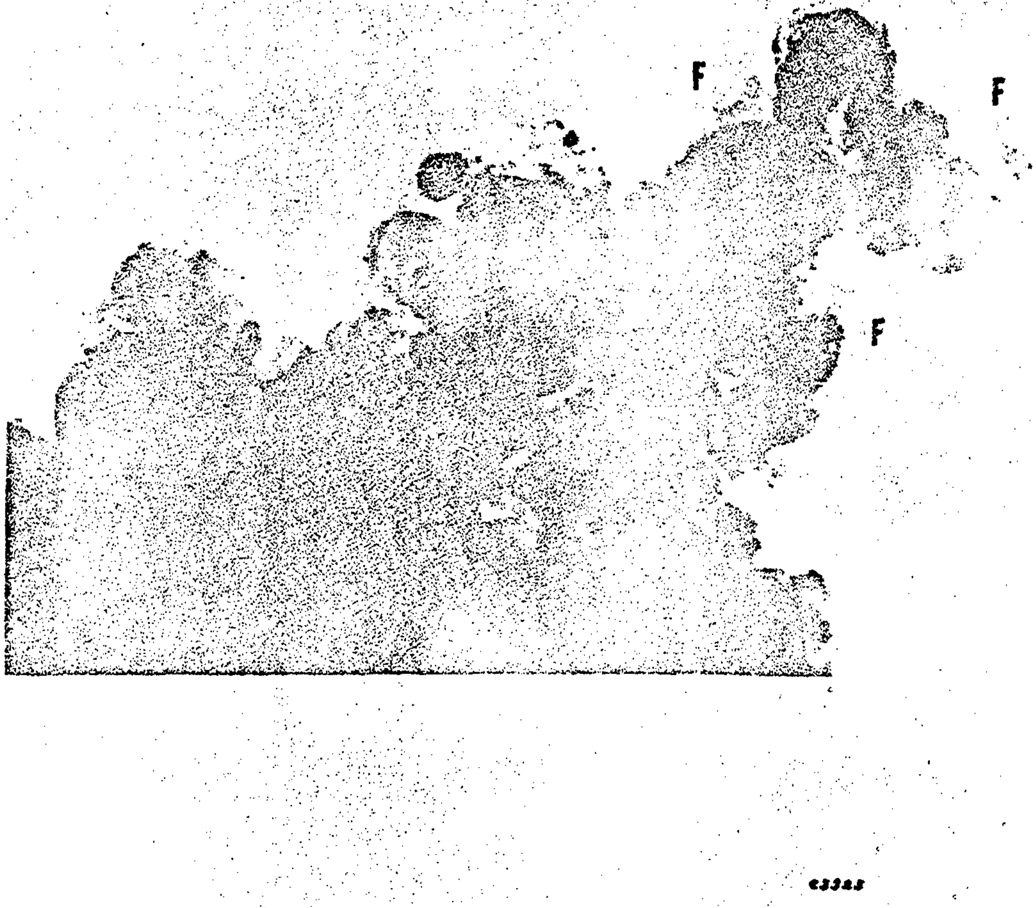


Figure 36. Electron Micrograph of Material Collected From SS-316 Bellows After Quenching and LF_2 Cycling Test. Note Areas That Presumably Depict Fluoride Coating Proper. Magnification 60,000X

TABLE XXIX. COMPUTED ELECTRON DIFFRACTION PATTERNS FOR PARTICULATES 1 THROUGH 6 OF SAMPLES FROM COPPER BELLOWS TEST NO. 1 AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (THE PRINCIPAL LINES ARE UNDERSCORED)

Specimen						Cu	$Cu(OH)_2$	CuO	CuF_2	FeO(OH)	Fe_2O_3	$Ca_3Al_2O_6$ nH_2O
1.	2.	3.	4.	5.	6.							
—	—	—	—	—	9.4	—	—	—	—	—	—	8.33
—	—	—	—	—	7.75	—	—	—	—	—	—	7.73
—	—	—	—	—	5.70	—	—	—	—	—	—	—
							5.30	—	—	—	—	—
—	—	—	4.86	4.87	—	—	—	—	—	4.97	—	—
—	—	—	—	4.10	—	—	—	—	—	4.18	—	4.02
—	—	3.86	—	3.90	—	—	3.75	—	—	—	—	3.38
—	(3.55)	—	3.65	—	3.65	—	—	—	—	—	—	—
—	—	—	3.36	—	—	—	—	—	—	3.36	—	3.60
—	3.20	—	—	—	3.20	—	—	—	3.22	—	—	3.29
—	—	—	—	—	2.92	—	—	—	—	—	—	2.87
—	2.80	—	—	—	—	—	—	2.75	2.82	—	—	—
2.68	2.63	2.68	2.68	2.63	—	—	2.64	2.53	2.66	2.69	2.69	2.69
—	2.50	—	—	—	2.50	—	2.51	2.52	2.53	2.58	2.51	2.45
—	2.25	2.35	2.34	2.30	—	—	2.36	2.32	2.39	2.30	—	2.36
—	2.26	—	—	—	2.23	—	2.26	—	2.21	—	—	2.22
2.19	—	2.15	2.19	2.19	—	—	—	—	—	2.18	2.19	—
—	—	2.12	—	—	2.12	—	—	—	—	—	—	—
2.05	1.98	2.09	—	—	2.06	2.09	2.08	—	2.04	2.01	—	2.04
—	—	—	1.96	—	—	—	—	1.96	—	1.92	—	1.97
1.83	—	1.83	1.83	1.83	1.85	1.81	—	1.86	1.82	1.80	—	1.86 1.81
1.80	1.80	—	1.80	1.77	—	—	—	1.78	1.77	1.77	—	1.74
—	1.73	1.76	—	—	1.75	—	1.73	1.71	1.69	1.69	1.69	—

(Continued)

TABLE XXIX. COMPUTED ELECTRON DIFFRACTION PATTERNS FOR PARTICULATES 1 THROUGH 6 OF SAMPLES FROM COPPER BELLOWS TEST NO. 1 AND REFERENCE LINES FOR THE COMPOUNDS IDENTIFIED (THE PRINCIPAL LINES ARE UNDERSCORED). (Continued)

Specimen						Cu	$Cu(OH)_2$	CuO	CuF_2	FeO(OH)	Fe_2O_3	$Ca_3Al_2O_6$ nH_2O
1.	2.	3.	4.	5.	6.							
— 1.56 —	1.62 1.58 1.54	— — —	1.68 — —	1.63 — —	— — 1.51	— — —	— — —	— 1.58 —	— — 1.51	— — —	— — —	— 1.54 —
— — — —	1.47 1.41 1.36 1.31	— — — —	1.46 — — 1.33	— 1.40 — 1.33	— — — 1.31	— — — —	1.48 1.45 1.38 —	1.50 1.41 1.37 —	— 1.44 1.42 1.38 1.33	— 1.42 — 1.32	1.48 — — —	— 1.43 — 1.34
1.28 1.25	— 1.25	1.29 1.27	— —	1.29 —	1.28 1.26	$\underline{1.28}$ —	1.29 1.26	— 1.26	— 1.27	1.29 —	— 1.27	— —
— 1.15	1.21 1.16 1.14	— 1.14	1.16 1.12	— 1.12	1.19 —	— — —	— — —	1.19 — 1.14	1.22 — —	— — —	1.23 — —	$\left.\begin{matrix}1.19\\1.16\end{matrix}\right\}$ —
1.09 1.06 1.02	1.08 — 1.04 1.02	— 1.05 —	1.09 — —	1.08 — 1.03	1.08 — 1.04	1.09 — 1.04	— — —	1.09 1.07 1.03	— — —	— — —	1.11 — —	1.09 — —
0.99 0.92 0.88	— 0.97 —	— 0.93 —	0.99 0.96 0.89	0.99 0.93 0.87	— — 0.86	— — 0.86	— — —	1.00 0.92 0.90	— — —	— — —	— — —	— — —
— — 0.72	— — —	— 0.83 0.77	0.85 0.83 0.78	— — —	— 0.81 —	— 0.83 0.80	— — —	— — —	— — —	— — —	— — —	— — —
0.76 0.74	— —	— —	— —	— 0.74	— —	— —	— —	— —	— —	— —	— —	— —

the liquid Freon used as a storage environment for the particulates collected. Virtually no parts of the passivating coating have been detached due to failing adhesion at the copper-CuF_2 interface.

Other crystalline fractions were identified among the particulates, such as Fe_2O_3, FeO(OH) and calcium aluminate hydrate approximating $Ca_3Al_2O_6 \cdot nH_2O$. See Table XXIX.

The computed diffraction patterns from particulates 1 through 6 and the X-ray powder data of interplanar spaces, d-spacings for a set of known compounds used as identification standards are also given. The principal lines are underlined. It should be noted that the experimental errors are large for the short radii in the electron diffraction rings and thus in the corresponding large d-spacings. The agreement between the experimental and theoretical spacings is optimum in the lower part of the columns and less accurate above 3.6 Å. The single crystal patterns are not well adapted for identification from electron diffraction since only selected planes diffract simultaneously and selected d-spacings are obtained. A more complete set of the crystallographic characteristics is obtainable in samples with randomly distributed submicroscopic crystals yielding diffraction rings rather than spot patterns.

It is concluded that only trace amounts of the passivating coating are susceptible to the flexing attack. A great majority of the particulate matter collected appears to originate from other parts of the reaction chamber than the passivated copper bellow surfaces.

The computed diffraction patterns 1 through 6 and the reference lines are listed in Table XXIX.

Visual observations of samples from copper bellows Test No. 3 procedure were similar to those from Test No. 1 procedure.

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Edwards Air Force Base, California 93523

13. ABSTRACT

This final technical report summarizes the studies conducted on halogen passivation. In the body of the report, general reaction behavior of fluorine and halogens with metal surfaces and contaminants, and cleaning and passivation procedures for systems and components using fluorine-containing oxidizers are outlined. A test conducted to evaluate the effectiveness of the cleaning and passivation procedure applied to a valve assembly is described. The experimental details have been included in the five appendices. These cover: (1) reaction of fluorine system contaminants, (2) impact sensitivity of organic residues left from passivation, (3) corrosive behavior of passivated metal surfaces, (4) gases absorbed on passivated surfaces, and (5) mechanical stability of passivation fluoride films.

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14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Fluorine						
Fluorinating Agents						
Passivation						
Fluoride Films						
Contamination						
Nickel Alloys						
Stainless Steel						
Aluminum Alloys						
Monel						
Copper						
Cleaning						
Hydraulic Fluid						
Halocarbon Grease						
Dye Penetrants						
Petroleum Jelly						
Acrylic Lacquer						
Corrosion						
Hydrogen Fluoride						
Bellows						
Fatigue						
Valve, solenoid						

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