

Final Report

May 18, 1966 to May 17, 1968

# DEVELOPMENT OF TECHNIQUES TO IMPROVE BLADDER MATERIALS AND TEST METHODS

Prepared for:

JET PROPULSION LABORATORY  
CALIFORNIA INSTITUTE OF TECHNOLOGY  
PASADENA, CALIFORNIA 91103

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UNDER NAS7-100

STANFORD RESEARCH INSTITUTE

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JPL Technical Representative: H. B. STANFORD

By: R. F. MURACA    J. S. WHITTICK    A. A. KOCH

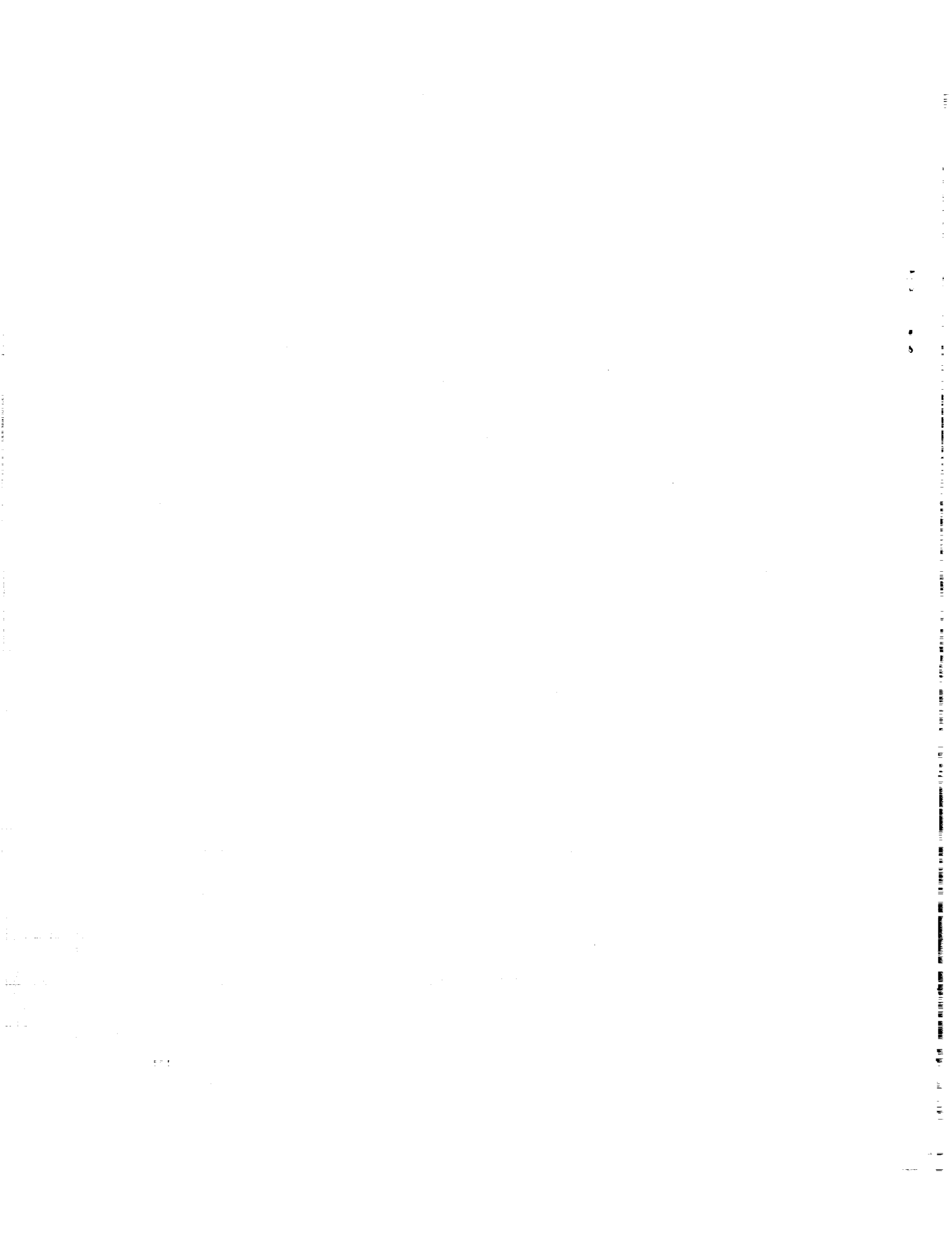
SRI Project PRD-6068

Approved:

A. G. BROWN, DIRECTOR  
CHEMISTRY & CHEMICAL ENGINEERING LABORATORY

This work was performed for the Jet Propulsion Laboratory,  
California Institute of Technology, sponsored by the  
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FOREWORD

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This Final Report summarizes in detail the work performed by Stanford Research Institute during the period May 18, 1967 to May 17, 1968 under Contract No. 951484 for the Jet Propulsion Laboratory of the California Institute of Technology. Prior work under this contract, described in Interim Report No. 1, June 17, 1967, is incorporated so that this document may provide for a complete understanding of program objectives and accomplishments without reference to the former report.

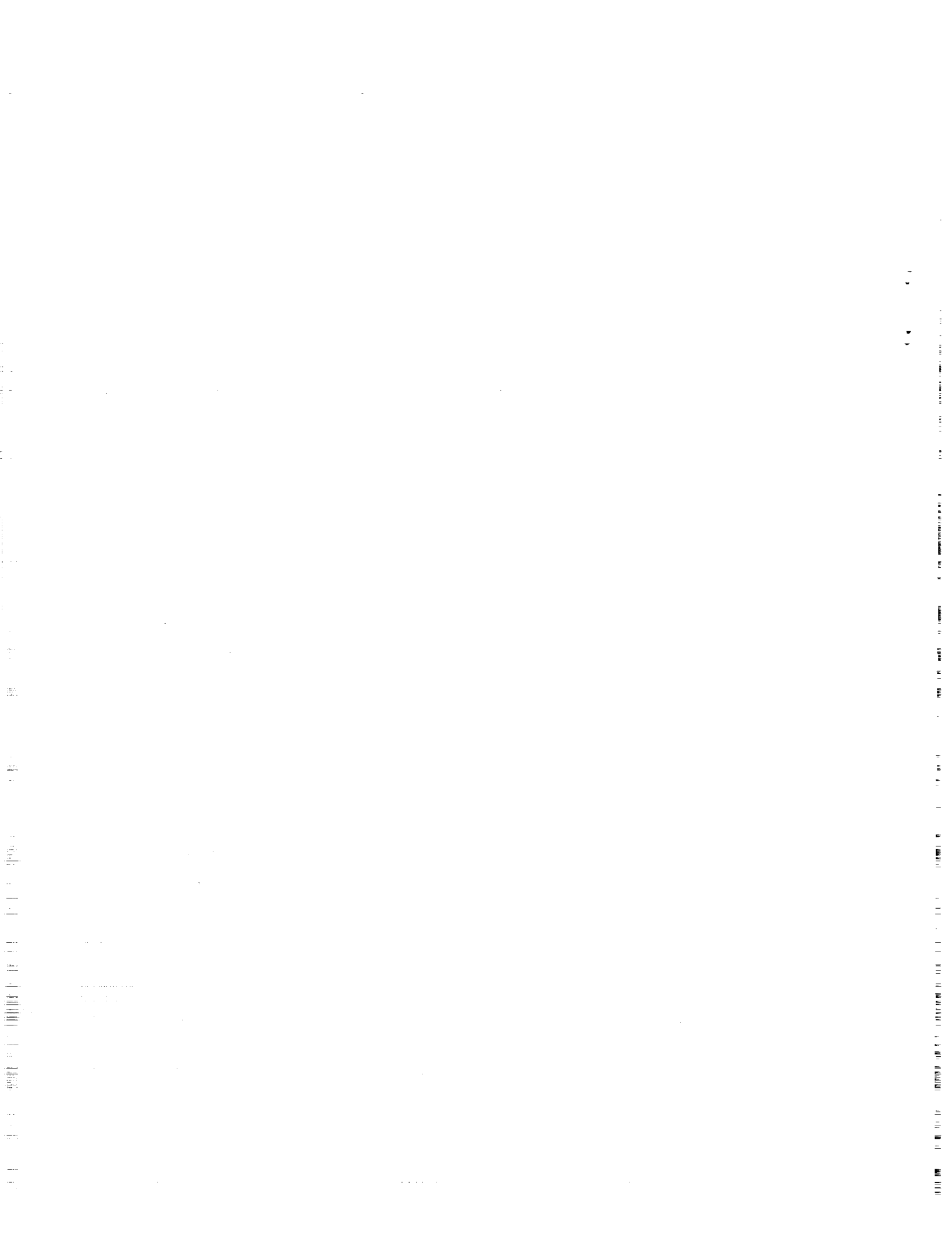
Technical Representative for the Jet Propulsion Laboratory was Howard B. Stanford of the Liquid Propulsion Section.

The technical effort at Stanford Research Institute was under the supervision and guidance of Dr. R. F. Muraca, Director, Analyses and Instrumentation. General program co-ordination was the responsibility of J. S. Whittick, Chemist-Program Co-ordinator; the major part of the work on preparing Teflon films was performed by A. A. Koch, Chemist.

Contributions to this report were made by the following Chemists of the Department of Analyses and Instrumentation:

C. A. Crutchfield	J. A. Neff
A. P. Longwell	E. Willis

Acknowledgment is made of the assistance of the Department's Chemical Technicians in support of this work.



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ABSTRACT

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Stanford Research Institute, Menlo Park, California  
DEVELOPMENT OF TECHNIQUES TO IMPROVE BLADDER MATERIALS AND TEST METHODS  
Final Report, May 1966-May 1968  
R. F. Muraca, J. S. Whittick, and A. A. Koch, June 17, 1968  
(JPL Contract No. 951484 under NAS7-100; SRI Project ASD-6068)

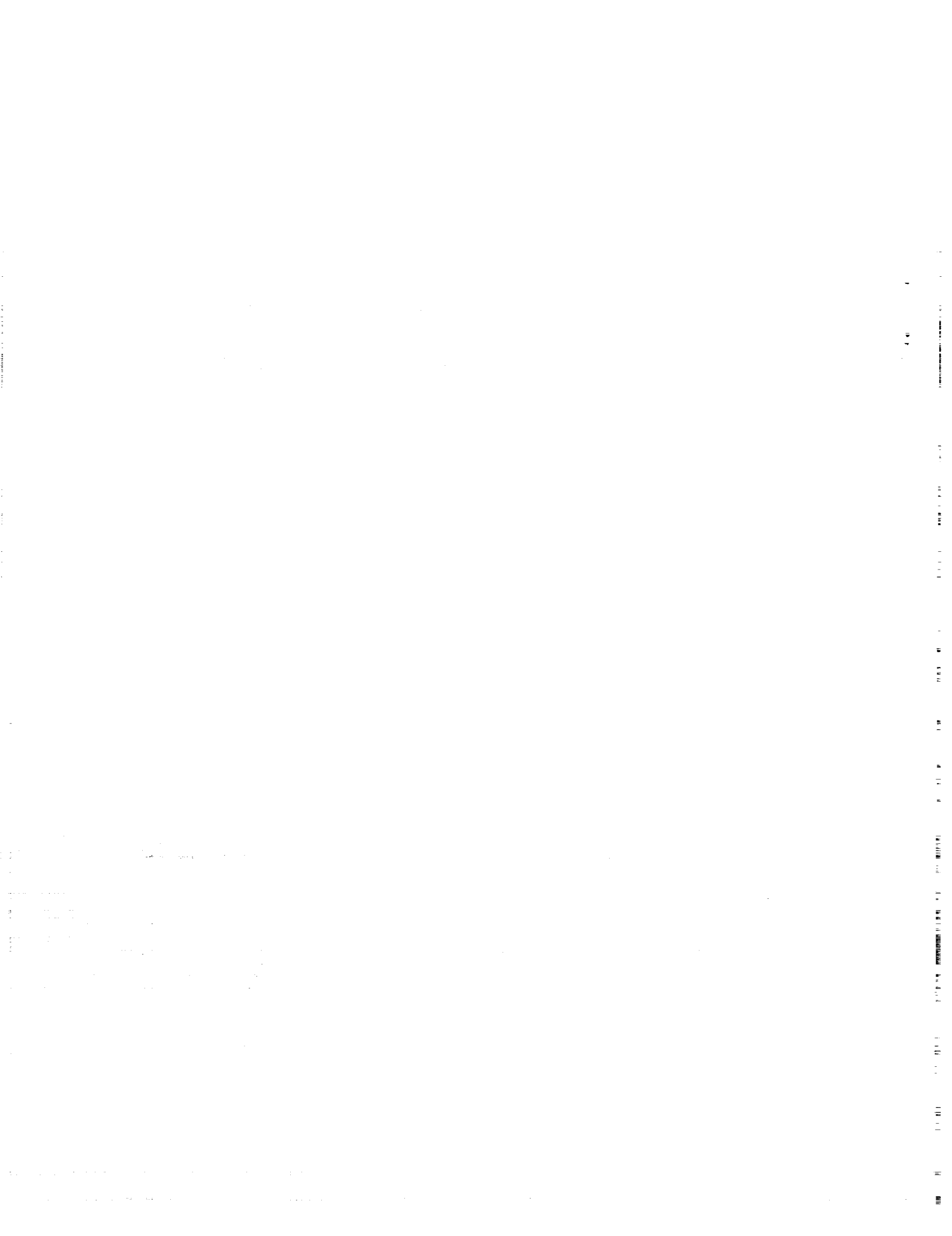
This report summarizes in detail the work performed during the contract period May 18, 1967 to May 17, 1968 and includes the essential features of the work performed in 1966-67 which provides for a thorough presentation in this report of program objectives and accomplishments. Background, objectives, and analyses of the program work are clarified in the Introduction and Summary section.

Process parameters are described for the fabrication of flexible Teflon films from aqueous dispersions; the experimental films have been characterized by electronmicrography, determinations of crystallinity, the measurement of crease-and-fold resistance, and other determinations. Analyses of original dispersions for impurities are also given.

The determination of Teflon crystallinity by several procedures is discussed and data are presented for the solubility of  $N_2O_4$  in Teflon, the swelling created by the solubility, and the relationship of density to crystallinity in compacted Teflon powders. Techniques are reported for the electroplating of Teflon films with lead in order to reduce their permeabilities to  $N_2O_4$ .

A description is given of an all-Monel vacuum system for handling  $OF_2$  and  $B_2H_6$ . Details of design and performance of a micro crease-tester for testing polymeric films while they are immersed in liquid propellants are also given.

Two "Reportable Items" under the NASA New Technology Clause are presented.





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## I. INTRODUCTION AND SUMMARY

The development of advanced liquid propulsion systems at the Jet Propulsion Laboratory requires the use of expulsion bladders for storable propellants in the space environment; the bladders must not only resist the corrosive action of liquid propellants, such as nitrogen tetroxide and hydrazine, but also must act as effective barriers against the loss of propellants. The materials from which bladders are made must be able to maintain their mechanical properties during prolonged storage with propellants so that they can withstand the sudden force of pressurization and must also be highly flexible and resistant to the creasing and folding which will occur during propellant expulsion.

Plans for more advanced propulsion systems include the use of cryogenic propellants such as oxygen difluoride and diborane. In these instances, expulsion bladders must have the same features of propellant resistance, flex-resistance, and impermeability, but they must also be able to maintain these properties at cryogenic temperatures.

### BACKGROUND

A short series of investigations by JPL indicated that a polymeric material such as Teflon was the most appropriate candidate for current propulsion systems because of its resistance to nitrogen tetroxide and hydrazine and because of its superior mechanical and thermal properties compared with other polymeric materials. The manufacture of seamless expulsion bladders from aqueous Teflon dispersions was accomplished successfully, and several space vehicles have been lofted with Teflon expulsion bladders aboard. However, the missions have been of short duration and have required expulsion only at mid-course guidance or at landing. Evidence at hand indicates that current fabrication processes are not producing reliably uniform bladders which can be entrusted for the longer-duration space missions which are planned. It is also apparent that the

tests performed on finished bladders or their control strips (tensile, crystallinity, flex) are not truly indicative of performance in service, because many bladders with excellent test results were ruptured on the very first expulsion cycle.

The requirements for longer-duration space missions dictate the need for far less permeable bladders than those which have been adequate for short missions. Permeation of  $N_2O_4$  through Teflon apparently has not been detrimental to short missions, but it will be of concern in future missions. For this reason, preliminary consideration has been given to the concept of using metal barriers in bladder construction, and experiments have been performed to attempt to cover Teflon films with electrodeposited lead; there is also a great deal of interest in laminates of aluminum (or other inert metal) foil and Teflon. Initial investigations at JPL indicated that electroplated films of lead must be burnished in order to provide a uniform hole-free surface; this is not too practical a procedure for rendering the interior surfaces of bladders impervious. Laminates of aluminum and Teflon are troubled with nonuniformity of adherence and formation of gas pockets; the molding of metal foils into adherent conformance with spherical bladders or hemispherical diaphragms has been found difficult and probably impractical.

Work with polymeric materials and  $OF_2$  and  $B_2H_6$  has been directed primarily toward simple compatibility studies with some work on shock or impact sensitivity.

#### PROGRAM OBJECTIVES

The work performed at SRI under this contract has been conducted with the following objectives as guide-lines:

- (1) The investigation of fabrication processes for Teflon films in order to determine which process parameters need modification or more rigid control;
- (2) The examination of procedures for the characterization of fabricated films in order to determine the effects of varying process parameters on the nature of finished films;



- (3) The investigation of procedures for cladding Teflon films with impermeable and inert metallic barriers;
- (4) The investigation of the performance of polymeric materials at cryogenic temperatures and in the presence of  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$ .

#### FABRICATION AND CHARACTERIZATION OF TEFLON TFE-30 FILMS

The great bulk of published information on Teflon relates to studies of pressed powders or extruded films; there is surprisingly little information on the properties of films fabricated from aqueous dispersions. However, review of these data suggested that the crystallinity of Teflon determines, in the main, properties such as permeability, tensile strength, elongation, etc. With this in view, the work at SRI commenced with the establishment of a facility for preparing experimental films from TFE-30 dispersions and the investigation of procedures for determining the crystallinity of Teflon films. Initial programs sought the correlation of crystallinity with flex resistance and tensile properties, since published data suggested that Teflon extruded films of low crystallinity are more flexible than those of higher crystallinity. (Flex resistance is considered to be more important than permeability to  $\text{N}_2\text{O}_4$ ; permeability will be higher for amorphous films.) As the work progressed, it became clear that the determining factor was not the degree of crystallinity, but the character of the orientation of the crystallites. This finding suggested a re-direction of the course of the program and led to a new approach for fabricating reproducible flexible films of superior quality.

Preliminary work on the fabrication of Teflon TFE-30 films involved the development of techniques to ensure application of uniform, thin layers from aqueous dispersions on the mandrel. Commercial dispersions had to be suitably modified to provide wetting and adherence to deposited TFE films and to furnish final films that would be even in clarity or opacity and free of mud-cracking. While basic fabrication techniques were being developed, a series of investigations established the optimum conditions for the determination of crystallinity in Teflon by x-ray diffraction, infrared spectrophotometry, differential thermal analysis, and density. Constant comparison was made of crystallinity results for Teflon powders

and commercial films to determine crystallinity ranges in which correlation could be had for all methods and some attempts were made to discern reasons for lack of correlation. The first acceptable films were made from aqueous dispersion of TFE as thin (2-3 mils) films (to provide samples transparent enough to permit infrared determinations). They were prepared by methods substantially similar to those employed by commercial fabricators, i.e., sintering of each layer of deposited dispersion for 20 minutes at about 360°C and quenching by spraying with liquefied carbon dioxide.

Having achieved some success with film fabrication and crystallinity determinations by the latter part of the first year of this program, a systematic series of experiments was set up to determine the effects of broad differences in the primary process parameters of sintering temperature, sintering time, and cooling (or quenching) rate and the conditions which would produce the least crystalline (most amorphous) film.

The three sintering temperatures chosen for study were (1) 330°C; the temperature just above the melting point of TFE (determined by DTA to be 327°C and sufficient for the flow of an amorphous species); (2) the temperature used in commercial fabrication of bladders, 360°C; and (3) a temperature at the point of incipient decomposition of TFE (determined by mass spectroscopy), 400°C.

The sintering times were based on (1) manufacturer's recommendations of 5 minutes; (2) fabricators' practice, 20 minutes; and (3) an extreme of 2 hours. (The time for conversion of crystalline film to an amorphous state was determined by infrared spectrophotometry to be more than 24 hours at 330°C, almost immediate at 360°C, and almost immediate at 400°C.)

Cooling rates were based on (1) a programmed rate of 3.7°C/min; (2) air-cooling at a rate of 50°C/min; and (3) rapid quenching in ice-water, 24°C/sec. The rapid quenching, accomplished by sudden plunging of the mandrel at sintering temperature into an ice/water bath, was designed to be more effective in "freezing" the film uniformly in its most amorphous state than fabricators' practice of trying to spray hot films quickly and evenly with liquefied carbon dioxide.

The results of the above series of experiments indicated that the most crystalline and least flex-resistant film resulted when the PTFE film was sintered after the application of the final layer for 20 minutes

at 360°C and then cooled slowly at a rate of 3.7°C/min. The most flexible film (one of the lowest crystallinities) was obtained when the PTFE was sintered at 400°C for 20 minutes and immediately quenched in ice/water. A similar low crystallinity and high flex resistance was obtained when a film was sintered at 360°C for 2 hours and quenched in ice/water. Thus, it was determined that immediate ice/water quenching was required to produce PTFE films of low crystallinity, and the experiments suggested that even longer sintering times at 360°C should yield films of better flex resistance.

Corroboration of the effect of rapid cooling on crystallinity and the reproducibility of the procedure was demonstrated by making two sets of films from two different batches of dispersions\* and comparing the results with those obtained for the first experimental films described above. All films were sintered for 20 minutes at 360°C after each spray application and air-cooled; after the final application, the films were sintered for 20 minutes at 360°C and cooled at different rates:

<u>Film</u>	<u>Cooling Rate</u>	<u>Crystallinity, %</u>
EX-A	0.028°C/sec	83.1
No. 10	0.033°C/sec	83.0
EX-1-S1	0.062°C/sec	79.0
EX-1-S2	0.8°C/sec	78.3
EX-B	1°C/sec	73.7
No. 8	1°C/sec	74.8
EX-C	20°C/sec	61.8
No.9	20°C/sec	60.1
EX-1-S3	24°C/sec	61.8

These data suggest that rapid quenching of the hot film and mandrel is essential for reproducibly fabricating films of low crystallinity.

Additional films were prepared by sintering each layer of dried dispersion at 360°C for 20 minutes and then varying the final sinter time from 20 minutes to 24 hours; all films were quenched in ice/water.

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\*One set of the films was delivered to JPL as documentation.

Representative data indicate that the flex resistance is a sharp function of sinter time but that the crystallinity does not vary in direct correlation with flex resistance:

<u>Film</u>	<u>Sinter Time</u>	<u>Crystal- linity, %</u>	<u>Cycles to Failure</u>
EX-1-S3	20 min	61.8	5
No. 11	5 hr	65.3	15
No. 14	6 hr	56.3	357
No. 16	12 hr	63.4	242
No. 17A	24 hr	48.0	487

The JPL crease tester has been used during this work; the tester and the reproducibility of test results are described in Section II.

Additional data like those given above, supplemented by the fact that many hours are required for the re-alignment of Teflon crystals at 350-370°C, provoked the thought that perhaps it was the character of orientation of crystallites in the films rather than the per cent crystallinity which was affecting flex resistance. A series of electronmicrographs were made of a large number of the films prepared for evaluating the process parameters; they suggested that this was a correct approach. The electronmicrographs show the progression from highly-crystalline random orientation (short sinter, slow cooling rate) to lesser-developed crystallite formation in more-or-less circular chains (short sinter, rapid quenching) to longitudinal and more amorphous structures which are intertwined and entangled (24-hr sinter, rapid quenching). With this confirmation, it is clear that work must continue toward examining the effects of even longer sintering times. As hinted in some of the data reported at this time and by some work recently performed, sufficiently-long sintering may negate the need for rapid quenching and permit simpler cooling techniques in the commercial fabrication of flexible Teflon-TFE films.

In line with the findings above, it appeared possible that stretching of Teflon films, such as is encountered in the expulsion cycles of Teflon

bladders, may cause an increase in crystallinity or increased orientation of crystal structure. An increase in directionally-oriented crystallinity will create embrittlement at a point of flexure and possibly lead to early failure. Linear orientation of crystallinity is readily possible in PTFE because of the lack of cross-linking in the polymer, leading to anisotropy; films may be stronger along the direction of applied force, but they will be weaker at  $90^{\circ}$  to the force, and thus under biaxial stress films may rupture readily. Laue photographs of films stretched for examination indicated that orientation takes place from as little as 75% elongation.

Tests performed at JPL with the permeation of hydrazine through commercial Teflon bladders indicated that the decomposition of the hydrazine occurs within the film; also, emission spectroscopic analysis of films showed the presence of  $\text{Cr}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in significant quantities. The presence of  $\text{Cr}_2\text{O}_3$  can be accounted for because commercial bladders are often prepared on a mandrel over-coated with a chromium-containing Teflon emulsion to promote adherence of the Teflon build-up. However, the presence of iron, phosphorus, etc. had to be attributed to impurities in the original Teflon emulsion. Co-ordinated with the work on preparing Teflon films from commercial aqueous dispersions were intense analyses of impurities present in the dispersions; as summarized in Section IV, the identified impurities are carried through in processing the dispersions and cannot be attributed to pick-up from long-term contact with storage containers.

Also in Section IV, some properties of Teflon pertinent to space storage with  $\text{N}_2\text{O}_4$  are discussed. The data illustrate the relationship of crystallinity to density, to the solubility of  $\text{N}_2\text{O}_4$ , and to the swelling caused by  $\text{N}_2\text{O}_4$ . Although the effects of swelling on physical properties have not been evaluated at this time, it is suggested that the swelling may lead to lowered tensile strengths and a greater tendency to undergo crystalline orientations under stress. Additionally, it is possible that swelling by  $\text{N}_2\text{O}_4$  can cause bond failure between the polymer and metal laminates.

#### CLADDING OF TEFLON FILMS AND PERMEABILITY

Examination of available information on the permeability of PTFE to  $\text{N}_2\text{O}_4$  especially at low crystallinity, suggested that it would be more

immediately practical to include barriers impermeable to  $N_2O_4$  in Teflon films by deposition of metals rather than by laminating processes. It had been reported that lead deposited from a fluoroborate bath onto a Brashear silver coating on Teflon needed burnishing to provide a uniform, hole-free surface, so the first approach was to seek a different bath; an alkaline lead bath was developed successfully to provide a smooth and uniform coating with metallic luster. Subsequently, it was found that the silver coating deposited by a Brashear method was not adhering to the PTFE. Initial work at JPL had shown that the coating was more tenacious when supersonic agitation was used in the processes, but no use was made of this technique at SRI since it was anticipated that a practical process for deposition of lead on the inside of a bladder could not employ supersonic agitation. A modification and simplification of the Brashear process provided for a more tenacious bonding of the silver coating to the Teflon surface. Then, when the alkaline lead bath was used for film surfaces as large as 10" X 15", the final lead plate was not uniform. Fortunately, the modified Brashear silvering led to the production of a uniform lead surface from a fluoroborate bath.

Since the final success of a lead cladding is dependent on the adhesion of the silver coating, it was surmised that a "porous" Teflon surface would provide a better keying-in of the initial silver coating than the smooth surface resulting from the usual Teflon film fabrication from aqueous dispersions. A special porous-surfaced film was prepared, and test results indicated that the bond was broken (at about 400 psi) at the silver-lead interface in contrast to the Teflon-silver break (about 185 psi) for a film with a smooth surface.

Several test films were prepared with lead coatings of 0.4 to 1.2 mils in thickness; resultant permeabilities to  $N_2O_4$  were of the order of 0.02 to 0.2 mg/hr-in<sup>2</sup> for 5.4-mil thick Teflon films compared with 13-20 mg/hr-in<sup>2</sup> for 5-mil thick Teflon films without lead cladding.

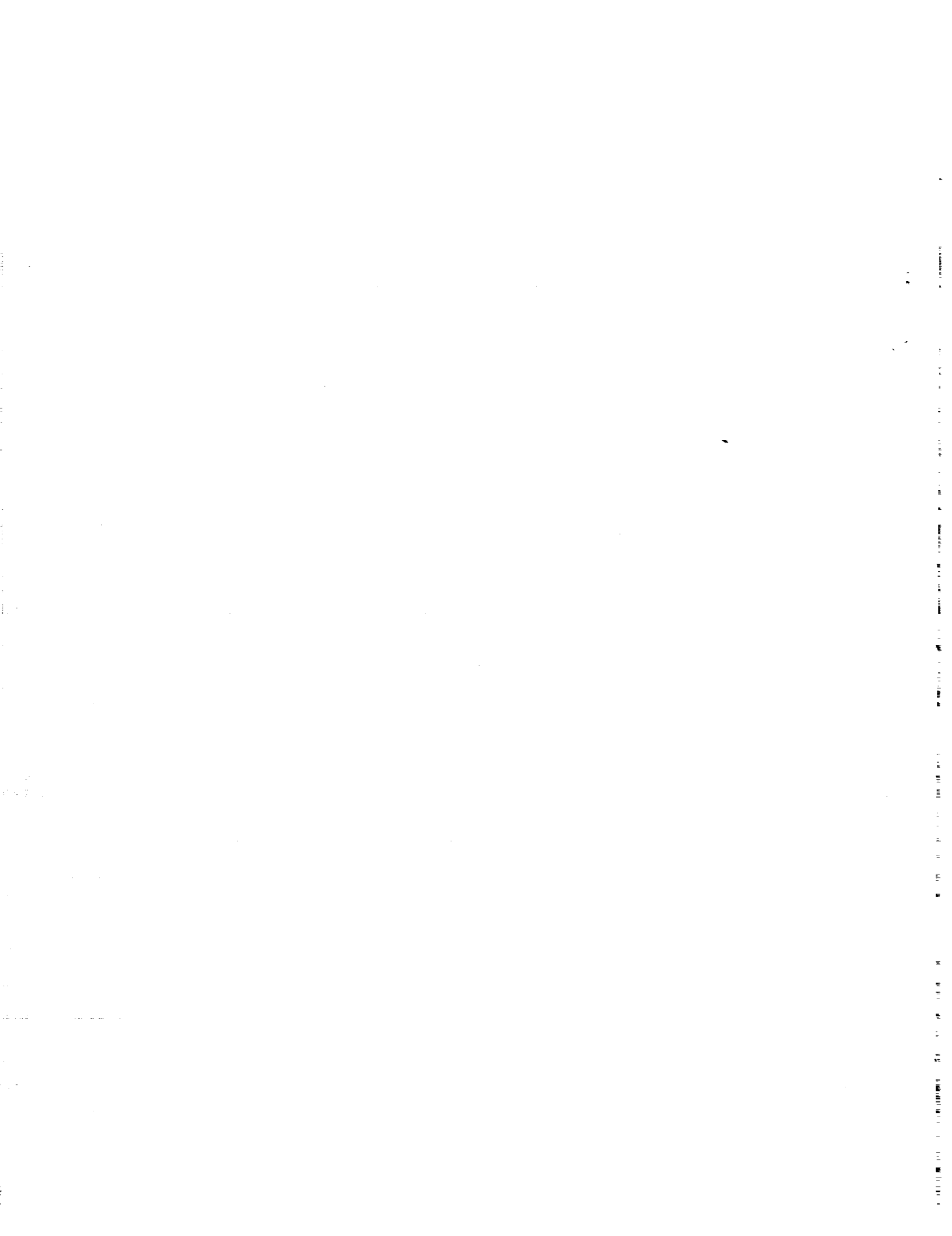
The above procedures and data are given in detail in Section V. Continuing work will involve the transfer of the plating techniques to prototype expulsion bladder spheres and hemispheres.

## POLYMERIC MATERIALS FOR USE WITH $\text{OF}_2$ and $\text{B}_2\text{H}_6$

Storable, high-energy liquid fuels and oxidizers are quite reactive with most organic materials. From available literature, it was discerned that Teflons were probably the only materials compatible with  $\text{OF}_2$ ; the literature also indicated that polyterephthalate, polycarbonate, and polyethylene materials were compatible with  $\text{B}_2\text{H}_6$ , but examination of polymeric materials under conditions of flex or stress had not been reported and thus it was not known if the polymers become embrittled at cryogenic temperatures or if they react violently with  $\text{OF}_2$  or diborane when flexed or torn in the presence of these liquids.

It was necessary to establish a test method which would provide short-term tests to determine the mechanical behavior of selected polymeric films at cryogenic temperatures and while immersed in  $\text{OF}_2$  or  $\text{B}_2\text{H}_6$ . A micro (small sample size and small propellant-volume) crease-and-fold tester was designed and constructed to perform such tests. It was found that none of the materials selected for test with either propellant had a flex resistance of more than a few cycles at temperatures less than  $-60^\circ\text{C}$  in an inert (Freon) medium. In tests with  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$  at  $-78^\circ\text{C}$  and  $-135^\circ\text{C}$ , the same low order of flex cycles (1 to 6) was recorded for the films tested; no signs of flaming or deflagration were observed during these tests under flex and strain in the propellants.

Complete details of the micro crease-and-fold tester are given in Section VI, and the work with  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$  is discussed in Section VII. Although further work is not contemplated with the  $\text{OF}_2$ - $\text{B}_2\text{H}_6$  system at this time, the micro tester will be of great value in evaluating Teflon films and lead-clad Teflon films in  $\text{N}_2\text{O}_4$  and  $\text{N}_2\text{H}_4$  under conditions of flexing during the continuing program.





II. PREPARATION OF TEFLON FILMS  
FROM TFE-30 DISPERSIONS

At present, seamless Teflon expulsion bladders are fabricated by processes which have been established more or less empirically. Briefly, one of these processes consists of spraying a suitably-prepared Teflon dispersion onto a thin-walled, rotating aluminum mandrel. Each layer of about 0.2-0.4 mil thickness is dried and then sintered. When the Teflon layer is of the desired thickness, caustic is pumped into the mandrel to dissolve the aluminum, leaving the bladder free-standing. A small percentage of bladders are discarded because of obvious imperfections, but the completed bladders are far from being reliable or uniform in quality. Disqualifying factors may be gross discoloration, mud-cracking, splitting, loss of mechanical properties, and pin-holes or excessive permeability.

The first activities in the study of the process of manufacture involved construction of a film-preparation facility so that the effects of process variables could be examined in detail. Then the basic techniques for handling and applying the dispersions were developed.

During the course of this year's program, process parameters have been developed for the fabrication of Teflon films from TFE-30 dispersions, which have low crystallinity and high resistance to flexures. The essential steps required to produce such films are as follows:

- (1) After the spray application of a layer of about 0.2 to 0.4-mil thickness, the film on the mandrel is sintered for 20-30 minutes at 360-370°C and then air-cooled. Additional layers are put on to form a film of the required thickness.
- (2) After the final spray application, when the final film of required thickness is completed, the film (still on the mandrel) is sintered for more than 24 hours at 360-370°C.
- (3) The film and mandrel at sinter temperature are quenched at a cooling rate of more than 20°C/second, accomplished by an immediate and total plunge into an ice/water bath.

Steps (2) and (3) are currently not employed in the commercial preparation of Teflon bladders.

#### EQUIPMENT

Spraying, sintering, and cooling operations are carried out in a small, isolated room which has been equipped to provide dust-free atmosphere. About 600 ft<sup>3</sup>/min of air enters the room through an MSA filter system and is exhausted at the rate of about 400 ft<sup>3</sup>/min through a hood over the spraying booth and 200 ft<sup>3</sup>/min under the doorway. By maintaining a positive pressure in the room, unfiltered air does not enter the room through fissures. (See Figure 1.)

A simple block diagram of the equipment used for the preparation of films is shown in Figure 2. The motor powering the lathe (Craftsman wood lathe) is equipped with a variable transformer so that the speed of rotation of the mandrel can be controlled over the range of 5-20 rpm; the mandrel is rotated at 15-20 rpm during the spray applications. The mandrel is fabricated as a right-cylinder from 4-inch diameter aluminum 6061-T6 alloy tubing (1/16" wall) and polished to a 16-32 micro-inch finish; the end plates are perforated to permit the passage of air or other coolant for uniform quenching. A thermocouple is embedded in the center of the mandrel on the inside; the leads come through holes in the end plates. The mandrel is supported between centers and is driven by a dog. The oven slides on one of the mandrel-supporting centers and can be positioned directly over the mandrel to permit in situ sintering. The oven temperature is controlled within  $\pm 2^{\circ}\text{C}$  with a Wilkens A-235 linear temperature programmer and a platinum resistance sensing element. In contrast to the prevalent commercial practice whereby infrared lamps are used to dry the sprayed films prior to sintering, the experimental Teflon films are baked dry and sintered by the oven which is at temperature when slid over the mandrel.

A 10-mv Varian G-10 recorder is used to measure the cooling rate of the mandrel after sintering a film. A precision potentiometer is used with the recorder to apply voltage when that generated by the thermocouple is in excess of 10 mv. By reading the applied and recorded voltages, the

actual temperature of the mandrel can be determined. The rate of cooling over the range of 370°C to about 275°C is of interest.

A Paasche AURF-1 air brush is used with a high-purity compressed air source for spraying the dispersion onto the mandrel. The prepared dispersion is contained in an 1/2-liter stainless steel container under a pressure of 25 psia, maintained by connection with the compressed air source used for spraying. This vessel was developed to prevent the evaporation of the dispersion on the walls above the liquid (as occurs in an open container), and subsequent contamination of the liquid by large, dried particles which fall into it. This problem may be peculiar to experimental work, where only small quantities of dispersions are used over relatively long periods of time.

#### FABRICATION PROCEDURE

The dispersion is fed to the spray gun via Teflon tubing, which eliminates the possibility of contamination by plasticizers which are easily extractable by water from most synthetic tubings. The line is fitted with a 40 $\mu$ -60 $\mu$  sintered glass filter in order to control particle size and reduce the possibility of large particles being imbedded in the film. The flow of the dispersion is metered at the gun, and the spray is applied to the mandrel perpendicular to its axis and in one progressive motion along the axis at a rate and distance established by practice. It has been found that each applied layer of Teflon must be no more than 0.2- to 0.4-mil thick in order to ensure uniformity of deposition and to prevent mud-cracking after sintering.

Note: The TFE-30 dispersions were applied directly to bare, polished aluminum surfaces without intermediary of a chromium-containing primer coating in prevalent use for the commercial fabrication of Teflon bladders. No problems were encountered with the adhesion of PTFE to the aluminum mandrels and it was found that films could be easily stripped without necessity of dissolving away the aluminum substrate.

The film is sintered under the prescribed conditions of time and temperature, the mandrel (and film) are cooled according to selected

conditions, and another layer of Teflon is deposited. Twenty or more applications are required to build a final film of 6-mil thickness.

#### DISPERSIONS

Aqueous Teflon dispersions manufactured by E. I. Du Pont de Nemours and Company, Inc. were used for this work. The choice of specific dispersions was made in order to investigate the same materials as those used in the commercial fabrication of expulsion bladders. At the outset of this program, three dispersions were obtained in one-gallon quantities for exploratory work and are described below:

Teflon TFE-30. - An aqueous dispersion containing 59-61% of tetrafluoroethylene solids with a particle size of 0.05 to 0.5 $\mu$  and 5.5-6.5%\* of a nonionic wetting agent. It is recommended for use as a general coating or impregnant where superior heat-aging characteristics are required [1].

Teflon TFE-30B. - An aqueous dispersion containing 59-61% of tetrafluoroethylene solids with a particle size of 0.05 to 0.5 $\mu$  and 5.5-6.5% of a nonionic wetting agent. It is recommended for fabric impregnation where superior dispersion wetting characteristics are needed [2].

Teflon TFE-3170. - An aqueous dispersion containing 59-61% of tetrafluoroethylene solids with an average particle size of  $\sim 0.2\mu$ . Ionic and non-ionic wetting agents are added.

The dispersions are at a nominal pH of 10 (adjusted with ammonium hydroxide), and contain Triton X-100 (octylphenoxy polyethoxy ethanol)<sup>†</sup> as the nonionic wetting agent; the ionic wetting agent in TFE-3170 has not been identified by Du Pont, but SO<sub>2</sub> and SO ions have been identified in the mass spectra of this dispersion, indicating the presence of a sulfate; sodium alkyl sulfates are often used as emulsifiers in Teflon dispersions.

All of the dispersions were obtained in one-gallon cube-shaped polyethylene containers. They arrived with (or developed) a surface film and

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\* Values for wetting agents are given as per cent of solids.

† Rohm and Haas.

sediment of rust-to-greenish colored matter, which was identified as iron hydroxide (see Section III for additional details).

Organic impurities (less than 0.02% by weight) in the dispersions were determined by mass spectroscopy to be squalene (TFE-3170) and dioctylphthalate (in all dispersions). The source of squalene is difficult to ascertain; its presence may be due to fingerprints or it may be a deliberate additive for plasticity or it may come from the polyethylene container. Dioctylphthalate is one of the most widely-used plasticizers in resin manufacture. Hence, its presence in the Teflon dispersions may be due to storage in a polyethylene container, but it has also been found in skived films and in samples prepared by the Dilectrix Corporation from dispersions stored in epoxy-lined drums. Incidentally, squalene has also been detected in FEP films.

It is interesting to note that, in contrast with whitish films produced from TFE-30 and 30B, films prepared from TFE-3170 were quite discolored, reminiscent of organic charring. Also, it was more difficult to prepare films from this dispersion.

#### Dispersion Modification

The fabrication of Teflon films centered largely about the use of diluted dispersions of TFE-30. It was found that a dispersion containing 30% solids by weight and 8% Triton X-100 (based on weight of solids) provided the best surface-wetting characteristics and the best control of the thickness of the sprayed layers. Table 1 indicates the ranges of concentrations used in the preparation of typical Teflon membranes used during the program of work.

The modified dispersions are prepared in 500-g batches. An amount of 2.25 g Triton X-100 is weighed into a small beaker and then transferred by washing with de-ionized water into a large beaker where it is further diluted to 250 g with de-ionized water and gently stirred into solution. The weight of the mixture is then brought to 500 g by the addition of 250 g of the TFE-30 dispersion in small amounts, stirring throughout the additions.

The modified dispersion is then filtered through a coarse sintered glass filter (40 $\mu$  to 60 $\mu$ ) into the steel dispersion container for immediate use or into a glass storage bottle.

#### Dispersion Storage

A settling-out of as-received Teflon dispersions was noted during storage for 4 to 6 months and initial failures in film preparation were easily ascribed to the agglomeration of particles initially about 0.5 $\mu$  into particles of about 60 $\mu$ . It has since been determined that raw dispersions should not be stored for more than 2 months, preferably less; also, it has been found that the storage life of a diluted or modified dispersion is of the order of less than one week. Settled particles cannot be re-dispersed with ease, and they appear to agglomerate further on agitation; gentle, daily agitation seems to reduce settling-out, but does not de-agglomerate particles.

The inclusion of a glass filter in the line from the dispersion container to the spray gun has been essential in this work for filtering out agglomerated particles.

#### PROCESS PARAMETERS

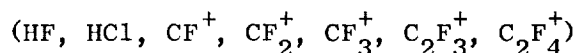
Subsequent to the development of an optimum dispersion for experimental work, films were prepared on a systematic basis in order to determine the process parameters which lead to the most flexible films possible from TFE-30 dispersions. Typical films made during the early stages of the work program are summarized in Table 2.

#### Sintering Temperature

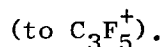
Three sintering temperatures were selected for evaluation: 330 $^{\circ}$ C, 360 $^{\circ}$ C, and 400 $^{\circ}$ C. The lowest temperature, 330 $^{\circ}$ C, was selected since it is just slightly above the melting point (327 $^{\circ}$ C) of TFE as determined by differential thermal analysis (DTA) and conceivably is sufficient to provide for the formation of an amorphous species. The highest temperature,

400°C, was selected on the basis of mass spectroscopic data as the maximum sintering temperature (the point of incipient decomposition). The 360°C temperature between the two extremes is just above a phase transition temperature for Teflon (356°C) and is the temperature used for commercial fabrication of bladders (355°C).

The decomposition temperature of TFE was determined by examining the mass spectra of the substances vaporized from a Teflon Film (TFE-3170) at incremental temperatures. The film sample, about 1 mg, was placed in the probe of the SRI direct introduction system for a 21-103C mass spectrometer (Consolidated Electrodynamics Corporation). Mass spectra of vaporizing substances were recorded at 25°C intervals from 200° to 500°C and show that the incipient decomposition occurs at 400°C:



and steady decomposition occurs at 425°C:



It is interesting to note that a number of commercial and experimental Teflon materials (TFE and FEP) which have been examined give off copious quantities of CO<sub>2</sub> at 95°C, and that CO<sub>2</sub> continues to be released as the sample temperature is raised, even at 425°C. A possible source of carbon dioxide may be de-carboxylation of end groups. Alternatively, it is also possible that carbon dioxide itself may be quite soluble in TFE or strongly adsorbed in the polymer matrix.

It was also necessary to prove that sintering of TFE at 400°C in an oxygen atmosphere does not lead to oxidative degradation. To this end, a small sample of a TFE film was maintained at 400°C in an oxygen atmosphere for as long as 48 hours in a thermogravimetry apparatus. The only weight loss incurred by the sample, about 0.5%, occurred in the early phases of heating; thereafter, no weight loss was detectable (±0.1%). Although the thermogravimetric determination suggests that little, if any, degradation takes place at 400°C., it is recognized that the molecular

weight distribution of the polymer may be affected by prolonged heating at elevated temperatures.

The uniformity of films prepared from Teflon dispersions may be quite dependent on the uniformity of the temperature of the mandrel. In order to determine the distribution of heat from the sintering oven at SRI, ten thermocouples were mounted on a 1/16-in wall aluminum mandrel which was placed in the oven. The sintering oven was pre-set for 360°C, and the oven and mandrel were allowed to equilibrate for 6 hours before any temperature measurements were made. The temperature measurements and the location of thermocouples are shown in Figure 3. The data indicate that temperature differences are within  $\pm 2.5\%$ .

### Sintering Time

Sintering times included manufacturer's recommendations (5 minutes) and fabricator's practice (20 minutes), as well as extremely long periods (e.g., 24 hours). The shorter sintering times provided for flowing together of the particles deposited from the emulsions, but it was found that these short times of sintering often led to pinholes or other discontinuities in the final films. The longer sintering times appeared to produce integral films.

Nearly all of the sintering times selected for study appeared to be long enough to permit conversion of crystalline PTFE to the amorphous state. In fact, the time required at a given temperature for Teflon films to be converted from a crystalline state to an amorphous state was determined by infrared spectrophotometry and found to be:

330°C	more than 24 hours
360°C	almost immediate
400°C	almost immediate

In these instances, a Teflon (TFE) film was maintained at a fixed temperature (in a dual heated-cell system) until it achieved equilibrium as indicated by the stabilization of the infrared spectrum. The per cent crystallinity at equilibrium is measured by the absorptions noted at  $12.85\mu$  ( $780\text{ cm}^{-1}$ ) and  $4.25\mu$  ( $2350\text{ cm}^{-1}$ ); the  $4.25\mu$ -band is a measure of



thickness and the 12.85- $\mu$  band is a measure of amorphicity. Infrared absorbance curves showing the differences in characteristics for a 90% crystalline film at room temperature and a film heated at 400°C are shown in Figure 4.

It must be remembered that although the sintering time at a given temperature is only the time required for conversion of crystalline particles to an amorphous film, the complete removal of water, wetting agents, and extraneous organics requires longer heating times. In fact, it has been shown by mass spectroscopy that a film sintered at 360°C for 2 hours (each layer) still contains a plasticizer and a residue of the wetting agent (or its decomposition product). (The possible effect of these "contaminants" will be discussed later.)

The relationship of sintering time at about 360-370°C to the flex resistance of Teflon films prepared by spraying from modified commercial dispersions is shown in Table 3. Although the recorded values were obtained from initial experiments, it is evident that sintering times of more than 24 hours are required for film crystallinities of less than 60% and flex resistances (JPL tester) of more than 500 cycles.

#### Cooling Rates

Three cooling rates were selected for evaluation in order to determine the effect of rapid temperature change on mechanical properties and crystallinity of the films. The rates were measured from sintering temperature to below the gel-point (327°C) of Teflon and were controlled by: (1) hand-operation of the controller to provide for a decrease of 10°C/min which resulted in a cooling rate of the oven of 3.7°C/min; (2) removing the sintering oven and allowing the mandrel to cool in air (50°C/min); and (3) plunging the mandrel at sintering temperature into an ice-water bath (at least 24°C/sec).

Rapid cooling is achieved as follows: After the final layer has been deposited, dried, and sintered for a short period of time, the mandrel is removed from the lathe and mounted in a vertical furnace (see Figure 6). The mandrel is held in the furnace on a shaft with a spring trigger; after

the requisite time of sinter, the lower part of the furnace is opened and the mandrel is triggered and allowed to fall into the lower bucket containing ice/water mixture.

The relationship of cooling rate/crystallinity/flex resistance for TFE films prepared at SRI is shown in Table 2. It is clearly seen that high degrees of crystallinity result in low values for flexure resistance and that crystallinity is a marked function of cooling rate. The immediate plunge of the PTFE film from sinter temperature into ice-water ensures a low degree of crystallinity and a uniform distribution of crystallites.

#### CHARACTERIZATION OF PREPARED FILMS

The films prepared during this program of work were examined for tensile strength and elongation, crease-and-fold resistance, and crystallinity. The permeability of the greater portion of the films fabricated was not determined because prior work had indicated that properly prepared TFE films would have permeability values (to  $N_2O_4$ ) governed almost entirely by the crystallinity of the PTFE in the range of 1.5 to 11 mg/hr-in<sup>2</sup> (Table 2 and Section V).

Tensile Strength and Elongation. - Tensile and elongation measurements of the Teflon films were made at about 70°F, using an Instron Model TTCIM-6; in order to conserve film supplies, a scaled-down tensile specimen was used. The test specimens had a gage length of 1,000 inch and a width of 0.125 inch. Six determinations were made on each film at a cross-head speed of 0.5 in/min; determinations included three specimens cut perpendicular and three specimens cut horizontal to the axis of the mandrel.

#### Crease-and-Fold Resistance

The flexure test employed at SRI is a severe three-cornered crease-and-fold test designed by the Jet Propulsion Laboratory of the California Institute of Technology to simulate the flexures of an actual expulsion bladder in spacecrafts. The test apparatus, loaned by JPL, is shown in Figure 5; it induces a traveling three-corner fold in a 2" x 8" sample. The sample is pulled back and forth under tension over two inclined blades which intersect at an angle with a fixed gap between. Materials were

supplied by JPL to detect pin-holes by means of a two-color dye system, i.e., a strongly-colored dye painted on the back surface of a film would become visible because of a developed pin-hole in the white dye painted on the top surface of a film. However, since Teflon is not easily wetted and the procedure was empirical at best, a spark-gap hole-detector system, similar to that described by King and Gregory [3] was adapted for use in the system.

Three stainless steel rollers have been incorporated as electrodes into the JPL tester in such a position that the film must pass between them as it is flexed by the reciprocating action of the tester (see Figure 5). High voltage is applied between the center and outside rollers from a source which can be adjusted at a level below the dielectric breakdown strength of the film. When a hole occurs in the film, ionization of the air between the rollers triggers the detector circuit, which then turns off the tester.

The electrical hole detector is basically more sensitive than dye penetration for the detection of even the tiniest holes in a Teflon membrane. Thus, tests with the JPL apparatus at SRI may tend to indicate a lower number of cycles to failure than reported previously by other workers [4]. Further, the detection of pinholes by dye penetration in laminates wherein separation of layers can afford pockets for dye accumulation appears to be questionable; it is submitted that some of the higher flex-resistance values reported may be in error.

An investigation was made of the effect of specimen width in tests conducted with the JPL crease tester. Teflon-FEP Type A (5 mil) was selected for this study because it was felt that its physical properties would be more uniform than the experimental films and a sufficient quantity was readily available for extensive testing. Three sets of 15 test specimens were prepared to have widths of 1.75, 2.00, and 2.25 inches. The results obtained in this study (Table 4) indicate that sample width does have a measurable effect on the flex resistance of Teflon films; while this effect is not very large, there is an apparent trend to be noted.

An investigation of the effect of gap width was also made with Teflon FEP Type A films. The results are given in Table 5; it appears that the gap width must be maintained to within 20%.

As a result of these investigations, the JPL test apparatus was operated under the following conditions:

Temperature	20-25°C
Tension	2.5 lb.
Blades	Flat
Included Angle	120°
Cant Angle	2°
Gap Width	0.006 inch
Sample Width	2.25 ± 0.05 inches
Film Thickness	5 + 1.0 mils
Electrical Hole Detection	

In order to determine the reproducibility of the crease-and-fold testing for sample strips taken at random from films produced at SRI, experimental films were prepared from a dispersion formulated as follows:

TFE-30 dispersion (Blend/Lot 6969)	50.0%
H <sub>2</sub> O, de-ionized	49.5%
Triton X-100 (Lot 1984)	0.5%

Triton X-100 was dissolved in the de-ionized water and the TFE-30 dispersion was added in small portions while the mixture was being stirred. The dispersion was then blended by stirring at slow speed for 30 minutes. The dispersion was filtered through a 40- to 60-micron sintered glass filter and analyzed:

Total solids	29.20%
Triton X-100*	11.20%
pH at 22°C	9.35
* as % of total solids wt.	

During film fabrication, each spray coat was sintered for 20 minutes at 370°C and air-cooled before the next application. After the final spray application, each film was sintered for 24 hours at 370°C and then

ice/water quenched from sinter temperature. Pertinent data for the films are given below:

<u>Film No.</u>	<u>No. of Spray Applications</u>	<u>Thickness, mils</u>	<u>Crystallinity, %</u>
22	20	6.0 ± 0.2	62.9
23	16	4.0 ± 0.2	60.1

The results of the tests, summarized in Table 6, indicate that a deviation of ±20 cycles-to-failure can be expected in test results for films which have a flex resistance of the order of 200 to 300 cycles, and that samples removed at random from the mandrels give substantially the same values (standard deviation 10 to 20%).

A micro crease-and-fold tester has been constructed in order to utilize smaller samples and to permit testing of films while immersed in a fluid or in a gaseous atmosphere other than air. Details of the test apparatus are given in Section VI. No crease-and-fold tests were performed on TFE films produced at SRI in  $N_2O_4$  or  $N_2H_4$  during this work period since it was felt that it would be best to wait and perform tests on the best films that could be produced.

#### Effects of Process Parameters on Crystallinity

Three Teflon films having low, intermediate, and high crystallinities were prepared from the TFE-30 dispersion for the crystallinity studies described below.\* The dispersion used for spraying was a modification of Blend/Lot No. 6325 with the following formulation:

TFE-30 dispersion	250.00 g
H <sub>2</sub> O, de-ionized	247.75 g
Triton X-100	2.25 g

Triton X-100 was dissolved in the de-ionized water and then the TFE-30 dispersion was added in small portions while the mixture was stirred. The diluted dispersion was then agitated gently on a mechanical shaker

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\* Duplicate films were prepared for retention by the JPL Technical Representative.

for 30 minutes and filtered through a 40- to 60-micron sintered-glass filter. Analysis of the final dispersion indicated:

Total solids	28.04%
Triton X-100	7.98%
pH	9.50 at 22°C

Ten spray applications were made on a 1/16"-wall mandrels; each layer was sintered for 20 minutes at 360°C and then air-cooled; after application of the last layer, the films were sintered at 360°C for 20 minutes and then cooled as follows:

Ice-water quenched	about 20°C/sec
Air-cooled	61.3°C/min
Programmed cooled	1.7°C/min

Each film had a thickness of  $2.8 \pm 0.2$  mils and was free of mud-cracking or occluded particles. The thin films permitted comparison of crystallinity determinations by X-ray and infrared techniques.

The degree and orientation of crystallinity of Teflon-TFE films influences the mechanical properties of the films (especially tensile strength and crease-and-fold resistance). The prevalence and orientation of Teflon crystallites in films with degrees of crystallinity of 83.1%, 73.7% and 61.8% are shown in Figures 7, 8, and 9 as electronmicrographs taken at a magnification of 8,000X; the films were prepared with 20-minute sinters at 360°C followed by cooling at 1.7°C/min, 61.3°C/min, and 20°C/sec, respectively. In Figure 7, the crystallites appear at random; in Figure 8, they are oriented in more-or-less circular chains. In Figure 9, individual crystallites are not seen because the rapid rate of cooling did not permit crystallinity to be developed to as high a degree as at low rates of cooling. If one ignores the filamentous white features (attributable to undissolved PVA used in preparing the electronmicrograph), a circular orientation of crystalline chains is evident. Also, the crystallites appear to be centered about the highly-crystalline TFE particles originally in the aqueous dispersions used to produce the films.

It has been shown by optical techniques [5] that Teflon-TFE crystals remain anisotropic for as long as 6 hours at a temperature of 350-375°C.

It was found also that the decay of anisotropy is a function of time, temperature, and molecular weight. Since the viscosity of a PTFE melt is extremely high ( $\rho = 1 \times 10^{11}$  at  $360^{\circ}\text{C}$ ), it is intuitively obvious that fusion of PTFE particles and re-alignment of PTFE chains cannot take place during short sintering times at  $360^{\circ}\text{C}$ . Given sufficient time to melt and flow, PTFE particles should become a homogeneous melt capable of long-chain re-alignment. Thus, films prepared with sinter times in excess of 24 hours at  $360^{\circ}\text{C}$  should exhibit a high degree of integration of PTFE particles and alignment of PTFE chains, leading to increased flexure resistance; Figure 9 suggests that original crystallite chains have had time to melt, flow, and become intermingled.

The effect on crystallinity of longer sinter times is shown in Figures 10, 11, and 12 (8,000X). Apparently, there is sufficient time for the crystallite chains to re-group themselves into longitudinal rather than circular formations; circularity gives way to elongation after 6-hour to 12-hour sinter times, and finally to a more amorphous structure after a 24-hour sinter. Degrees of crystallinity for the films shown in Figures 10 to 12 are 56.3%, 63.4%, and 49.4%, respectively; although the crystallinity of 63.4% appears to be in nonsequence, it is verified by the stronger appearance of crystallites in the electronmicrograph and the relative decrease in flex resistance (Table 3). Apparently, the cooling rate during fabrication was not adequate and, consequently, the amorphous phase had a chance to re-group and crystallize. In spite of the crystallinity, however, the flex resistance is higher than is usually obtained for such a crystallinity value; this suggests that the inter-twining or entanglement of crystallite centers is the prominent factor in membrane behavior. The result of low crystallinity and chain orientation is an increase in flex resistance, shown clearly in Table 3.

The effect of long sinter time and slow cooling rate on crystallinity is most interesting. As shown in Figure 13, the film structure is highly crystalline and tends toward an intermingled array of linear crystallites.

## VACUUM SINTERING OF TEFLON FILMS

Analysis by mass spectroscopy has shown that all of the Teflon films produced thus far contain contaminant organic compounds which might create undesirable effects when such bladder materials are in contact with oxidizers or fuels, and which might interfere with the deposition of adherent metallic coatings. In an attempt to eliminate organic contaminants, a film was prepared by the standard procedure, heat-treated in vacuo, and then sintered as usual and cooled by quenching in ice/water.

The Teflon film was prepared from a modified TFE-30 dispersion (Blend/Lot No. 6708) with the following formulation:

TFE-30 dispersion	250.00 g
H <sub>2</sub> O, deionized	247.75 g
Triton X-100	2.25 g

Analysis of the final dispersion prior to spraying indicated:

Total solids	29.75%
Triton X-100	7.97%
pH	9.52 at 22°C.

A total of sixteen spray applications were made on a 1/16" wall aluminum mandrel. Each layer was sintered 20 minutes at 360°C and air-cooled. After the final layer was sintered, the mandrel was transferred to the vacuum system specially-constructed for the work. The vacuum sintering process consisted of holding the temperature of the mandrel at 100°C for 8 hours at  $1 \times 10^{-5}$  torr, at 255°C for 16 hours at  $2 \times 10^{-6}$  torr, and at 330°C for 24 hours at  $2 \times 10^{-6}$  torr. Following the vacuum-sintering treatment, the mandrel was removed from the chamber, re-heated for 20 minutes at 360°C, and then ice/water quenched.

The final film (11" x 12") had a thickness of  $4.5 \pm 0.3$  mils and was transparent and free of mud-cracking. As shown in Table 7, physical and mechanical properties were comparable to those for a film which had not undergone vacuum treatment and had been sintered for only 20 minutes.



Mass spectrometric analysis of the vacuum-sintered film indicated that organic contamination had been removed; only carbon dioxide was released from the film at 100° and 125°C.

Vacuum-sintered films may be a requisite for the successful deposition of metal interfaces on TFE films.

Table 1  
PREPARATION OF TFE-30\* DISPERSIONS FOR MAKING  
FLEXIBLE TEFLON FILMS

SRI FILM NO.	SRI BATCH NO.	TFE-30 BLEND/LOT	TRITON X-100 LOT	FORMULATION			ANALYSIS, Wt-%		
				TFE-30	T-X-100	H <sub>2</sub> O	Solids	T-X-100	pH
11	10	6708	1110	50.0%	2.2%	47.8%	29.4	7.4 <sup>†</sup>	9.65
12B	10	6708	1110	50.0	2.2	47.8	29.4	7.4	9.65
13B	10	6708	1110	50.0	2.2	47.8	29.4	7.4	9.65
14	12	6708	1110	50.0	2.3	47.7	29.9	8.9	9.43
15	13A	5782	1984	50.0	2.3	47.7	28.3	8.7	9.64
16	13AB	5782	1984	50.0	2.3	47.7	28.3	8.7	9.64
17A/B	14	5782	1984	50.0	2.3	47.7	29.5	7.4	9.43

\* E. I. Du Pont de Nemours and Company, Inc.

† Triton X-100 values are as % of solids content.

Table 2  
 CHARACTERIZATION OF PRELIMINARY FILMS PREPARED FROM TFE-30 DISPERSION\*

	THICKNESS, mils	TENSILE, psi	ELONGATION, %	CREASE-AND-FOLD TEST				DENSITY, g/cc	CRYSTALLINITY, % (X-Ray, Av.)	PERMEABILITY TO N <sub>2</sub> O <sub>4</sub> , mg/hr/in <sup>2</sup>
				5 cycles	10 cycles	15 cycles	20 cycles			
<u>EX-1-S1</u> sintered 20 min/360°C cooled 3.7°C/min	4.7	3,550	512	3 holes	-	-	-	2.174	79.0	3.08
<u>EX-1-S2</u> sintered 20 min/360°C cooled 50°C/min	3.5	3,480	440	1 hole	8 holes	-	-	2.160	78.3	7.48
<u>EX-1-S3</u> sintered 20 min/360°C cooled 24°C/sec	4.0	4,310	415	1 hole	1 hole	2 holes	-	2.141	61.8	-
<u>EX-2-S5</u> sintered 20 min/400°C cooled 24°C/sec	6.6	3,100	346	0	0	0	0	2.141	61.9	9.12
<u>EX-3-S7</u> sintered 2 hr/360°C cooled 24°C/sec	4.6	4,340	422	0	0	0	1 hole	2.138	61.8	9.66

\* E. I. Du Pont de Nemours and Company, Inc., Batch No. 6325.

Table 3  
 CHARACTERIZATION OF TEFLON FILMS:  
 TYPICAL EFFECTS OF SINTERING TIME ON FLEX RESISTANCE

SRI FILM NO.	THICKNESS, mils	SINTER TIME AND TEMPERATURE	COOLING RATE	CRYSTAL-LINITY	CYCLES TO FAILURE, JPL CREASE TEST <sup>c</sup>
EX-1-S3 <sup>a</sup>	4.0	20 min/360°C	24°C/sec	61.8%	5
EX-3-S7 <sup>a</sup>	4.6	2 hr/360°C	24°C/sec	61.8	5
11	4.9	5 hr/360°C	20°C/sec	65.3	15
12B	4.0	5 hr/360°C, +5 hr/360°C <sup>b</sup>	20°C/sec	55.4	35
13B	3.9	5 hr/360°C, +6 hr/360°C <sup>b</sup>	20°C/sec	55.2	65
14	4.8	6 hr/360°C	20°C/sec	56.3	357
15	4.2	24 hr/360°C	20°C/sec	49.4	1023
16	3.8	12 hr/360°C	20°C/sec	63.4	242
17A	4.8	24 hr/360°C	20°C/sec	48.0	487
17B	4.8	24 hr/360°C	20°C/sec	51.7	521

<sup>a</sup> Data from Interim Report No. 1, June 17, 1967, page 24.

<sup>b</sup> Films were quenched in ice/water after 5 hours, then re-sintered for 5 or 6 hours and quenched again.

<sup>c</sup> Appearance of one pin-hole constitutes a failure. Values represent single determinations.

Table 4  
 EFFECT OF SPECIMEN WIDTH ON MEASUREMENTS  
 MADE WITH THE JPL CREASE TESTER\*  
 (Teflon-FEP Type A, 5-mil)

SPECIMEN NO.	CYCLES TO FAILURE		
	2.25" Wide	2.00" Wide	1.75" Wide
1	83	57	101
2	106	79	38
3	87	84	50
4	91	94	55
5	89	86	81
6	98	58	67
7	123	77	63
8	76	60	47
9	69	77	38
10	98	64	52
11	55	100	85
12	94	62	106
13	89	86	67
14	91	61	78
15	63	61	74
Range	68	42	68
Average	88	74	67
Standard Deviation	25%	20%	30%

\* At 23°C.

Table 5  
 EFFECT OF BLADE GAP WIDTH ON CREASE-AND-FOLD  
 MEASUREMENTS MADE WITH THE JPL CREASE TESTER\*  
 (Teflon-FEP Type A, 5-mil)

SPECIMEN NO.	CYCLES TO FAILURE	
	0.006" Gap	0.060" Gap
1	83	63
2	106	58
3	87	72
4	91	66
5	89	73
6	98	58
7	123	73
8	76	53
9	69	53
10	98	67
11	55	50
12	94	36
13	89	46
14	91	60
15	63	75
Range	68	39
Average	88	60
Standard Deviation	25%	20%

\* At 23°C.

Table 6  
 REPRODUCIBILITY OF CREASE-AND-FOLD TESTS\* OF TWO TEFLON  
 FILMS PREPARED FROM TEFLON TFE-30 DISPERSIONS

SPECIMEN NO.	FILM NO. 22		FILM NO. 23	
	Direction	Cycles to Failure	Direction	Cycles to Failure
1	equat.	273	axial	212
2	equat.	224	axial	197
3	equat.	261	axial	221
4	equat.	210	axial	204
5	axial	241	equat.	234
Range	63		37	
Average	241		214	
Standard Deviation	11%		11%	

\* JPL crease tester: 23°C.

Table 7  
 COMPARISON OF PROPERTIES OF TEFLON FILMS  
 PREPARED BY SINTERING IN VACUUM VS. SINTERING IN AIR

PROPERTY	VACUUM SINTERED*	AIR SINTERED
Thickness, mils	4.5	4.0
Crystallinity, %	63.9	61.8
Tensile Strength, psi	4,145	4,310
Elongation, %	495	415
Permeability to N <sub>2</sub> O <sub>4</sub> (mg/hr/in <sup>2</sup> )	1.49	1.00
Crease-and-fold, 5 cycles	0 holes	1 hole
10 cycles	1 hole	1 hole
15 cycles	13 holes	2 holes

\* Removed from vacuum; reheated to 360°C for 20 minutes; ice-water quenched.



FIG. 1 PHOTOGRAPH OF FACILITY FOR PREPARING TEFLON FILMS

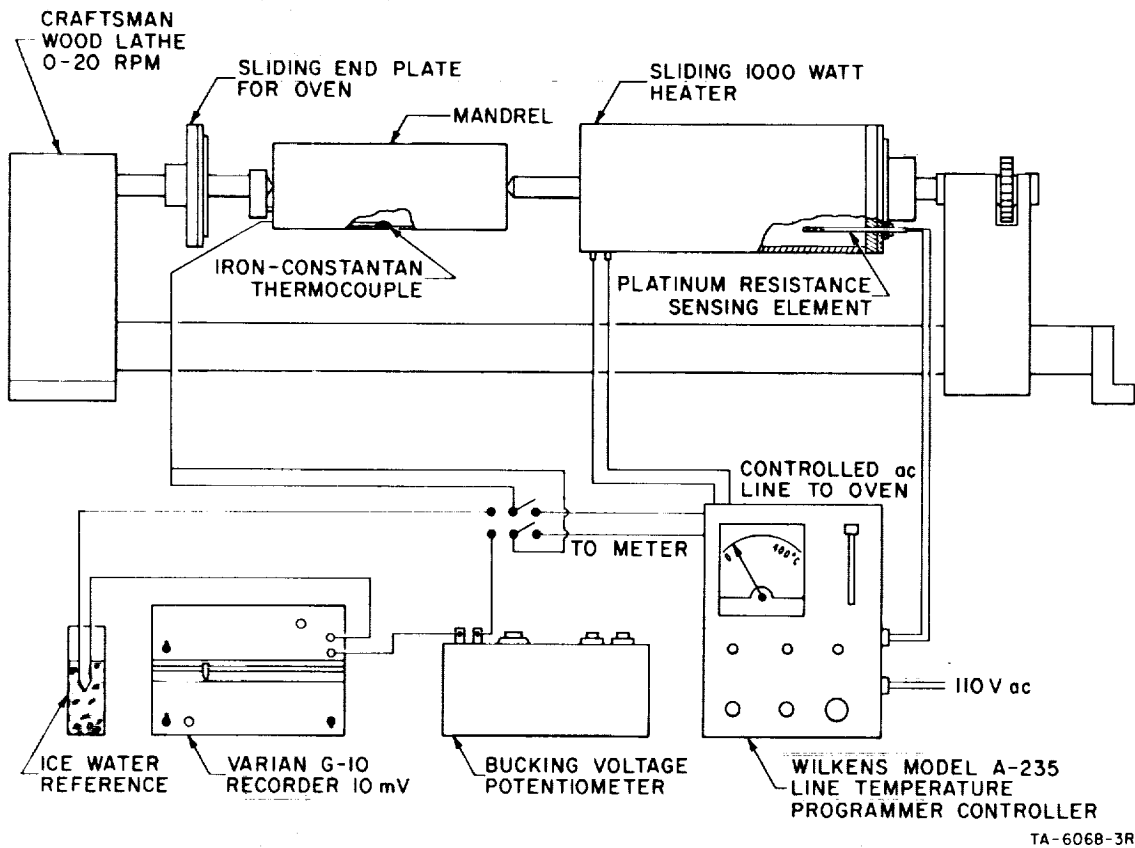
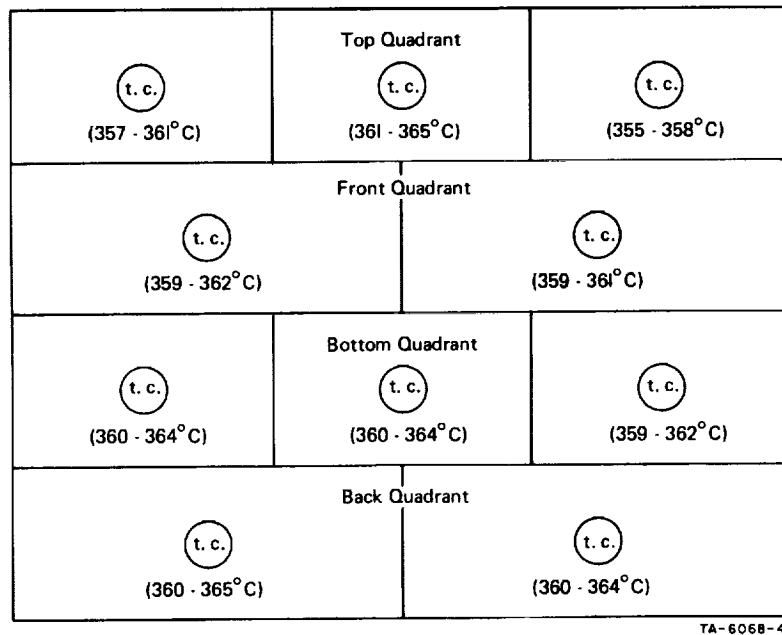


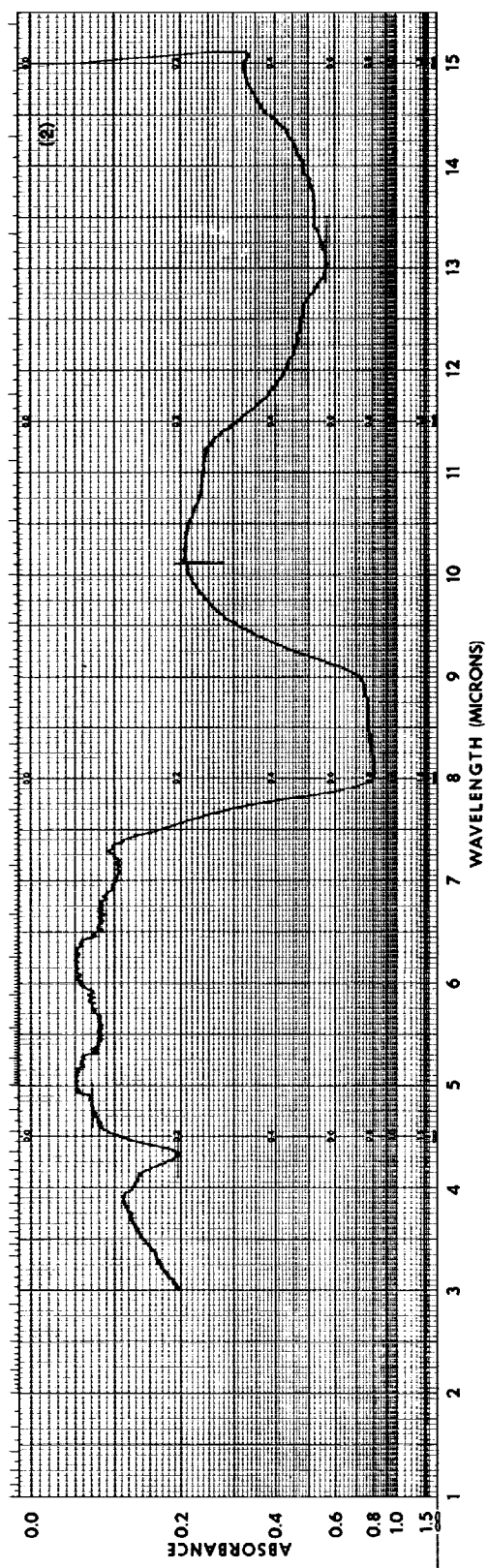
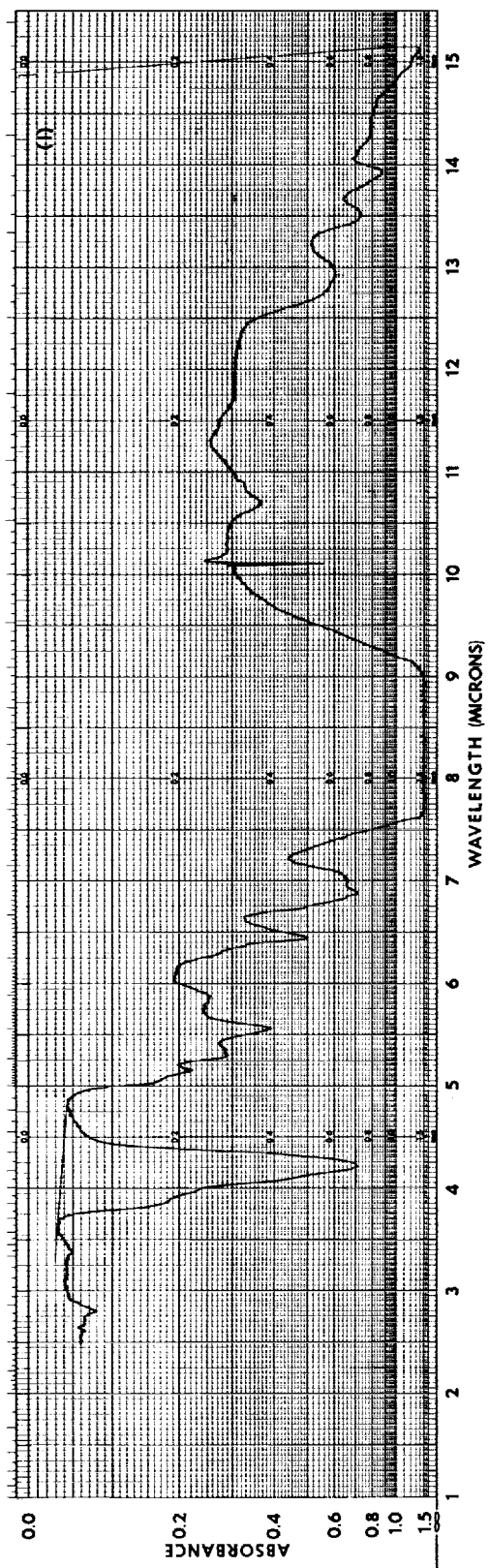
FIG. 2 DIAGRAM OF EQUIPMENT FOR PREPARING TEFLON FILMS





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FIG. 3 PLANAR VIEW OF MANDREL INDICATING THERMOCOUPLE LOCATIONS AND TEMPERATURE RANGES  
 Mandrel is 4.0 in. O.D. aluminum, 11.0 in. long, with 0.625 in. wall.



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FIG. 4 INFRARED ABSORBANCE CURVES OF TEFLON FILMS SHOWING THE RELATIONSHIP OF THE 4.25 $\mu$  BAND TO THE 12.85 $\mu$  BAND FOR CRYSTALLINE AND AMORPHOUS SPECIES (Upper) About 90% crystalline, at room temperature. (Lower) Essentially amorphous, at 400°C.

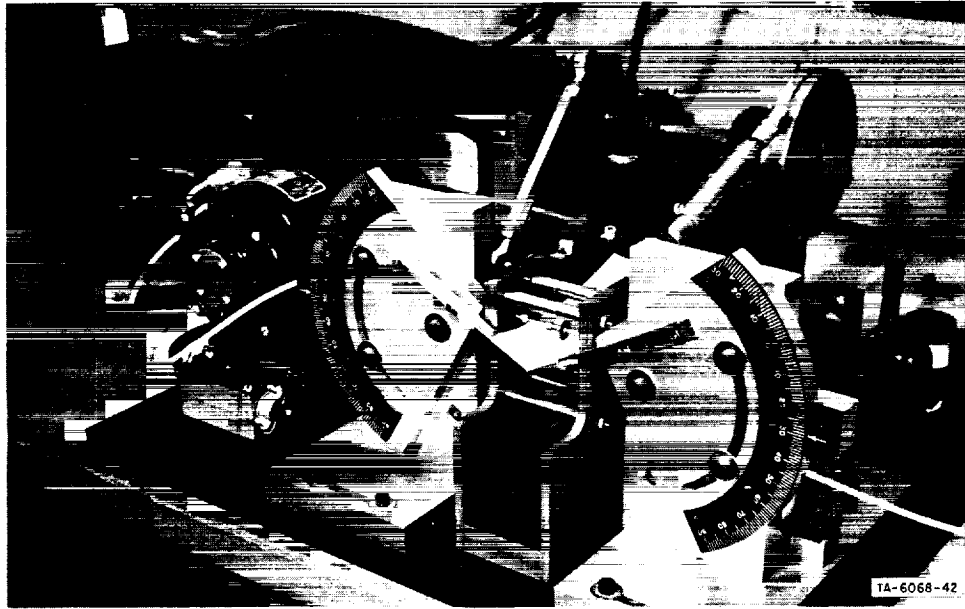


FIG. 5 JPL CREASE-AND-FOLD TESTER INSTALLED AT SRI  
WITH ELECTRICAL HOLE DETECTION DEVICE

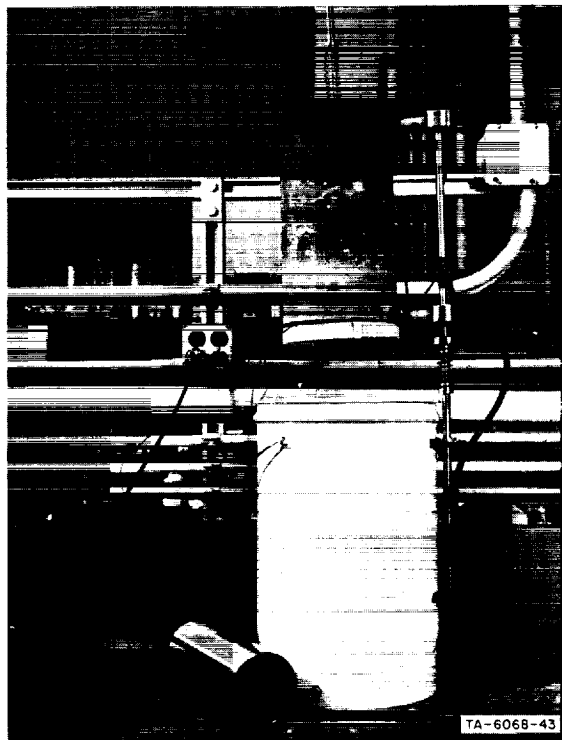


FIG. 6 ARRANGEMENT FOR PLUNGING  
THE HOT MANDREL  
INTO AN ICE/WATER BATH



FIG. 7 ELECTRONMICROGRAPH (Reversed Image) OF TEFLON-TFE FILM WITH 83.1% CRYSTALLINITY (8,000X)

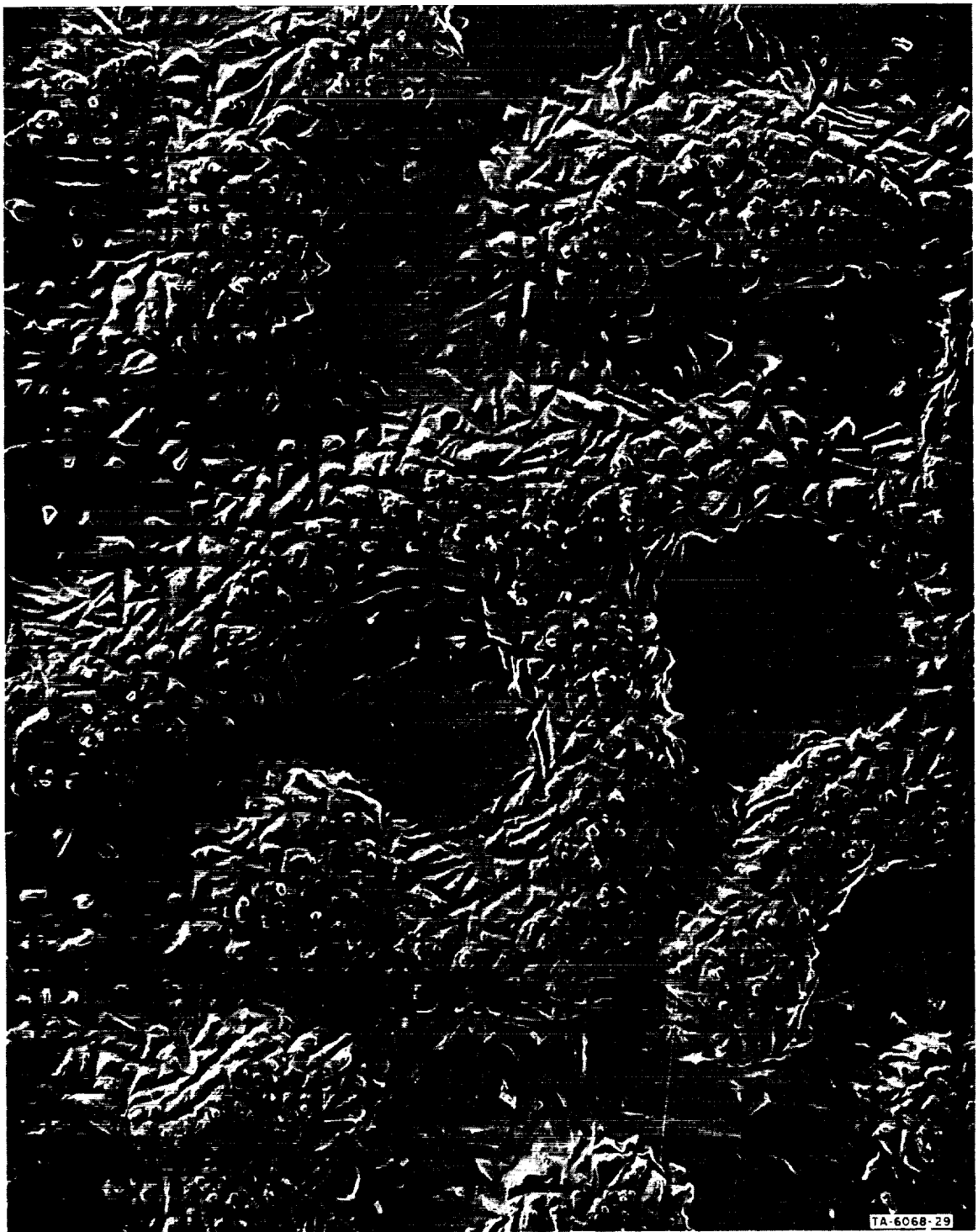


FIG. 8 ELECTRONMICROGRAPH (Reversed Image) OF TEFLON-TFE FILM WITH 73.7% CRYSTALLINITY (8,000X)

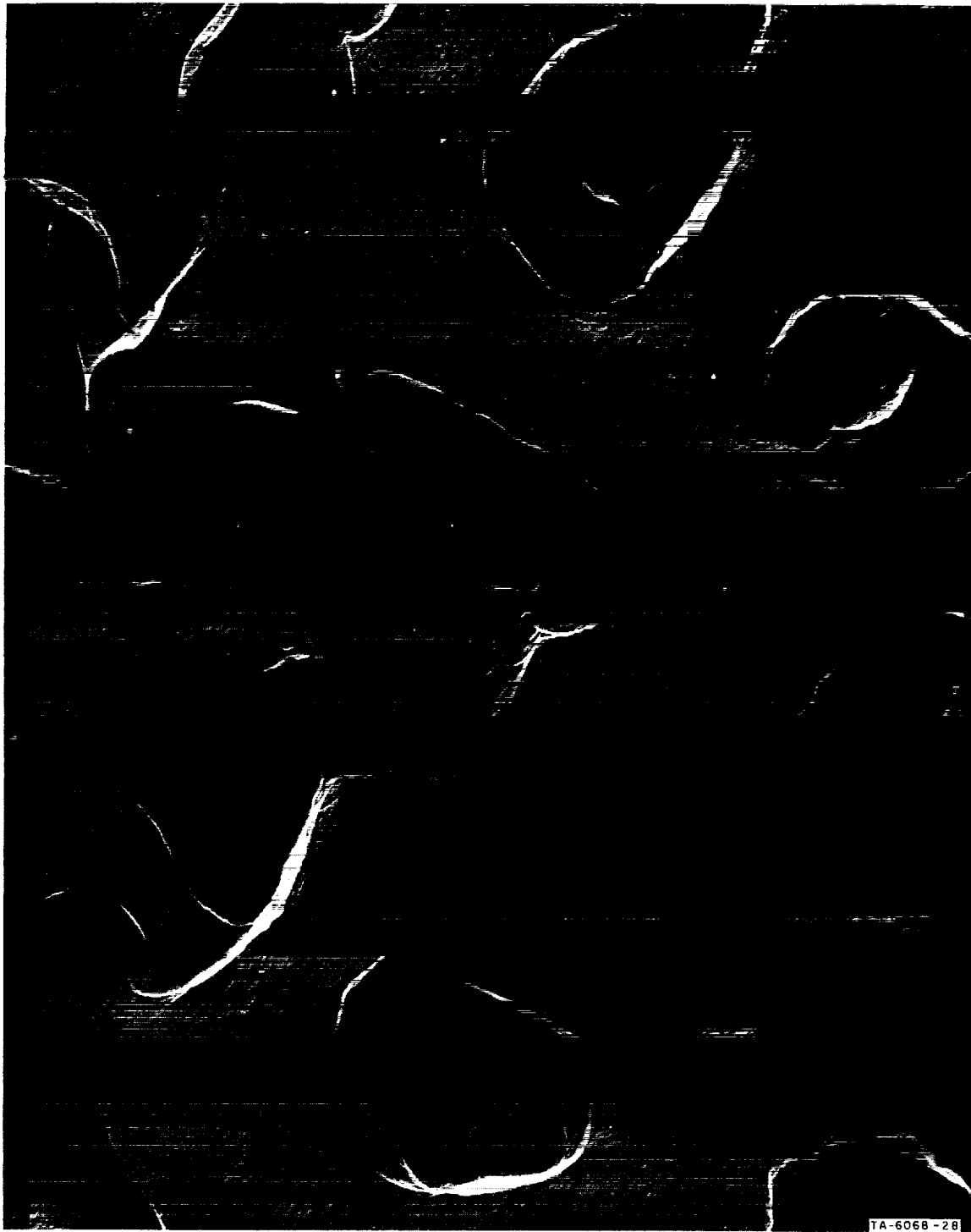


FIG. 9 ELECTRONMICROGRAPH (Reversed Image) OF TEFLON-TFE FILM WITH 61.8% CRYSTALLINITY (8,000X)



FIG. 10 ELECTRONMICROGRAPH (Direct Image) OF TEFLON-TFE FILM  
SINTERED 6 HOURS AT 370°C (8,000X)

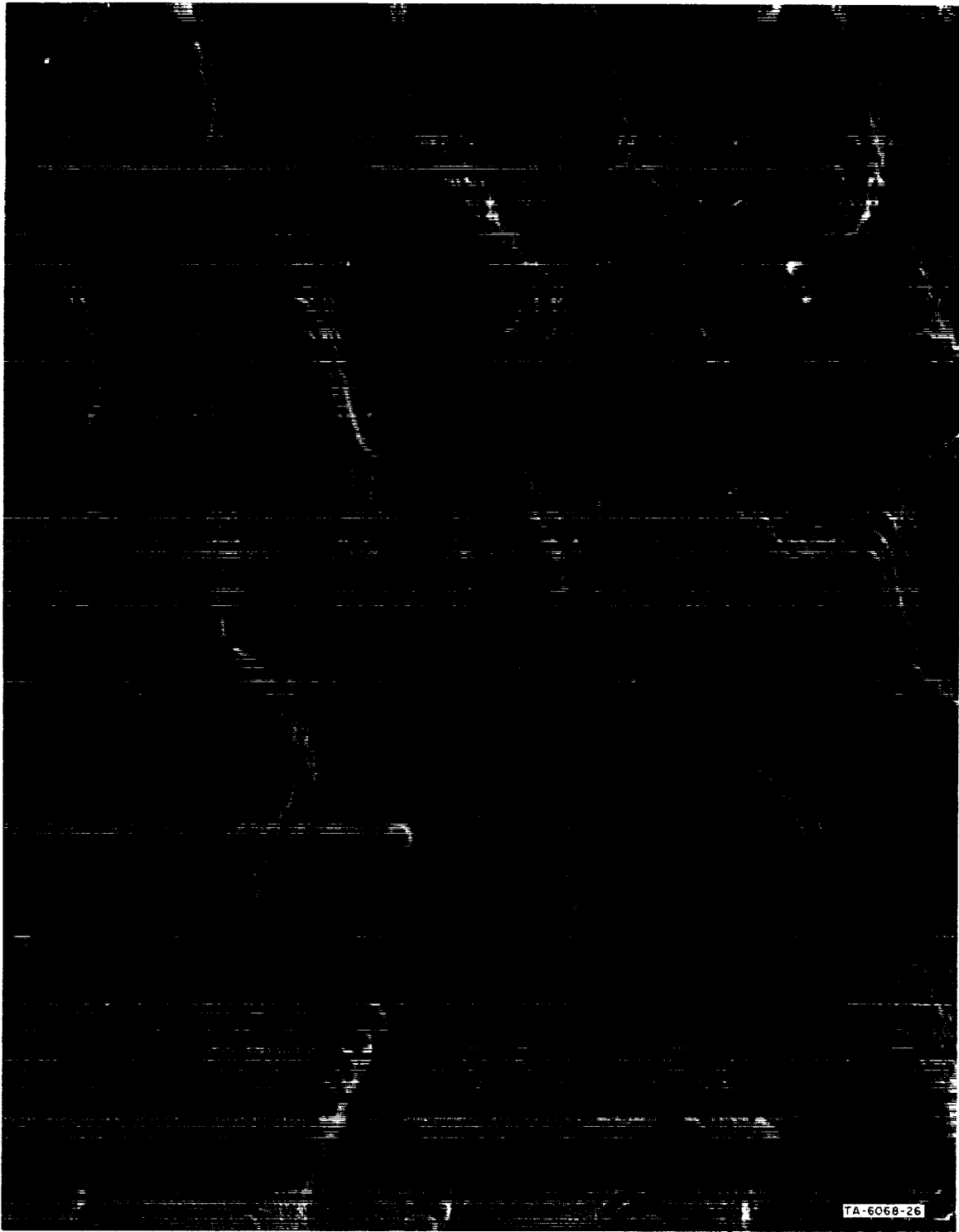


FIG. 11 ELECTRONMICROGRAPH (Direct Image) OF TEFLON-TFE FILM  
SINTERED 12 HOURS AT 370°C (8,000X)





FIG. 12 ELECTRONMICROGRAPH (Direct Image) OF TEFLON-TFE FILM  
SINTERED 24 HOURS AT 370°C (8,000X)



FIG. 13 ELECTRONMICROGRAPH OF TEFLON-TFE FILM SINTERED AT 350-370°C FOR 72 HOURS AND COOLED AT 2°C/MIN (8,000X)

### III. ANALYSES OF TEFLON DISPERSIONS AND PELLETS

A comprehensive study of the preparation of Teflon films for expulsion bladders requires a knowledge of the properties of Teflon in its various forms. To this end, the Teflon dispersions have been analyzed for contaminants and the relationships of crystallinity, density, and solubility in and swelling with  $N_2O_4$  have been determined for highly-compacted Teflon pellets.

#### CHEMICAL ANALYSES OF DISPERSIONS

During discussions at the Du Pont organization, attended by representatives from Du Pont, SRI, JPL, and Dilectrix, speculation was made on the source of impurity components in the Teflon dispersions (see Figure 14) and whether the impurities were inadvertently introduced by storage in metal containers or were derived from additives in the manufacturing processes. In a co-operative effort, Du Pont provided SRI with four kinds of dispersions which were taken from an old inventory, and subsequently supplied four equivalent dispersions from freshly-produced stock.

A comparison of the impurity contents of the several dispersions, summarized in Table 8, indicates that there are no significant differences between old stock and new stock for TFE-42, and no significant differences for FEP-120 (which has the highest impurity content) except for larger contents of calcium and magnesium in the new stock. The older batch of TFE-30 has a higher level of total residue, iron, sodium, and phosphorus than the new stock, whereas the new batch of TFE-30B has a higher level of total residue, calcium, magnesium, and phosphorus than the old stock. In no case does the total impurity content (as determined) of any dispersion exceed 100 ppm; in the work involved with film preparation at SRI thus far, the effect of impurities has not been studied, but it is anticipated that impurities will affect catalytic decomposition of hydrazine.

## PROPERTIES OF HIGH-DENSITY TEFLON PELLETS

High-density Teflon pellets were prepared from Du Pont's TFE-7 casting powder for determinations of crystallinity, density, solubility of  $N_2O_4$ , and swelling caused by  $N_2O_4$ . In accord with modern theory, it was found that the density, solubility for  $N_2O_4$ , and swelling of Teflon in  $N_2O_4$  are a function of crystallinity.

The press for making Teflon pellets is illustrated in Figure 15. The base-plate die was fastened to the body of the press and about 2 grams of Teflon casting powder were introduced through a powder funnel; then the press was connected to a vacuum system with appropriate fittings and the press nut was tightened about the ram until an hermetic seal was effected. (Glass wool and stainless steel wire screen were put in the side-arm to prevent entry of powder into the vacuum system.) The valve between the press and vacuum system was opened slowly to prevent eruption of the powder from occluded gases; it was found that many hours at room temperature are required to complete the outgassing of Teflon powder.

When the powder was outgassed, a thermocouple was affixed to the press body and the press was wrapped with a heating tape and insulating material. Thence, the temperature of the press was controlled by the input from a variable transformer. After being held at a temperature of  $250^{\circ}$  to  $260^{\circ}C$  overnight while the press with the powder charge was being evacuated, the press temperature was raised to  $350^{\circ}$ - $360^{\circ}C$  and maintained at this temperature for at least two hours. Then a C-clamp was positioned about the press and the ram was forced down; positive pressure was maintained on the ram for at least 15 minutes at the press temperature of  $350^{\circ}C$ . The heating tape was removed; pressure was applied continuously by means of the C-clamp while the measured temperature decreased to the order of  $125^{\circ}C$  (about 20 minutes). When the temperature fell below  $70^{\circ}C$ , the press was removed from the vacuum system and dismantled so that the pellet (about  $1/4''$  thick) could be removed.

Different degrees of crystallinity in the prepared pellets were obtained by heating two of them for 3/4 hour in air at 340°C followed by cooling to room temperature at 2°C/minute, and by heating two others for one hour in air at 340°C and cooling them rapidly by quenching in ice/H<sub>2</sub>O. Then the pellets were milled to provide two plane-parallel surfaces so that accurate measurements could be made before and after immersion in N<sub>2</sub>O<sub>4</sub>; measurements were made with a micrometer; the thickness of the finished pellets varied from 0.136 to 0.139 inches.

The crystallinity of the pellets was determined by x-ray diffraction and the density of material received from the machining of the pellets was determined by pycnometry. The pellets were placed in glass ampoules with several milliliters of N<sub>2</sub>O<sub>4</sub> and the ampoules were sealed-off in the absence of air. After storage for one week at about 25°C, the ampoules were opened. The final thickness of the pellets was measured and then, as rapidly as possible, the N<sub>2</sub>O<sub>4</sub> droplets adhering to the surfaces were wiped off and the pellets were dropped into stoppered flasks containing a dilute solution of hydrogen peroxide in distilled water. After the pellets had soaked in this solution overnight, the acid formed by hydrolysis of the N<sub>2</sub>O<sub>4</sub> was determined by acid-base titration and computed as wt-% solubility of N<sub>2</sub>O<sub>4</sub> in Teflon.

The results of the determinations for crystallinity, density, solubility, and swelling are given in Table 9. The abnormally low density of the pellet of 47.6% crystallinity is almost certainly due to the presence of internal voids. Comparison of the measured density with the theoretical "true" density derived from the %-crystallinity determined by x-ray diffraction indicates that the void content is approximately 9%. Internal voids in this pellet are indicated also by the unusually high "solubility" of N<sub>2</sub>O<sub>4</sub> in it. Data for the other three pellets vary smoothly with crystallinity. As shown in Figure 16, the theoretical curve plotted for crystallinity vs density is a straight line from 0% at ~2 g/cc to 100% at 2.305 g/cc; the data points obtained for the three pellets are in good agreement with the theoretical curve (based on

exhaustive x-ray studies). It is also of interest to note that a crystallinity of less than 50% (38%) was easily obtained. The solubility of  $N_2O_4$  in low-crystallinity material (the most flexible) is so great that high permeation rates will of necessity be observed in bladders made from this material; further, the swelling caused by  $N_2O_4$  may prove troublesome when laminates of TFE and metals are used in propellant systems.

Table 8

COMPARISON OF IMPURITY CONTENTS OF DU PONT TEFLON DISPERSIONS FROM OLD INVENTORY AND NEW INVENTORY

Description	Residue, ppm		Iron, ppm		Calcium, ppm		Magnesium, ppm		Sodium, ppm		Potassium, ppm		Phosphorus, ppm		Ammonia wt-%					
	Blend/Lot	Aqueous	Solid	Total	Aqueous	Solid	Total	Aqueous	Solid	Total	Aqueous	Solid	Total	Aqueous						
Dispersions, New Inventory																				
TFE-30	6969 (1)	8.0	5.0	13	0.37	0.065	0.44	0.27	0.014	0.28	0.062	0.109	2.85	0.090	2.94	0.125	0.146	0.271	2.14	0.0303
	(2)	8.0	6.0	14	0.39	0.036	0.42	0.28	0.020	0.30	0.063	0.099	2.86	0.095	2.81	0.178	0.029	0.206	2.00	0.0304
TFE-30B	7082 (1)	80	29	109	0.16	0.12	0.28	0.66	0.014	0.67	0.087	0.27	16.3	0.64	17.0	0.380	0.30	0.68	13.1	0.0259
	(2)	68	9	77	0.14	0.10	0.24	0.46	0.029	0.49	0.070	0.25	16.4	0.59	17.0	0.30	0.04	0.34	12.8	0.0251
TFE-42	6971 (1)	11	9	20	0.46	0.087	0.55	0.08	0.03	0.110	0.05	0.08	0.32	0.11	0.43	0.124	0.05	0.17	<1	0.0496
	(2)	7	7	14	0.49	0.03	0.52	0.07	0.004	0.074	0.02	0.08	0.30	0.10	0.40	0.104	0.05	0.15	<1	0.0490
FEP-120	127 (1)	163	13	176	0.63	0.49	1.12	0.88	0.02	0.90	0.35	0.42	15.4	0.91	11.3	39.4	1.46	40.9	11.6	0.0427
	(2)	134	61	195	0.50	0.39	0.89	0.88	0.04	0.92	0.30	0.35	15.7	0.83	16.5	34.0	1.94	35.9	11.6	0.0416
Dispersions, Old Inventory																				
TFE-30	6862 (1)	38	2	40	0.62	0.11	0.73	0.25	0.009	0.26	0.01	0.016	90.1	22.8	112.9	0.15	0.09	0.24	5.50	0.0286
	(2)	40	8	48	0.52	0.14	0.66	0.13	0.08	0.21	0.12	0.13	81.3	9.3	90.6	0.10	0.12	0.22	5.40	0.0280
TFE-30B	5943 (1)	22	16	38	0.05	0.09	0.14	0.15	0.01	0.16	0.04	0.05	16.7	1.0	18.7	0.30	0.045	0.35	3.1	0.0296
	(2)	17	10	28	0.10	0.14	0.24	0.09	0.10	0.19	0.03	0.04	20.3	4.5	24.5	0.28	0.06	0.34	3.0	0.0293
TFE-42	6864 (1)	16	16	32	0.13	0.70	0.83	0.12	0.01	0.13	0.03	0.06	0.35	0.10	0.45	0.04	0.16	0.20	<1	0.0572
	(2)	5	14	19	0.11	0.40	0.52	0.10	0.01	0.11	0.01	0.02	0.50	0.001	0.50	0.02	0.16	0.12	<1	0.0579
FEP-120	120 (1)	98	83	181	1.7	0.17	1.9	0.26	0.002	0.26	0.01	0.020	19.9	0.89	20.9	49.7	10.0	59.7	6.00	0.0619
	(2)	145	45	180	1.6	0.14	1.7	0.08	0.007	0.09	0.007	0.017	20.0	0.70	20.7	25.1	27.8	52.9	5.0	0.0619

Table 9  
 CRYSTALLINITY OF TEFLON VS. DENSITY,  
 SOLUBILITY OF N<sub>2</sub>O<sub>4</sub>, AND SWELLING BY N<sub>2</sub>O<sub>4</sub>

CRYSTAL- LINITY, %(X-RAY)	DENSITY, g/cc	SOLUBILITY OF N <sub>2</sub> O <sub>4</sub> , wt.-%	SWELLING BY N <sub>2</sub> O <sub>4</sub> , THICKNESS, %
74.7	2.229	0.624	0
56.0	2.150	1.59	1.10
(47.6)*	(1.949)	(7.68)	(1.46)
38.1	2.105	2.59	2.91

\* Estimated 9% void content; see text.



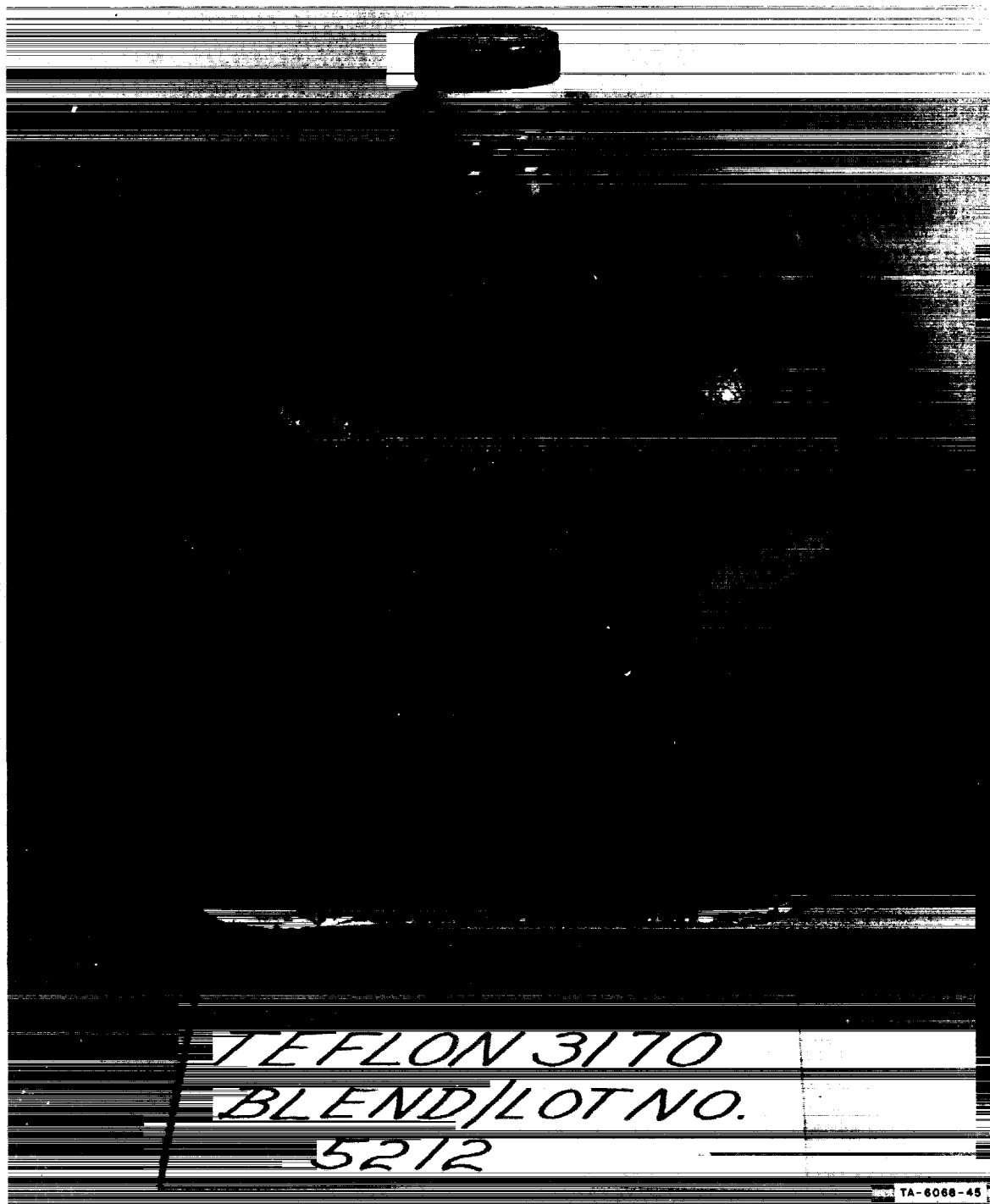


FIG. 14 PHOTOGRAPH OF TEFLON DISPERSION IN ONE-GALLON POLYETHYLENE CONTAINER; NOTE PRECIPITATE OF IRON HYDROXIDE

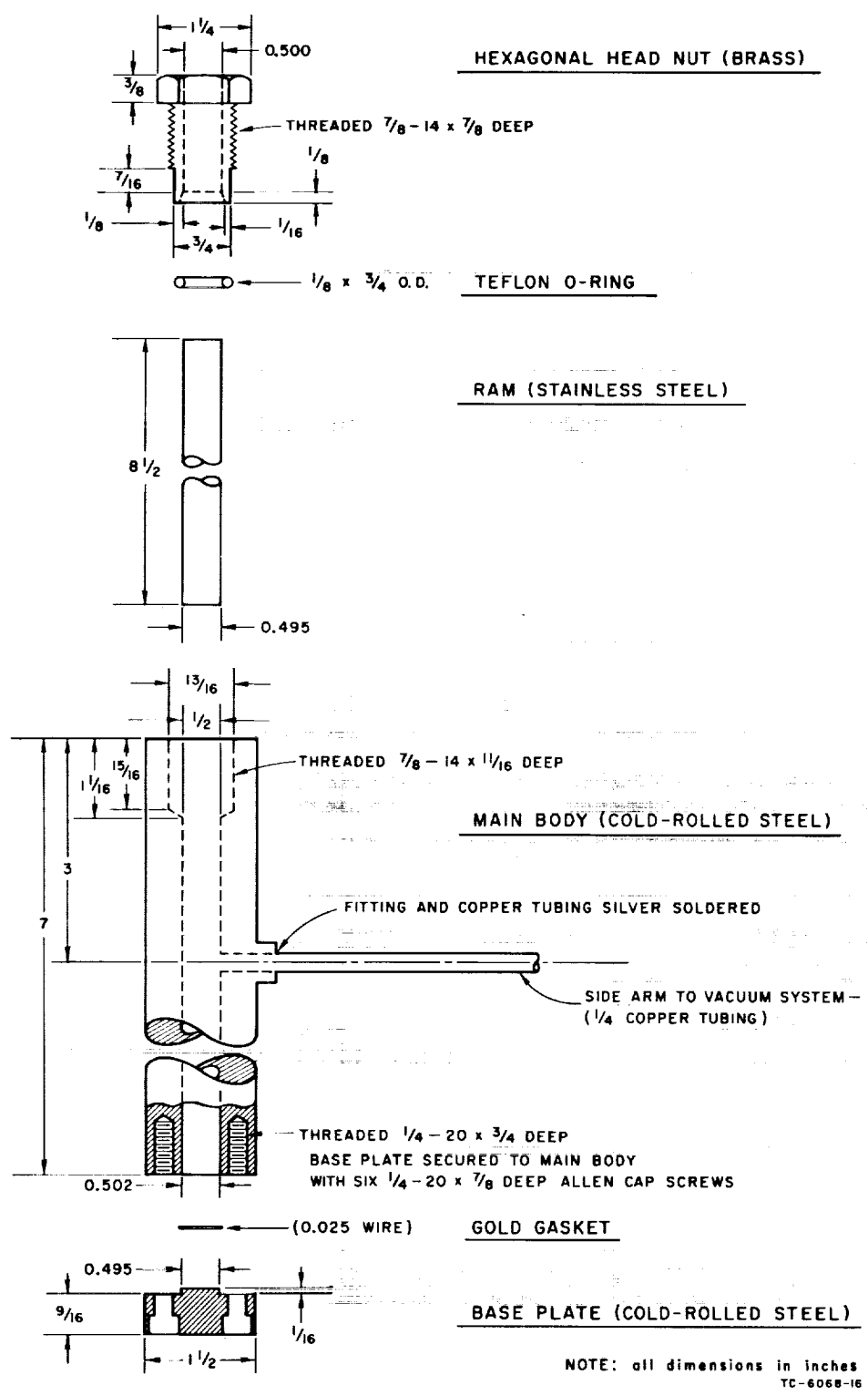


FIG. 15 PRESS BODY, BASE-PLATE DIE, AND RAM FOR MAKING TEFLON PELLETS

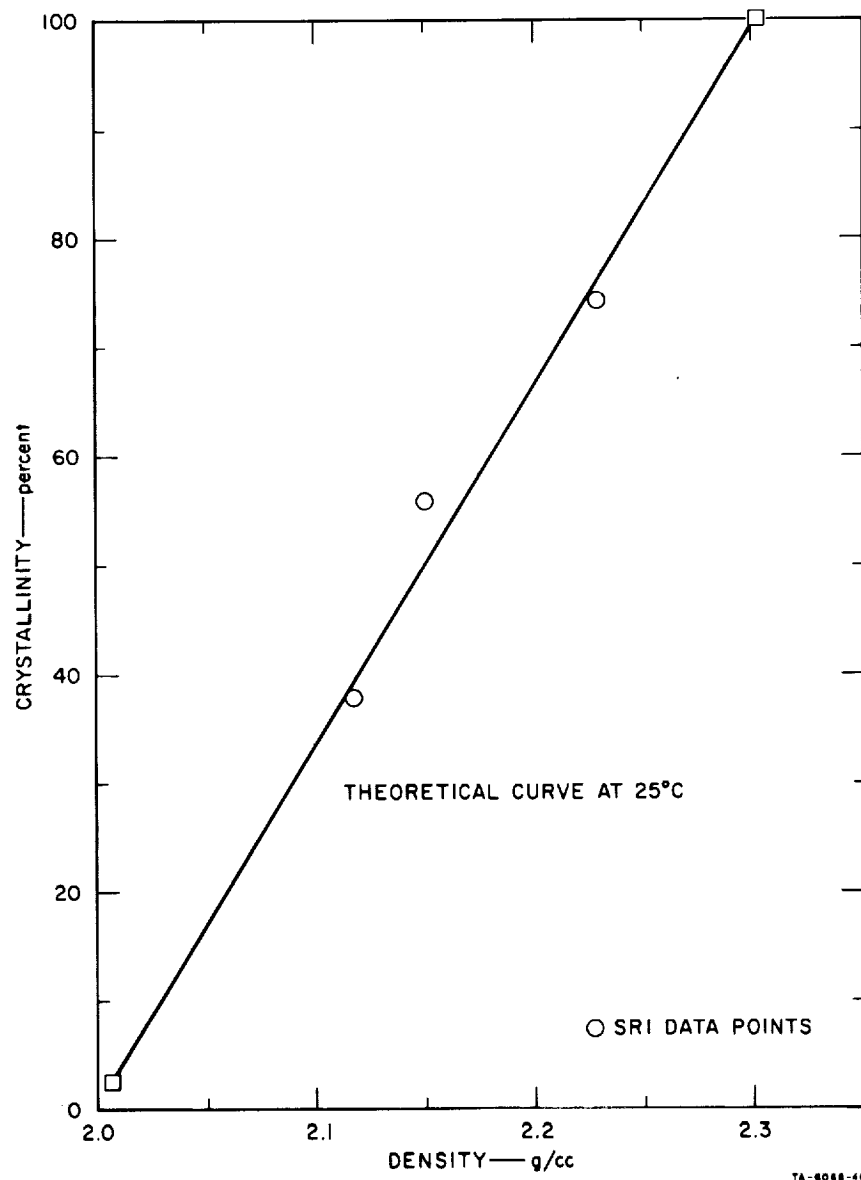


FIG. 16 CRYSTALLINITY OF TEALON-TFE vs. DENSITY



## IV. CRYSTALLINITY OF TEFLON FILMS

The extent and distribution of crystallinity in Teflon films appears to be an important parameter in the production of bladders exhibiting reproducible mechanical properties. Therefore, it was considered important to have available a series of independent and accurate methods for determining the crystallinity of PTFE films. Several methods for determining crystallinity were investigated and compared: (1) X-ray diffraction, (2) Infrared spectrophotometry, (3) Calorimetry, (4) Density.

## X-RAY DIFFRACTION

The determination of crystallinity by x-ray diffraction involves comparing the intensities of the crystalline 100 reflection with that of the amorphous halo associated with this reflection. Teflon, a substance containing a large amount of highly-ordered matter, exhibits an x-ray diffraction pattern indicating a constant, well-defined distance between planes of a crystal lattice. In addition to this well-defined x-ray scattering (limited to a very small angular range), there is another, more diffuse type of scattering, indicating a random distribution of distances between planes of a similar crystalline character. This type of scattering represents a lower degree of order within the crystal, and is referred to as the "amorphous" halo. In fact, this scattering does not represent a completely amorphous state, but one approaching a liquid type of ordering.

The amount of crystalline material in Teflon is assumed to be directly proportional to the intensity of the x-rays scattered by the well-defined 100 d-spacing, while the amount of amorphous material is assumed to be directly proportional to the intensity of x-rays scattered by the random 100 d-spacings. In the case of Teflon, the sharp, crystalline peak is found at  $2\theta = 18.9^\circ$  for copper  $K_\alpha$  ( $\lambda = 1.542$ ) radiation, whereas the "amorphous halo" reaches a maximum intensity at  $16.6^\circ$  for the same

wavelength of radiation, although it extends beyond the crystalline peak for some angular distance. A typical x-ray pattern for a Teflon film is given in Figure 17.

There are other types of disorder present in crystalline Teflon, and these have been discussed by Killian and Jenkel [6] Bunn and Howells [7] and Bunn [8]. However, it is believed that the disorder represented by the randomization of the 100 d-spacing is that most similar to the disorder of "liquid" Teflon. For example, the 110 planes of the Teflon crystal are nearly completely randomly spaced at temperatures over 30°C (indicating a change from pure hexagonal to a partially-disordered pseudo-hexagonal state), but there is essentially no change in the distribution of spacing of 100 planes until near the melting point, indicating that this type of randomization occurs chiefly by melting.

Although the method of comparing the amorphous halo with the 100 crystalline reflection has been accepted by many workers [6, 9, 13], there is some disagreement as to the value of the correction factors that must be applied in order to get true x-ray intensity from measured intensity; Ryland [10] uses a factor of 1.8 and Killian and Jenckel [6] uses the factor 1.0. At SRI, it has been estimated that the factor is 1.18, taking into account angle factors such as polarization and Lorentz factor, thermal vibrations, absorption within the film, and assuming that structure amplitude and number of equivalent reflections were identical for both amorphous halo and crystalline peak. It was also assumed that the amorphous halo was symmetrical about  $2\theta = 16.6^\circ$ .

The calculations of per cent crystallinity from x-ray intensity data are:

$$1.18 \left( \frac{I_c}{I_a} \right)_{\text{meas}} = \frac{I_c}{I_a} = \frac{M_c}{M_a}$$

$$\%C = \frac{M_c/M_a}{1 + M_c/M_a}$$

where

$I_{c,meas}$  = experimentally determined intensity of the crystalline 100 peak

$I_{a,meas}$  = experimentally determined intensity of the amorphous halo associated with the crystalline 100 peak

$I_c$  = "true, corrected" crystalline intensity

$I_a$  = "true, corrected" amorphous intensity

$M_c$  = mass of material in the crystalline state

$M_a$  = mass of material in the amorphous state

%C = crystalline material, wt-%

### Experimental

A Norelco powder diffractometer with scintillation-counter detector and rotating holder is used for these determinations. The counter is connected with a pulse-height analyzer, with the base-line set at 0.8 volts and the window set at 3.50 volts; the response of the pulse-height analyzer is linear throughout the range of intensities anticipated for the Teflon films. Copper  $K_{\alpha}$  radiation is used, with a nickel filter to eliminate copper  $K_{\beta}$  radiation.

The scintillometer scans over a range of  $10^{\circ} = 2\theta$  to  $24^{\circ} 2\theta$  at a rate of  $1/4^{\circ} 2\theta$  per minute. Often, two scans are necessary, one at a high attenuation for examining the crystalline peak, and one at a lower attenuation for determining the intensity of the amorphous halo. Receiving slits of  $1/2^{\circ}$  are used.

The sample is mounted in a hollow stainless steel holder that presents only Teflon film to the x-ray beam; thus, no extraneous scattering from other materials is involved in the determination.

Measurements are made by integrating the area under each curve with a polar planimeter, and multiplying by the appropriate scale factors. Selection of base lines is somewhat arbitrary, and seems to introduce the maximum error involved in the determinations.

## Effects of Film Stretching on Crystallinity and Crystal Orientation

The film holder used initially for the x-ray determination of crystallinity required that the film be stretched. It was then considered that the stretching of the films might be effecting orientation of crystals. A new holder was fabricated, which would contain films under virtually no tension, and many determinations were repeated. A review of the data summarized in Table 10 for 2 films indicates that apparent crystallinity is 5 to 10% higher for films which are held under tension.

This finding suggested that orientation of PTFE crystals may occur during the flexures required by the expulsion bladders, and may lead to an alteration of mechanical properties, for example, an increase in crystallinity may occur at a crease and lead to a brittleness of the film at that point. Infrared examination of one film which had been stretched 100% along the axial direction of manufacture revealed no difference in the infrared spectrum as compared with that obtained with the film in the as-received state. This was not surprising since it is not expected that a change in crystal orientation would be detectable by the IR procedure. On the other hand, x-ray measurements can be made sensitive to the orientation of crystals or the "lining-up" of crystallites in an orderly pattern, with like faces parallel.

A series of transmission Laue photographs were made by a modified method in order to determine whether stretching of the Teflon films would enhance orientation. In this method, monochromatic x-rays strike the sample and are diffracted; the film plate is placed behind the sample. Rings are formed where the plane of the sample intersects the cone of diffracted rays and are recorded on the film (Figure 18). For a sample composed of randomly oriented crystallites, the rings formed will be of uniform optical density throughout their circumferences. However, as crystallites assume some definite orientation, a circumferential distribution of density will develop; portions of the arcs will fade, and other portions will grow denser. In the case of maximum orientation (i.e., a single crystal) only spots, not arcs, will remain on the film.



A sample holder was constructed to hold the Teflon films under any tension desired. Using the Laue method, photographs were taken of unstretched film (Figure 18) and of films stretched 20% (Figure 20), 75% (Figure 21), and 100% (Figure 22) of their original length. All films were stretched in the direction parallel to the axis of the mandrel on which they were formed. The unstretched film appears to consist of randomly oriented crystallites, and stretching the film 20% seems to have no effect on the circumferential distribution of intensity in the rings, hence no detectable effect on orientation. In Figures 21 and 22, however, a selective distribution of intensity becomes apparent. Therefore, these samples (75% and 100% stretching) are beginning to display orientation. The fact that the arc of the diffracted beam becomes a smaller segment of a circle as stretching increases indicates that the degree of orientation is increasing as stretching is increased. In the ultimate, the circle segments become sharply defined spots.

#### Effect of Film Orientation on Crystallinity Determinations

Since the polymer film cools faster than the mandrel and has a much larger coefficient of thermal expansion, there exists the possibility that the crystallinity of the film is greater along one axis than another. Determination of crystallinity in the two directions was undertaken. Although the actual crystallinity values are at some variance between those computed from x-ray diffraction data and those obtained from infrared determinations (based on published x-ray data), examination of the three films prepared as indicated above indicated that no differences in crystallinity in the two axes are detectable. These data are shown in Tables 11 and 12.

#### Effect of Mill-Rolling on a Film Sample

Part of the effort on the determination of crystallinity by x-ray was devoted to the correlation of results with infrared spectrophotometric procedures. Although the thickness of a film is of no consequence in the determination of crystallinity by x-ray diffraction (so long as thickness is constant in a specimen), experimental films had to be rolled to less

than 3 mils in order to provide measurable absorbance (transmission) in the infrared. The x-ray data obtained for films examined as-received after rolling are summarized in Table 13. As indicated by the data, the rolled samples have lower crystallinity values by x-ray than the original samples. This suggests that crystallinity determinations on thick films can not be performed by infrared techniques, for the rolling or pressing actions destroy crystallinity.

#### INFRARED SPECTROPHOTOMETRY

Several investigations of the use of infrared spectrophotometry to determine the crystallinity of Teflon films have been reported in the literature [11-13]. The determinations are based on the measurement of an absorption band at  $12.85\mu$  ( $780\text{ cm}^{-1}$ ) which is due to the amorphous transitions of the polymer; the absorption at this wavelength is linear with crystallinity. Another absorption band at  $4.25\mu$  ( $2350\text{ cm}^{-1}$ ) is often used as an internal thickness standard since it is not influenced by the degree of crystallinity; it is due to an overtone of the intense  $\text{CF}_2$  stretching vibrations. The amorphous absorption bands are preferable to crystalline bands for measuring crystallinity because they are broad (thus requiring less resolution) and are less subject to polymer orientation [12].

According to the work of Moynihan [13], the ratio of the absorbance of the amorphous band at  $12.85\mu$  to density and thickness of the polymer is related to the degree of crystallinity as determined by x-ray diffraction. In order to corroborate these results and obviate the need for density and thickness measurements of individual samples, the relationship  $d_{\text{mm}} \sigma$  was computed with the use of Lambert's Law:

$$A = E \times C \times L$$

where

- A = absorbance
- E = extinction coefficient
- C = concentration
- L = path length.

By determining carefully the area and weight of a piece of smooth TFE film, E at 4.25 $\mu$  was calculated as follows:

$$\frac{\text{weight}}{\text{area}} = \text{cm} \times \frac{\text{g}}{\text{cm}^2} = d_{\text{cm}} \times \sigma$$

and

$$d_{\text{cm}} \times \sigma \times 10 = d_{\text{mm}} \times \sigma$$

where

$$d_{\text{mm}} = \text{thickness in mm}$$

$$\sigma = \text{density.}$$

Since

$$A = E \times C \times L$$

$$\frac{A}{L \times C} = E_{4.25\mu}$$

then

$$\frac{A_{4.25\mu}}{d_{\text{mm}} \times \sigma} = E_{4.25\mu} = 1.41 \text{ (this work).}$$

Assuming that  $E_{4.25\mu}$  is the same for all Teflon samples:

$$d_{\text{mm}} \times \sigma = \frac{A_{4.25\mu}}{E_{4.25\mu}} \quad \text{and} \quad \frac{A_{12.85\mu}}{d_{\text{mm}} \times \sigma} = \frac{A_{12.85\mu}}{A_{4.25\mu}} \times E$$

the ratio of absorbance at 12.85 $\mu$  with respect to the product of thickness and density can be plotted as a linear function vs degree of crystallinity as obtained by x-ray diffraction data; for example:

$A_{12.85\mu/d} \sigma$	Crystallinity by X-Ray	
	Moynihan <sup>5</sup>	SRI (this work)
2.54	44	53.4
0.344	90.5	94.1

## CALORIMETRY

Calorimetry has been used to determine the per cent crystallinity of nylon-6 [14] and polyethylene [15]. This method is based on the assumption that the heat of fusion (in cal/g) required to melt a given sample of semi-crystalline polymer is proportional to the fraction of the sample which is in the crystalline state, and thus to the per cent crystallinity [16].

$$\% \text{ crystallinity} = 100 \times \frac{\Delta H_f \text{ experimental}}{\Delta H_f \text{ theoretical}}$$

This equation assumes a linear relationship between heat of fusion and per cent crystallinity; it is also assumed that the amorphous fraction does not "melt," i.e., has no effect on the heat required to melt the crystalline fraction. To apply this method, it is necessary to know the heat of fusion of a 100% crystalline sample; this has been reported for Teflon as 14.6 cal/gram [17].

A study of the kinetics of melting of PTFE was made by Hellmuth *et al.* [18]. In this work, the relative heat of fusion of several samples of PTFE which had been cooled from the melt at various rates were measured. Although no absolute values are given, the relative  $\Delta H_f$  values are related to the thermal history of the samples and thus to the degree of crystallinity.

### Experimental Work

The instrument used in this work was a Du Pont Model 900 Differential Thermal Analyzer with a calorimeter attachment.

The instrument response (calorimeter constant) was calibrated by using pure standard substances with known heats of fusion. Cadmium was used since its melting point, 321°C, is close to that of PTFE (327°C) and the determined instrument response for Cd may be considered equal to that of PTFE. In order to compensate for small run-to-run instrumental variations, a small amount of tin (m.p. 232°C) was always run with the PTFE as an internal standard.

The instrument response was determined and heats of fusion calculated in the following manner:

$$\Delta H_f = \frac{E \cdot A \cdot T \cdot \Delta T}{M \cdot R}$$

where

E = instrument calibration constant

= m cal/°C-min

A = peak area, in<sup>2</sup>

R = heating rate, °C/min

H<sub>f</sub> = heat of fusion, cal/g

M = mass of sample, mg

T, ΔT = chart expansion on X and Y axes, respectively

To determine the instrumental constant E, for the condition and temperature of interest (327°C), small weighed samples of Sn and Cd were run simultaneously in the same sample cup, using the same conditions to be used for PTFE measurements. Calibration runs performed in this manner agreed within ±2.7% and  $E_{Cd}(PTFE)/E_{Sn} = 1.06$ .

The heats of fusion of PTFE samples were determined as follows: A small disk of aluminum foil was formed into a cup by pressing around the end of a metal rod. A small amount (1-2 mg) of pure tin was weighed into the cup on a microbalance and then about 4-8 mg of the PTFE sample was weighed into the cup. The sides of the cup were folded down about the samples and the cup was placed in the sample chamber of the calorimeter. The air in the calorimeter was replaced with argon and the instrument

was started. Since tin melts at 232°C and Teflon at 327°C, only the range between 200°C and 400°C was recorded.

The instrument operating conditions used were: heating rate = 5.5°/min with scale expansion of 20°C/inch on the X(T) axis and 0.2°C/inch on the Y(ΔT) axis.

At the end of each run, the peak areas of the melting endotherms of tin and PTFE were measured by a polar planimeter and the heat of fusion of the PTFE sample calculated in cal/g as follows:

$$\Delta H_{f,PTFE} = \frac{E_{PTFE} \cdot A_{PTFE} \cdot T\Delta T}{M_{PTFE} \cdot R}$$

$$\Delta H_{f,Sn} = \frac{E_{Sn} \cdot A_{Sn} \cdot T\Delta T}{M_{Sn} \cdot R}$$

Since T, ΔT, and R are the same for both Sn and PTFE in all cases, these two equations may be added together and re-arranged so that:

$$\Delta H_{f,PTFE} = \Delta H_{f,Sn} \frac{A_{PTFE} \cdot M_{Sn}}{M_{PTFE} \cdot A_{Sn}} \cdot \frac{E_{PTFE}(Cd)}{E_{Sn}}$$

As stated above, it is assumed that  $E_{PTFE} = E_{Cd}$ . All quantities on the right side of the above equation being known, the  $\Delta H_f$  of the PTFE sample may be calculated.

In order to determine the most convenient conditions of operation, several thermograms of PTFE were made at various heating rates and scale expansions. At heating rates of 10° and 20° per minute, very broad and diffuse melting endotherms appeared, similar to those reported by Hellmuth et al. [18]. A heating rate of 5.5°C/min was chosen since the endotherms found at this rate had fairly definite starting and final points. Scale expansions of 20°C/inch (X axis) and 0.2°C/inch (Y axis) were found suitable for the temperature range and the sample size used.

As shown in a typical thermogram (Figure 23), there is a shift in the base line before and after the PTFE melting transition, which complicates the evaluation of the area. The baseline for integration was selected somewhat arbitrarily [19] as shown on the thermogram.

A few preliminary experiments were made to ascertain whether the changes in heat of fusion of PTFE following heat treatment could be made quantitative with reasonable precision. It was found that the changes could be easily measured and that the changes were in the correct sense, i.e., the rapidly-cooled samples had lower heats of fusion than those which had been cooled slowly.

Reproducibility from run-to-run was also tested by measuring the heats of fusion of three separate portions from the same PTFE sample; the values agreed within  $\pm 3\%$ .

A sample of PTFE which was expected from other data to have a crystallinity of about 95% was examined. The heat of fusion value for this sample was 13.92 cal/g which corresponds to an apparent crystallinity of 95.4% when compared with the literature value of 14.6 cal/g to theoretically 100% crystalline PTFE [14].

A series of PTFE film samples from a common source was heat-treated in the calorimeter and then removed and cooled from the melt (370°C) at various rates to produce samples of known thermal history and presumably of known relative crystallinity. The heats of fusion of these samples were determined and compared with the thermal history and with crystallinity determinations obtained by infrared examination. The data are summarized in Table 14.

#### Discussion of Results

It is seen from Table 8 that there is a relationship between the heat of fusion data, the thermal history, and the infrared crystallinity values. It is also obvious that the calorimetric data furnishes much lower crystallinity values than does the infrared and that the calorimetric values for crystallinity are not linearly related to values obtained by other methods; for example, in Table 15 are listed calorimetry and

x-ray results for crystallinity measurements. It is of interest that the relative heats of fusion obtained in this work are similar to those found by Hellmuth et al. [18]. It is anticipated that the explanation for the lack of correlation between DTA and x-ray or IR crystallinities will cast a valuable insight into the underlying reasons for the variability observed in the mechanical properties of PTFE films.

#### DENSITY

The correlation of density and crystallinity was determined initially with pressed sintered pellets as indicated in Section III. Occasional spot checks were made on films, and it was found that densities and x-ray crystallinities were always in close accord at high crystallinities, but not at lower. The densitometric method offers an independent check on x-ray crystallinity when films are so thick that they do not permit sufficient infrared transmission.



Table 10  
EFFECT OF SAMPLE TENSION ON THE DETERMINATION  
OF CRYSTALLINITY BY X-RAY DIFFRACTION

SRI FILM NO.	PERCENT CRYSTALLINITY	
	Under Tension	No Tension
EX-1-S2	87.9	78.3
EX-1-S3	66.7	61.8

Table 11  
EFFECT OF FILM ORIENTATION ON X-RAY  
DETERMINATION OF CRYSTALLINITY

FILM	BEAM RELATION TO EQUATORIAL AXIS	% CRYSTALLINITY
Ice/H <sub>2</sub> O quenched	rotated	61.8
	perpendicular	62.1
	parallel	61.2
Air-cooled	perpendicular	73.9
	parallel	73.5
Programmed cooled	perpendicular	82.9
	parallel	83.3

Table 12  
EFFECT OF FILM ORIENTATION ON INFRARED  
DETERMINATION OF CRYSTALLINITY

FILM	CRYSTALLINITY,* Av-%	RANGE, %
Ice/H <sub>2</sub> O quenched	51	50-52
Air-cooled	57	56-58
Programmed cooled	69.5	68-71

\* Average of axial and equatorial measurements.

Table 13  
 COMPARISON OF CRYSTALLINITY OF  
 ROLLED VS. ORIGINAL FILMS  
 BY X-RAY DIFFRACTION

SRI FILM NO.	PERCENT CRYSTALLINITY	
	Rolled	Original
EX-1-S3	53.4	61.8
EX-1-S1	64.8	79.0

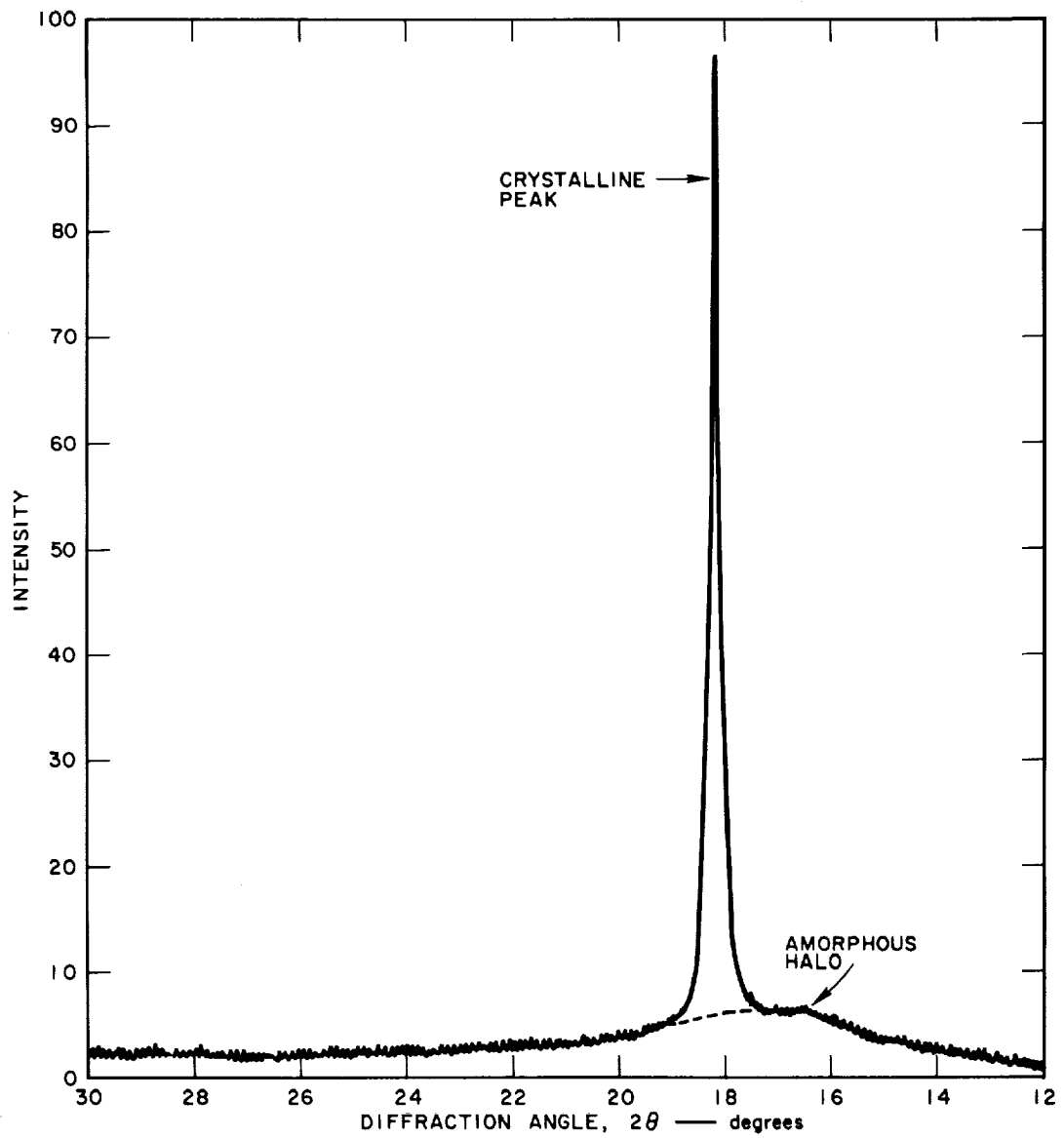
Table 14  
 COMPARISON OF CRYSTALLINITY DETERMINATIONS  
 ON SMALL STRIPS OF FILM:  
 CALORIMETRY VS. INFRARED

SAMPLE	$\Delta H_f$ , cal/g	% CRYSTALLINITY, CALORIMETER	% CRYSTALLINITY, INFRARED*
H	7.65	52	62
E	5.45	37	62
B	5.72	39	59
F	4.59	31	56
J	4.42	30	56
G	4.19	29	53
A	3.99	27	49
TFE-30	13.92	95	90.5

\* Computed from IR absorbance and X-Ray data of Moynihan (5).

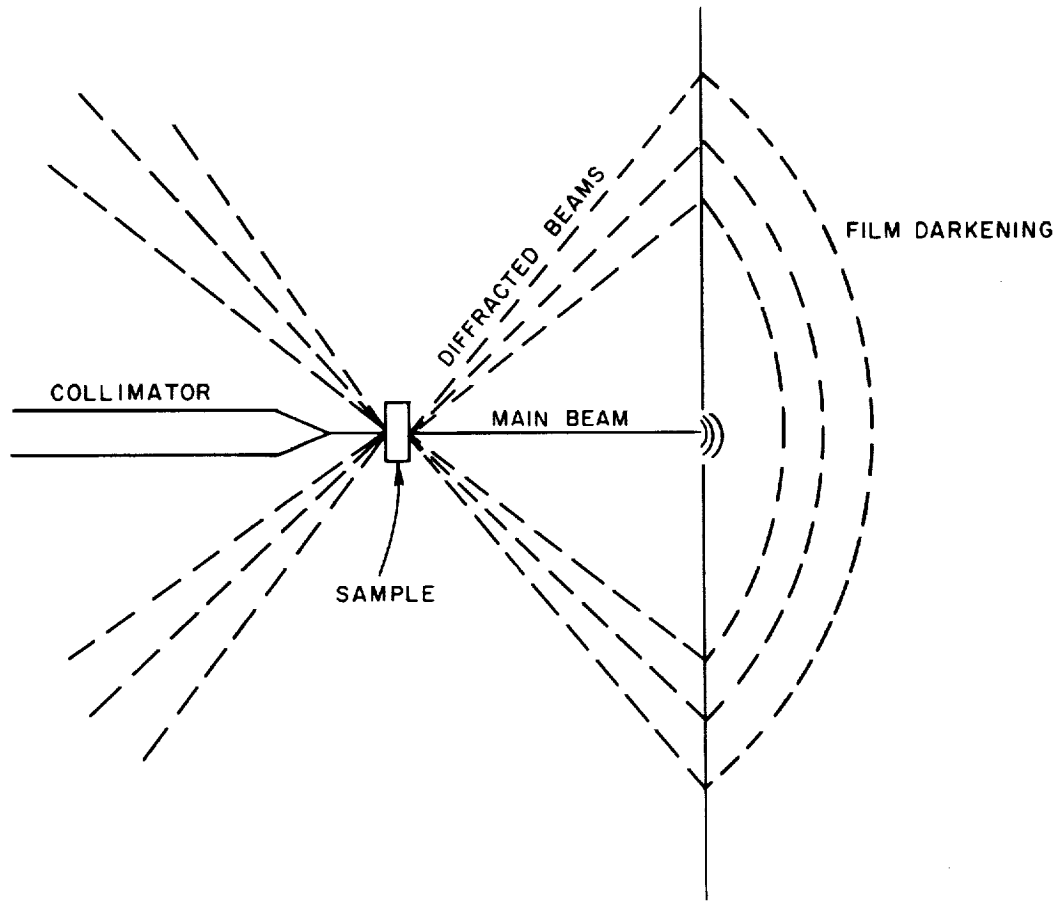
Table 15  
 COMPARISON OF CRYSTALLINITY DETERMINATIONS  
 ON EXPERIMENTAL FILMS:  
 CALORIMETRY VS. X-RAY DIFFRACTION

SAMPLE FILM	$\Delta H_f$ , cal/g	% CRYSTALLINITY, CALORIMETER	% CRYSTALLINITY, X-RAY (SRI)
EX-1-S3	4.88	33	62
EX-2-S5	6.89	47	65
EX-1-S1	7.59	52	79
TFE-30 (powder)	13.92	95	94



TB-6068-2R

FIG. 17 X-RAY DIFFRACTION PATTERN OF TYPICAL TEFLON-TFE FILM  
(Copper  $K_{\alpha}$  Radiation)



TA-6068-11

FIG. 18 MODIFIED TRANSMISSION (Monochromatic Beam) LAUE X-RAY DIFFRACTION DIAGRAM

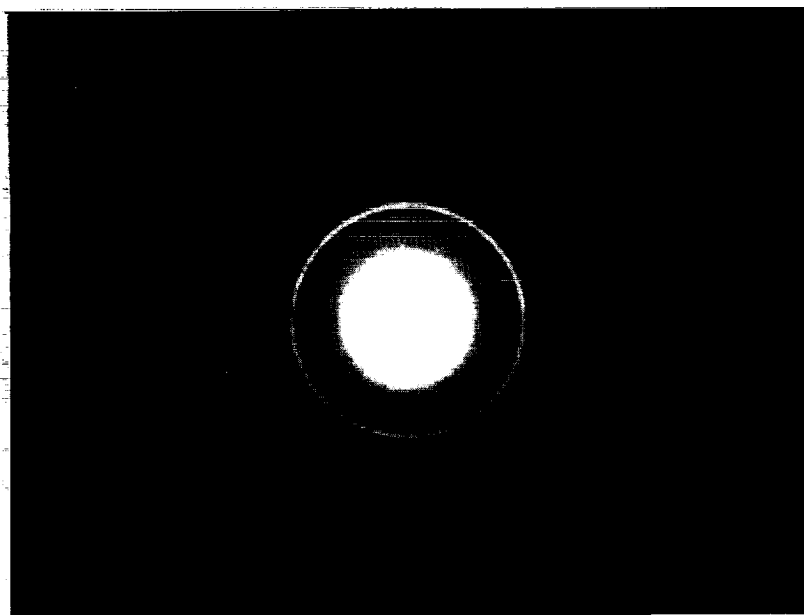


FIG. 19 MODIFIED LAUE X-RAY PHOTOGRAPH OF TEFLON FILM AS RECEIVED (CuK $\alpha$  radiation, 6-hr exposure)

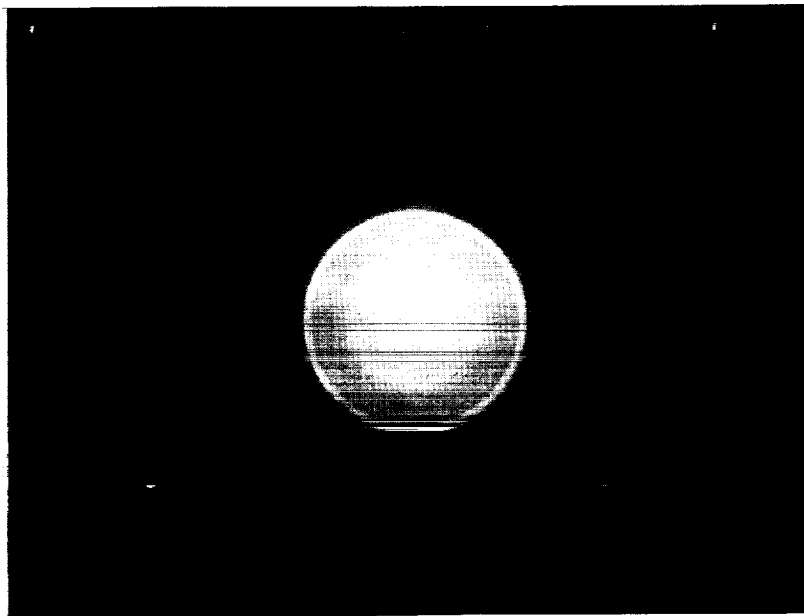
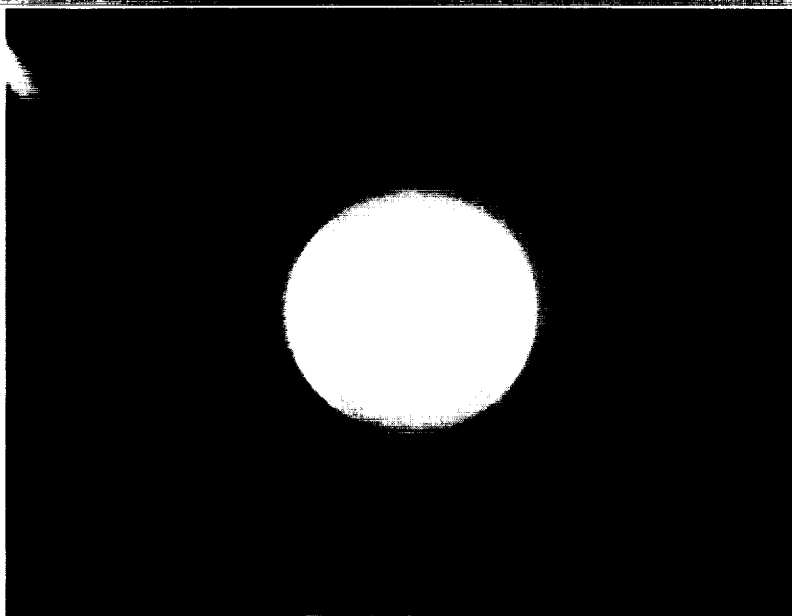


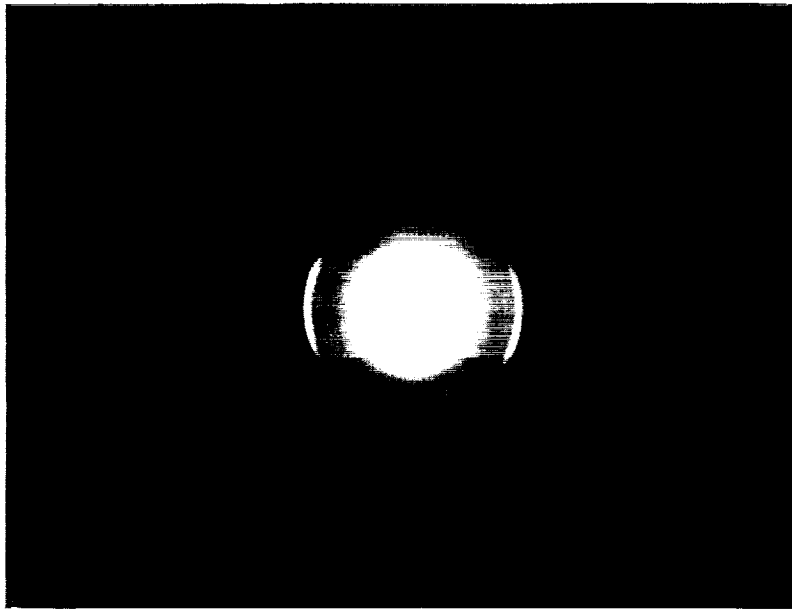
FIG. 20 MODIFIED LAUE X-RAY PHOTOGRAPH OF TEFLON FILM STRETCHED 20% OF ORIGINAL LENGTH (CuK $\alpha$  radiation, 6-hr exposure)



TB-6068-14

← STRETCH →

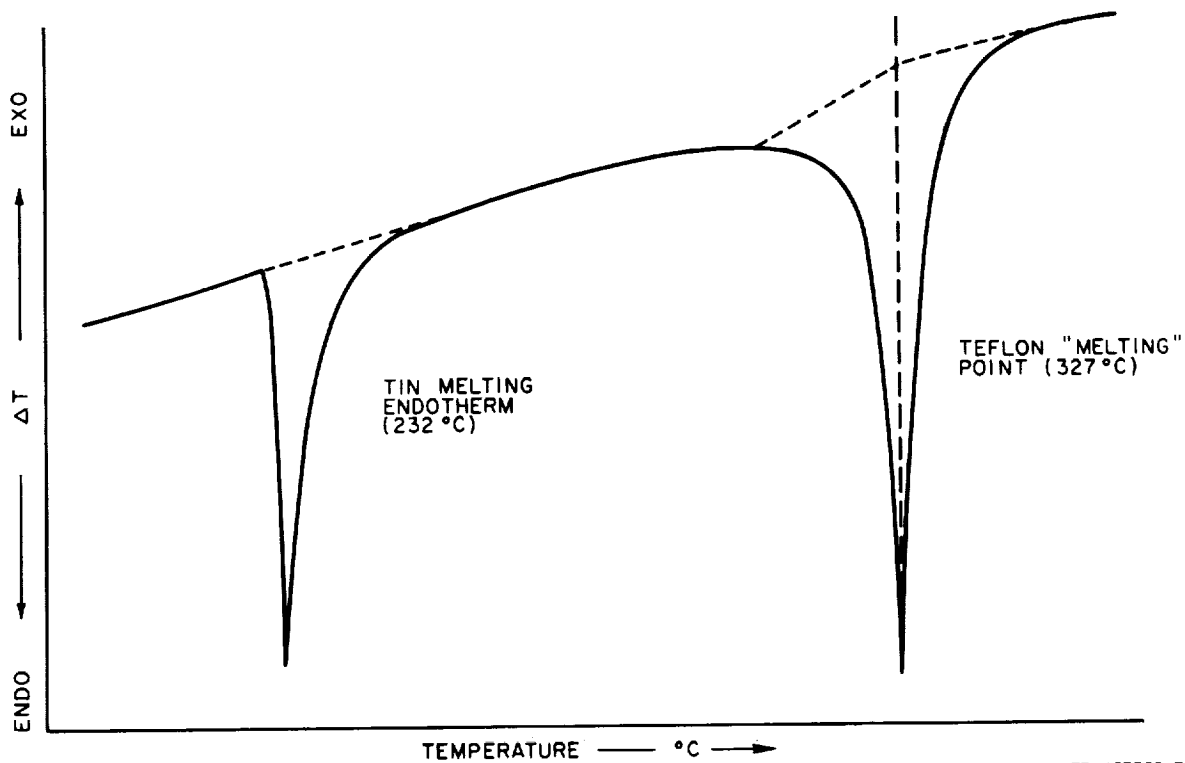
FIG. 21 MODIFIED LAUE X-RAY PHOTOGRAPH OF TEFLON FILM STRETCHED 75% OF ORIGINAL LENGTH (CuK<sub>α</sub> radiation, 6-hr exposure)



TB-6068-15

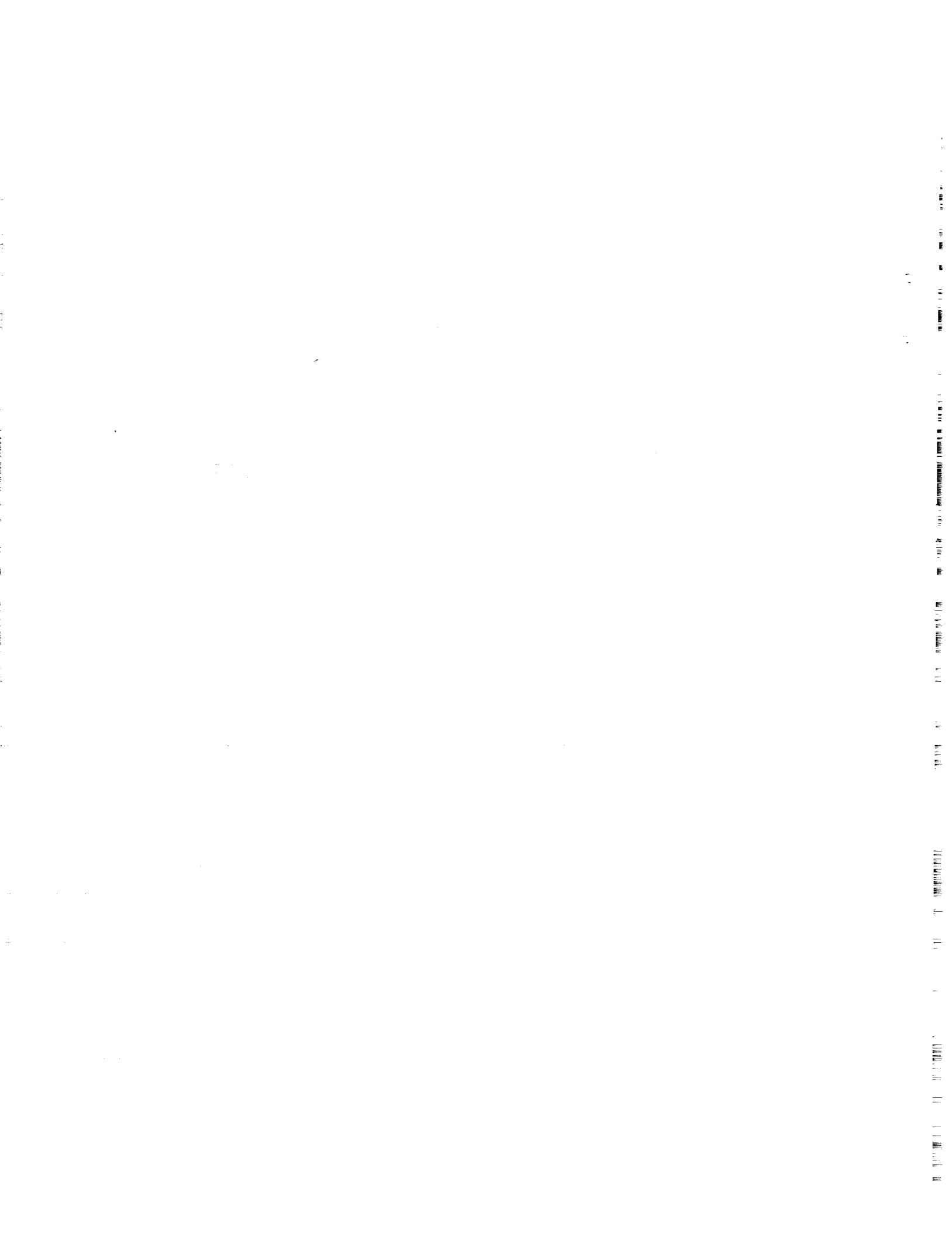
← STRETCH →

FIG. 22 MODIFIED LAUE X-RAY PHOTOGRAPH OF TEFLON FILM STRETCHED 100% OF ORIGINAL LENGTH (CuK<sub>α</sub> radiation, 5-hr exposure)



TB-105522-7

FIG. 23 THERMOGRAM SHOWING ENDOTHERMS OF TIN STANDARD AND TEFLON SAMPLE





PRECEDING PAGE BLANK NOT FILMED.

## V. CLADDING OF TEFLON FILMS AND PERMEABILITY

All polymeric films are permeable in varying degrees to gases and liquids. In order to render Teflon films suitable for long-term use in space-propellant expulsion bladders, it is advisable to incorporate a continuous inert metallic barrier to eliminate or reduce permeability. In the past, attempts to prepare laminates of a metal foil and Teflon have met with little success; an alternate approach is the cladding of the film by the deposition of lead or some other compatible metal on the film surface. The work described below includes the techniques established for the deposition of lead on a film by electroplating, and the results of the determinations of the permeability of lead-clad films to  $N_2O_4$ .

### LEAD CLADDING BY ELECTRODEPOSITION

Electroplating techniques for the deposition of lead on Teflon have been established to provide unburnished coatings which are thin, smooth, uniform, and impermeable. The procedure is patterned after the techniques employed for over 50 years to deposit metals on nonconductors, and was applied to Teflon by Vango and Krasinsky [20] in preliminary work at the Jet Propulsion Laboratory. The current procedure requires etching of the Teflon surface with sodium, coating with silver by a modification of the original Brashear process, and final plating with lead from a fluoroborate bath. Modifications of the procedure originally used at JPL have permitted the elimination of sonic plating-bath agitation, the 2-stage silvering procedure, and mill-rolling of the final lead plate. The latter is most important since the interior surface of a balloon-type bladder or even the curved surface of a hemispherical diaphragm would be extremely difficult to roll or burnish effectively.

The projected end-use of lead-plated Teflon requires that the thinnest coating possible be applied in order to keep weight at a minimum, preserve expulsion bladder flexibility, and yet provide maximum resistance

to the permeation of nitrogen tetroxide. Another consideration is, of course, the proposed length of time in which  $N_2O_4$  will be in contact with a lead barrier since the corrosion rate of lead in anhydrous  $N_2O_4$  is 2 mils per year [20]. The work reported at this time has had the objective of producing an integral and adherent lead coating of about 1-mil thickness; once the plating parameters were established to produce this coating via simplified and reproducible procedures, it was anticipated that there should be no difficulty in applying coatings of thicknesses required by the extent of space missions.

#### Electroplating Techniques

A commercially-available, skived Teflon film (Saunders S-25) was used for the work directly related to the establishment of plating techniques. Teflon films prepared at SRI from TFE-30 dispersions were used for additional studies on permeability and adherence of the lead coatings. In general, sample squares of the order of 3" x 3" were used.

Etching. - The Teflon film is washed in a mild detergent solution, thoroughly rinsed with de-ionized water, and air-dried. Etching is accomplished by immersion for 30 to 60 seconds at room temperature in Tetra-Etch (W. L. Gore and Assoc., Inc.); the Tetra-Etch is stored under refrigeration and thoroughly shaken before use. After the film is removed from the etching bath, it is inspected for uniformity, determined by the depth of the brown color. If spots appear to be un-etched or only lightly-etched, the film is immersed again. (It is recommended that the etching process for the interior of a sphere, such as an expulsion bladder, include a preliminary etch followed by acetone rinsing and drying, and then a second etch.)

The Teflon film is washed finally in a mild detergent solution, rinsed thoroughly with de-ionized water, and dried by four treatments with acetone.

Silver Coating. - The preliminary work on the application of a silver coating to the etched Teflon surface was performed in accordance with a Bra-shear's formula [21]; however, it was found that the deposited silver lifted immediately in tests with the JPL crease tester. A brief search

of the literature revealed that a more tenacious deposit could be formed if the silver-coating solution were more concentrated and the etched film were immersed for 15-20 minutes in the solution maintained at 65°C [22]. Not only was this treatment effective in strengthening the silver-Teflon bond, but it also permitted elimination of a reducing step in the Brashear process. The recommended formulation is: Dissolve 15 g AgNO<sub>3</sub> in 200 ml of distilled (or de-ionized) water, add 5 g KOH, take up precipitated silver oxide with ammonium hydroxide (leaving a slight excess in suspension), dilute the bulk to 600 ml, and heat to 65°C.

Lead Plating. - During the preliminary work on lead plating, an alkaline lead bath was developed which provided a satisfactorily smooth and integral plate; however, it was found that the plate could not be deposited uniformly when test strips as large as 5" x 10" were employed. Thus, continuing work has been involved with the determination of optimum operating procedures for a standard lead fluoroborate bath, and much more uniformity of coating thickness has been achieved.

The bath is prepared with the use of Lead Fluoroborate Concentrate (Baker and Adamson reagent, 27.2% lead) and peptone in the following formulation:

Lead fluoroborate concentrate	200 g/l
Peptone	0.5 g/l
De-ionized water to make	1000 ml

and was operated at first under the following conditions:

Bath temperature	25°C
Current density	20 amp/ft <sup>2</sup>
Anodes	Lead

By analyzing the lead deposits (vide infra), the time required to produce a lead coating of about 1-mil thickness was determined to be adequate at 15 minutes:

<u>Plating Time</u>	<u>Thickness of Pb, mils</u>	
	<u>5 samples at random, Av.</u>	<u>5 samples from very edges, Av.</u>
45 min.	1.3	1.5
30 min.	0.83	1.2
20 min.	0.70	1.1
15 min.	0.54	0.87

In order to provide for the optimum grain-size of the lead coating, operating conditions were varied and the coated films were tested later for permeability to  $N_2O_4$  (in this instance, TFE-30 films prepared at SRI were used for the substrates):

<u>SRI Film No.</u>	<u>Current Density, amp/ft<sup>2</sup></u>	<u>Plating Time</u>	<u>Plating Temp.</u>	<u>Plate Thickness, mils</u>
1	20	15 min.	25 <sup>o</sup> C	0.8
2	10	20 min.	25 <sup>o</sup> C	0.4
3	10	20 min.	50 <sup>o</sup> C	0.75
4	20	15 min.	50 <sup>o</sup> C	1.2

Subsequent tests indicated that film No. 4 was the least permeable to  $N_2O_4$  (Table 18), and thus final operating conditions were established as:

Bath temperature	50 <sup>o</sup> C
Current density	20 amp/ft <sup>2</sup>
Anodes	Lead

#### Thickness of Lead Coating

A chemical method has been developed for determining the thickness of the lead coating: Five discs of 0.499 cm<sup>2</sup> are punched out of the lead-clad Teflon film and the lead is dissolved from the discs in 8N nitric acid. The solution is diluted, decanted from the discs, treated with 10% sodium-potassium tartrate solution (the presence of silver is indicated by a brown precipitate), neutralized with 10% sodium hydroxide solution, diluted further, and the pH adjusted to 10 with an ammonium buffer. The

silver is complexed by the addition of 5% potassium cyanide solution, and the lead is titrated with 0.01M EDTA, using Eriochrome Black-T as indicator. Milligrams of lead found are then converted to mil-thickness.

#### Adherence of Lead Coatings

A Teflon test film was prepared from TFE-30 (#5783) as described previously, sintered for 24 hours at 370°C, and quenched in an ice/water bath. One half of this film, 17A, was removed from the mandrel for direct electroplating with lead. The half of the film remaining on the mandrel, 17B, was re-heated at 370°C for 30 minutes; then, while it was still at a temperature between 275°C-225°C, an additional spray application of the dispersion was made. Finally, the film was sintered at 370°C, again for 30 minutes, and quenched in the ice/water bath. The final application of dispersion to the hot film surface resulted in a porous layer of Teflon of about 0.001-in. thickness, tenaciously bonded to a relatively nonporous film. It was felt that such a porous layer would provide a "keying" surface for the lead electroplate, ensuring an interlocked and stronger bonding of the silver coat and lead plate to the Teflon surface.

The contrast in surface appearance of the smooth and porous surfaces of films 17A and 17B are shown clearly in the photomicrographs of Figures 24 and 25. A cross-sectional view of the porous layer of Film 17B (0.001-inch thick) is shown in Figure 26.

Films 17A (smooth) and 17B (porous) were electroplated with lead on one side. Then, three samples of each film were cemented to fixtures fabricated for the bond-strength determinations.

The bond-strength fixtures were machined in pairs from aluminum round stock as 0.5-inch diameter rods 5 inches in length which terminate in 0.5-inch long flat heads of 1.25-inch and 0.785-inch diameters. The face of each flat head was sandblasted, washed with a detergent solution and rinsed in de-ionized water. Then the fixtures were oven-dried at 100°C for 24 hours.

The etched surface of each test film was cemented to the 1.25-inch flat head of a bond-strength fixture with Scotchweld, Structural Adhesive EC-2216A/B under a load of 5 pounds. The adhesive was allowed to cure

for 24 hours at room temperature--then, adhesive was applied to the 0.785-inch flat head which was centered against the film cemented to the other part of the fixture in a metal lathe. A pressure of about 5 pounds was applied and the adhesive was allowed to cure for 16 hours at room temperature. After removal from the lathe, the completed test assembly was stored for one week at room temperature for final curing of the adhesive.

The test assemblies were pulled apart at a speed of 0.1 in/min on an Instron Model TTCLM-6 tester. The recorded load-at-break was used to calculate the psi required to separate the test fixture from the plated film. As shown in Table 16, the bond strength of the primary silver coating to the Teflon is greater for the film with the porous surface. The lowest value (245 psi) for the porous film is attributed to surface discontinuities which were apparent prior to plating.

#### PERMEABILITY AND TEFLON FILMS

The development of the all-stainless steel permeability cell described in Interim Report No. 1 (June 17, 1967) was delayed in order to obtain data which could be compared directly with the extensive work already performed at JPL with the "Vango" permeability apparatus [23]. Hence, several of these all-glass apparatuses were constructed (see Figure 27).

##### System Efficiency

Since a long-term permeability system operating at ambient temperature would be preferable to one requiring the liquid-nitrogen cooling described by Vango, investigation was made, using a skived film (Saunders S-25) of the efficiency of two means for collecting the  $\text{NO}_2$  which has permeated through the test membranes: (1) condensation at liquid nitrogen temperature, and (2) bubbling through 1% of  $\text{H}_2\text{O}_2$  in distilled water (adjusted to pH 7).

As shown in Table 17, there is little difference in determined leak rates when the  $\text{NO}_2$  is collected at  $\text{LN}_2$  temperature or in 1%  $\text{H}_2\text{O}_2$  solution at room temperature. At present, the latter appears more amenable

to continuous monitoring--provided the peroxide is present in sufficient quantity to oxidize quantitatively the nitrous acid which is formed.

#### Permeation of Unclad and Lead-Clad Films

As described earlier in this Section, four test squares from a TFE-30 film prepared at SRI were clad with varying thicknesses of lead plates and the permeabilities of the test films to  $N_2O_2$  were determined. At the same time, permeability determinations were made also for similar films as-prepared (without plating). The results of the determinations, summarized in Table 18, demonstrate the differences due to differences in plating procedures and the 500-fold difference between clad and unclad films. These data compare most favorably with those reported by Vango for 6-mil lead coatings which were mill-rolled to close the gaps in the lead deposit [20]. (The final lead-plating procedure was based on the result for film No. 4.)

Table 16

COMPARISON OF ADHERENCE STRENGTHS OF LEAD PLATE  
BONDED TO SMOOTH AND POROUS TEFLON FILM SURFACES

SRI FILM NO.	PSI AT BREAK	TYPE OF FAILURE
17A (smooth surface)	260	Silver to Teflon
	160	Silver to Teflon
	135	Silver to Teflon
	Av 185	
17B (porous surface)	245	Surface failure of lead
	370	Lead to silver
	420	Lead to silver
	Av 345	

Table 17

PERMEABILITY TO  $N_2O_4$  OF TFE FILMS AT 25°C AS  
DETERMINED BY DIFFERENT COLLECTION SYSTEMS  
(Saunders S-25 Teflon)

SAMPLE NO.	FILM THICKNESS, mils	DURATION OF TEST, hrs	LEAK RATE, mg/hr-in <sup>2</sup>	
			in LN <sub>2</sub>	in 1% H <sub>2</sub> O <sub>2</sub>
1	15	26.5	1.05	1.06
2	15	23.0	1.00	0.99
3	15	23.0	1.17	1.05

Table 18

PERMEABILITY TO  $N_2O_4$  OF FLEXIBLE TFE-30 FILMS (SRI):  
THE EFFECT OF LEAD CLADDING

SRI FILM NO.	TFE FILM THICKNESS, mils	LEAD THICKNESS, mils	DURATION OF TEST, hrs	LEAK RATE, mg/hr-in <sup>2</sup>	
				in LN <sub>2</sub>	in 1% H <sub>2</sub> O <sub>2</sub>
A	5.4	0	20.5	11.0	13.1
B	4.6	0	17.0	19.5	--
1	5.4	0.8	20.5	0.023	--
			+68.5	--	0.027
			+232.0	--	0.116
2	5.4	0.4	20.5	0.033	--
			+68.5	--	0.27
3	5.4	0.75	68.5	--	3.57
4	5.4	1.2	68.5	--	0.012
			+232.0	--	0.017



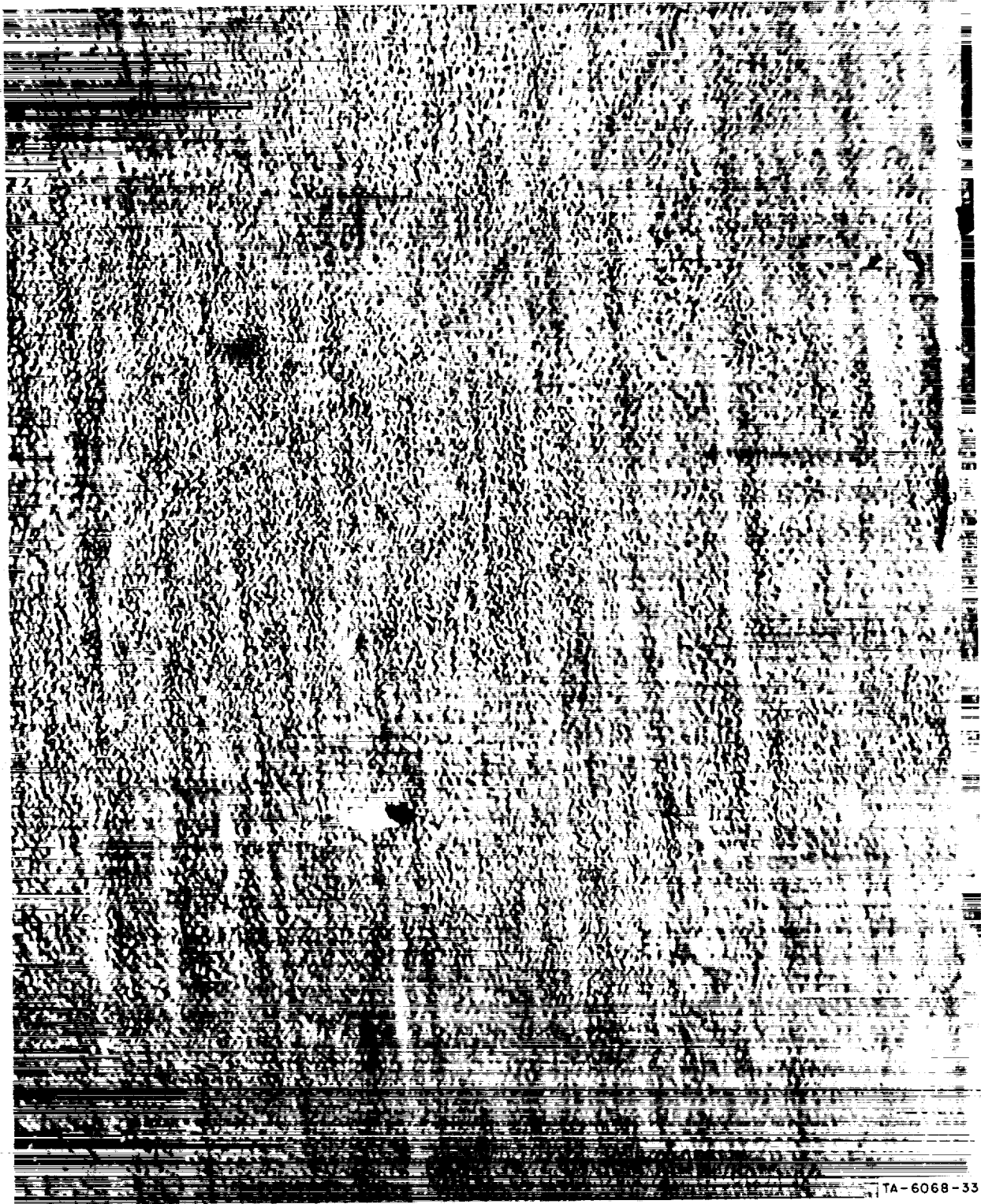


FIG. 24 PHOTOMICROGRAPH OF TEFLON-TFE FILM 17A (Smooth Surface);  
CHROMIUM-SHADOWED, 200X

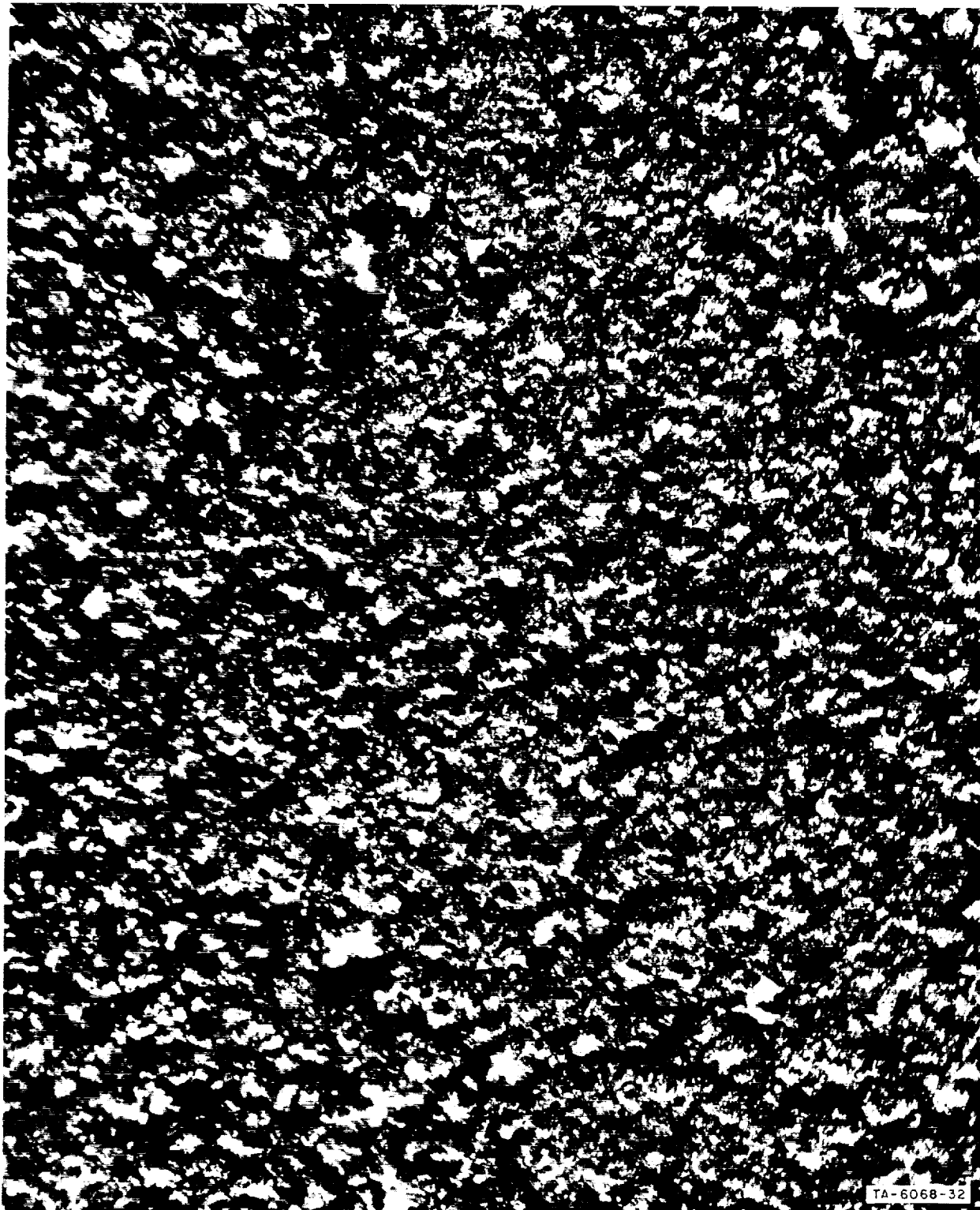


FIG. 25 PHOTOMICROGRAPH OF TEFLON-TFE FILM 17B (Porous Surface);  
GOLD-SHADOWED, 170X

POROUS LAYER  
0.001"

SUBSTRATE  
0.0048"

TA-6068-31

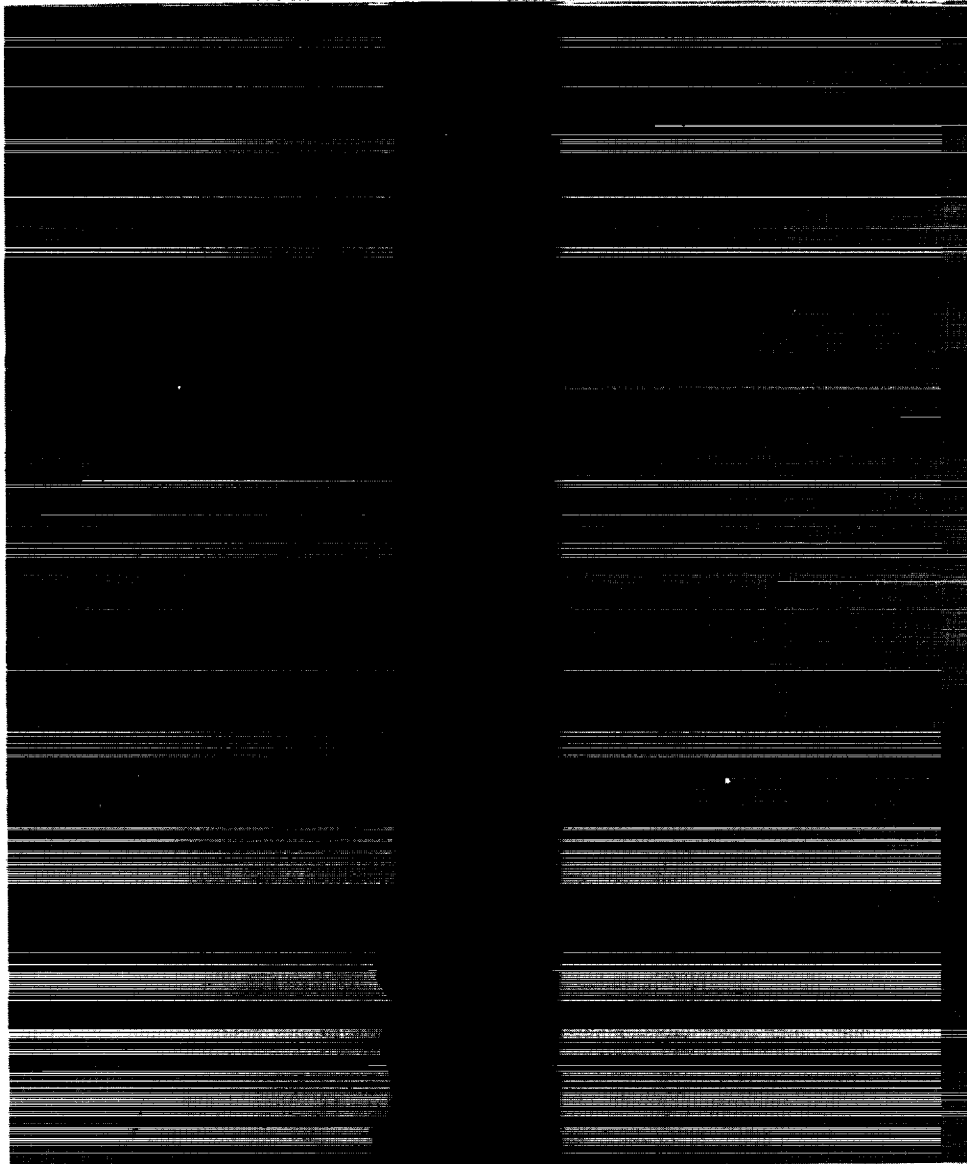
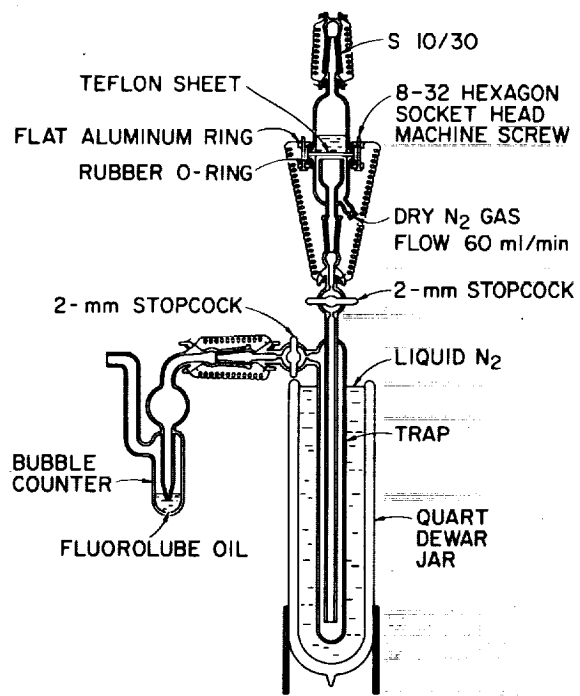


FIG. 26 PHOTOMICROGRAPH OF CROSS-SECTION OF FILM 17B



TA-6063-128

FIG. 27 PERMEABILITY APPARATUS

## VI. MICRO CREASE-AND-FOLD TEST APPARATUS FOR POLYMERIC FILMS

One of the objectives of this reported work was to evaluate the crease-and-fold resistance of candidate polymeric expulsion bladder materials in the presence of the propellants at cryogenic temperatures and at pressures of 0-40 psia. It was required that the tester provide the severe three-cornered creases which would be experienced by propellant expulsion bladders in spacecrafts. In view of the potential hazards inherent in flexing polymeric materials in the presence of highly-reactive propellants, it was also required that the volume of propellant be as small as possible.

The design of the crease-and-fold test fixture is a miniature three-cornered-crease tester which provides nearly identical flexing parameters as the tester developed at the Jet Propulsion Laboratory [4] (see Section II). The fixture is incorporated in an apparatus which permits testing over a wide temperature range (as low as  $-196^{\circ}$ ). The detection of failure (appearance of pinhole) is accomplished by an electric spark technique, similar to that described by King and Gregory [3] (see Section II).

### TEST APPARATUS

A detailed assembly drawing of the crease-and-fold test apparatus is shown in Figure 28. The tubular connection (1) is attached to a multi-purpose vacuum line to permit transfer of propellants or cryogenic coolants into the bell jar (21). The crease test fixture is driven by a variable-speed motor attached to the drive shaft (2) passing through Teflon O-ring compression seals (5). Couplings connected with this shaft rotate approximately  $120^{\circ}$  to cause the test sample to slide across the crease fitting (10) approximately 1.25 inches for a complete stroke or cycle. It is possible to pre-select the tension on the test sample

with the calibrated spring plunger gage (18). The narrow band attached to the gage and around the drive pulley (14) is a 5-mil thick nickel foil (11) and is secured at the top center of the pulley by a machine screw (30).

Details of the crease fitting over which the test sample is flexed are shown in Figure 29. This removable fitting can be replaced with another having different reference angles (A and B).

Specifications for the prototype micro crease-and-fold test apparatus are given in Table 19.

Figures 30 and 31 are photographs of the test apparatus which illustrate the difference in size and shape of a regular 3-inch bell jar and another version used to permit testing in a minimum quantity of fluid. The larger (200 cc) volume is used for testing in relatively inert fluids, such as Freons; the smaller (10 cc) volume is used for testing in reactive fluids, such as liquid oxygen difluoride or liquid diborane. In either instance, sufficient liquid volume is used to immerse the sample completely while it is under test.

In Figure 32, the positioning of the spark probe used for the detection of pinholes is shown with its tip at the sample crease line. The probe consists of a conducting wire (insulated by quartz tubing) attached to a 0-1000 volt/30 milliamp neon-sign transformer. Current is passed through the probe during the flexing of materials in inert gases or liquids; when a pinhole is formed, a spark passes from the probe through the hole to the metallic surface of the crease fitting. The formation of the spark can be seen by close observation but is also evident by observing the ammeter in the circuit.

The efficiency of the test fixture for production of 3-cornered creases is shown clearly by the marks on a typical film sample (Figure 33).

#### OPERATING PROCEDURES

Test samples are cut to the dimensions shown in Figure 34, degreased with methylene chloride or trichloroethylene and dried under vacuum. A sample is then clamped in the sample holder (Figure 28) and the crease

fitting is bolted in a position selected to draw the desired tension on the strip. After a sample is cooled to a low temperature, it will have changed because of sample shrinkage; thus, it is necessary to make several trials to establish the correct tension at room temperature.

For samples which are being tested in air at ambient temperature, a preliminary check for holes is made with the high-voltage probe and then the tester and the probe are activated; observation is made of the number of cycles to failure (appearance of one pinhole).

For samples which are to be tested at temperatures less than ambient, an inert liquid (such as a Freon) is placed in the bell jar after the preliminary hole-check to provide efficient heat transfer with the coolant maintained at desired temperature in a Dewar flask surrounding the bell jar. Samples may be tested in gaseous atmospheres at cold temperatures, but heat transfer is poor and as long as one hour may be required for the sample to reach the desired temperature. Results obtained in gaseous atmospheres are questionable because the temperature at a flexure point will be undoubtedly higher than ambient.

For tests with hazardous or toxic gases, e.g., propellants, the bell jar is clamped in place and connected to the vacuum system by the tabulation shown in Figures 28 and 30. The gas is then vacuum-transferred to the bell jar. If the test is to be conducted at low temperature, the evacuated bell jar is cooled by a bath at the desired temperature prior to filling; bath temperature must not be cooler than desired test temperature since the test sample may be weakened or embrittled prematurely.

Although it is possible to operate the hole-detecting probe during tests conducted in air, the probe must not be operated in media in which burning or explosion will be initiated by the electric spark. For testing in liquid  $\text{OF}_2$ , for example, after a few test cycles of  $\text{OF}_2$  is withdrawn under vacuum into a storage vessel, the bell jar is warmed and flushed with nitrogen or an inert gas, and then the probe is activated. If a hole is not detected, the system is again evacuated, cooled, filled with  $\text{OF}_2$  and the test continued for a few more cycles.

## PERFORMANCE

The geometry of the micro crease fitting was patterned after the JPL tester in order that an equivalent test might be performed; then a series of experiments were carried out to determine the appropriate tension which would ensure equivalent results. It was found that a 500-g tension on the one-inch wide test strips in the micro tester would provide the same results as those obtained with the JPL tester for test strips of 2.5-inches wide under 2.5 pounds of tension. The comparative test data are summarized in Table 20 for a commercial Teflon film; high-voltage hole detection was used with each apparatus.

The amount of tension applied to the sample is an important variable. As shown in Table 21, the number of cycles to failure for a PTFE film can be increased by a factor of 10 simply by decreasing applied tension from 700 to 500 grams, while maintaining crease-fitting geometry at the same Ref. angles ( $A = 120^\circ$ ,  $B = -2.5^\circ$ ). A decrease in the number of cycles to failure can also be effected by changing the geometry of the crease fitting; about 3 times the resistance to wear has been observed (Table 22) for the same film when applied tension was unchanged but Ref. angle B was changed from  $-2.4^\circ$  to  $0^\circ$ .

One of the most profound causes of failure of polymeric films in crease-and-fold testing is due to brittleness caused by low temperatures. This can be seen by examining the results which are summarized in Table 23 for PTFE films tested from  $25^\circ\text{C}$  to  $-135^\circ\text{C}$ .

Because of the stiffness and memory characteristics of polymeric films at low temperatures, these tests are not equivalent to those conducted at the higher temperatures. As a test sample is cooled, it tends to conform less to the crease fitting geometry and also requires additional force or tension to be set in motion. Such force increases with decreasing test temperature. Figure 35 shows the results of a study to evaluate the effect of temperature on this force requirement. The tension added beyond pre-set tension of 500 grams to start the crease cycle was measured as a function of temperature for two polymeric materials which were selected



to represent extremes of stiffness: Mylar 500 D (polyterephthalate), very stiff at low temperatures, and Zedel (polyethylene) found to be most flexible at low temperatures. Since the spring scale sensitivity was about 50 grams, the Zedel film was tested over the temperature range within the sensitivity limit of the tester, but as much as 200 grams additional was required to initiate the tests for the Mylar film at low temperatures.

Table 19

DESIGN PARAMETERS OF MICRO CREASE-AND-FOLD TEST APPARATUS\*

ITEM	DETAIL
<u>Test Fixture</u> Metals for construction (for propellant contact surfaces) Gasket seals Drive mechanism Length of flex stroke Range of tension Normal test tension Motor drive Normal test rate Crease fitting Normal test design	Monel metal or nickel-plated metal Teflon Eccentric coupling on circular pulley 1/4" (fixed; could be varied to 2 inches) 0-4.5 pounds 1.0 pounds Bodine type NSH-12R, 0-173 rpm 60 rpm Replaceable and variable Angle A = 120°, B = -2.5°
<u>Encasement</u> Normal bell jar Reduced-volume bell jar	3" x 12" Pyrex pipe; liquid volume to cover sample, 200 cc. 3" x 12" Pyrex pipe tapered to 1" diameter at bottom well, about 2" diameter at top of sample area; liquid volume to cover sample, 10 cc

\* See Figure 28.

Table 20  
 COMPARATIVE TEST RESULTS AT 24°C FOR MICRO  
 CREASE TESTER AND JPL CREASE TESTER<sup>a</sup>  
 (Teflon-FEP, Type A, 5-mil)<sup>b</sup>

SAMPLE NO.	CYCLES TO FAILURE	
	JPL Tester	Micro Tester
1	83	129
2	106	139
3	87	103
4	91	94
5	89	89
6	98	121
7	123	90
8	76	88
9	69	104
10	98	118
11	55	108
12	94	76
13	89	78
14	91	99
15	63	84
Range	68	63
Average	88	101
Standard Deviation	±16	±18

<sup>a</sup> Ref. Angle A = 120°  
 Ref. Angle B = -2.5°

<sup>b</sup> E. I. DuPont de Nemours and Company

Table 21  
 EFFECT OF TENSION ON CREASE RESISTANCE  
 OF FILMS IN AIR AT 24°C  
 (PTFE Film S-24, 3.5 mil)<sup>a</sup>

TRIAL	CYCLES TO FIRST HOLE <sup>b</sup>	
	700-g tension	500-g tension
1	15	258
2	19	253
3	19	256
4	44	354
5	19	306
6	27	296
7	12	237
8	24	288
9	12	227
10	24	360
11	16	
12	19	
13	16	
14	33	
15	21	
16	31	
17	13	
18	38	
19	18	
20	24	
Average	22	289
Std. Dev.	±9	±32

<sup>a</sup> Saunders Engineering Company  
<sup>b</sup> Ref. Angle A = 120°, B = -2.5°

Table 22  
EFFECT OF CREASE FITTING GEOMETRY ON CREASE RESISTANCE  
OF FILMS IN AIR AT 24°C, (700-g Tension)  
(PTFE Film S-24, 3.5 mil)<sup>a</sup>

TRIAL	CYCLES TO FIRST HOLE	
	Ref. angle A = 120° Angle B = 0°	Ref. angle A = 120° Angle B = -2.5°
1	15	15
2	15	19
3	23	19
4	17	44
5	21	19
6	26	23
7	48	12
8	49	24
9	42	12
10	40	24
11	43	16
12	102	19
13	52	16
14	108	33
15	152	21
16	85	24
17	98	23
18	146	31
19	91	13
20	64	38
Average	62	22
Std. Dev.	±42	±9

<sup>a</sup> Saunders Engineering Company

Table 23  
EFFECT OF TEMPERATURE ON FLEX RESISTANCE  
OF TEFLON FILMS

SAMPLE	THICKNESS	TEMP., °C	NUMBER OF CYCLES TO FAILURE <sup>a</sup>
FEP-100A <sup>b</sup>	5-mil	25	108 ± 18
		-29	20.4 ± 7.7
		-59	6.6 ± 1.8
		-78	5.8 ± 1.4
		-135	1. (1 sample)
Saunders S-24 <sup>c</sup>	3-mil	25	289 ± 42
		0	121 ± 50
		-29	71. ± 47
		-59	1.
Saunders S-25 <sup>c</sup>	4-mil	-78	1.
		25	486 ± 135
		0	110 ± 48
		-29	15 ± 10
		-59	1.
		-78	1.

<sup>a</sup> Average of 10 determinations

<sup>b</sup> E. I. DuPont de Nemours and Company

<sup>c</sup> Saunders Engineering Company

- NOTES:
1. REMOVE ALL BURRS AND SHARP EDGES APPROX. .0100.
  2. GENERAL FINISH  $\sqrt{\text{V}}$  EXCEPT AS NOTED.
  3. DRILL & TAP TO SUIT ON ASSEMBLY.
  4. ALL STOCK ITEMS NOT OF NICKEL OR MONEL MATERIAL MUST BE NICKEL PLATED.
  5. SEE DWG. NO. C-6068-52 FOR WELD ASSEMBLY.

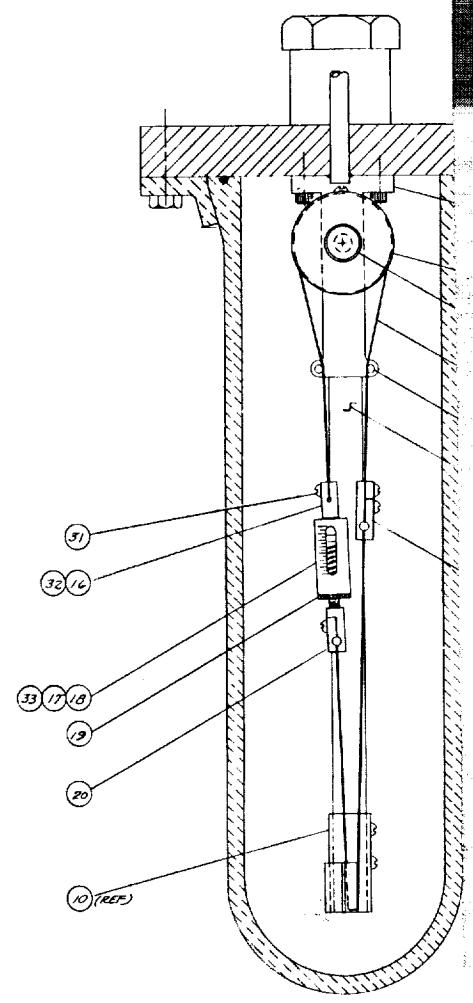


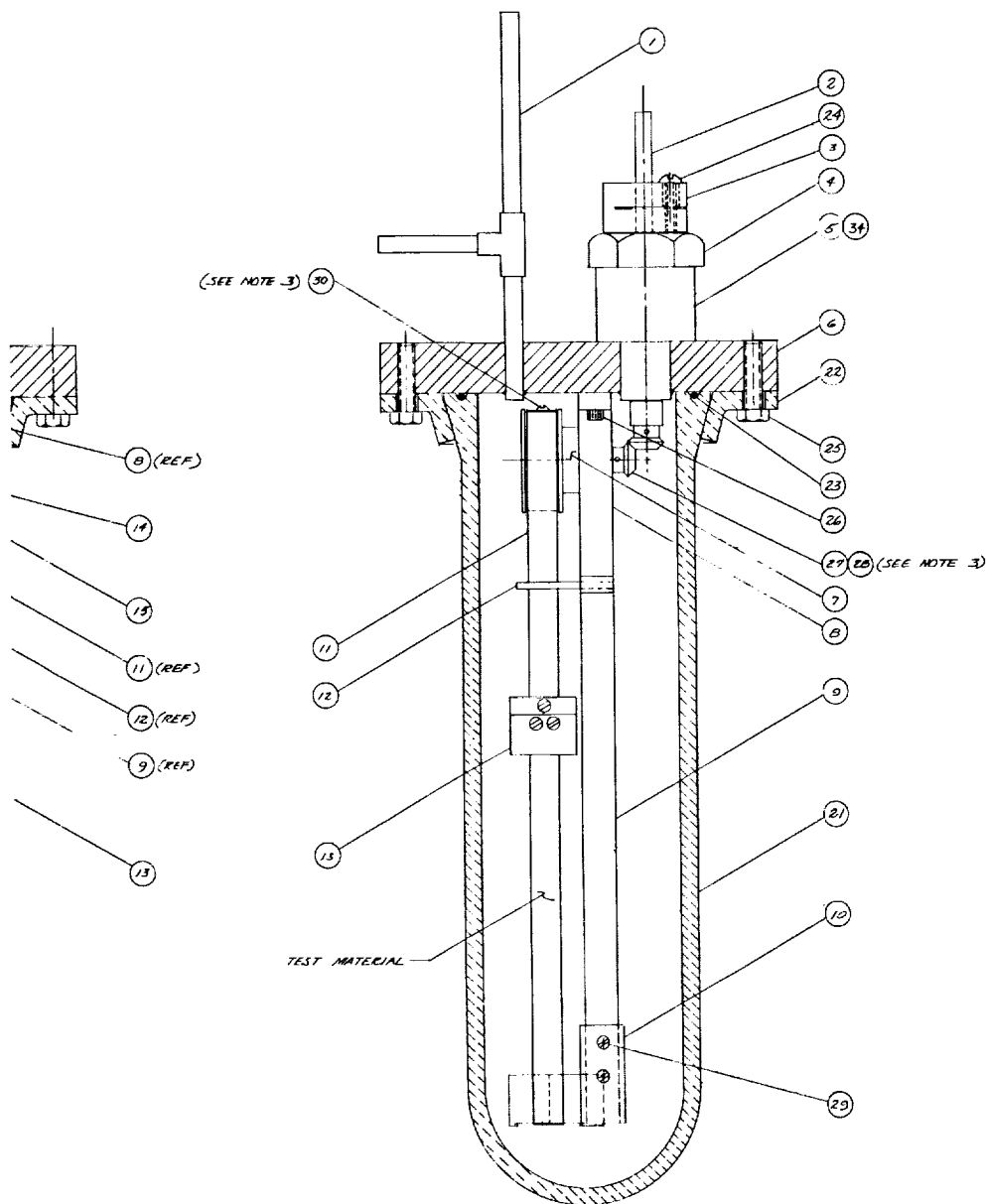
FIG 28 A

95

**EXHAUST FRAME**

10/10/10

10/10/10



34	O-RING-TEFLON, #30 I.D. x .500 O.D.	2
33	SPRING-COMPRESSION	1
32	STUD-THREADED 5-40 x 1/2	1
31	MACHINE SCREW 6-32 x 1/2	1
30	MACHINE SCREW 4-40 x 1/2	1
29	MACHINE SCREW 2-56 x 1/2	2
28	SOC. HD. SET SCREW 1-40 x 1/2	2
27	GARY-BROOKHOLM MITER GEAR - BRASS	2
26	MACHINE SCREW 8-32 x 1/2	2
25	MACHINE SCREW 1-20 x 1	6
24	MACHINE SCREW 1-20 x 1/2	1
23	O-RING-TEFLON, 1.250 I.D. x 3.000 O.D.	1
22	PIPE CLAMP - GLASS - 3"	1
21	BELL JAR - GLASS 3" I.D.	1
20	B-606B-51 CLAMP	1
19	B-606B-50 END CAP - GAUGE	1
18	B-606B-49 PLUNGER - GAUGE	1
17	B-606B-48 BODY - GAUGE	1
16	B-606B-47 CLAMP	1
15	A-606B-37 PULLEY SHAFT	1
14	A-606B-36 PULLEY	1
13	B-606B-46 CLAMP	1
12	A-606B-45 PIN	2
11	B-606B-44 BAND	1
10	B-606B-38 WEAR FITTING	1
9	A-606B-35 BLOCK EXTENSION	1
8	A-606B-34 PULLEY BLOCK	1
7	B-606B-43 SPACER	1
6	B-606B-31 PLATE	1
5	A-606B-32 GLAND	1
4	A-606B-33 GLAND NUT W/SUPPORT BEARING	1
3	B-606B-42 COLLAR - LOCKING	1
2	A-606B-38 DRIVE SHAFT	1
1	A-606B-40 GAS INLET BLEEDER PIPE ASS'Y	1

ITEM	QTY.	DESCRIPTION	SCALE	DATE	BY	CHKD.
TITLE: ASSEMBLY DRAWN: J. G. ... CHECKED: ... APPROVED: ... DATE: 10-19-69 STANFORD RESEARCH INSTITUTE MEMO PARK, CALIF.						

TB-7041-47

FIG. 28 B ASSEMBLY DRAWING FOR MICRO CREASE-AND-FOLD TEST APPARATUS

96

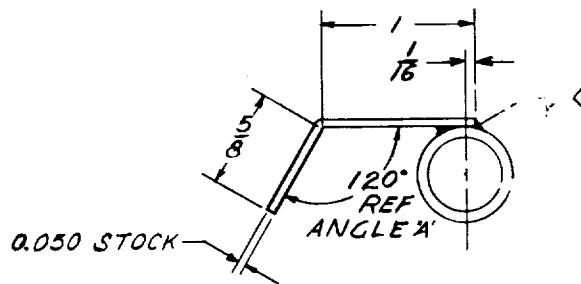
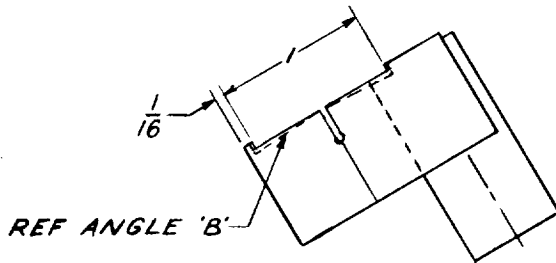
FOLDOUT FRAME 2



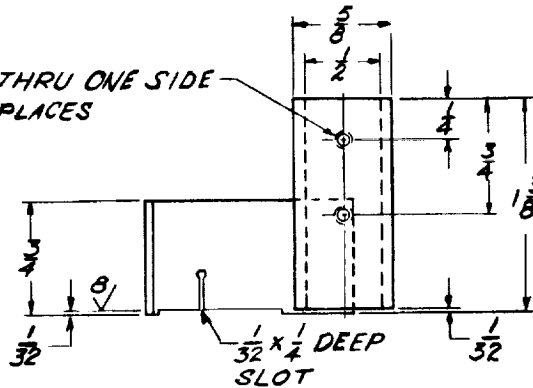


**NOTES:**

1. REMOVE ALL BURRS AND BREAK SHARP EDGES APPROX. .010R.
2. GENERAL FINISH  $\sqrt{125}$ , EXCEPT AS NOTED.



#50 (0.070) DRILL THRU ONE SIDE  
2-56 THREAD 2 PLACES



ITEM	DWG. NUMBER	DESCRIPTION	QTY.
MATL:	NICKEL	TOLERANCES: UNLESS OTHERWISE SPECIFIED	BASIC DIMS.
FINISH:		ANGULAR TOL: ± 1/2°	FRACT. TOL.
DR.	V. Lopez		DECIMAL TOL.
CKD.			
APPD.			
APPD.			
		TITLE:	SCALE
		NEXT ASSEMBLY:	
STANFORD RESEARCH INSTITUTE MENLO PARK, CALIF.			DWG. NO. B-6068-39
			ISSUE

PRINTED ON DIEP0 NO. 1000H CLEARPRINT

7A-6068-23A

FIG. 29 DESIGN DRAWING OF CREASE FITTING

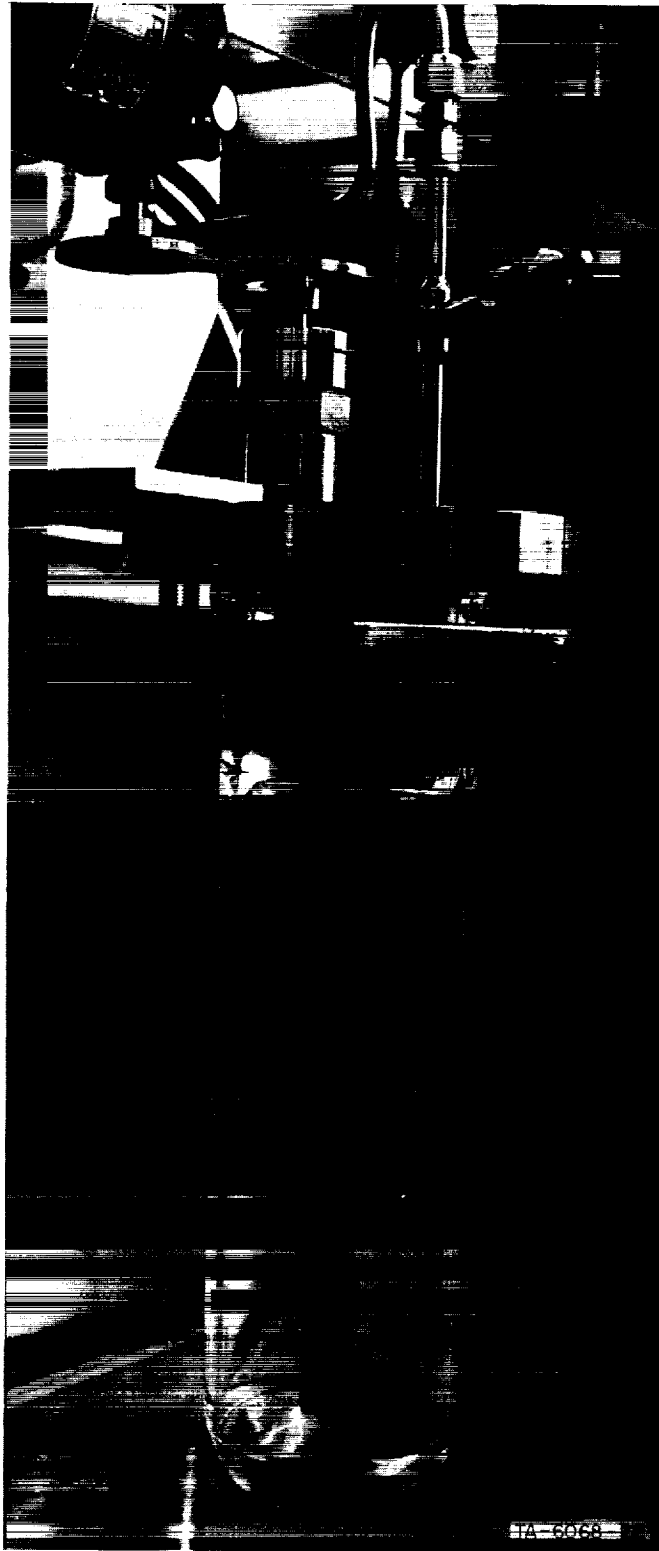


FIG. 30 MICRO CREASE-AND-FOLD TEST  
FIXTURE WITHIN THREE-INCH  
BELL JAR



FIG. 31 MICRO CREASE-AND-FOLD TEST  
FIXTURE WITHIN LOW-VOLUME  
BELL JAR

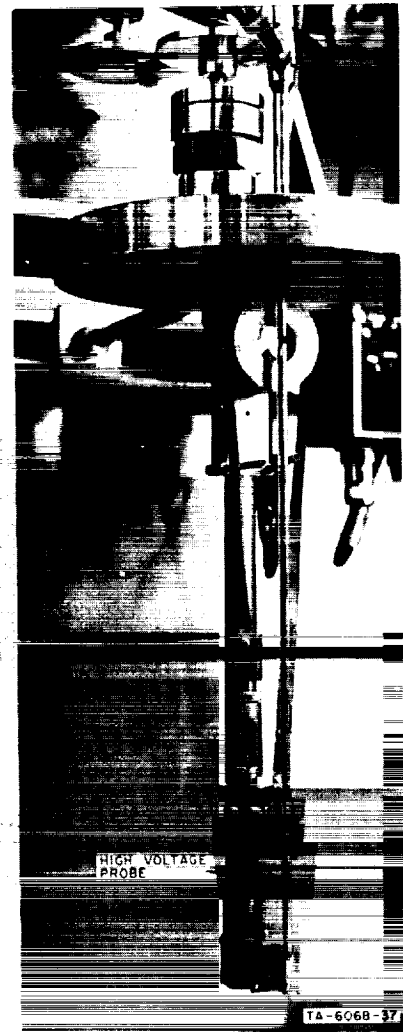


FIG. 32 MICRO CREASE-AND-FOLD TEST  
FIXTURE WITH HIGH-VOLTAGE  
PROBE IN PLACE FOR PINHOLE  
DETECTION

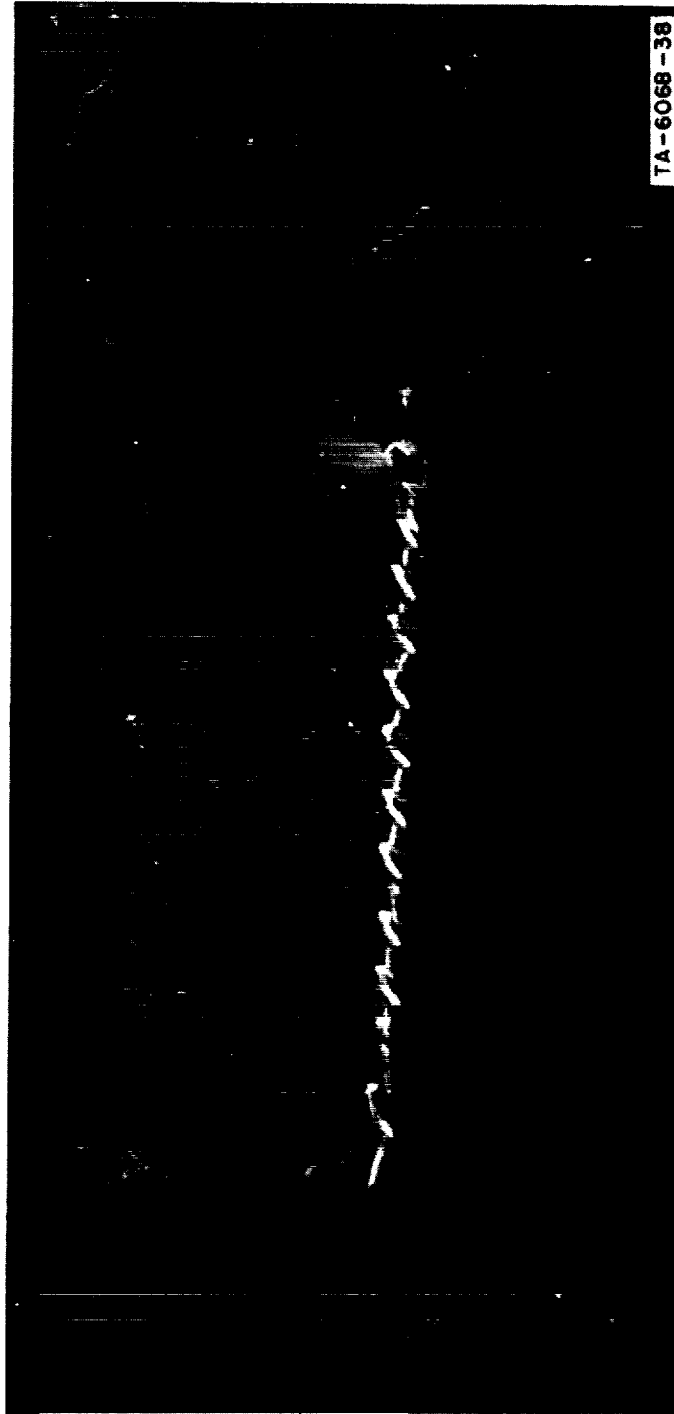


FIG. 33 TEFLON TEST STRIP AFTER CREASE-AND-FOLD TEST;  
NOTE THREE-CORNERED WEAR IMPRINTS

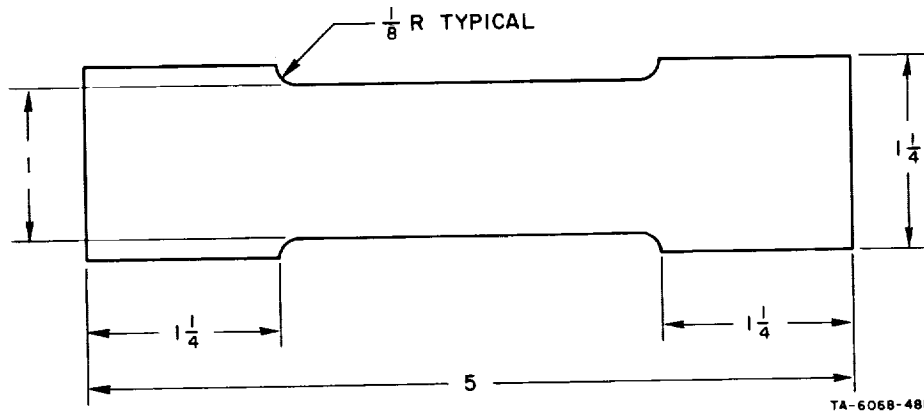


FIG. 34 SAMPLE DIMENSIONS FOR MICRO CREASE-AND-FOLD TESTING

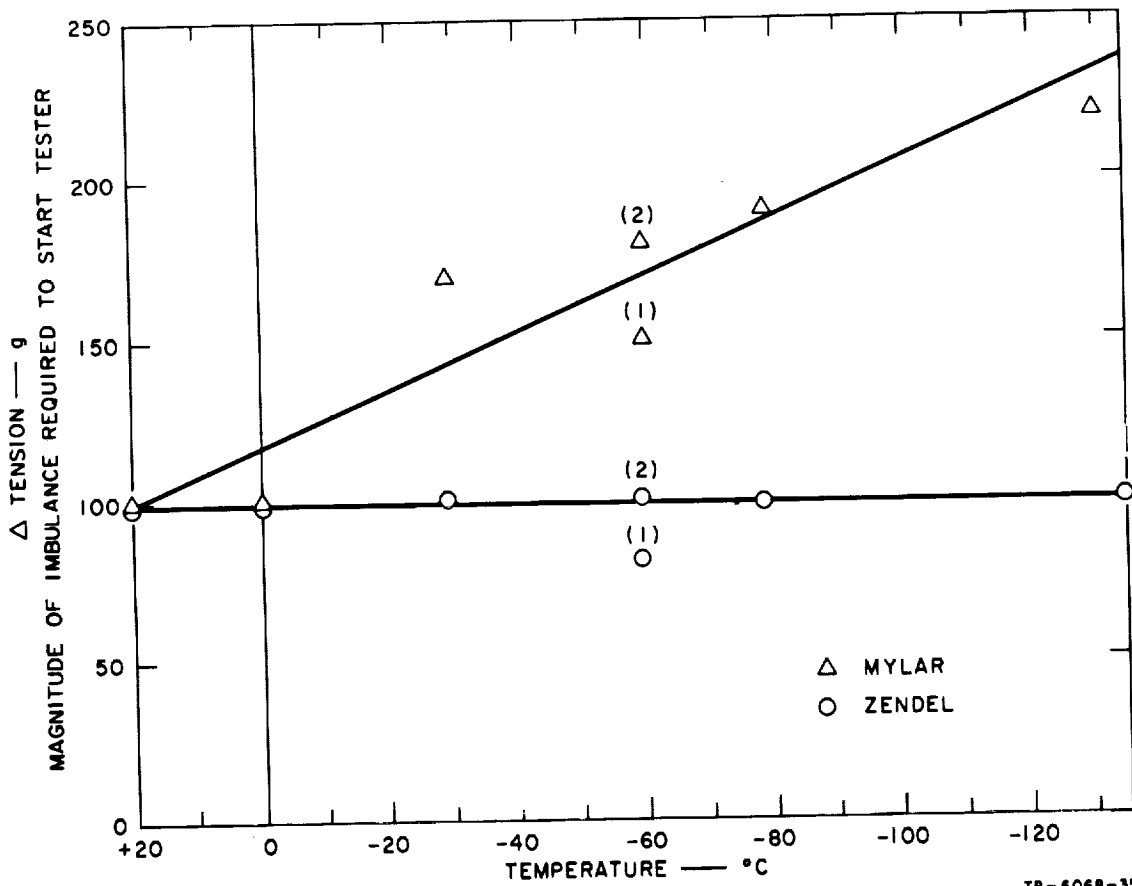


FIG. 35 EFFECT OF TEMPERATURE ON TENSION REQUIRED TO INITIATE CREASE-AND-FOLD TESTING



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## VII. COMPATIBILITY OF MATERIALS WITH OXYGEN DIFLUORIDE AND DIBORANE

Consideration of advanced (and cryogenic) space propulsion systems, such as oxygen difluoride-diborane ( $\text{OF}_2\text{-B}_2\text{H}_6$ ), requires a detailed investigation into materials selection for flexible expulsion bladders and high-strength propellant tanks, both of which must be relatively inert to the highly-reducing or -oxidizing propellants and must maintain required properties at cryogenic temperatures.

The work reported at this time has been involved with an examination of available information on materials compatibility with  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$ , the fabrication of a vacuum propellant-handling system, the design and fabrication of a micro crease-and-fold tester, and preliminary testing of polymeric materials considered for use in propellant expulsion bladders.

(The design and performance of the micro crease-and-fold tester is described in detail in Section VI.)

### COMPATIBILITY REVIEWS

Information on file concerning the compatibility of  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$  with metallic and nonmetallic materials was supplemented by a search in the (unclassified) technical literature, using reference sources such as Chemical Abstracts, STAR Abstracts, AIAA Abstracts, and DMIC Abstracts. The information derived has contributed to the design of a reliable vacuum system for handling the potentially-hazardous propellants and to the preliminary selection of polymeric materials to be tested for use in expulsion bladders.

#### Compatibility of Oxygen Difluoride

Several studies and reviews can be cited [24-27] in which the storability and compatibility of  $\text{OF}_2$  with selected metals and plastics have been evaluated. At the present state-of-the-art, the most promising

liquid oxidizer propulsion bladders are laminates of relatively porous fluorocarbons and thin metallic coatings [4, 28-30] but problems of fabrication have not been solved. Folded metal diaphragms at this time appear to be least desirable because they cannot be flexed repeatedly and because flexure may rupture the metal and lead to ignition. [Many metals (and glass) can be used for short-term storage of  $OF_2$  if clean and free of water and HF and not subjected to shock.]

The compatibility of metals and plastics with  $OF_2$  under flex and shearing action has not been studied adequately. Generally, the user of fluorine oxidizers is cautioned to passivate metals with the oxidizer before use and not to shock or subject the containers to flexing action under moderate pressures because the disturbance may lead to an increased rate of corrosion and even ignition of the metal.

Passivation of metal surfaces prior to pressure loading is presumed to form a nonvolatile, relatively adherent fluoride coating which prevents further corrosion. On thick metal surfaces, heat of reaction from the initial attack by the oxidizer is dissipated by the good heat conduction of metals, but since thin metals and metal powders can not conduct heat away from the surface at a sufficient rate, ignition is more probable. Studies need to be made to determine the thickness of metal required to prevent ignition to within acceptable reliability limits. Porter and Stanford [4] point out that "storability" data on metals is practically useless for selecting materials for expulsion service; testing of materials under flexure or stress should be performed in the propellant to be used. Krusos [30] notes that the statistical data to-failure to double-fold dynamic tests lead to the recommendation that Teflon bladders are suited for  $N_2O_4$  propulsion bladders and that similar data should be obtained for other oxidizer systems.

Some discussion of the problem of compatibility of  $OF_2$  with fluorocarbon materials is appropriate since  $OF_2$  and fluorocarbons can react violently, although fluorocarbons are widely used with  $OF_2$ . An accidental explosion of Teflon storage containers and  $OF_2$  was reported [31] and the same workers showed that reactions of fluorocarbons and fluorine



oxidizers can be initiated by shock [32], and impact [33]. However, the initiation of these reactions is difficult. Some attention to purity and condition of the Teflon should be made. Also, it appears that a small quantity of  $OF_2$  may be dissolved in Teflon or will at least react slightly in liquid storage; fluorocarbon samples show a slight increase in weight in storage [30]. Terminal groups on Teflon chains are potential reaction sites; for example, carboxyl groups may convert to acryl hypo-fluorites [32] which would be undesirable. Hydrocarbons have also been identified as impurities in Teflon. Irradiation of bulk Teflon produced [34] radicals which were reported to be stable up to the melting point. Oxygen reacts with these radicals to produce peroxides which can be removed by heating at low pressure to regenerate the original free radicals. The free radicals may provide sites which initiate fluoridation of the polymer. Flexing action may also cause chain scission, producing terminal groups which would be subject to reaction with  $OF_2$ . These observations indicate that purified Teflon should be used and that the material should be heat-treated to drive off carboxyl, peroxide, and hydrocarbon impurities before use. A final fluorine passivation before use should help eliminate most of the residual reactive spots.

#### Compatibility of Diborane

The selection of materials compatible with diborane fuel is not as difficult as with oxidizers. The low-temperature requirement for positive expulsion systems, however, poses considerable difficulty; but the materials for low-temperature tank lines and expulsion bladders which are reported to show promise are the polyterephthalate, polyester polymers [35]. Degradation studies [36] of polyethylene terephthalate indicate that hydrolysis at elevated temperatures is the most important degradation mechanism. However, it must be pointed out that polyester polymers have exposed hydroxyl groups which diborane can attack; carboxyl groups in non-rigid materials are attacked readily by  $B_2H_6$  at elevated temperatures. If any unsaturation is present in polymers,  $B_2H_6$  can saturate the bonds (addition); migration of the added  $-BH_2$  group is known to occur [36], but in the liquidus range for diborane these reactions may

not be important or sufficiently rapid to cause difficulty. Teflon may be useful, but it is recognized that the heat of reaction of Teflon with  $B_2H_6$  is much greater than with fluorine oxidizers. Mixtures of chlorinated hydrocarbons and boron hydrides can detonate if shocked; conditions for detonation are not known for Teflon-boron hydrides.

#### PROPELLANT-HANDLING SYSTEM

A vacuum system for handling  $OF_2$  and  $B_2H_6$  was designed and fabricated from Monel metal (except for special traps). All integral tubulations are joined by welded flanges sealed with pure-gold wire gaskets. The system is designed so that short sections can be isolated and disassembled easily for cleaning or replacement; additionally, the possible isolation of sections provides for individual experiments, with only the primary manifold being common.

The system is equipped with soda-lime traps (in copper casings) which prevent contamination or possible detonation by fluorine oxidizers of the forepump system; also included are direct tie-lines with a fluorine storage tank for passivation prior to  $OF_2$  handling and with a nitrogen storage tank for flushing of the system after propellants are removed. The fluorine tank, stored a few feet away from the system, was installed according to manufacturer's recommendations and SRI Safety Office regulations.

The entire system is contained within a high-speed exhaust hood. The two sides of the hood are made of heavy-walled Lucite, and the front of the hood is fitted with sliding double-doors made of heavy-walled Lucite; the back of the hood butts against a wall sheathed with stainless steel. The hood floor is made of stainless steel and is designed as a 4-inch deep trough with a 4-inch wide drain line so that unexpected spills may be contained and flushed immediately with copious amounts of water.

An over-all view of the vacuum handling system is shown in Figure 36. At each end, one can distinguish the copper-walled traps containing soda-lime; adjacent to these traps are Kel-F pre-traps which permit observation of the liquid level of released propellants. The  $OF_2$  supply is stored

(not visible) above the large-face Wallace & Tiernan pressure gage. (Diborane is stored in a freezer in an isolated area, far removed from the laboratory being described.) At the left of the photo can be seen another gage; this is the temperature controller for dispensing liquid nitrogen to a bath in order to maintain the temperature of test.

#### COMPATIBILITY OF POLYMERIC MATERIALS

Preliminary work on determining the compatibility of polymeric materials with oxygen difluoride and diborane has involved the determination of crease-and-fold resistance of selected materials in contact with either propellant. Because of the fire, impact, and explosion hazard of polymeric hydrocarbons with  $\text{OF}_2$ , only polyfluorocarbons were considered for testing. On the other hand, a variety of hydrocarbon polymers could be considered for testing in  $\text{B}_2\text{H}_6$  since they are not likely to be dangerous in use; however, oxidizing types of films (such as fluorocarbons) were not considered for test because of possible reactions with the strongly-reducing diborane.

Film samples of 3-5 mils thickness were used for test since they would conform moderately well to the micro crease tester jaw configuration (Section VI); it was felt that thinner materials would not withstand the sloshing action in partially-filled tanks. Test strips were cut and cleaned according to the procedures described in Section VI.

The data summarized in Table 24 indicate that an FEP film prepared at SRI displays better flex resistance in  $\text{OF}_2$  vapor at  $-78^\circ\text{C}$  than a commercially-available skived FEP film. Tests in  $\text{OF}_2$  at  $-135^\circ\text{C}$  were not performed on the SRI film. None of the Teflon FEP samples flexed in  $\text{OF}_2$  showed any signs of deflagration.

Crease-and-fold test data are given in Table 25 for several types of polymeric films in diborane at  $-135^\circ\text{C}$ . Mylar 500D (5 mil thick) can be cycled 5 to 7 times at  $-135^\circ\text{C}$  in liquid  $\text{B}_2\text{H}_6$ . As expected, the infrared pattern of the material after test shows no evidence of chemical attack (loss of OH peaks or appearance of -BH stretching peaks). Carbonyl attack is not readily assayed by this method in 5-mil samples because of the

strength of the CO peak; however, carbonyl reduction by  $B_2H_6$  would have been seen as increased OH and -BH peaks (to within  $\pm 1\%$ ). Pinholes formed in polyethylene (UCC Zendel, 4-mil) during the first cycle at  $-135^\circ C$  in liquid  $B_2H_6$ ; there was evidence of surface conductivity which interfered with the electrical pinhole detector (reaction?). A 5-mil polycarbonate film (GE 2346-L3) tore on the first cycle.

The over-all conclusion derivable from the tests in  $B_2H_6$  or  $OF_2$  is that the selected polymeric films appear to be inert in the propellants but are embrittled by the cryogenic temperatures. Thus, polymeric materials cannot be recommended for storage and use in expulsion bladders which are maintained at cryogenic temperatures. At this time, it appears that propellant-expulsion for the  $OF_2$ - $B_2H_6$  system will have to be accomplished by all-metal systems.

Table 24  
 CREASE-AND-FOLD RESISTANCE OF TEFLONS  
 IN OXYGEN DIFLUORIDE  
 (Ref. Angle A = 120°; Ref. Angle B = 0°;  
 Tension = 1.0 lb.)

SAMPLE	NO. OF TESTS	SAMPLE THICKNESS	TEST TEMP.	CYCLES TO FAILURE
FEP-500A*	3-4	5 mils	-78°C	3.5 ± 0.9
FEP-500I*	3-4	5 mils	-78°C	3.5 ± 0.9
SRI-FEP	3-4	5 mils	-78°C	7.6 ± 1.7
FEP-100A*	3-4	4 mils	-135°C	1-3
FEP-500L*	3-4	4 mils	-135°C	1-3

\* E. I. Du Pont de Nemours, Inc.

Table 25  
 CREASE-AND-FOLD RESISTANCE OF POLYMERIC  
 MATERIALS IN DIBORANE  
 (Ref. Angle A = 120°; Ref. Angle B = 0°;  
 Tension = 1.0 lb.)

SAMPLE	NO. OF TESTS	SAMPLE THICKNESS	TEST TEMP.	CYCLES TO FAILURE
Mylar 500D <sup>a</sup> (polyester)	3-4	5 mils	-135°C	5-7
Zendel <sup>b</sup> (polyethylene)	3-4	4 mils	-135°C	1
GE 2346-63 <sup>c</sup> (polycarbonate)	3-4	5 mils	-135°C	1

<sup>a</sup> E. I. Du Pont de Nemours, Inc.

<sup>b</sup> Union Carbide Chemicals, Inc.

<sup>c</sup> General Electric Company.

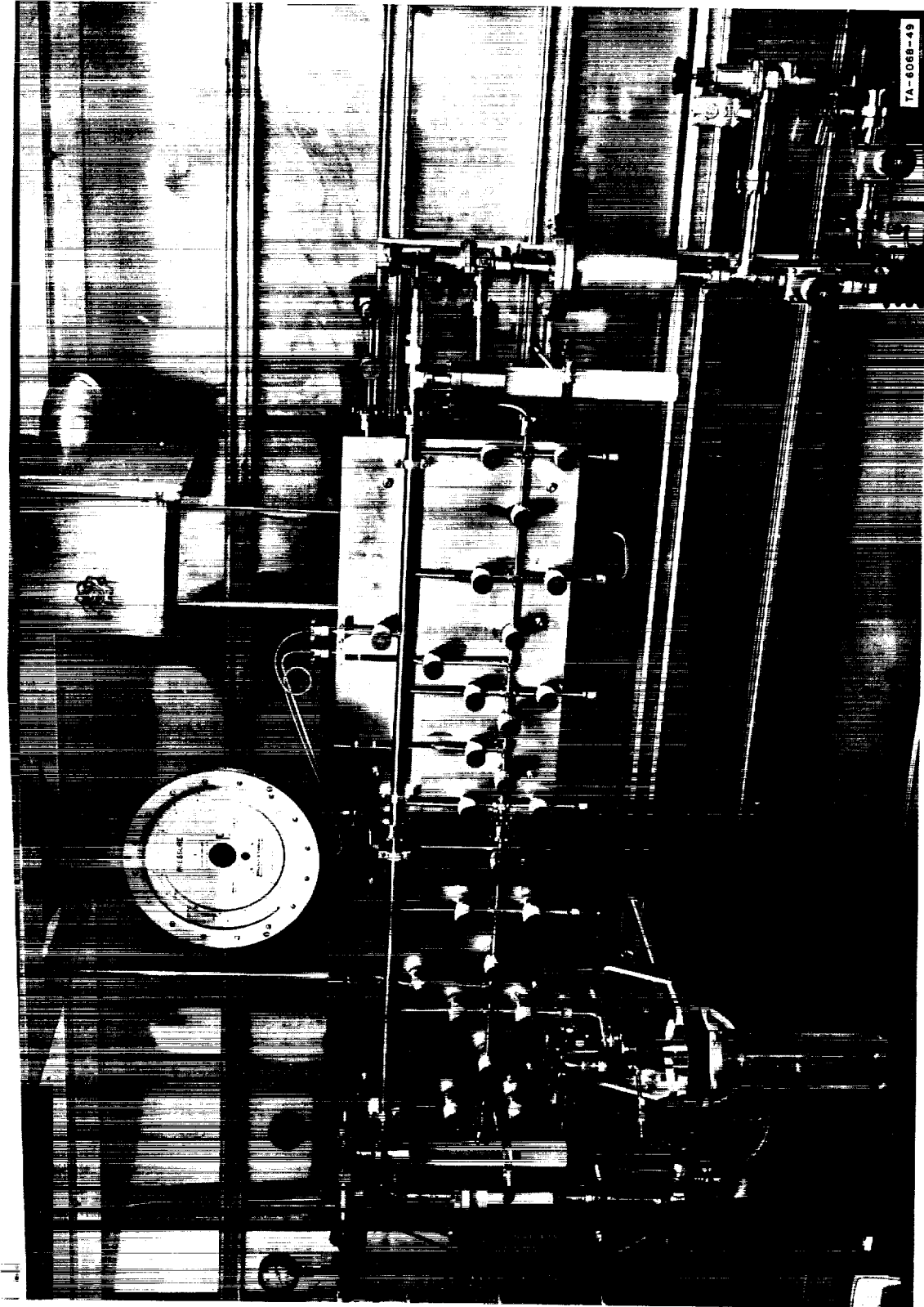


FIG. 36 MONEL METAL VACUUM SYSTEM FOR HANDLING PROPELLANTS

## VIII. REVIEW AND CONTINUING WORK

Flexible films can be fabricated from TFE-30 dispersions by following the process parameters established during this program of work. However, in order to assure the uniformity and reproducibility of fabricated films, it is necessary that all procedures be rigidly controlled, especially the conditions of sintering temperature, sintering time, and quenching. For example, some of the deviations from film properties expected because of planned changes in the process variables could be traced to small variations in the process parameters.

It has been shown that the structure of prepared films as revealed by x-ray crystallinity and electronmicrography is of major importance in deducing the effects of process variables and determining the development route. Continuing work with TFE-30 has indicated that longer sintering times (greater than the presently-recommended 24 hours) may result in superior films. It is planned to optimize all parameters and then prepare a series of spherical bladders for evaluation.

Recent work has suggested some interesting aspects of the correlation of crystal orientation, heat of fusion measurements, and film performance. It is planned to probe these correlations in depth so that the successful production of films will be based on sound theory and experimental proof.

It has been demonstrated that a well-bonded, uniform, and integral lead plate can be deposited on Teflon film as a permeation barrier. This work will be continued to prepare lead-clad films which will be tested for crease resistance while immersed in  $N_2O_4$  or  $N_2H_4$ . The work will include the plating of the interior of Teflon spherical bladders.

Recent work with films made from TFE-FEP co-dispersions (performed under another JPL Contract, No. 951581) has resulted in some extremely interesting findings which require immediate and thorough investigation since films made from TFE-FEP co-dispersions or made as laminates are already in production as expulsion bladders. The work was performed to

provide some basic information to permit discernment of the cause for rupture of an experimental bladder and was necessarily brief. A substantial contribution to expulsion bladder development will be made by including this investigation in the continuing program.

A micro crease-and-fold tester was designed which permits testing small strips (1" x 5") of sample films; small sizes are important when a number of characterizations must be made on one test film for thorough evaluation. The tester also provides performance of flex tests on films immersed in propellants, a necessity in continuing work.

Preliminary work with the behavior of polymeric materials in  $\text{OF}_2$  and  $\text{B}_2\text{H}_6$  has shown that the flex resistance of the films is drastically reduced at the low temperatures required to store the propellants in the liquid state. Thus, low temperature properties are as important a factor as the compatibility of the films with the propellants. Unless new films are identified or developed, it appears that the  $\text{OF}_2$ - $\text{B}_2\text{H}_6$  expulsion system will have to be metallic; thus, no further work is contemplated with polymeric films. In order to qualify metals for the system, both as structural members and as expulsion diaphragms or bellows, a large scale program must be undertaken to examine all parameters thoroughly in the shortest time possible to meet flight schedules. It is recommended that tests be performed at a remote site fully-equipped for safe handling of cryogenic and potentially-hazardous materials, and that it be conducted by an organization which can provide a work team experienced in handling the materials and clearly aware of the significance of test procedures.



## IX. NEW TECHNOLOGY ANNOUNCEMENTS

In accordance with the New Technology Clause of Contract No. 951484, reportable items have been identified clearly in various monthly reports. The items are summarized formally in the following paragraphs.

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### FABRICATION OF FLEXIBLE FILMS FROM TEFLON TFE-30 DISPERSIONS

Innovator: R. F. Muraca, assisted by A. A. Koch  
First Used: October 1967  
Reported as January 1, 1968 (Monthly Report No. 19)  
New Technology: June 17, 1968 (Final Report)

Several films have been fabricated from Teflon TFE-30 dispersions which have the characteristics necessary for use as expulsion bladders for spacecraft propellant systems. Process parameters have been developed to provide Teflon films of low degrees of crystallinity and high degrees of resistance to flexure. (See Section II of this report.)

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### MICRO CREASE-AND-FOLD TEST APPARATUS FOR POLYMERIC FILMS

Innovator: J. A. Neff and R. F. Muraca  
First Used: October 1967  
Reported as March 1, 1968 (Monthly Report No. 21)  
New Technology: June 17, 1968 (Final Report)

A micro test apparatus has been developed to evaluate the crease-and-fold resistance of polymeric materials in the presence of propellants at temperatures of +25°C to -195°C and pressures from 0 to 40 psia. A

detailed description of the design and performance of the tester is given in Section VI of this report.

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Separate reports of the above items are being submitted to the NASA/JPL Technology Utilization Officer.

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