Interim Report No. 1 | *May 18, 1966 to May 17, 1967*

DEVELOPMENT OF TECHNIQUES TO IMPROVE BLADDER MATERIALS AND TEST METHODS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA 91103

CONTRACT NO. 951484
UNDER NAS7-100

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

June 17, 1967

Interim Report No. 1 | May 18, 1966 to May 17, 1967

DEVELOPMENT OF TECHNIQUES TO IMPROVE BLADDER MATERIALS AND TEST METHODS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA 91103

CONTRACT NO. 951484
UNDER NAS7-100

JPL Technical Representative: H. B. STANFORD

SRI Project Supervisor: R. F. MURACA

SRI Project ASD-6068

Approved: R. F. MURACA, DIRECTOR
ANALYSES AND INSTRUMENTATION

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

Copy No. 4

PRECEDING PAGE BLANK NOT FILMED.

FOREWORD

This Interim Report summarizes the work performed by Stanford Research Institute during the period May 18, 1966 to May 17, 1967 under Contract No. 951484 for the Jet Propulsion Laboratory of the California Institute of Technology.

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 coordination was the responsibility of J. S. Whittick, Chemist-Program Coordinator.

The work was performed by the following chemists of the Department of Analyses and Instrumentation:

F. M. Church
C. A. Crutchfield
J. A. Havir
A. A. Koch
A. P. Longwell
C. H. Martin
E. Willis

Acknowledgment is made of the technicians and machinists who contributed to this program.

ABSTRACT

Stanford Research Institute, Menlo Park, California
DEVELOPMENT OF TECHNIQUES TO IMPROVE BLADDER MATERIALS AND TEST METHODS
Interim Report No. 1, May 1966 to May 1967
R. F. Muraca, et al., June 17, 1967
(JPL Contract No. 951484 under NAS7-100; SRI Project No. ASD-6068)

This report summarizes the work performed during the contract period May 18, 1966 to May 17, 1967. The investigation of process parameters for the preparation of films from Teflon dispersions is described and data are presented on the characterization of experimental films; these data include values for physical and mechanical properties, such as tensile strength, permeability, degree of crystallinity, and identification of impurities or additives in the raw dispersions. Various approaches to the long-term detection of permeation of N_2O_4 or N_2H_4 through Teflon membranes are discussed and the laboratory procedures for testing the permeability of Teflon films to N_2O_4 is described in detail. The determination of crystallinity of Teflon films by X-ray diffraction, infrared spectrophotometry, and differential thermal analysis has been examined and preliminary correlations are expressed. A bibliography has been compiled for the preparation and characterization of Teflon films.

CONTENTS

FOREWORD iii
ABSTRACT v
TABLES ix
ILLUSTRATIONS xi

I INTRODUCTION 1

II PREPARATION OF TEFLON FILMS 3
    Equipment 3
    Fabrication Procedure 5
    Dispersions 5
    Process Parameters 8
    Metal Cladding of Teflon Films 14
    References 19

III CHARACTERIZATION OF TEFLON FILMS AND SOME CORRELATIONS . . . 21
    Process Parameters and Mechanical Properties 21
    Mechanical Properties and Crystallinity 22
    Density 22
    Permeability 23
    Organic Impurities 23

IV PERMEABILITY OF TEFLON FILMS 27
    Investigation of Techniques 27
    Permeability Determinations 34
    References 38

CONTENTS (Concluded)

V CRYSTALLINITY OF TEFLON FILMS 39

X-Ray Diffraction 39

Calorimetry 43

Infrared Spectrophotometry 47

References 53

VI FUTURE WORK 55

VII NEW TECHNOLOGY 57

Appendix BIBLIOGRAPHY 59

TABLES

Table 1 Identification and Mechanical Properties of TFE-30 Films 15

Table 2 Characterization of Films Prepared from TFE-30 Dispersion 24

Table 3 Summary of Suitable Techniques for Detecting the Permeation of N_2O_4 and N_2H_4 through Teflon Membranes . . 36

Table 4 Permeability of Experimental Films to N_2O_4 at 25°C . . . 36

Table 5 Effect of Sample Tension on the Determination of Crystallinity by X-Ray Diffraction 49

Table 6 Comparison of Crystallinity of Rolled *vs* Original Films by X-Ray Diffraction 49

Table 7 X-Ray Determination of Crystallinity in Experimental Films 49

Table 8 Comparison of Crystallinity Determinations on Small Strips of Film: Calorimetry *vs* Infrared 50

Table 9 Comparison of Crystallinity Determinations on Experimental Films: Calorimetry *vs* X-Ray Diffraction . . 50

ILLUSTRATIONS

Fig. 1 Diagram of Equipment for Preparing Teflon Films 16
Fig. 2 Photograph of Facility for Preparing Teflon Films 17
Fig. 3 Infrared Absorbance Curves of Teflon Films Showing the Relationship of the 4.25μ Band to the 12.85μ Band for Crystalline and Amorphous Species. 18
Fig. 4 Relationship of Crystallinity to Tensile Strength of Teflon Film (TFE-30) 25
Fig. 5 Permeability Cell and Apparatus 37
Fig. 6 X-Ray Diffraction Pattern of Typical Teflon Films (Copper K_α Radiation) 51
Fig. 7 Thermogram Showing Endotherms of Tin Standard and Teflon Sample 52

I INTRODUCTION

This Interim Report summarizes the work performed during the period May 18, 1966 to May 17, 1967 under JPL Contract No. 951484, entitled "Development of Techniques to Improve Bladder Materials and Test Methods."

Plans for liquid propulsion systems at the Jet Propulsion Laboratory require the use of expulsion bladders for storable propellants in the space environment which not only resist the corrosive action of liquid propellants, such as nitrogen tetroxide and hydrazine, but also act as effective barriers against the loss of propellants or premature mixing. Because the bladders are exposed either to intermittent or prolonged periods of pressure, they must be made of light, highly-flexible materials which can undergo repeated creasing and folding. Although some metals, such as titanium, steel, or aluminum alloys are resistant to corrosion by propellants, they cannot withstand flexing when formed into thin-walled bellows or bladders. After a series of investigations by JPL, it was determined that a polymeric material such as Teflon was the most appropriate candidate for this purpose because of its resistance to N_2O_4 or N_2H_4 and because its mechanical and thermal properties are superior to most polymeric materials, such as other fluorocarbons, silicones, or fluorosilicones. Teflon film is available in sheet-form, prepared by skiving extruded stock; however, these sheets cannot be used to manufacture bladders because reliable methods have not been found for making seams which are leak-tight and strong. Aqueous Teflon dispersions, used since 1958, appear to provide a means for producing seamless bladders, but rigid process controls needed to assure reliable and uniform bladders have yet to be defined.

One of the objectives of the program of investigation at SRI is to optimize the processes for the fabrication of expulsion bladders made from Teflon dispersions. In order to examine at first hand the effects of process variables, an experimental film preparation facility has been established. A description of this facility, of preliminary work with

Teflon dispersions, and of a schedule designed to prepare films on a systematic basis are described in Section II of this report. Data are tabulated for the preparation, appearance, and mechanical properties of experimental films, and work leading to concepts for cladding Teflon films with metals is also discussed.

In Section III, a summary is provided of the characterization of experimental films and a concept for a nondestructive quality-control test is discussed.

Another objective of the program is the investigation of methods for detection of permeation of Teflon films by N_2O_4 or N_2H_4 in order to provide a basis for the development of a long-term constant-readout detection system. This work is summarized in Section IV; also included is a description of the procedure for establishing quantitative values for the permeation of experimental films, which is adaptable to automation.

The dominant role of crystallinity in Teflon films for expulsion bladders has required that several procedures for its determination be investigated in order to select the most accurate and reproducible one. A description of these procedures and cross-correlations are given in Section V.

Section VI is devoted to the plans for continuing work and Section VII is concerned with reportable items under the "new technology" clause of the contract.

In the Appendix, a bibliography is given, alphabetically by author, of the literature which has been accumulated during the program of work.

II PREPARATION OF TEFLON FILMS

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 0.3-0.4 mil thickness is dried, sintered, and quenched. 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 large 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 latter part of this contract period, a two-phase schedule was designed for the selection of the best process parameters for the preparation of films from Du Pont's dispersion TFE-30. At the time of writing this report, Phase I has been completed (determination of best sintering temperature, sintering time and cooling rate), and preparations have been made for continuing with Phase II (sintering in vacuum).

EQUIPMENT

All spraying, sintering, and cooling operations are carried out in a small, isolated room which has been equipped to provide a dust-free atmosphere. About 600 ft^3/min of air enters the room through an MSA filter system and is exhausted at the rate of about 400 ft^3/min through a hood over the spraying booth and 200 ft^3/min under the doorway. By maintaining a positive pressure in the room, unfiltered air does not enter through the doorway whenever the door is opened. (See Figure 2.)

A simple block diagram of the equipment used for the preparation of films is shown in Figure 1. 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 ± 2°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.

The 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.

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 40μ-60μ 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 0.3-mil thick in order to ensure uniformity of deposition and to prevent mud-cracking after sintering.

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, four dispersions were obtained in one-gallon quantities for exploratory work and are described below:

Teflon FEP-120. - An aqueous dispersion containing 53-57% of fluorinated ethylene-propylene solids with a particle size of 0.10 to 0.25μ and 5-7% of a mixture of nonionic and ionic wetting agents.* It is recommended for use as a coating or sealant and for molded electronic and mechanical parts.[1]

---

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

Teflon TFE-30. - An aqueous dispersion containing 59-61% of tetrafluoroethylene solids with a particle size of 0.05 to 0.5μ 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 charactersitics are required.[1]

Teflon TFE-30B. - An aqueous dispersion containing 59-61% of tetrafluoroethylene solids with a particle size of 0.05 to 0.5μ 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 ~ 0.2μ. Ionic and nonionic wetting agents are added.

The dispersions have a nominal pH 10 (adjusted with ammonium hydroxide), and contain Triton X-100 (octylphenoxy polyethoxy ethanol)* as the nonionic wetting agent; the ionic wetting agent in FEP-120 and TFE-3170 has not been identified by Du Pont, but SO_2 and SO ions have been identified in the mass spectra of these dispersions, 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 sediment of rust-to-greenish colored matter, which was identified as iron hydroxide.

Organic impurities (less than 0.02% by weight) in the dispersions were determined by mass spectroscopy to be squalene (in FEP-120 and 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. However, this substance has also been detected in skived films of FEP.[3] Dioctylphthalate is one of the most

---

* Rohm and Haas

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.

It is interesting to note that, in contrast with whitish films produced from TFE-30 and 30B, the films prepared from FEP-120 and TFE-3170 were quite discolored, reminiscent of organic charring. Also, it was more difficult to prepare films from these two dispersions. The additive common to both TFE and FEP dispersions is the ionic wetting agent.

Dispersion Storage

A settling-out of Teflon dispersions was noted during their storage while the experimental facility and equipment was being constructed, (from 4 to 6 months) but a gross effect on film preparation was not anticipated. The first failures in film preparation were easily ascribed to the agglomeration of particles initially about 0.5μ into particles of about 60μ. It has since been determined that raw dispersions should not be stored for more than 2 months, preferably less, if they are going to be used for spray applications. Also, it has been found that the storage life of a diluted or modified dispersion is of the order of less than one week. Unfortunately, the particles cannot be re-dispersed, and only agglomerate further with agitation; gentle, daily agitation simply reduces 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.

Dispersion Modification

The examination of process parameters for the fabrication of Teflon films has been initiated with the aqueous dispersion TFE-30. It was found that a modified 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.

The modified dispersions are prepared in 500-g batches. An amount of 225 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 (40μ to 60μ) into the steel dispersion container for immediate use or into a glass storage bottle.

PROCESS PARAMETERS

Subsequent to the development of an optimum dispersion for experimental work, a program was planned to prepare films on a systematic basis in order to determine the process parameters which lead to the least permeable and most flexible films possible from the TFE-30 dispersion. Phase I of the program provides for the selection of the best sintering temperature, sintering time, and cooling rate for preparing 4- to 6-mil films on a polished mandrel. The best parameters from Phase I will be used to prepare a film which will be sintered in vacuo.

As each film is prepared, it is examined for mechanical properties, physical characteristics, and impurities. The results of this program provide guidelines for similar work with the other dispersions.

Sintering Temperature

Three sintering temperatures were selected for evaluation: 330°C, 360°C, and 400°C. The lowest temperature, 330°C, was selected since it is just slightly above the melting point (327°C) of TFE as determined by differential thermal analysis (DTA) and conceivably is sufficient to provide for the flow 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 by some commercial fabricators 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 incipient decomposition occurs at 400°C:

$$(\mathrm{HF},\ \mathrm{HCl},\ \mathrm{CF}^+,\ \mathrm{CF_2}^+,\ \mathrm{CF_3}^+,\ \mathrm{C_2F_3}^+,\ \mathrm{C_2F_4}^+)$$

and steady decomposition occurs at 425°C:

$$(\text{to } \mathrm{C_3F_5}^+).$$

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_2 at 95°C, and that CO_2 continues to be released as the sample temperature is raised, even at 425°C.

Sintering Time

Three sintering times for evaluation were selected on the basis of (1) manufacturer's recommendations (5 minutes); (2) fabricator's practice (20 minutes); and an extreme (2 hours). Concurrently, 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 12.85μ (780 cm^{-1}) and 4.25μ (2350 cm^{-1}); the 4.25-μ band is a measure of thickness and the 12.85-μ 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 3.

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.)

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 (24°C/sec).

Mechanical Properties

Tensile Strength and Elongation.

- Tensile and elongation measurements of the Teflon films were made at about 70°F, using an Instron Model TTCLM-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. - Resistance to creasing and folding was determined with the aid of the JPL crease tester[4] (loaned by JPL). The tester induces a traveling three-corner fold in a 2" × 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. The failure of a material after a given number of cycles is indicated by the appearance of a pinhole, generally detected by a dye penetrant; however, it was found that detection by a high-voltage source was more sensitive and rapid, and an improved hole-detection system is being constructed.

PHASE I SUMMARY

The first set of films from TFE-30 were prepared with a fixed sintering temperature and time; the cooling rates were varied:

temp., °C	time, min	cooling rate
360	20	3.7°C/min (air)
360	20	50°C/min (air)
360	20	24°C/sec (ice-water quench)

The best cooling rate was then selected on the basis of mechanical properties, such as tensile strength, elongation, and crease-and-fold resistance. As shown in Table 1, this is a rate of 24°C/sec (film EX-1-S3).

Then, films were prepared with a fixed sintering time and cooling rate while the sintering temperature was varied:

temp., °C	time, min	cooling rate
330	20	24°C/sec
400	20	24°C/sec

Since the evaluation for 360°C sintering temperature had already been made, it was necessary to prepare only two films for comparison. On the basis of mechanical properties (Table 1) EX-1-S3 is again superior, and thus sintering temperature could be fixed at 360°C.

Continuing, films were prepared with fixed sintering temperatures and cooling rates while time was varied; again, only two films were needed for comparison. In this instance, as shown in Table 1, there is no difference in tensile strength or elongation for the films sintered at 360°C for 20 minutes (EX-1-S3) or 120 minutes (EX-3-S7), but there is a marked difference in crease-and-fold resistance. Thus, it would seem that maximum mechanical properties result from the conditions of:

Sintering temperature	360°C
Sintering time	2 hours
Cooling rate	24°C/sec (ice-water quench)

It may be that the crease-and-fold resistance of EX-3-S7 (Table 1) is due to provision of sufficient time at temperature for the evolution of gases or substances which are responsible for microvoids. It has been reported[5] that a maximum change due to an increase in microvoid content may be as much as -1000 in the case of flex fatigue life, while crystallinity, for comparison, affects it only as much as -100. By like token, although the tensile strength and elongation of EX-2-S5 are very low, the crease-and-fold resistance is very high--perhaps in this instance due to the evolution of void-creating substances at the elevated sintering temperature of 400°C.

It is interesting to note that another film sintered at 400°C for 20 minutes actually split during a slow cooling rate of 50°C/min. Additional films will be prepared to determine the reasons for failure.

A summary of the mechanical properties of the films with other characteristics, such as crystallinity and permeability, are given in the following Section.

Phase II Initiation

Phase II of the systematic program for preparing and evaluating Teflon films has been designed to investigate whether films which have been sintered in vacuum will be completely free of organic impurities and whether films which have been prepared this way will have superior characteristics *per se* or for subsequent metal cladding.

The presence of organic impurities in the Teflon dispersions is considered to be of extreme importance in the preparation of Teflon films for expulsion bladders. For example, the vaporization and partial elimination of these relatively simple molecules during sintering may be responsible for the micro-voids which occur in the final films. On the other hand, if these substances remain, they will leave a network of low-molecular-weight materials which are attacked easily by oxidizers or fuels, thus creating open pathways for permeation or they will be responsible for the formation of holes in the final film.

In the work planned, each applied layer of dispersion will be evacuated at a temperature below sintering, in order to remove organic impurities and to reduce the probability of occurrence of voids. Then, the films will be fired at sintering temperatures to produce uniform, integral membranes. It will also be established whether the films need to be sintered in vacuum after each layer is applied, or whether evacuation is required only after the film has been built up to the desired thickness.

Modifications have been made to a 2-inch portable vacuum system (SRI) to accommodate an oven and trapping system for the sintering of Teflon films. The oven has been fabricated of sufficient size to hold the mandrel on centers while it and the applied film are heated in vacuum. The trap is of a large size (6" diameter and 3' length) in anticipation of the work described below.

METAL CLADDING OF TEFLON FILMS

It has been found, in other work, that bonds made between Teflon and metal in vacuum are firm; this may provide a basis for an integral bond of Teflon and aluminum, for example, in laminates for expulsion bladders. Just as one cannot apply an adherent coat of paint on an oily surface or one cannot electroplate successfully over fingerprints, it is reasonable to assume that an integral bond of metal to aluminum (for example) cannot be achieved if the Teflon surface is contaminated with organic impurities or protected by a monomolecular layer of adsorbed gases. Thus, after a film has been sintered in vacuum, it will be maintained in vacuum while the vapors of an aluminum alkyl compound are decomposed on the film to form what is hoped to be an extremely tenacious, ductile deposit of aluminum metal.

It is anticipated that successive coatings of Teflon emulsion can not be as tightly bound to the intervening aluminum deposit since oxidation by air (when the assembly is removed to the spraying booth) will inactivate the aluminum surface, and the same problems of adhesion noted by others will be encountered. In order to obviate such difficulties, the aluminum film may be treated so as to expose fresh aluminum surfaces through medium of oxide-removing complexations as afforded by oxalato-, fluorido-, or phosphato-alkaline moieties applicable as pre-treatments or as deliberate additions to the next Teflon emulsion to come into contact with the aluminum. The possibility of activating *in vacuo* the aluminum film under the next Teflon emulsion layer (before sintering) has attractive features. Other concepts for the preparation of tight films and/or cladded films *in vacuo* are under consideration.

Table 1

IDENTIFICATION AND MECHANICAL PROPERTIES OF TFE-30 FILMS[a]

FILM NO.	SINTERING TEMP., °C	SINTERING TIME, MIN	COOLING RATE, °C /TIME	APPEARANCE	THICKNESS, mils	TENSILE STRENGTH, psi[a]	ELONGATION, %[b]	CREASE-AND-FOLD TEST[c]			
								5 cycles	10 cycles	15 cycles	20 cycles
EX-1-S1	360	20	3.7/min (air)	Milk-white, opaque	4.7 ± 0.1	3,550	512	3 holes	-	-	-
EX-1-S2	360	20	50/min (air)	Semi-transparent	3.5 ± 0.1	3,480	440	1 hole	8 holes	-	-
EX-1-S3	360	20	24/sec (ice)	Transparent	4.0 ± 0.1	4,310	415	1 hole	1 hole	2 holes	-
EX-2-S4	330	20	24/sec (ice)	Partial sinter; discarded	--	--	--	-	-	-	-
EX-2-S5	400	20	24/sec (ice)	Transparent	6.6 ± 0.1	3,100	346	0	0	0	0
EX-3-S6	360	5	24/sec (ice)	Partial sinter; discarded	--	--	--	-	-	-	-
EX-3-S7	360	120	24/sec (ice)	Transparent	4.6 ± 0.1	4,340	422	0	0	0	1 hole

a) Batch No. 6325.

b) Average of 6 determinations, 3 crosswise and 3 lengthwise.

c) 2.5 lbs tension, 30° blade angle, -2.0° cant, flat blades.

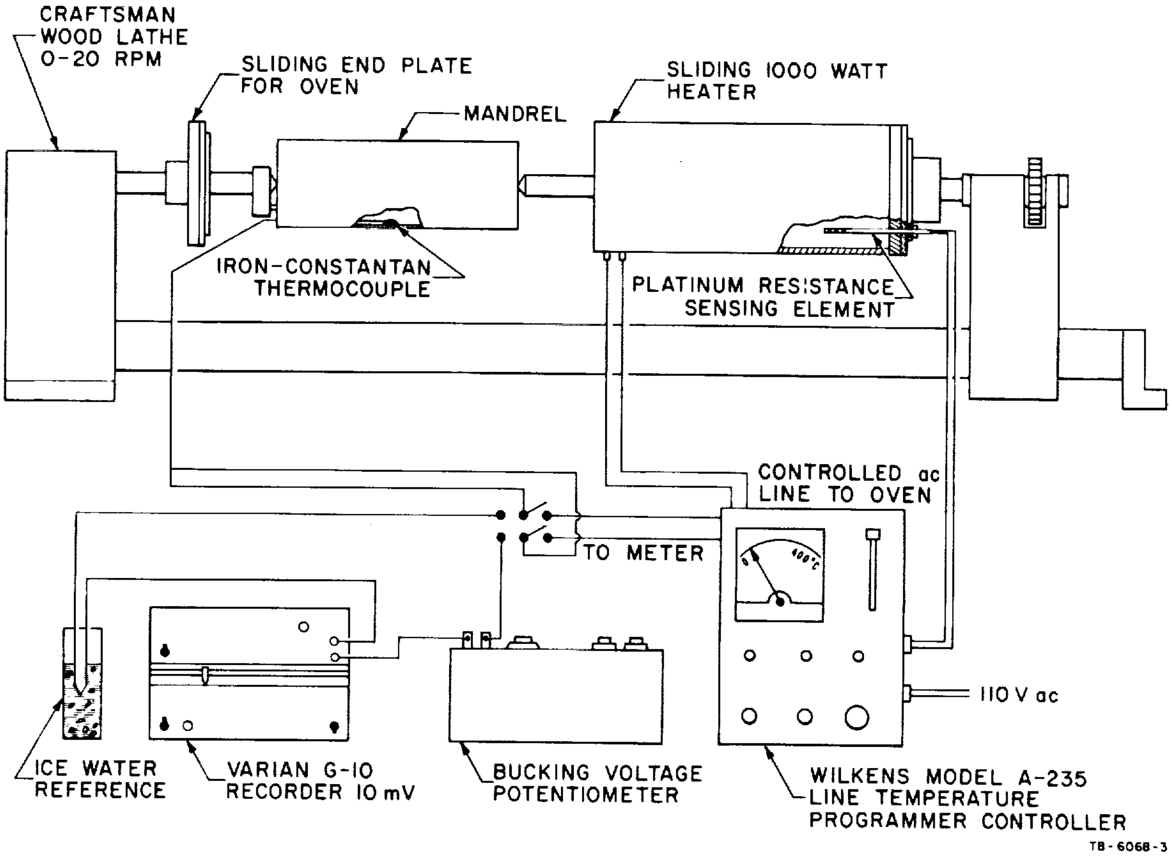

FIG. 1 DIAGRAM OF EQUIPMENT FOR PREPARING TEFLON FILMS

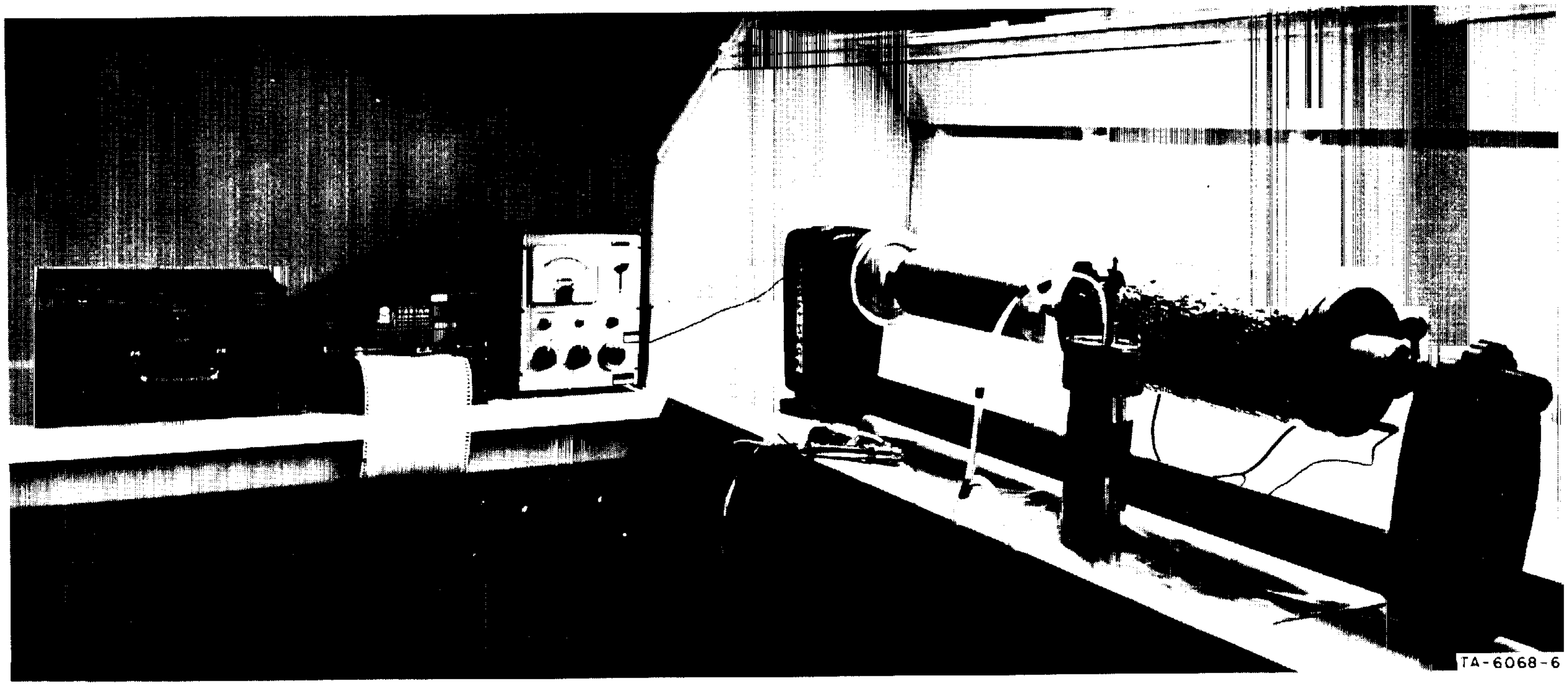
TA-6068-6

FIG. 2 PHOTOGRAPH OF FACILITY FOR PREPARING TEFLON FILMS

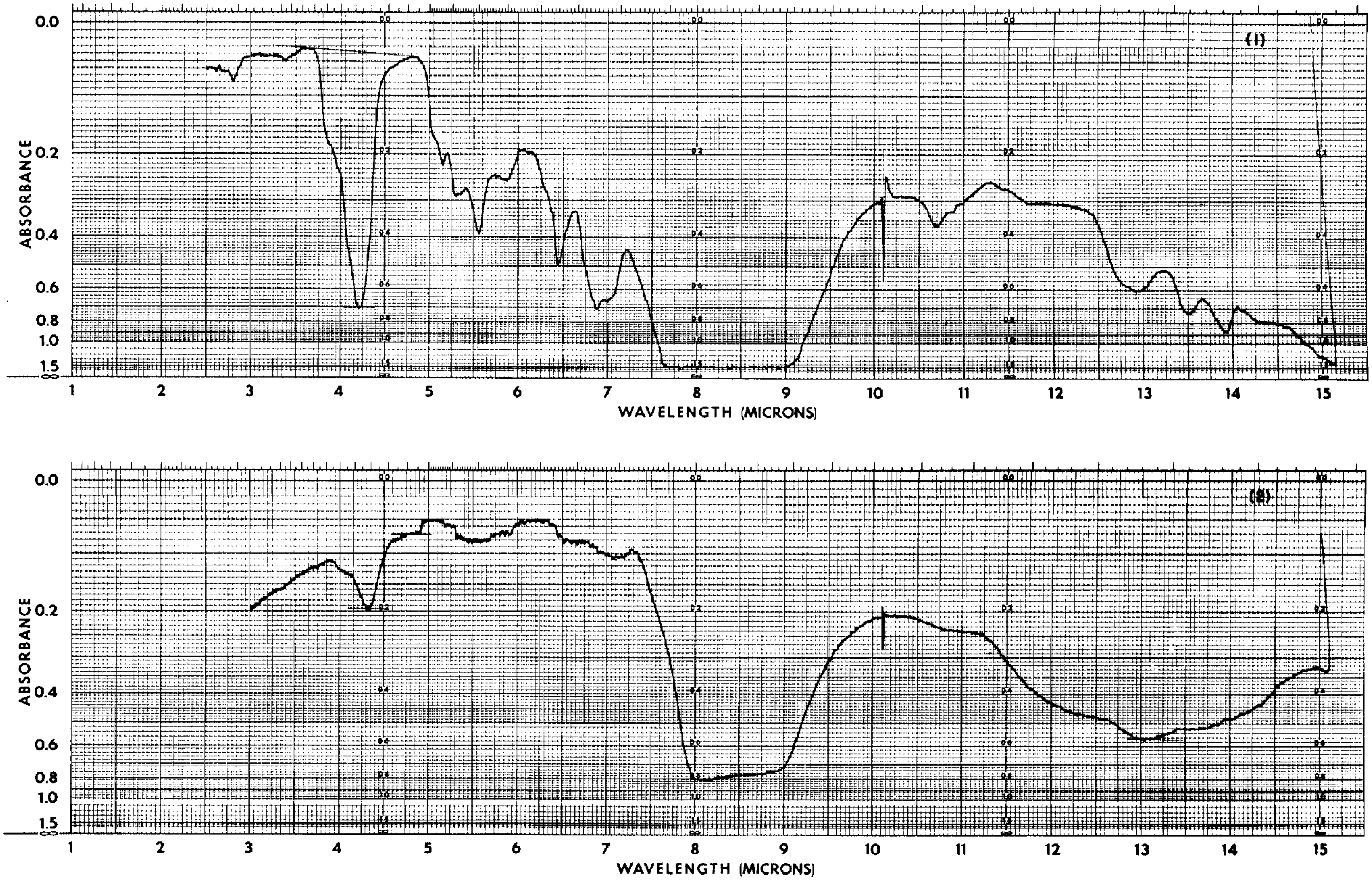

FIG. 3 INFRARED ABSORBANCE CURVES OF TEFLON FILMS SHOWING THE RELATIONSHIP OF THE 4.25μ BAND TO THE 12.85μ BAND FOR CRYSTALLINE AND AMORPHOUS SPECIES
(1) About 90% Crystalline, at Room Temperature (2) Essentially Amorphous, at 400°C

REFERENCES

1. Du Pont Bulletin A-21458, August 1961.
2. Du Pont Bulletin A-25040.
3. Under JPL Contract No. 950745, "Polymers for Spacecraft Applications."
4. Porter, R. N., and Stanford, H. B., Jet Propulsion Laboratory, *T. R. No. 32-899*, July 1, 1966.
5. Anon., *Machine Design*, September 5, 1957, p. 86.

III CHARACTERIZATION OF TEFLON FILMS AND SOME CORRELATIONS

During the course of developing the process parameters which provide for supple and strong Teflon films, the aim was to produce films which have:

(1) Resistance to acceleration forces as high as 5 to 10 g;
(2) Resistance to damage by stretching;
(3) Resistance to damage by flexing during at least 10 expulsion/filling cycles;
(4) Resistance to permeation by fuels or oxidizers.

A summary of test data for mechanical properties, physical properties, and permeability to N_2O_4 for the experimental films is given in Table 2.

PROCESS PARAMETERS AND MECHANICAL PROPERTIES

Assuming that the modified dispersions and the application of sprayed-on layers, etc. are maintained constant, the mechanical properties of Teflon films appear to be predictable and controllable by the basic process parameters of sintering time, sintering temperature, and cooling rate. With experimental films, it is a simple matter to remove any desired section for characterization; however, since a finished Teflon bladder cannot be cut for testing, it has been the commercial practice to prepare test materials on small mandrels alongside of the actual bladder mandrels, following the same procedures at the same time for spraying, sintering and quenching. It is assumed that spraying and sintering of the test material in this fashion duplicates the film on the larger mandrel. On the other hand, the films on the smaller mandrels are quenched by hand-sprayed CO_2 or by water at about 70° F. In these cases, there is considerable doubt that a small test mandrel and a large bladder mandrel will be cooled uniformly at the same rate, and thus equivalent mechanical properties will not be obtained; this may be a reason why test specimens pass acceptance tests but bladders often fail proof-tests. Thus, processing should include the recording of cooling rates of each test mandrel at several locations and each of the bladder mandrels at many locations in order to verify uniformity of the bladder films and conformity with the test materials.

MECHANICAL PROPERTIES AND CRYSTALLINITY

As shown in Table 2, there is also a direct relationship between the average crystallinity of the experimental films and the process parameters. Consequently, a straight-line can be drawn for the relationship of crystallinity (as determined by x-ray diffraction) to mechanical properties, as shown by the curve for tensile strength vs crystallinity in Figure 4. (The anomalous values for 1 out of 5 films, EX-2-S5, are not included in the curve.) Therefore, it is conceivable that a portable x-ray scanning unit can provide a nondestructive test for the uniformity of crystallinity (and thus the mechanical properties) over the entire surface of a finished bladder. It has been shown already that a film which was cooled nonuniformly at 50° C/min (because of differences in heat transfer at various segments of the mandrel) had a variation in crystallinity of as much as 10% over a 6-inch length of test section.

Based on the above relationships, and the adaptability of x-ray techniques to pin-point scanning, the development of a miniaturized, portable x-ray unit for the determination of crystallinity of Teflon films is under consideration.

DENSITY

Density determinations were made by a pycnometric technique, using de-aerated water containing a small amount of surfactant. The values cited in Table 2 appear to be related to crystallinity and mechanical properties, but insufficient information exists at this time for further utility, such as determining microvoid contents.

PERMEABILITY

Permeability of the experimental films to N_2O_4 was determined by the procedure described in Section IV. The anomalous values do not permit any correlation to be made with crystallinity or other properties at this time. The extent of microvoids and the influence of organic and inorganic impurities is undetermined at present.

ORGANIC IMPURITIES

All of the prepared films were examined by mass spectroscopy for organic impurities. Since there was no difference in the substances released from any of the films at 125°C in vacuum, the data are not summarized in Table 2 with other characterizations. In each case, identification was made of carbon dioxide, dioctylphthalate, and a form of octyl-phenol (either a resistant impurity in the wetting agent or a product of decomposition during sintering).

Table 2

CHARACTERIZATION OF FILMS PREPARED FROM TFE-30 DISPERSION*

	THICK-NESS, mils	TENSILE, psi	ELONGA-TION, %	CREASE-AND-FOLD TEST				DENSITY, g/cc	CRYSTAL-LINITY, % (X-Ray, Av.)	PERMEABILITY, TO N_2O_4, $mg/hr/in^2/mil$
				5 cycles	10 cycles	15 cycles	20 cycles			
EX-1-S1 sintered 20 min/360°C cooled 3.7°C/min	4.7	3,550	512	3 holes	-	-	-	2.174	79.0	0.66
EX-1-S2 sintered 20 min/360°C cooled 50°C/min	3.5	3,480	440	1 hole	8 holes	-	-	2.160	78.3	2.13
EX-1-S3 sintered 20 min/360°C cooled 24°C/sec	4.0	4,310	415	1 hole	1 hole	2 holes	-	2.141	61.8	0.41
EX-2-S5 sintered 20 min/400°C cooled 24°C/sec	6.6	3,100	346	0	0	0	0	2.141	61.9	1.38
EX-3-S7 sintered 2 hr/360°C cooled 24°C/sec	4.6	4,340	422	0	0	0	1 hole	2.138	61.8	2.10

---

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

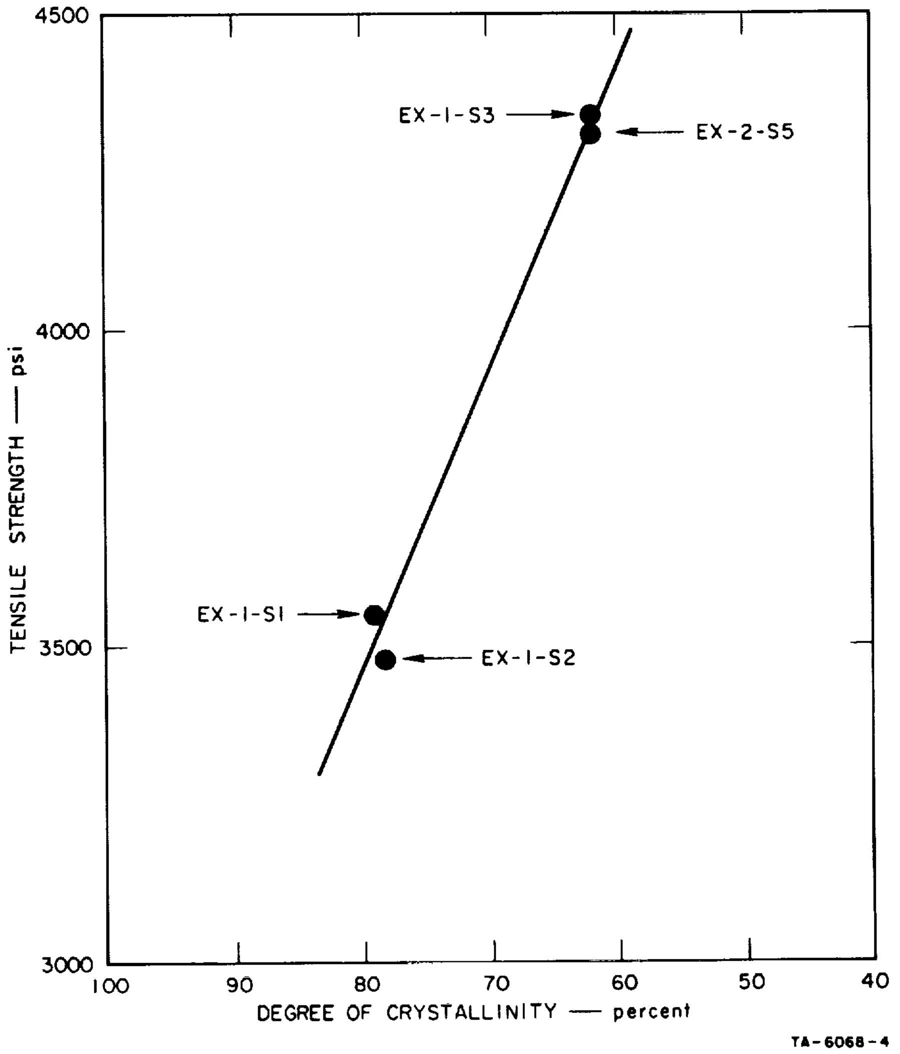

FIG. 4 RELATIONSHIP OF CRYSTALLINITY TO TENSILE STRENGTH OF TEFLON FILMS (TFE-30)

IV PERMEABILITY OF TEFLON FILMS

The ultimate objective of this phase of the program of work is to provide a test fixture for Teflon membranes and a detection system for permeation of these membranes by N_2O_4 or N_2H_4 which will operate continuously for periods of several months with a sensitivity of 0.1 $\mu g/hr/in^2$ of either propellant at working pressures up to 300 psig and with essentially zero drift or baseline displacement. The detection system is to perform reliably with a limited amount of attention from trained, but nontechnical personnel. It is understood that although batch sampling may have the advantage of sensitivity, continuous sampling and recording will offer the advantages of simplicity and reliability.

INVESTIGATION OF TECHNIQUES

A number of detection techniques have been examined for sensitivity, long-term stability, reliability, and availability of commercial instrumentation. It was assumed that the measurable leak rate would be 0.2 $\mu g/hr$ and that no substances would be present in a flushing or pressurized atmosphere of helium other than N_2O_4 or N_2H_4, so that the methods need not be very specific or selective. Five techniques considered suitable for further investigation were: (1) Helium ionization; (2) Clathrate reaction; (3) Electrolytic conductivity; (4) Mass spectrometry, and (5) pH measurement. The characteristics of these techniques are summarized in Table 3, and details are given in the following paragraphs.

Helium Ionization

The helium ionization detector might be considered the simplest and most sensitive of these investigated; it was first described by Deisler et al.[1] with α-particle excitation and is almost identical in principle to the commercially-available "Lovelock argon detector" for gas chromatography. High-purity helium is passed continuously at about 50 cc/min between two closely-spaced electrodes. One of the electrodes is a

250-millicurie tritium foil which serves as an anode and the other is a metal cathode; the potential between the electrodes is in the range of 4,000 to 7,000 volts/cm. The principle of operation of this detector has not been definitely established, but is thought to be as follows:

The tritium beta particles (0.018 Mev) raise some of the helium atoms to an excited state (ionization potential of 19.8 e.v.). The excited helium atoms ionize "impurity" atoms or molecules (e.g., NO_2 or N_2H_4) on collision, as long as the ionization potential of the impurity is lower than the helium excitation potential ($I.P._{NO_2} = 11.0$; $I.P._{N_2H_4} = 9.0$). The electrons lost by the ionized impurities are accelerated by the applied potential and, by further collisions, excite additional helium atoms. Therefore, the concentration of excited helium atoms will be considerably greater than the concentration of impurity atoms, and minute amounts of impurities give rise to relatively large flows of electric current between the electrodes. The detector is almost completely nonspecific since any substance with an ionization potential less than the helium excitation potential will be detected. Under appropriate conditions, a nearly linear response of ionization current vs concentration of impurity can be obtained.

An instrument utilizing this technique has been developed only recently, and has not yet been tested with NO_2 or N_2H_4[2]. A leak of about 0.2μ g/hr through a membrane will give a concentration of about 20 ppb at a helium flow rate of 50 cc/min, and if the sensitivity of the developed device for other gases can be maintained for NO_2 and N_2H_4, adequate sensitivity under continuous flow operation can be assured.

Highest-purity helium must be used with this technique since the detector is quite sensitive to impurities; at 50 cc/min flow rate, a standard cylinder of helium will last about 80 days. The flow rate of helium may be decreased to as low as 5 cc/min, which will increase sensitivity, but then back-diffusion may become a problem if the permeability fixture is to be operated at atmospheric pressure or below.

Clathrate Reaction

As shown in Table 3, the clathrate system is not as sensitive as the other techniques; however, it is readily available, economical, and appears to be reliable under long-term operation. Delivered units are calibrated by the manufacturer, but flushing or pressurizing gas must be of constant and known relative humidity. The gas stream, containing traces of NO_2, for example is passed at a constant rate through a detector head containing a "catalyst" and a bed of hydroquinone-krypton 85 clathrate. The hydroquinone is oxidized to quinone, liberating the radioisotopic krypton 85 which is detected "downstream" by a Geiger-Muller counter and ratemeter[3]. For detection of other gases (such as N_2H_4) a different detector head and different catalyst system would be used; the end result is still the release and detection of krypton^{85}. The reactions taking place in the detector head are uncertain, but are perhaps:

(1) (a) NO_2 + "catalyst" (diethyl chlorophosphate?) $\longrightarrow$ products + Cl_2

(b) $Cl_2 + C_6H_4(OH)_2(Kr) \longrightarrow 2\ HCl + C_6H_4O_2 + Kr^{85}$

(2) (a) $3\ N_2H_4 \xrightarrow{350^0} 4NH_3 + N_2$
(b) $2\ NH_3 + KClO_3 \xrightarrow{380^0} Cl_2 + KCl + 3\ H_2O + KNO_3$
(3) $Cl_2 + C_6H_4(OH)_2(Kr) \longrightarrow 2\ HCl + C_6H_4O_2 + Kr^{85}$

The reactions of the gases with the clathrate and perhaps the catalyst are thought to take place in a layer of water absorbed on the surface of the clathrate crystal, since the response of the detector to any gas is somewhat dependent on the relative humidity of the gas passing through the detector. Thus, it is necessary that the relative humidity of the gas be known and constant.

The sensitivity of the device is about the same for all gases, i.e., about 0.1 ppm. Using a flow rate of 100 cc/min of helium past the membrane under test, and a 2-minute time constant on the ratemeter, a leak rate of about 1 μg/hr of NO_2 or N_2H_4 should be detectable. This would yield a count rate of 2000 cpm which is twice the normal background of about 1000 cpm; a decreased helium flow rate of 50 cc/min would double the concentration of propellant gases, but the normal background due to clathrate leakage will also increase so that the sensitivity will not be improved.

A complete breakdown of the test membrane would destroy the clathrate; a sealed-on mica window in the Geiger Muller counter may also be destroyed, but a thin-wall all glass tube should not be harmed. Destruction of the clathrate will, of course, release Kr^{85} to the atmosphere; however, the radioisotope is nonreactive chemically, the radiation hazard is small, and the area can be decontaminated simply by ventilation. A built-in adjustable high-level alarm is built into the device to actuate shut-off valves to isolate the membrane test cell at any pre-determined leak rate.

Electrolytic Conductivity

Electrolytic conductivity detection is quite sensitive and relatively inexpensive, but would require a considerable amount of design, development, and testing since units for this purpose are not commercially available. The propellant gases leaking through the test membrane are flushed out of the test chamber by a continuous flow of helium. The gas stream then passes through a scrubber where the NO_2 or N_2H_4 is dissolved in a continuous stream of high-quality deionized water which is then passed through a conductivity cell. The change in conductivity of the water due to the dissolved gases is determined by comparison of the conductivity of the water before and after it passes through the scrubber. The two conductivity cells are two arms of an A.C. conductivity bridge.

The minimum detectable leak rate of NO_2 should be of the order of 0.04 μg/hr under continuous operation at a water flow rate of 150 cc/hr through the conductivity cell. The sensitivity to N_2H_4 should be about the same order of magnitude, but slightly inferior; this estimate is based on results available to us on the detection of HCl and CO_2 by this method. Sensitivity can be somewhat improved by decreasing the rate of water flow through the scrubber.

Some investigation into scrubber design may be required because of the rather slow rate of solution and reaction of NO_2 with water. An ion-exchange column may have to be incorporated into the apparatus in order to provide a water of high and constant purity, about 10^{-6} mhos. Rupture of a test membrane would require cleaning of water and gas lines, but the conductivity cells should not change their calibration.

Mass Spectrometry

Mass spectroscopic residual gas analyzers (RGA) provide high sensitivity and selectivity and are readily available. The helium stream leaves the test chamber and a small portion of it enters a capillary or controlled leak which is connected to the sample inlet of the RGA. The height of the peak of interest is recorded either by continuous monitoring or by cyclic scanning.

A leak rate of 0.2 μg/hr of NO_2 or N_2H_4 collected in a stream of helium at a flow rate of 100 cc/hr will yield a concentration of about 1 ppm by volume. If this gas mixture is now expanded in the sample inlet system of a mass spectrometer to a total pressure of 10^{-4} torr, the partial pressure of the NO_2 or N_2H_4 will be about 10^{-10} torr. Since commercial RGA units have a sensitivity of 2 to 5×10^{-12} torr per division, this means that a leak rate of 0.2×10^{-6} g/hr through a membrane will be indicated as at least 20 to 30 divisions on the RGA peak monitor or recorder. The minimum detectable leak rate will depend very much on the particular instrument used, but it seems that a rate or 0.2×10^{-6} g/hr can be detected fairly simply.

It is not practical to try to increase the detectability by decreasing the helium flow rate, as 100 cc/hr is about the lowest flow rate which can be maintained accurately for extended periods. It may, however, be possible to increase the NO_2 or N_2H_4 concentration in the gas stream entering the mass spectrometer by using molecular separators. These devices have been used successfully to increase the sample to helium ratio by a factor of 100, and would permit an RGA to be used at somewhat below its maximum sensitivity, which would probably improve stability and accuracy. This might also allow the use of a simpler and less expensive instrument.

One decided advantage mass spectrometers have over all other methods considered is that the comparison of signal with background can be carried out by the instrument itself without the need for extra hardware. The only disadvantage posed by this system is that the apparatus is complex and thus furnishes a psychological barrier; on the other hand, the RGA is no more complex than a helium leak detector. The possibility of blockage of the leak must be taken into consideration; a system of continual checking can be established merely by use of a helium supply containing an internal calibrant.

pH Detection

The propellants leaking through the membrane into helium or argon are scrubbed by a continuous flow into pure water. The resulting pH change is monitored, or the solution is neutralized by adding the required amount of acid or base; standard reagents may be stored in reservoirs or generated coulometrically. (Coulometric generation of reagents would require an additional set of electrodes and associated electronics.) It is necessary to use two sets of electrodes of excellent stability. Neutralization of the solution requires only very small amounts of titrant; for example, for 0.2 μg of NO_2 or N_2H_4 dissolved in 10 ml of water initially at pH 7:

Gas	pH	10^{-3}M titrant required
NO_2	6.36	4.35 μ liter
N_2H_4	7.72	6.15 μ liter

The pH system offers simplicity of operation and the possibility of utilizing a differential voltage of as much as 40 mv to trigger digitized, incremental neutralization currents.

Rejected Methods

Several other methods were examined and rejected as unsuitable for various reasons. These are discussed in the following paragraphs.

Spectrophotometry in Gas Phase. - The molar absorptivity of NO_2 and N_2H_4 is too small to be useful[4,5]; for example:

Gas	Wavelength	Molar Absorptivity
NO_2	394 mμ	152
NO_2	6.2 μ	46
N_2H_4	10.5 μ	54

For a leak of 0.2 μg/hr and a helium flow of 10 cc/hr past the test membrane flowing continuously into a low volume cell (22 cc, 60-cm path length) or into a long path cell (4000 cc, 10-m path length), the resulting optical absorbancy for NO_2 at 394 mμ would be

22 cc, 60-cm path length	$A = 0.003$
4000 cc, 10-m path length	$A = 0.07$

The latter would be easily measurable, but at 10 ml/hr helium flow, 40 hours would be required to fill the cell, and detection of leak-rate changes would be equally slow.

Colorimetry with Various Reagents. - Gases leaking through the membrane are scrubbed into an appropriate reagent solution which is then passed into a colorimetric cell for measurement of optical density. This type of detection is quite specific and sensitive; however, the reagents are not very stable, solutions in reference cells change with time, and color-forming reactions are not immediate. Additionally, reagents must be slowly and accurately metered with the entering gas stream, which requires complexity of equipment.

Polarography. - The gases are scrubbed into a stream of supporting electrolyte which then passes into a flow-type polarographic cell. If 0.2 μg of NO_2 or N_2H_4 are collected in 10 ml of supporting electrolyte, the resulting concentrations would be much too dilute for polarographic measurement:

Gas	Molar Concentration
NO_2	4.36×10^{-8} $\underline{M}$
N_2H_4	6.15×10^{-8} $\underline{M}$

Further, polarographic equipment is too delicate for use in an industrial or field environment.

PERMEABILITY DETERMINATIONS

From the evaluation of the foregoing procedures for the determination of permeability, it was concluded that the procedure using a pH determination (or acid-base equivalence) would be the most economical and reliable for adaptation to automation. Subsequently, a prototype permeability cell was designed which would ensure containment of a film sample without undue stress or laceration. A schematic diagram of this cell in relation to the apparatus for routine permeation measurements is shown in Figure 5.

The procedure employed for the permeability determination by measurement of pH or neutralization of ionic species is basically that described by Vango[6], and further supplemented by Vango and Krasinsky[7,8,9], whereby the propellant permeating through a Teflon membrane is swept by an inert gas into pure water or an aqueous solution where it can be measured by the change in pH or by titration with a suitable acid or base.

Routine Procedure (N_2O_4)

A sample film is placed in the permeability cell and the apparatus is assembled as shown in Figure 5. The flow-rate of argon is adjusted to about 20 cc/min and the collector is filled with 25 cc of CO_2-free H_2O at 25°C. When the pH of the collector solution has stabilized (about 7.0), 5-6 ml of N_2O_4 are transferred with a syringe into the cup of the sample cell, over and in contact with the sample film. The cell is capped and the $N_2O_4 \rightleftharpoons 2\ NO_2$ (at 25°C) permeating through the film is swept out of the cell by argon into the collector. The test is run for a pre-selected time; during this time, the change in pH is recorded primarily to indicate that permeation is continuing. (In the future, as data are accumulated, the change in pH may provide the basis for an automated system.) Then, the collector solution is treated with hydrogen peroxide (to oxidize nitrous acid to nitric) and the total nitric acid content is titrated with 0.1 N NaOH. The permeability rate of the sample film is then computed as follows:

$$\text{Permeability/hr} = \frac{\text{ml}_{\text{base}} \times \underline{\text{N}}_{\text{base}} \times 46.01}{\text{time, hr}}$$

$$\text{Permeability/hr/in}^2 = \frac{\text{P/hr}}{\text{area (0.78'')}}$$

$$\text{Permeability/hr/in}^2\text{/mil} = \frac{\text{P/hr/in}^2}{\text{thickness, mil}}$$

Permeability data are summarized in Table 4 for a number of the experimental films described in Section II. From the two films which were examined in duplicate, permeability rates between different areas of the films may vary from 0.2 to 0.3 mg/hr/in^2/mil (abs.).

Correlation of these permeability rates with other properties are discussed in Section III.

Table 3

SUMMARY OF SUITABLE TECHNIQUES FOR DETECTING THE PERMEATION OF N_2O_4 AND N_2H_4 THROUGH TEFLON MEMBRANES

PARAMETER	HELIUM IONIZATION	CLATHRATE REACTION	MASS SPECTROMETRY	ELECTROLYTIC CONDUCTIVITY	pH
Sensitivity, μg/hr	0.01	1.0	0.1	0.04	0.03
Calibration Stability, ±10%	weeks	3 mos.	weeks	months	months
Development Required	none	moderate	none (needs vacuum system)	considerable	moderate
Linear Range	10^4	10^3 +	10^4	10^4	10^6
Restraints	hi-purity helium	humidified gas	none	conductivity water	stable electrodes
Availability	prototype	commercial (Tracerlab)	commercial (several)	components only	components and pH meter

Table 4

PERMEABILITY OF EXPERIMENTAL TEFLON FILMS* TO N_2O_4 (at 25°C)

EXPERIMENTAL FILM NO.	THICKNESS, mils	DURATION OF TEST, HR	PERMEABILITY		
			mg/hr	mg/hr/in^2	mg/hr/in^2/mil
EX-1-S1	4.7	144	2.42	3.08	0.66
EX-1-S2	3.5	50	5.39	6.87	1.96
EX-1-S2	3.5	92	6.35	8.09	2.31
EX-1-S3	4.0	41	0.91	1.15	0.29
EX-1-S3	4.0	144	1.68	2.14	0.53
EX-2-S5	6.6	49	7.16	9.12	1.38
EX-3-S7	4.6	49	7.58	9.66	2.10

---

* See Section II for preparation of films.

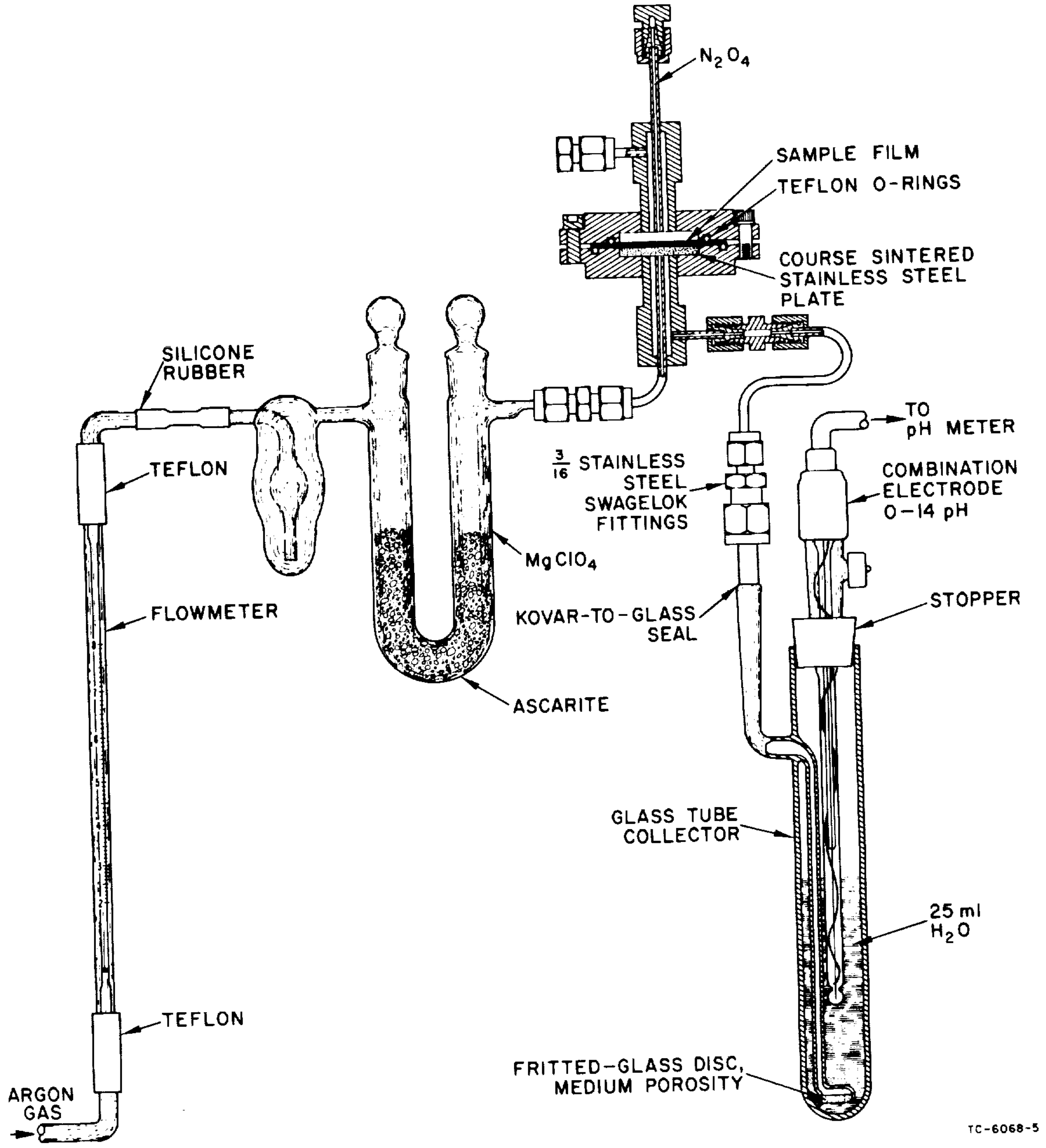

FIG. 5 PERMEABILITY CELL AND APPARATUS

REFERENCES

1. Deisler, P. F., McHenry, K. W., and Wilhelm, R. H., Anal. Chem., 27, 1366 (1955).
2. Hartmann, C. H., and Dimick, K. P., J. Gas Chrom., 4, 163 (1966).
3. Gudzinowicz, B. J., and Smith, W. R., Anal. Chem., 35, 465 (1963).
4. Pierson, R. H., Fletcher, A. N., and Gantz, E. St. Cl., Anal. Chem., 28, 1239 (1956).
5. Norris, M. S., Fleck, S. A., and Lichtenfels, D. H., Anal. Chem., 27, 1565 (1955).
6. Vango, S. P., Jet Propulsion Laboratory, TM No. 33-55, August 25, 1961.
7. Vango, S. P., and Krasinsky, J. B., Jet Propulsion Laboratory, Space Science Summary, No. 37-21, Vol. IV, June 30, 1963.
8. Vango, S. P., and Krasinsky, J. B., Jet Propulsion Laboratory, Space Science Summary, No. 37-23, Vol. IV, October 31, 1963.
9. Vango, S. P. and Krasinsky, J. B., Jet Propulsion Laboratory, Space Science Summary, No. 37-26, Vol. IV, April 30, 1964.

V CRYSTALLINITY OF TEFLON FILMS

The degree and uniformity of crystallinity in Teflon films is a determining factor in the uniformity and reproducibility of mechanical properties. Therefore, it is important that the crystallinity determination be accurate and reproducible. For that reason, several methods for determining crystallinity were investigated and compared: (1) X-ray diffraction, (2) Infrared spectrophotometry, (3) Calorimetry.

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 $2\theta = 18.9^0$ for copper $K_\alpha (\lambda = 1.542)$ radiation, whereas the "amorphous halo" reaches a maximum intensity at 16.6^0 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 6.

There are other types of disorder present in crystalline Teflon, and these have been discussed by Killian and Jenkel,[1] Bunn and Howells,[2] and Bunn.[3] 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[1,5,6], 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[5] uses a factor of 1.8 and Kilian and Jenckel[1] use 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 $2\theta = 16.6^0$.

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

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

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

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_α radiation is used, with a nickel filter to eliminate copper K_β radiation.

The scintillometer scans over a range of $10^0 = 2\theta$ to 24^0 2θ at a rate of $1/4^0$ 2θ 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 $1/2^0$ 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.

Effect of Tension on a Film Sample

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 5 for 2 films indicates that apparent crystallinity is 5 to 10% higher for films which are held under tension.

This finding immediately poses questions about the inducement of orientation of crystals during the flexures required by the expulsion bladders, accompanied by a subsequent loss in mechanical properties. This possibility is being examined systematically by a combination of mechanical and instrumental techniques.

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 and examined after rolling are summarized in Table 6. As shown by the data, the rolled samples have lower crystallinity values by x-ray than the original samples. This may be due to irregularities in the surfaces of the rolled films. Irregular surfaces tend to increase the background scattering, which might be indistinguishable from the amorphous halo, thus raising its intensity. The effect of rolling on crystallinity will be examined in detail.

Results for Experimental Films

The degree of crystallinity for the experimental films is summarized in Table 7. All data were obtained for samples as-received and held under no tension during x-ray analysis.

CALORIMETRY

Calorimetry has been used to determine the per cent crystallinity of nylon-6[8] and polyethylene.[9] 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 function of the sample which is in the crystalline state, and thus to the per cent crystallinity[7]:

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

This equation presupposes a linear relation between heat of fusion and per cent crystallinity; it is 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.[11]

A study of the kinetics of melting of PTFE was made by Hellmuth et al.[10] 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 ΔH_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/^{0}C-min
A = peak area, in^2
R = heating rate, ^{0}C/min
H_f = heat of fusion, cal/g
M = mass of sample, mg
$T, \Delta T$ = 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 $E_{Cd}(\mathrm{PTFE})/E_{Sn} = 1.06$.

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 were recorded.

The instrument operating conditions used were: heating rate = 5.5^0/min with scale expansion of 20^0C/inch on the X(T) axis and 0.2^0C/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 ΔH_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 10^0 and 20^0 per minute, very broad and diffuse melting endotherms appeared, similar to those reported by Hellmuth et al.[10] A heating rate of 5.5^0C/min was chosen since the endotherms found at this rate had fairly definite starting and final points. Scale expansions of 20^0C/inch (X axis) and 0.2^0C/inch (Y axis) were found suitable for the temperature range and the sample size used.

As shown in a typical thermogram (Figure 7), 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[12] 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 ±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.[11]

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 8.

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. The latter are probably closer to the "correct" crystallinity since it is reported that such low values as, e.g., 27% (sample A) for PTFE do not exist. It seems also that the calorimetric values for crystallinity are not linearly related to values obtained by other methods; for example, in Table 9 are listed calorimetry and x-ray results for crystallinity measurements on films made in Phase I studies. It is of interest that the relative heats of fusion obtained in this work are similar to those found by Hellmuth et al.[10]

INFRARED SPECTROPHOTOMETRY

Several investigations of the use of infrared spectrophotometry to determine the crystallinity of Teflon films have been reported in the literature.[5,13-16] The determinations are based on the measurement of an absorption band at 12.85μ (780 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 4.25μ (2350 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 CF_2 stretching vibrations. The amorphous absorption bands are preferable to crystalline bands for measuring crystallinity because they are more broad, thus requiring less resolution, and also are less subject to polymer orientation.[15]

According to the work of Moynihan,[5] the ratio of the absorbance of the amorphous band at 12.85μ 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 $d_{mm}\sigma$ 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 4.25μ 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_{mm} = thickness in mm
σ = 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 12.85μ with respect to the product of thickness and density can be plotted as a linear function <u>vs</u> degree of crystallinity as obtained by x-ray diffraction data; for example:

$A_{12.85\mu}/d_{\text{mm}}\sigma$	Crystallinity by X-Ray	
	Moynihan[5]	SRI (this work)
2.54	44	53.4
0.344	90.5	94.1

Table 5

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 6

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

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

Table 7

X-RAY DETERMINATIONS OF CRYSTALLINITY IN EXPERIMENTAL FILMS

FILM NO.	AREA	CRYSTALLINITY, %
EX-1-S1	Center	79.0
EX-1-S2	Edge	76.0
	Edge	80.6
EX-1-S3	Center	61.8
EX-2-S5	Edge	63.6
	Center	60.2
EX-3-S7	Edge (a)	62.0
	Edge (b)	58.8
	Center	64.6

Table 8

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

SAMPLE	COOLING RATE	ΔH_f, cal/g	% CRYSTALLINITY, CALORIMETER	% CRYSTALLINITY, INFRARED*
H	0.1°/min	7.65	52	62
E	1.7°/min	5.45	37	62
B	3.3°/min	5.72	39	59
F	17°/min	4.59	31	56
J	quenched, LN_2	4.42	30	56
G	quenched, LN_2	4.19	29	53
A	quenched, ice-H_2O	3.99	27	49
TFE-30	(pressed powder)	13.92	95	90.5

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

Table 9

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

SAMPLE FILM	ΔH_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

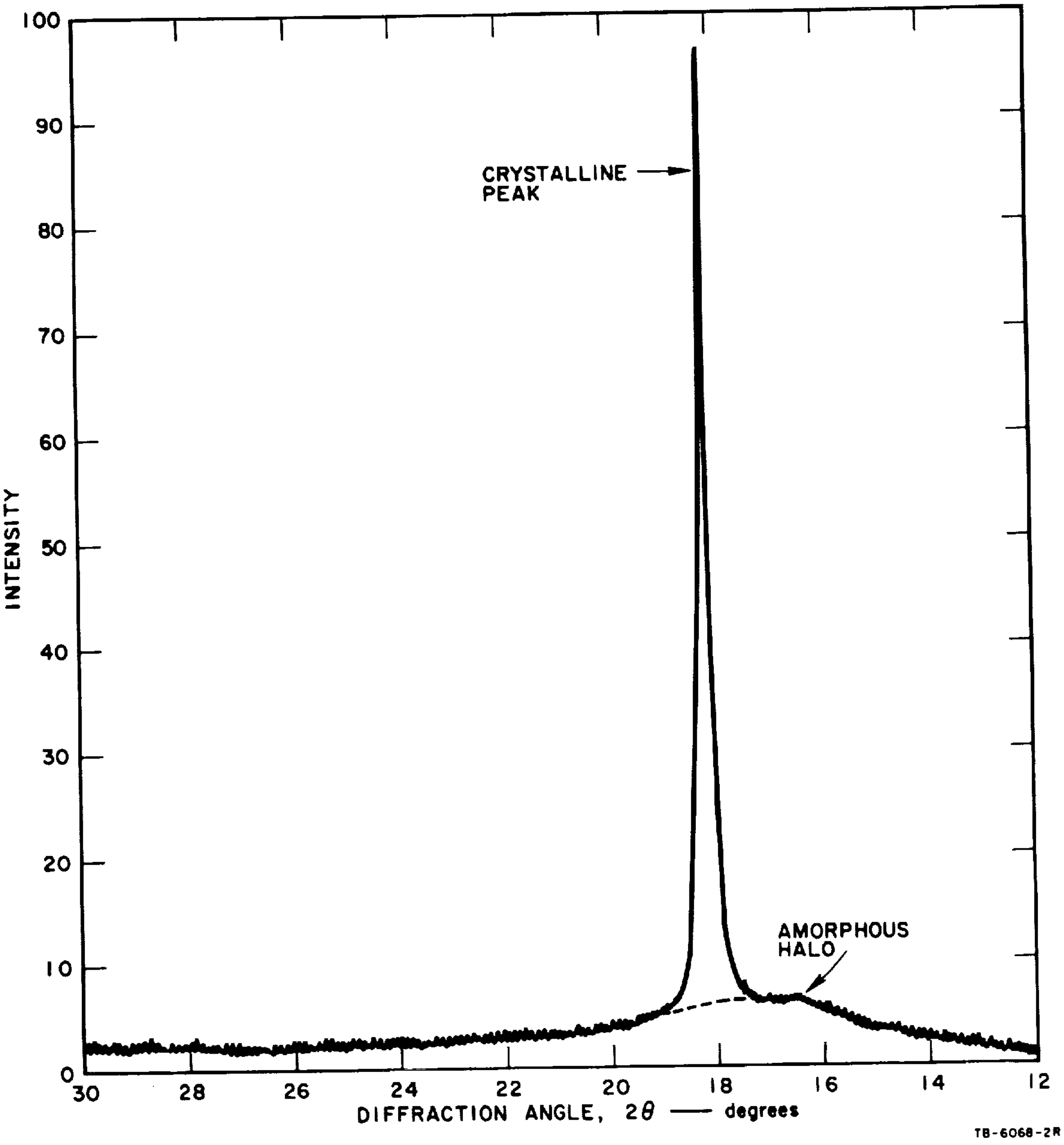

FIG. 6 X-RAY DIFFRACTION PATTERN OF TYPICAL TEFLON FILMS (Copper K_α Radiation)

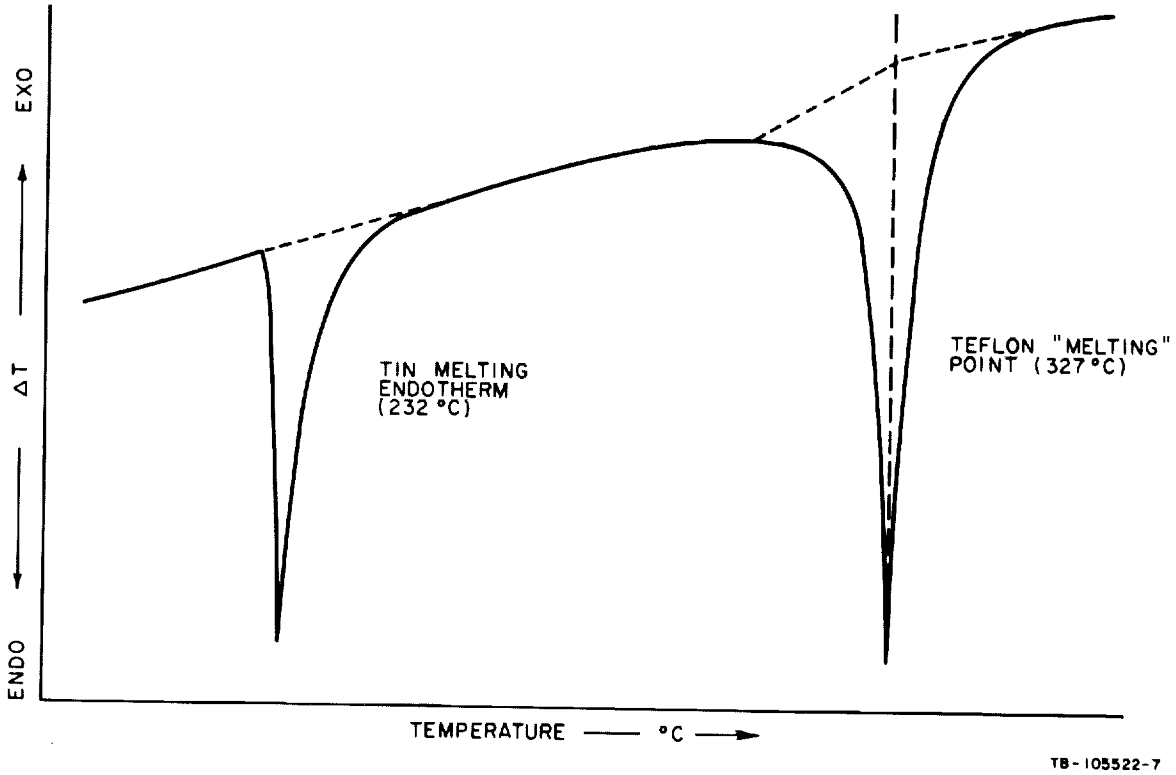

FIG. 7 THERMOGRAM SHOWING ENDOTHERMS OF TIN STANDARD AND TEFLON SAMPLE

REFERENCES

1. Kilian, H. G., and Jenckel, E., *Z. Electrochem.*, **63**, 308 (1959).
2. Bunn, C. W., and Howells, E. R., *Nature*, **174**, 549 (1954).
3. Bunn, C. W., *Chemical Crystallography*, Oxford, Clarendon Press, 1946, Ch. VII, pp. 190-209.
4. Ryland, A. L., *J. Chem. Educ.*, **35**, 80 (1958).
5. Moynihan, R. E., *J. Am. Chem. Soc.*, **81**, 1045 (1959).
6. Miller, R. L., in *Encyclopedia of Polymer Science and Technology*, **4**, Interscience Publishers, New York, 1966, pp. 449-528.
7. Ke, B., in *Encyclopedia of Polymer Science and Technology*, Interscience Publishers, New York, 1966, Vol. 5.
8. Inoue, M., *J. Poly. Sci., Part A*, **1**, 2697 (1963).
9. Ke, B., *J. Poly. Sci.*, **42** 15 (1960).
10. Hellmuth, E., Wunderlich, B., and Rankin, J. M., Jr., *Appl. Polymer Symposia*, *No. 2*, **10** (1966).
11. McGeer, P. L., and Dunns, H. C., *J. Chem. Phys.*, **20**, 1813 (1952).
12. Berg, L. G., *Compt. Rend. Acad. Sci. U.R.S.S.*, **38**, 24 (1943).
13. Robinson, T. S., and Price, W. C., *Proc. Phys. Soc.*, **B66**, 969 (1953).
14. Liang, C. Y., and Krimm, S., *J. Chem. Phys.*, **25**, 563 (1956).
15. Miller, R.G.J., and Willis, H. A., *J. Polymer Sci.*, **19**, 485 (1956).
16. Krimm, S., *Fortsch. Hochpolym.-Forch.*, **2**, 51 (1960).
17. Brown, R. G., *J. Chem. Phys.*, **40**, 2900 (1964).
18. Parker, C. J., and Nordberg, M. R., Jr., *J. Opt. Soc. Am.*, **49**, 856 (1959).

VI FUTURE WORK

Work will continue toward fulfilling the primary objective of this program: the development of techniques to improve bladder materials. This will include the determination of the effects of sintering Teflon membranes in vacuum in order to remove organic impurities and the development of techniques for cladding films with tightly-bonded metals which are resistant to fuels and oxidizers. Work is also planned for the vapor deposition of Teflon as a protective coating for "clean" metallic surfaces. As possible, the presence and effect of inorganic impurities, such as iron compounds, will also be investigated.

As more data are accumulated on the permeation of Teflon membranes, particularly by N_2O_4 and through membranes which are metal-clad, design concepts for a long-term constant-readout permeation-detection system will be more firmly crystallized.

Various physical properties of Teflon membranes will be investigated in depth as they seem especially applicable to the success and reliability of expulsion bladders. This implies particular attention to possible effects on the integrity of the Teflon-to-metal bond which is a pre-requisite for long-term-storage of fuels and oxidizers in polymeric expulsion bladders. Already under investigation are solubility constants for N_2O_4 in Teflon, extent of swelling, and the effect of flexing on crystallinity (and therefore mechanical properties).

The concept of a portable x-ray instrument for quality control of crystallinity of fabricated bladders (and therefore quality-check of mechanical properties) will be exploited as fully as possible.

In addition to work with Teflon membranes for use with nitrogen tetroxide and hydrazine, investigation will be made of bladder materials which can be used with oxygen difluoride (OF_2) and diborane (B_2H_6). This work will include compatibility tests with candidate bladder materials for periods up to one year, the determination of interaction (if any) of such materials with titanium, steel, or aluminum propellant-tank materials, the possible effects of candidate materials on the stress corrosion of tank alloys, and the investigation of cladding of candidate bladder materials with suitable metals.

VII NEW TECHNOLOGY

The accomplishment of the basic objectives of this program will lead directly into new technology, or at least technology beyond the present state-of-the-art. Unfortunately, at this time, although the work is proceeding on apparently commendable lines, there is no new technology to report.

The program has been organized on a scientifically systematic basis. Appropriate equipment has been assembled and the various parameters involved in the work are being explored methodically. However, out of this work a number of concepts for processes, techniques, and designs are being evolved. It is anticipated that some of these concepts will materialize into genuine "new technology" during the next year. At such times, these items will be reported promptly, in accordance with the policies of the Analytical Department at Stanford Research Institute.

Appendix

BIBLIOGRAPHY

Pertinent references have been given at the end of each section of this report for specific subject matter. However, these references do not reflect the broader scope of literature which has been examined and evaluated relative to the preparation, characterization, and testing of Teflon films. It is emphasized that no attempt was made to collect all references; only those pertinent to the investigation described in this report.

This compendium of information is listed alphabetically by author in the following pages. Complete titles of the reports and articles are given so that the nature of the subject matter is clearly evident.

BIBLIOGRAPHY

Anon., "Designing with Teflon. Part 1. How Processing Affects Properties." Machine Design, September 5, 1957, p. 86.

Anon., "Designing with Teflon. Part 2. Strength Properties and Effects of Time," Machine Design, September 19, 1957, p. 162.

Anon., "Designing with Teflon. Part 3. Thermal, Chemical, and Wear Properties," Machine Design, October 3, 1957, p. 124.

Anon., "Designing with Teflon. Part 4. Methods of Fabrication," Machine Design, October 17, 1957, p. 124.

ASTM Method D-1505, "Test for Density of Plastics by Gradient-Density Technique," American Society for Testing Materials, Philadelphia, Pennsylvania.

ASTM Method D 882-64T, "Tensile Properties of Thin Plastic Sheeting," American Society for Testing Materials, Philadelphia, Pennsylvania.

ASTM Method D 792-64T, "Specific Gravity and Density of Plastics by Displacement," American Society for Testing Materials, Philadelphia, Pennsylvania.

Aggrawal, S. L., and Tilley, G. P., "Determination of Crystallinity in Polyethylene by X-Ray Diffractometer," J. Polymer Sci., **18**, 17 (1955).

Araki, Y., "Thermal Expansion Coefficient of Polytetrafluoroethylene in the Vicinity of its Glass Transition at about 400^{0}K," J. Appl. Polymer Sci., **9**, 421 (1965).

Bauman, A. J., "Some Design Considerations: Large Expulsion Bladders for Nitrogen Tetroxide and Hydrazine," Jet Propulsion Laboratory, T. R. No. 32-862, January 15, 1966.

Berman, L. D., "Compatibility of Materials with Storable Propellants," SAMPE, National Symposium, Los Angeles, Nov. 13, 1962.

Brown, R. G., "Vibrational Spectra of Polyethylene: Effects of Temperature and Pressure," J. Chem. Phys., **40**, 2900 (1964).

Bunn, C. W., and Howells, E. R., "Structures of Molecules and Crystals of Fluorocarbons," Nature, **174**, 549 (1954).

Bunn, C. W., Cobbold, A. J., and Palmer, R. P., "The Fine Structure of Polytetrafluoroethylene," J. Polymer Sci., 28, 365 (1958).

Burt, R., and Minkoff, G., "The Analysis of Combustion Products. V. The Use of Infrared Spectrometry For Following High-Temperature Kinetics," Anal. Chim. Acta, 16, 259 (1957).

Case, L. C., "Viscosity of Polytetrafluoroethylene Above the Melting Point," J. Appl. Polymer Sci., 3, 254 (1960).

Clark, E. S., and Muus, L. T., "Partial disordering and crystal transitions in polytetrafluoroethylene," Z. Kristallogr., 117, 119 (1962).

Clark, R. M., "Positive Expulsion Systems. Design Data and Performance Characteristics," Joclin Manufacturing Company, T. R. No. 2-B-1, June 1, 1963.

Deisler, P. F., McHenry, K. W., and Wilhelm, R. H., "Rapid Gas Analyzer Using Ionization by Alpha Particles," Anal. Chem., 27, 1366 (1955).

DeWolff, P. M., Taylor, J. M., and Parnisk, W., "Experimental Study of Effect of Crystallite Size Statistics on X-Ray Diffractometer Intensities," J. Appl. Phys., 30, 63 (1959).

Du Pont, E. I. de Nemours and Co., "Teflon 100, 110, 120," Bulletin No. A-21458 (8/61).

Du Pont, E. I. de Nemours and Company, "Teflon 30, 30A, and 41BX," Bulletin No. A-25040.

Du Pont, E. I. de Nemours and Company, "TFE-Fluorocarbon Resin Dispersions. Properties and Processing Techniques," Information Bulletin No. X-50e.

Eby, R. K., and Sinnott, K. M., "Transitions and Relaxations in Polytetrafluoroethylene," J. Appl. Phys., 32, 1765 (1961).

Gorelik, B. M., Zhikharevich, I. G., and Bukhium, M. F., "A technique for Obtaining Thin Sections of Rubber-Like Polymers," Industrial Laboratory, 32, 245 (1966). (English translation)

Gudzinowicz, B. J., and Smith, W. R., "New Radioactive Gas Chromatographic Detector for Identification of Strong Oxidants," Anal. Chem., 35, 465 (1963).

Hartmann, C. H., and Dimick, K. P., "Helium Detector for Permanent Gases," J. Gas. Chromat., 4, 163 (1966).

Hellmuth, E., and Wunderlich, B., "Superheating of Linear High-Polymer Polyethylene Crystals," J. Appl. Phys., 36, 3069 (1965).

Hellmuth, E., Wunderlich, B., and Rankin, J. M., "Superheating of Linear High Polymers. Polytetrafluoroethylene," *Applied Polymer Symposia*, No. 2, 101 (1966).

Hermans, P. H., and Weidinger, A., "Estimation of Crystallinity of Some Polymers from X-Ray Intensity Measurements," *J. Polymer Sci.*, **4**, 709 (1949).

Hermans, P. H., and Weidinger, A., "Crystallinity of Precipitated Cellulose," *J. Polymer Sci.*, **5**, 565 (1960).

Heslam, J., and Willis, H. A., *Identification and Analyses of Plastics*, D. van Nostrand Co., Inc., Princeton, N.J., 1965, Ch. 5.

Inoue, M., "Studies on Crystallization of High Polymers by Differential Thermal Analysis," *J. Polymer Sci.*, **1A**, 2697 (1963).

Kast, W., and Flaschner, L., "Eine rontgenographische Methode zur Bestimmung das Verhaltnisses von kristalliner und amorpher Substanz in Zellulosefasern," *Kolloid-Z.*, **111**, 6 (1948).

Ke, B., "Characterization of Polyolefins by Differential Thermal Analysis," *J. Polymer Sci.*, **42**, 15 (1960).

Ke, B., "Differential Thermal Analysis of High Polymers. II. Effects of Diluents on Melting Behavior of Polyethylenes," *J. Polymer Sci.*, **50**, 79 (1961).

Ke, B., "Differential Thermal Analysis of High Polymers. VI. Comments on Some Material and Experimental Factors," *J. Polymer Sci.*, **1A**, 1453 (1963).

Ke, B., "Differential Thermal Analysis," *Encyclopedia of Polymer Science And Technology*, Interscience Publishers, New York, 1966, Ch. V.

Killian, H. G., and Jenckel, E., "Schmelzen Kristallisieren einiger Hochpolymer Nach rontgenographischen Messungen," *Z. Elektrochem.*, **63**, 308 (1959).

Krimm, S., and Tobolsky, A. V., "Quantitative X-Ray Studies of Order in Amorphous and Crystalline Polymers. Quantitative X-Ray Determination of Crystallinity in Polyethylene," *J. Polymer Sci.*, **7**, 57 (1952).

Krum, F., and Muller, F. H., "Vorbehandlung und dielectric Verhalten Hochpolymerer," *Kolloid-Z.*, **164**, 81 (1959).

Lanzavecchia, G., Morlacco, G., Ceraloni, F., "Transizioni a temperatura ambiente del politetrafluoro-etilene," *L. Chimica e L'Industria*, **46**, 160 (1964).

Leborits, A., "Permeability of polymers to gases, vapors, and liquids," Modern Plastics, 43 (7), 139 (March 1966).

Liang, C. Y., and Krimm, S., "Infrared Spectra of High Polymers. III. Polytetrafluoroethylene and Polychlorotrifluoroethylene," J. Chem. Phys., 25, 563 (1956).

Longworth, R., and Morawetz, H., "Measurement of the Infrared Spectra of Solids at Varying Temperatures by the Pressed Alkali Halide Disc Technique," Chem. and Ind., 1955, 1470.

Lontz, J. F., and Happoldt, W. B., Jr., "Teflon Tetrafluoroethylene Resin Dispersions," Ind. and Eng. Chem., 44, 1800 (1952).

Mackenzie, J. D., McDonald, R. S., and Murphy, W. K., "Infrared Spectroscopy of Metals and Hygroscopic Glasses," Rev. Sci. Inst., 32, 118 (1961).

Mandelkern, L., Crystallization of Polymers, McGraw-Hill Book Company, New York, 1964.

McCrum, N. G., "An Internal Friction Study of Polytetrafluoroethylene," J. Polymer Sci., 34, 355 (1959).

McCrum, N. G., "A Study of Internal Friction in Co-polymers of Tetrafluoroethylene and Hexafluoropropylene," Makromoleculare Chemie, 34, 50 (1959).

McGeer, P. L., and Duus, H. C., "Effect of Pressure on the Melting Point of Teflon Tetrafluoroethylene Resin," J. Chem. Phys., 20, 1813 (1952).

Matthews, J. L., Peiser, H. S., and Richards, R. B., "The X-Ray Measurement of the Amorphous Content of Polythene Samples," Acta Cryst., 2, 85 (1949).

Miller, R. G. J., and Willis, H. A., "An Independent Measurement of the Amorphous Content of Polymers," J. Polymer Sci., 19, 485 (1956).

Miller, R. L., "Crystallinity," in Encyclopedia of Polymer Science and Technology, Interscience Publishers, New York, 1966.

Moynihan, R. E., "Molecular Structure of Perfluorocarbon Polymers. Infrared Studies on Polytetrafluoroethylene," J. Am. Chem. Soc., 81, 1045 (1959).

Norris, M. S., Fleck, S. A., and Lichtenfels, D. H., "Ultraviolet Absorption Determination of Nitrogen Dioxide," Anal. Chem., 27, 1565 (1955).

Pacor, P., "Applicability of the Du Pont 900 DTA Apparatus in Quantitative Differential Thermal Analysis," Anal. Chim. Acta, 37, 200 (1967).

Pierson, R. H., Fletcher, A. N., and Gantz, E. St. C., "Catalog of Infrared Spectra for Qualitative Analysis of Gases," Anal. Chem., 28, 1218 (1956).

Pistorius, C. W. F. T., "Transitions and Melting of Polytetrafluoroethylene under Pressure," Polymer, 5, 315 (1964).

Porter, R. N., "The Fabrication of Seamless Teflon Propellant Expulsion Bladders," Jet Propulsion Laboratory, T. R. No. 32-914, June 15, 1966.

Pokrovskii, G. I., and Kotova, I. P., "Investigation of Crystallinity of Some Polymers by Infrared Spectroscopy," Soviet Phys. Tech. Phys., 1, 1417 (1957). (Engl. transl.)

Porter, R. N., and Stanford, H. B., "Propellant Expulsion in Unmanned Spacecraft," Jet Propulsion Laboratory, T. R. No. 32-899, July 1, 1966.

Preuss, H. P., "Synthetic Resins. Part V - Fluorocarbon Resins," Metal Finishing, October 1960, p. 62.

Roldan, L. G., Rahl, F., and Patterson, A. R., "Investigation of Polymer Order by X-Ray Diffraction," J. Polymer Sci., 8, 145 (1965).

Ruland, W., "X-Ray Determination of Crystallinity and Diffuse Disorder Scattering," Acta Cryst., 14, 1180 (1961).

Ryland, A. L., "X-Ray Diffraction," J. Chem. Ed., 80 (1958).

Starkweather, H. W., Jr., and Boyd, R. H., "The Entropy of Melting of Some Linear Polymers," J. Phys. Chem., 64, 410 (1960).

Thomas, P. E., "Quality Control Check-List and Procedures for Flurocarbon Resins," SPE J., 16, 1248 (1960).

Thomas, P. E., Lontz, J. F., Sperati, C. A., and McPherson, J. L., "Effects of Fabrication on the Properties of Teflon Resins," SPE J., 12, 89 (1956).

Vango, S. P., "Determination of Permeability of Cast Teflon Sheet to Nitrogen Tetroxide and Hydrazine," Jet Propulsion Laboratory, T.M. No. 23-55, August 25, 1961.

Vango, S. P., and Krasinsky, J. B., "Metal Plating of Teflon Sheet as a Means of Reducing Permeation," Jet Propulsion Laboratory, Space Programs Summary, No. 37-21, Vol. IV, June 30, 1963.

Vango, S. P., and Krasinsky, J. B., "Continued Effort in Metal Plating of Teflon Sheet as a Means of Reducing Permeation," Jet Propulsion Laboratory, Space Programs Summary, No. 37-23, Vol. IV, October 31, 1963.

Vango, S. P., and Krasinsky, J. B., "Additional Results on Metal Plating of Teflon Sheet," Jet Propulsion Laboratory, Space Programs Summary No. 37-26, Vol. IV, April 30, 1964.

Wada, Y., "Mechanical Dispersions and Transition Phenomena in Semicrystalline Polymers," J. Phys. Soc. Japan, 16, 1226 (1961).

Wunderlich, B., and Dole, M., "Specific Heat of Synthetic High Polymers. VIII. Low Pressure Polyethylene," J. Polymer Sci., 24, 201 (1957).

Wunderlich, B., and Kashdan, W. H., "Thermodynamics of Crystalline Linear High Polymers. I. Comparison of the Melting Transitions of Solution and Melt-Crystallized Polyethylene," J. Polymer Sci., 50, 71 (1961).