NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Technical Report No. 32-914

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N66 27182
(ACCESSION NUMBER)
32
(PAGES)
CR-75332
(NASA CR OR TMX OR AD NUMBER)
FACILITY FORM 602
(THRU)
1
(CODE)
15
(CATEGORY)

GPO PRICE $ ______
CFSTI PRICE(S) $ ______
Hard copy (HC) 2.00
Microfiche (MF) .50
ff 653 July 65

jpl
JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

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The Fabrication of Seamless Teflon Propellant Expulsion Bladders

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Prepared Under Contract No. NAS 7-100
National Aeronautics & Space Administration

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*Photos courtesy Dilectrix Corp.

ABSTRACT

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Seamless Teflon bladders of TFE, FEP, or a combination of both are fabricated by several firms for the NASA Space Program. The process involves mixing aqueous dispersions of Teflon particles, spraying this dispersion onto a metal mandrel, sintering the particles into a film and then etching out the metal mandrel. Teflon bladders made in this manner are reasonably compatible with propellants and capable of repeatedly expelling propellants, but they are somewhat permeable to propellants. Production of defect-free bladders requires a concerted quality control program to monitor every step in the process.

Author

I. INTRODUCTION

This Report describes the processes by which seamless bladders of Teflon[1] are fabricated. Teflon bladders, presently the subject of intensive interest, are used more widely than bladders of any other material in the current generation of NASA space vehicles. Their function is to provide positive control over the liquid rocket propellants which must be forced from the propellant tanks, under pressure, and fed to the rocket engines while the spacecraft is in free-fall, i.e., at zero gravity.

To visualize exactly how these bladders perform their task, it is only necessary to realize that they are essentially bags inside the propellant tanks which have their openings fastened to the tank outlet ports. All of the liquid propellants are contained inside the bags so that when gas pressure is applied to the outside, the liquid is squeezed out through the ports as the bladders are collapsed. Figure 1 illustrates a typical bladder installation in a propellant tank.

This form of positive propellant feed is desirable when liquid rocket systems are operated under 0 g since it prevents any of the pressurizing gas from becoming entrained as bubbles in the propellant streams flowing out of the tank to the engine. Such bubbles can cause rough combustion, or even explosions, in the engine. By acting as flexible mechanical barriers which separate the liquid from the gas and thus allow only liquid to be fed to the engine, these bladders help assure smooth, positive operation of the rockets, Ref. 1.[2]

The popularity of seamless Teflon bladders for this application is due to: 1) the inherent compatibility of these bladders with the highly reactive propellants, such as nitric acid, nitrogen tetroxide, etc., for which suitable

[1]Teflon is the registered Trade Mark of the E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware, who supply Teflon resins and dispersions.

[2]Ref. 1 discusses this approach to positive propellant expulsion in greater detail than is feasible in this Report.

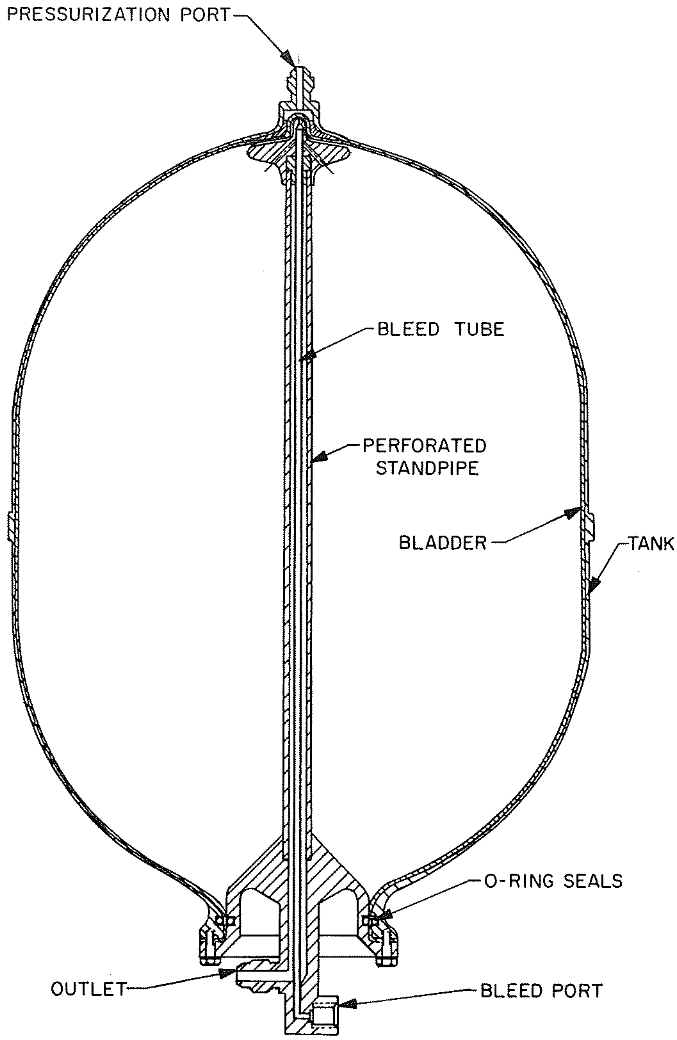


Fig. 1. Typical seamless Teflon bladder installation

elastomers are not available at this time; 2) the inherent structural integrity of bladders of one-piece construction which are free of all joints and seams; and 3) the nearly-limitless variety of shapes and sizes of bladders which can be made by the current fabrication process.[3]

The descriptions which follow of the processes for making sprayed and sintered bladders are typical but not necessarily specific to all commercial firms in this field of technology. In this case, the details are specific to Dilectrix Corporation, Farmingdale, Long Island, New York, who generously spent their time to reveal their methods and to help the writer prepare this Report. Although a preliminary version of the manuscript was reviewed by them, it should not be interpreted as being a definitive statement of their techniques. Firstly, the construction of sprayed and sintered bladders is an art which at the present time would be difficult to reduce to narrative description. Secondly, the brief outline of the methods given herein is not meant to be a process specification but only a summary of background information for the project personnel who will be designing, ordering, testing, and using these bladders. And thirdly, Dilectrix, like its competitors, is constantly searching for and implementing changes which improve their product, Ref. 2.[4]

Dilectrix was chosen as representative of the field for this Report because at the present time they are the major supplier of sprayed and sintered bladders for the NASA space program. Their contracts call for delivery of bladders for *Apollo, Gemini, Lunar Orbiter, Saturn* and *Surveyor,* among others.[5]

The choice of Dilectrix to supply the information for this report should not be construed as being in any way an exclusive endorsement of the Company or its products. Other firms known by the writer to be in this business include Joclin Manufacturing Company of Wallingford, Connecticut and Calcor Space Facility, Inc., Whittier, California.

The fabrication process by which these companies make seamless Teflon bladders can be described as consisting of five basic steps. First, a dispersion made up of very fine Teflon particles suspended in water is obtained. Second, a metal mandrel is made; this mandrel is machined so that its outside contour is the same as the desired inside contour of the bladder. Next, the Teflon dispersion is sprayed onto the mandrel so as to form a thin coating over the entire outside surface of the mandrel. Then this film is dried and sintered in an oven so that all of the Teflon particles coalesce into a continuous film. These later two steps, the coating and sintering, are repeated several times to build up the total film thickness to the desired dimension. Finally, the mandrel is chemically dissolved leaving the Teflon film intact as a complete, free-standing bladder. Figure 2 shows a

[3]This statement, while true, gives the false impression that seamless Teflon bladders are free of shortcomings. Many problems, such as permeability, susceptibility to damage by creasing, etc., do in fact exist. However, the primary purpose of this Report is not to discuss the drawbacks of the finished articles but to describe the manufacturing process.

[4]Ref. 2 discusses some of the new constructions which Dilectrix has tested.

[5]In most cases these bladders are ordered by NASA prime contractors or subcontractors rather than directly by NASA field centers.

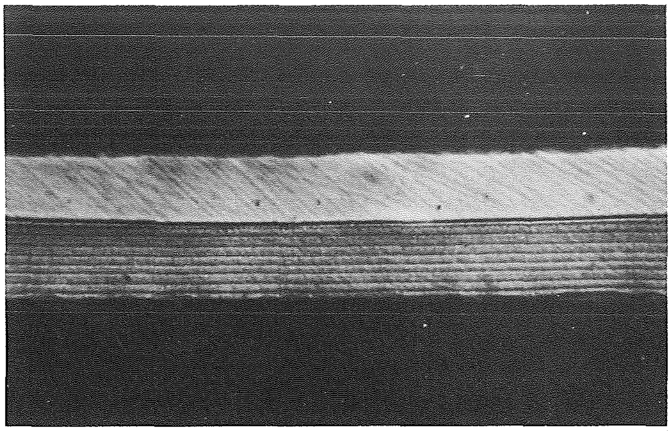


Fig. 2. Cross-section of a built-up film of Teflon (photo courtesy Dilectrix Corp.)

cross-section of a bladder wall made by this process. Note that several individual but inseparable layers, each built up by a separate spraying and sintering cycle, are visible in the TFE portion of the film; the thicker layer with no visible lamination was made in the same way but of FEP in which the layers flow together to form a more uniform film.

Certain practical limitations and detailed operations necessary to assure a good quality film make the actual process somewhat more complicated than this abbreviated explanation implies but essentially this description is correct. Each of these steps is narrated in greater detail on the following pages. The order of presentation roughly parallels the chronological order in which the work is accomplished.[6] Although newer materials are now under development, this Report is restricted to bladders constructed solely of Teflon.

[6]A few supplementary comments and details, thought to be pertinent to an understanding of the materials, processes, and problems involved, are included in the two Appendices.

II. TEFLON AND ITS DISPERSIONS[7]

Teflon is currently available in two chemical forms: TFE, tetrafluoroethylene; and FEP, fluorinated ethylene-propylene. TFE was the first type of Teflon to become available. Its chemical formula is: $(CF_2\ CF_2)_n$. The monomer can be shown diagrammatically as:

$$\begin{array}{ccc} F & & F \\ | & & | \\ C & = & C \\ | & & | \\ F & & F \end{array}$$

Thousands of these monomers join together to form long chains of polytetrafluoroethylene:

$$\begin{array}{cccccccccccccccccc} & F & & F & & F & & F & & F & & F & & F & & F & & F \\ & | & & | & & | & & | & & | & & | & & | & & | & & | \\ - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C & - & C\,- \\ & | & & | & & | & & | & & | & & | & & | & & | & & | \\ & F & & F & & F & & F & & F & & F & & F & & F & & F \end{array}$$

[7]Most of the information in this Section was taken from Ref. 3–6.

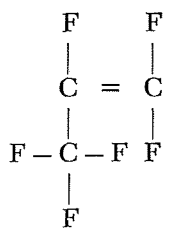
Thick pieces of TFE are opaque and milk white in color. Thin pieces are translucent and very thin films are almost transparent. Any coloring, other than the milk white, is due to foreign materials such as residual wetting agent, fillers, etc., which may have been added during processing or to fluids which have permeated into the structure after processing.

TFE is supplied by the manufacturer in the form of molding powder or aqueous dispersion. Processors form these raw materials into solid pieces of Teflon by pressure molding (the powder) or dip coating (with the dispersion). The parts so formed can be strengthened by sintering to coalesce the particles. Postforming, by the application of pressure at temperatures approaching but below the *transition* temperature (620°F), can be used to slightly alter the shape of the sintered parts but radical re-shaping is difficult. This difficulty stems from the fact that, above the transition temperature, TFE resins enter into a gel state (at 621°F) which limits the melt flow.[8] Because of

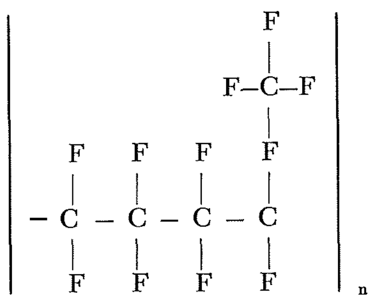
[8]Some additional details of the nature and properties of TFE and FEP films are given in Appendix A of this report.

its unresponsiveness to heat forming methods, TFE is not considered to be a true thermoplastic.

FEP was marketed to satisfy the demand for a genuine thermoplastic with Teflon's properties. This material is the copolymer of TFE and hexafluoropropylene (HFP). This monomer TFE, shown as the first of the two diagrammed on the preceding page, combines with the monomer HFP shown as:



to form the copolymer fluoroethylene-propylene (FEP) with the structural formula:



Thousands of these copolymers are connected together in the solid FEP material. Pure FEP tends to be more nearly colorless and transparent than TFE. FEP film has a tendency to look more brownish than TFE however, because it is less permeable and therefore the wetting agents do not escape as readily during the sintering process as they do from TFE. Also, FEP film is sintered at lower temperatures than TFE so there is less active volatilization of the wetting agents.

FEP, like TFE, is supplied both as a solid (in pellets) and in a dispersion. Unlike TFE, however, the FEP can be melt-processed since it is thermoplastic. Extrusion, injection molding, and vacuum forming are common methods of making parts of FEP. It can also be dip coated onto many different substrate materials and heat sealed, either to itself or to TFE.

While both of these varieties of Teflon, TFE and FEP, have individual characteristics, they share some important general properties. The most useful property of Teflon, for the rocket engineer, is its inertness. Only molten alkali metals, fluorine, and certain halogenated compounds will react with it. Teflon will be physically affected by some substances, including nitrogen tetroxide, which permeate into it and cause swelling; removal of the permeant will restore Teflon to its original condition.

Teflon's second most valuable property is its very low coefficient of friction—because of this the surface has a slippery feeling even when chemically clean. Its lubricity is so outstanding that solid pieces of Teflon or Teflon-base materials are used as journal bearings, piston rings, etc., without additional lubricants. Teflon also is applied by dip coating or spraying from an aerosol bomb to form thin, solid lubricating films on solid substrates.

Related to its low-friction characteristic is the difficulty in attaining a really secure bond between Teflon and other materials using conventional techniques. (This freedom from stickiness has recently been commercially exploited in the production of Teflon-coated cookware which is easily cleaned after use.) Special processes (involving primer layers, chemical treatment of the Teflon surface, or etching of the surface to which the Teflon is to be bonded) are a necessary prerequisite to producing high quality structural joints. A moderate degree of success has been achieved in heat bonding Teflon to thin metal foils[9] but such bonds usually fail when, for example, the Teflon is saturated with nitrogen tetroxide.

Early attempts to build bladders of Teflon were limited by the available fabrication processes. Firstly, small diaphragms were machined from solid pieces. Later, TFE film, made by skiving,[10] was cut into gores and sewn together. Finally, about 1958, the process of making bladders by spraying a thin coating of Teflon dispersion onto a metal mandrel, sintering it, and etching out the mandrel was developed.

The Teflon dispersions used for spraying and sintering films are either straight or slightly modified commercially-available dispersions which are normally composed of three ingredients: Teflon particles, wetting agent, and water. du Pont describes their Teflon 30 as a dispersion of TFE, having hydrophilic, negatively charged colloids containing particles of 0.05 to 0.5 micron

[9]This problem of achieving a secure connection to metal is being studied as part of the development of Teflon-metal foil laminate bladders but it is of little interest to those developing all-Teflon bladders, such as those which are the subject of this Report.

[10]Sheets, tapes, etc., of Teflon are produced by skiving, the process of peeling or shaving a thin sheet from a rotating round bar with a sharp cutting edge.

(μ) diameter suspended in water and containing 59–61% TFE by weight and 5.5–6.5% (based on weight of TFE resin) Triton X-100,[11] a non-ionic wetting agent; the pH is about 10. This commercial dispersion is shipped to the plant of the bladder fabricator in 30-gal metal drums.

FEP dispersion from du Pont Teflon 120 is "....an aqueous dispersion containing 53–57% by weight of FEP solids having a particle size of approximately 0.10 to 0.25 μ and 5–7% of a mixture of volatile, non-ionic and anionic wetting agents....a nominal pH of 10 and a viscosity of about 25 centipoise (cp) at room temperature."

When batches of the dispersion are prepared for spraying, the commercial dispersion is mixed with additional water and any other specified ingredients, such as more wetting agent, special additives, etc., to get the required mixture. The exact formulation used is based on previous experience; this experience is gained by a trial and error process in which determinations are made of the relationship between the composition of mixtures, the spraying characteristics, and the physical properties of the resulting films.[12]

Mixed batches of dispersions are usually small enough to be used up within several days. The dispersions normally do not suffer from settling of the solids until several weeks after mixing.[13]

[11]Triton X-100, a surfactant consisting of alkylated aryl polyether alcohols, is marketed by Rohm and Haas, Philadelphia, Pennsylvania; it is reputed to leave no residue after volatilization. See Appendix A of this report for more data on this product.

[12]It was experimentation of this sort that led to the discovery of the usefulness of the codispersion of TFE and FEP. Still other experiments have yielded Teflon films filled with powdered metals, carbon, etc., which have properties that are considerably different from those ordinary TFE films. The properties of TFE, FEP and laminate films are discussed in Appendix A of this Report.

[13]The shelf life of the commercial dispersion is 6 mo or longer, but prompt application of the mixed dispersion to the mandrel is desirable since it does minimize the chance of changes in the spraying properties.

III. THE MANDREL AND ITS PREPARATION

The mandrel onto which the Teflon dispersion is coated must possess certain qualities. Obviously it must be a suitable surface for receiving the dispersion, and holding the dispersion evenly without any tendency to puddle or cause the film to break; this quality is largely a function of the surface preparation to be discussed below. The mandrel must be dimensionally stable, being able to survive several temperature cycles during the sintering process, since the outer contour of the mandrel becomes the inner contour of the bladder. Finally it must be easily and quickly dissolved, leaving no residue and in no way harming the bladder.

The commonly-used mandrels are made of type 1100 aluminum. Wall thicknesses are nominally 0.050 to 0.060 in.; this is a good compromise between the requirements for dimensional stability and speed of chemical removal. Tolerances on the mandrel's external dimensions are held within $\pm$ 1/64 in. These dimensions must be sized to allow for the 1.7–2.2% shrinkage in the bladder which occurs when the mandrel is etched out.

As mentioned previously, the contour of the external surface of the mandrel becomes the internal surface contour of the bladder. An area of exception to this is the neck where flanges perpendicular or nearly perpendicular to the axis of the outlet tube are desired. Because it is very difficult to spray dispersion evenly onto such flanges, a conical section is produced instead and later spun to the flat configuration.

The mandrels are produced largely from flat sheet metal. Hemispherical, elliptical and other end shapes are usually spun while cylindrical sections are rolled. Joints are welded using inert gas processes. All surfaces to be coated are then machined and polished to a standard 32-microinch (μin) finish.

When received by the bladder fabricator, the mandrel is carefully inspected to assure conformance with the drawing. Dimensions are checked with micrometers and templates. Welds are tested for porosity with dye penetrant. Every square inch of surface is visually examined to be sure it is free of defects.

Surface finish requires special attention primarily because flaws in the bladder may originate from surface discontinuities. For example, pits are troublesome since TFE does not readily bridge over them but rather contracts from the pits to leave holes in the film. Scratches are thought to be nucleation sites for flaws in the film which act as stress risers.

In order to be sure that a properly smooth finish exists, the mandrel is polished again by buffing it until all areas to be coated have a 16- to 32-μin finish.[14] Final acceptance is based on visual comparison with a General Electric surface gauge.

The polished mandrel is then cleaned by immersion for a specific time in a caustic bath, a solution of sodium hydroxide; an even cleaning is secured by rotating the mandrel while it is immersed. After removal from the bath it is rinsed with tap water, a chromic acid solution (to neutralize the caustic), tap water, and finally deionized water. Then the mandrel is dried. Clean mandrels are stored in polyethylene bags until they are removed for installation in the holding fixture in the coating facility. Figure 3 shows a typical mandrel as it appears when ready to be coated with Teflon.

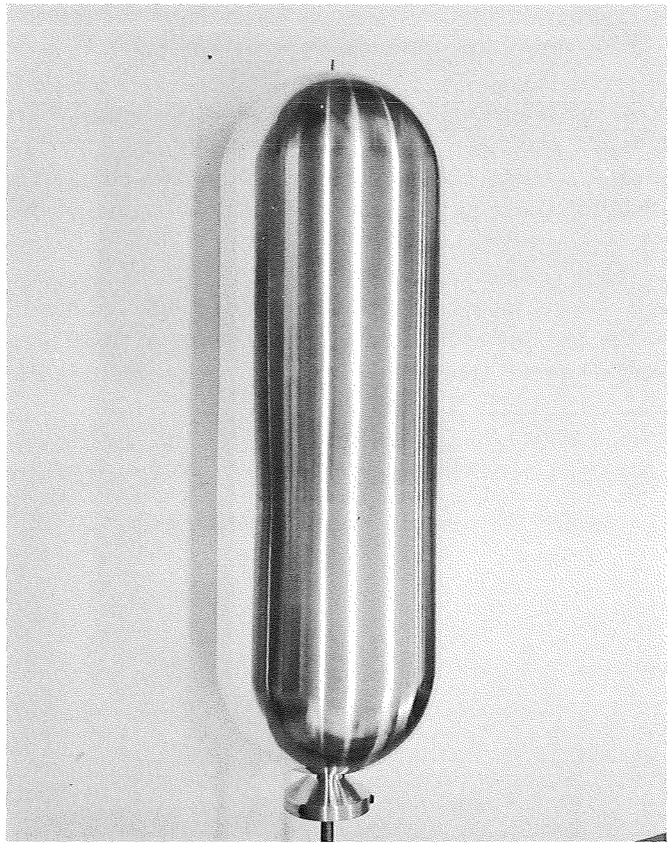


Fig. 3. A typical mandrel after being polished (photo courtesy Dilectrix Corp.)

[14]Smoother finishes have been tried experimentally but no particular advantage was evident from the results. Greater difficulty in preserving the better finish during the necessary handling of the mandrel was experienced.

IV. THE SPRAYING AND SINTERING PROCESSES

Actual creation of the bladder occurs when the mandrel is coated with Teflon. This process is carried out in a special facility which is equipped with: (1) tooling for holding and rotating the mandrel while the coating is applied, (2) drying areas where batteries of infra red lamps heat the newly applied coating, and (3) ovens for sintering.

At Dilectrix, this equipment is located in a single area which is kept clean by use of air locks, positive pressurization and the wearing of *white* suits by personnel. Although no specific *clean room* cleanliness rating is sought, these precautions are felt to be essential to the avoiding of inclusions in the bladders.[15]

The first step in coating the mandrel is to apply a thin (0.0001–0.0002 in. thick) layer of primer. Usually a primer such as du Pont No. 850-202 is used when TFE is to be put on an aluminum mandrel. This primer is a mixture of du Pont's Teflon 30 dispersion, chromic acid, phosphoric acid, and other ingredients. For very thin bladders, a 0.0003–0.0004 in. layer of FEP dispersion might be substituted. This primer layer is sintered, as described below, and then the Teflon dispersion is sprayed on.

Of all the steps in fabricating seamless Teflon bladders, the most critical step is the application of the Teflon onto the mandrel. This is accomplished with an air-powered spray gun, similar to the conventional paint spray gun, that atomizes the liquid dispersion into a directed stream of fine mist. This mist impacts the surface being coated while the individual droplets are still liquid so that a very thin wet film is deposited. Great care is required in applying the film in order to avoid exceeding a *critical thickness* of film and to build up an even film.

Critical thickness is defined as the maximum thickness of a layer of dispersion that can be sintered without the development of *mud cracking*. The term *mud cracking* is a verbal picture of surface damage characterized by criss-crossed cracks, much like the familiar cracked mud in the bottom of a dried river or lake. TFE is subject to mud cracking because the film shrinks as it is dried and sintered. Since TFE is not a thermoplastic in the conventional sense, the cracks do not heal over upon re-heating. Experience has shown that if a layer of dispersion which is ¾ mil or greater in thickness is dried and sintered, mud cracking will develop. The actual thickness at which mud cracking is incipient depends upon several variables. Substituting additional wetting agent for some of the water in the dispersion, for example, will increase the critical thicknness; this procedure has the drawback of increased difficulty in baking off the wetting agent during the sintering process. At Dilectrix, normal practice is to apply the dispersion in layers which are 0.0003–0.0004 in. thick. Such thin layers are well below the critical thickness so mud cracking is usually avoided.

It is this limitation, on the thickness of film which can be successfully laid down with a single spraying and sintering cycle, that makes it necessary to construct bladders by laying down several successive films. Each of these films requires a repetition of the spraying and sintering processes. Thus, if a 0.0003 in. film is added during each cycle, 20 complete cycles (neglecting the primer) must be completed to build up a total film thickness of 6 mils. Obviously, for a given final film thickness, the number of cycles is inversely proportional to the thickness of each layer, therefore there is some incentive to apply the thickest layers that will assuredly result in high-quality film. It is unconservative, however, to attempt to apply layers approaching the critical thickness because of uncertainties as to the exact point of incipient mud cracking and difficulties in spraying layers with precisely even thickness over the entire surface of the bladder. Mud cracking, when it does occur, is usually confined to areas which are particularly difficult to coat evenly.

Most of the spraying is done by hand. Spraying is an art or skill which must be acquired by practice. It closely resembles the art of top-grade automobile painting. A few specific points will be mentioned here.

First, a spray with nearly optimum droplet sizes and velocities must be produced. Actual droplet sizes and velocities are not measured but, instead, operating conditions that consistently give good results are maintained. The controlled variables in this case are the temperature, density and viscosity of the dispersion, and the flow rates of air and dispersion through the spray gun. Second, the gun must be kept at the proper distance from the surface. The gun must be close enough to deposit a wet film yet far enough away to avoid too rapid build-up in local areas and excessive air stream shear stresses in the film. Third, the gun must be kept pointed perpendicular to the

[15] Appendix B, Inspection and Quality Control, discusses this matter.

surface since tangential spraying causes *orange peel*; orange peel, another picture word, describes a roughened surface texture similar to that on an orange. Fourth, the gun must be constantly in motion relative to the surface to obtain an even layer which is free of puddling or bald spots. The operator moves the gun with smooth, jerk-free motions. In most cases the mandrel is chucked in a machine resembling a lathe so that it can be rotated uniformly during the spraying process. Figure 4 shows a mandrel being spray-coated with Teflon dispersion in the manner described.

Right cylinders can be sprayed by machine. The mandrel is chucked in the machine as with hand spraying, but the spray gun is mounted on a tool holder which is translated parallel to the mandrel surface at constant speed by a lathe feed mechanism. As yet, such automated methods have not been adequately developed to do high quality work on other shapes. All of the ends, necks, flat surfaces and nonsymmetrical shapes are sprayed by hand.

Immediately after a layer of dispersion has been applied, the mandrel is slowly rotated under a battery of infrared lamps which heat the film to slightly above +120°F in order to drive off the excess water. Figure 5 shows a coated mandrel being dried.

Once dried, the layer is ready to be sintered. The mandrel is hung from a portable frame which is placed in an electrically-heated oven, Fig. 6, where a slight circulation of air carries the heat to the Teflon layer being

Fig. 4. Spraying Teflon dispersion onto the mandrel (photo courtesy Dilectrix Corp.)

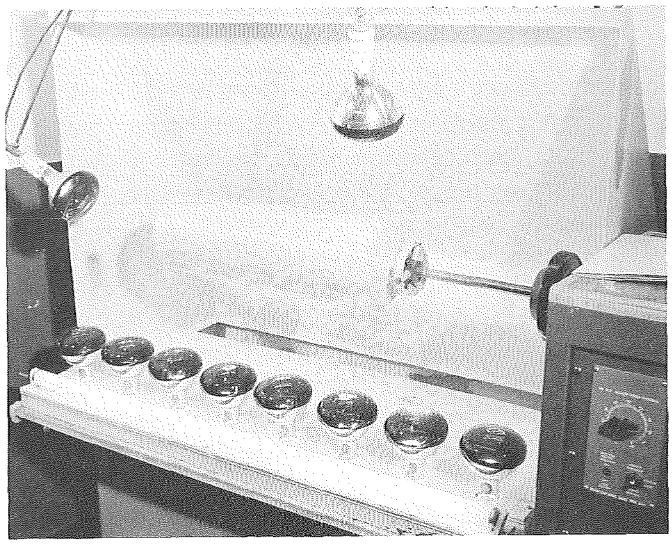


Fig. 5. Drying the coating under infra-red lamps (photo courtesy Dilectrix Corp.)

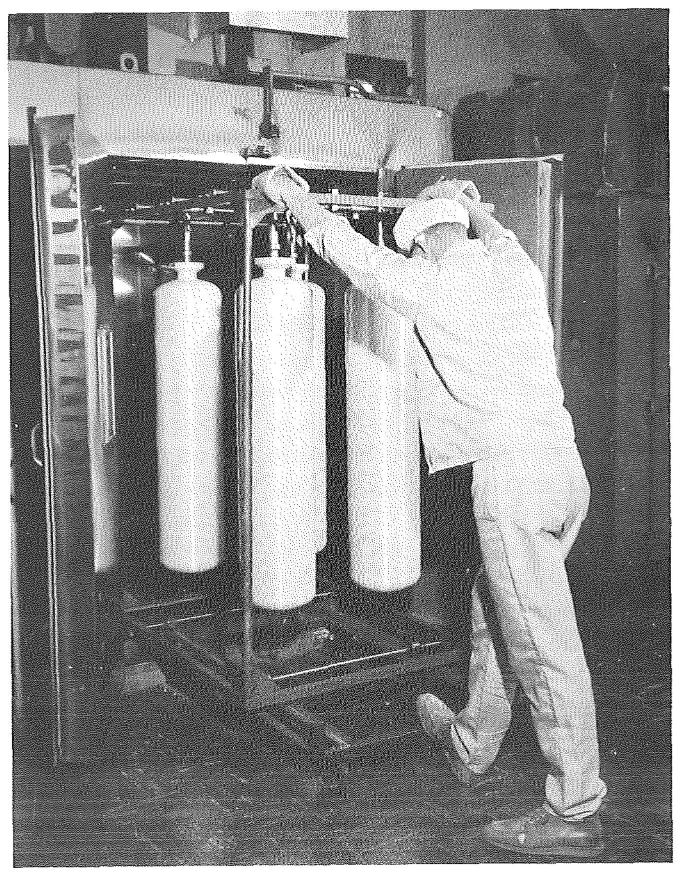


Fig. 6. Coated mandrels being put into the sintering oven (photo courtesy Dilectrix Corp.)

sintered. At about +400°F the X-100 wetting agent begins to volatilize and its rate of volatilization reaches a peak at approximately +450°F. The threshold of TFE sintering is reached at +620°F. Degradation begins if the film temperature exceeds +734°F, so the oven controller is often set at +670 ±10°F; for FEP, the oven is set for approximately +580 ±10°F. Sintering temperature is maintained for about 20 min.

The fact that FEP sinters at a lower temperature than TFE is an important factor to be considered when composite films or codispersions of TFE and FEP are being made. Sintering TFE after previously sintering an undercoating of FEP is very difficult and the problem is intensified by the need in most cases to apply more than a single layer of TFE because each layer requires a sintering operation. Progressive degradation of the underlying FEP is quite likely to occur as the sintering cycle is repeated over and over at a temperature approaching the upper limit for high quality FEP. Even with the oven control setting near the lower limit for full sintering of the TFE, local temperature variations in the oven may exceed the safe limit for FEP.[16] For this reason, conventional practice is to make composite-film bladders, sometimes called *laminated*, with the layers of TFE on the inside and with the FEP layers on the outside. This arrangement means that all of the higher temperature sintering of the TFE is completed before the first layer of FEP is applied.

Thermal degradation is an important thing to avoid since it manifests itself as a lowering of the strength of the film as a result of shortening of the polymer chains.

TFE film will have better physical properties if it is quenched immediately after the final sintering rather than being allowed to cool gradually. Dilectrix reduces the temperature from 670°F to below the gel point (621°F) in 3 to 5 sec by spraying the film with CO_2. This step minimizes the crystallinity. A fast quench can be expected to keep the crystallinity below 55% and the flexural modulus[17] below 65,000 psi. Slow cooling to the annealed condition can result in crystallinity as high as 75% or higher and a flexural modulus of 85,000–90,000 psi.[18]

FEP film is only slightly affected by the rate of cooling. Crystallinity can range from 40 to 57% but usually is between 45 and 47% in bladders.

After cool-down to room temperature, the total film thickness is measured. Details of this measurement and the detailed inspection the bladder undergoes are given in Appendix B of this Report. If more layers are to be added, the mandrel is returned to the coating facility for the next spraying operation.

If markings, such as serial numbers, part numbers, etc., are to be permanently imbedded in the bladder wall, they are sprayed on during one of the intermediate spraying operations. The pigment is chromic oxide.

After the final spraying, sintering, and cool-down operations are completed, i.e., when the required total thickness of film has been built-up, the Teflon-covered mandrel is taken to the finishing area.

[16]Dilectrix states that their ovens keep local temperatures to within ±20°F of the controller setting.

[17]Flexural modulus is defined in ASTM 790 as the modulus of elasticity measured by bending the material, taking the appropriate load and deflection measurements, and then solving for the modulus of elasticity in an appropriate beam deflection equation.

[18]Procurement specifications sometimes limit the flexural modulus to 75,000 psi or less.

V. FINISHING THE BLADDER

The bladder is ready to be finished when the Teflon coating on the mandrel is complete. At Dilectrix, before any further operations are performed, a protective layer of vinyl is applied. This has been found by experience to substantially reduce the incidence of damage to finished bladders during handling.

If the bladder design has a flat flange on the end of the outlet neck, the bladder is made on a mandrel with a flared conical section terminating the neck. To obtain the final desired flange configuration, the conical section of the coated mandrel must be spun to shape. This spinning operation is performed in a spinning lathe as shown in Fig. 7; the mandrel is internally supported in position by a pole that passes down through the neck to the opposite end of the mandrel. A hard-rubber split collar is fitted to the neck to act as the form against which the end of the mandrel is spun. As the mandrel is rotated by the lathe, a blunt-ended spinning tool is forced against the surface to be deformed so that the conical section is gradually worked until it conforms to the shape of the hard-rubber form.[19] After spin back, the stresses in the Teflon coating must be relieved so that it will remain a flat flange once the mandrel has been removed; this stress relief operation is a simple annealing process from a temperature below the transition point. At this stage the Teflon coating on the mandrel is a complete bladder of the desired size, plus shrinkage allowance, and shape, which has only to be separated from the mandrel.

[19]The edge of the flange is rough trimmed to size after this process.

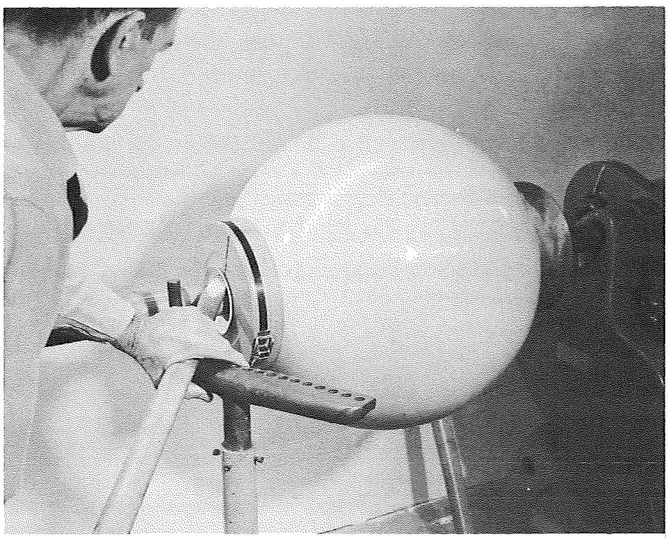


Fig. 7. Spinning back the neck flange (photo courtesy Dilectrix Corp.)

Due to the shape of the bladder and the tenacity of the bond between the bladder and mandrel, the safest process for separating the two is to chemically etch the mandrel out. This is done by immersing them in a bath of caustic, sodium hydroxide. It is very important to keep the bladder from collapsing as the supporting mandrel is removed because sharp feather edges can develop as the mandrel becomes quite thin. To keep the bladder distended, so these edges do not cut the inner surface of the bladder, a slightly greater hydrostatic pressure is maintained on the inside. This differential hydrostatic pressure may be achieved simply by holding the bladder upright with the neck a few inches above the surface of the caustic bath. Caustic solution is piped into the bladder so that the flow circulates inside then rises and flows out over the flange; thus the level inside is even with the neck flange, a few inches above the outside level in the bath. This process of circulating caustic inside the bladder continues until the mandrel is completely dissolved. Most mandrels can be removed in 3–10 hr. During this period the temperature of the bath varies between +140 and +190°F.

When the free-standing bladder is removed from the caustic bath it is given a preliminary rinse with tap water and the vinyl coating is stripped off. This is followed by a thorough washing with tap water, a chromic acid solution, and finally tap water again to neutralize the caustic.

After the bladder has been dried and the flange given its final trimming, it is ready for final inspection – or interim inspection if it is but one ply of a multiply bladder – and cleaning and packaging for shipment. All of these steps are accomplished according to varying procedures designed to meet the specific requirements of the customers' specifications.

VI. SUMMARY AND CONCLUSIONS

Aqueous dispersions, containing minute particles of Teflon, can be sprayed onto metal mandrels and then sintered to form seamless Teflon films of practically any shape suitable for propellant expulsion bladders.

The techniques presently being used to make these seamless bladders fall into the category of an art, although a number of scientifically monitored controls are being used, because reproducibility and quality are highly dependent upon the skill of the operator. This entire process must be carefully monitored and the final product thoroughly inspected for the several kinds of flaws that jeopardize the integrity and durability of the finished bladder.

Agreement between the fabricator and his customers is essential in the areas of establishing the range of acceptable properties of the bladder and deciding upon the quality control and inspection procedures to be used to determine compliance with the purchase specification. This need is especially important because of the current lack of recognized standards for film properties and methods of checking bladders.

APPENDIX A

Characteristics of Teflon Films Made by Spraying and Sintering

In the following discussion of the properties of Teflon films, frequent reference is made to three basic factors which exert a controlling influence on the physical properties of the films. These three factors are the average molecular weight (mol. wt.), crystallinity, and void content.[20]

In Section II of this Report, the monomer and copolymer of the two forms of Teflon were diagrammed and mention was made of the fact that the long polymer chains consist of thousands of these individual units connected together. Figure A-1 is a photograph of a Godfrey molecular model of a short segment of the TFE Teflon structure. The molecular weight of a given chain is obviously the number of monomer or copolymer units in the chain multiplied by the molecular weight of each unit.[21] An *average* mol. wt. is specified in connection with the bulk properties of Teflon because not all of the chains are of the same length.

The bulk properties of Teflon can also be related to the spatial orientation of the polymer chains. In many regions the chains are in random orientation relative to each other; this portion of the film is said to be in the *amorphous* state. In the remaining regions, chains are

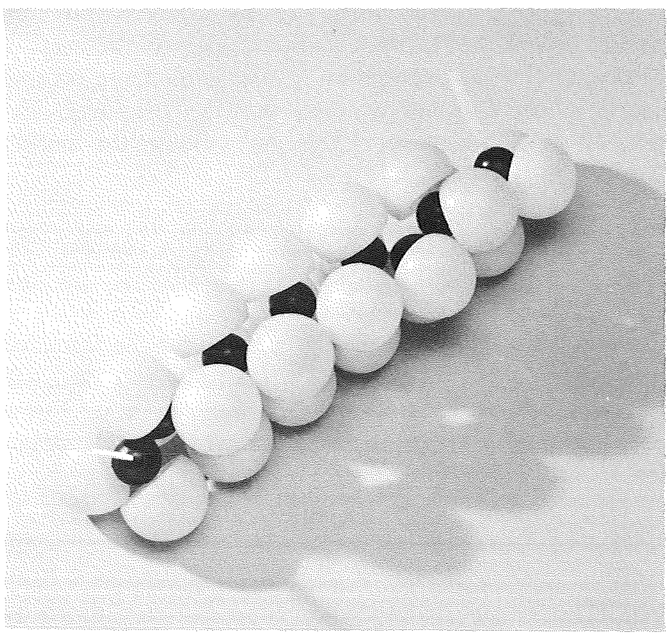


Fig. A-1. Godfrey molecular model of a short segment of the TFE Teflon structure

[20]While some of the details in this short discussion may not be precisely accurate in all respects they are sufficiently correct to permit an understanding of the gross correlations to be presented later.

[21]Monomer mol. wt. = 100 and copolymer mol. wt. = 250.

arranged in a more or less orderly fashion which is described as the *crystalline* state; it is believed that the chains tend to orient themselves parallel to each other in the regions of crystallinity to form clusters much like bundles of rods. These two states are co-existent in all Teflon material.

Crystalline regions and amorphous regions are interspersed so the bulk properties reflect an averaged response of both states. For example, the more ordered portions of the chains are less free to be reoriented by external forces than the random parts so they contribute a degree of rigidity to the entire mass and it follows that the rigidity becomes greater as the proportion of crystalline to amorphous content increases. Other properties are also affected by this same proportion. To numerically express this proportion, the percentage of the total mass which is in the crystalline state is termed the *crystallinity* of the Teflon; e.g., if 53% by weight of the total is crystalline, then the crystallinity is 53%.

Not all of the volume apparently occupied by the Teflon is packed with polymer chains. Vacant spaces occur because Teflon is not a completely uniform crystalline substance. The degree to which all of the space is occupied in a finished piece of Teflon depends upon a number of factors including the size, shape and porosity of the particles in the resin and the processing the resin undergoes as it is formed into the solid film. By measuring the specific gravity of the finished material and comparing it with the theoretical specific gravity for voidless Teflon of the same crystallinity, the percentage of void space in the finished material can be calculated. Expressed as a percentage of the total volume, the answer is called the *void content.*

When Teflon is being processed into a bladder, the three factors of molecular weight, crystallinity, and void content should be adjusted within the available limits to develop a film with the best properties for the intended use. Exactly how these variables may be controlled will be discussed below where the specific kinds of Teflon are described. But first, some of the desirable characteristics of a bladder film will be enumerated.

There are four characteristics that are most important in films chosen for the construction of expulsion bladders. The first is the chemical compatibility of the films with the propellant and pressurant. Second, the mechanical properties that determine their structural suitability for performing the operations required of a bladder. Third, the permeability of the films to the propellant and pressurant. And lastly, their fabrication characteristics.

The term *compatibility* is used here to refer to the degree of mutual interaction between the film and propellant or pressurant; a completely compatible film would have no effect whatever on the fluids and vice versa. Few bladder films are completely compatible with the most reactive propellants so some degree of interaction usually occurs.

The most common kind of interaction between ordinary polymers and propellants is direct chemical attack during which the fluid oxidizes or reduces the bladder material. This attack may take the form of replacing single atoms or complex groups attached to the polymer chains, breaking cross-links between chains, or even breaking the bonds in the backbone of the chain. Polymers that have been attacked in this fashion will harden, crack, become gummy or sticky, foam, or simply disintegrate. Sometimes a composite or a material containing impurities may experience selective attack. For example, if the composite is made in discrete layers, the susceptible layers may be stripped off or disintegrated so as to cause the film to delaminate. If there are non-compatible ingredients interspersed throughout an inert film, such as Teflon, these substances may react with the permeating propellant, or pressurant, to form gas bubbles or pockets of residue within the film. A less severe change occurs when the fluid is merely soluble in the film; this results in swelling and loss of film strength.

The film or some ingredient in it may, on the other hand, cause changes in the fluid. Constituents in the film may dissolve into the fluid and thus change its characteristics. Or worse yet, the film or its constituents may cause the fluid to decompose into several components. A particularly troublesome problem is the wide range of substances which act as catalysts for hydrazine and hydrogen peroxide; the decomposition of hydrazine produces ammonia, nitrogen, and hydrogen, while hydrogen peroxide breaks down into water and oxygen.

Predicting the likelihood of reactions which may occur when given propellants and films come into contact can be accomplished with a fair degree of assurance if all of the constituents are known. This is seldom the case, however. Trace impurities are almost always present and these substances may not be detected in the normal course of production inspection of film, propellant, etc. This means that tests must be performed to check the actual compatibility. Fortunately, valid tests can be made easily using only small patch samples of film if the samples are carefully chosen so as to be fully representative of all the film conditions and compositions, and if the fluids are an equally accurate sampling of the extremes of composition.

The job of determining the structural suitability of films for bladder applications is not so straightforward. No simple patch sample tests are known that yield definitive answers. This uncertainty is partly due to the lack of a complete mathematical analysis of the loads and strains which the bladder must survive in order to reliably perform its function; without such an analysis, the relative importance of the measurable physical properties is unknown. Until the proper relationships between the physical parameters are defined, the selection process must remain essentially a trial and error procedure. The current method for completely assessing a film consists of subjecting bladders of the film to tests which closely simulate the operations that the projected bladder will perform. These tests include filling and expulsion cycles, periods of sloshing and vibration, etc.

Meanwhile, empirical attempts are being made to develop criteria for judging the films. Observations of bladders during the various operations reveal that nonelastomeric bladders are subjected to severe rolling and folding. Complex fold patterns develop which usually cause creases to form; these creases may be static, fixed location; or they may be dynamic, the so-called rolling or travelling creases. Further, aside from obvious causes such as cuts, almost all mechanical failures in bladders are attributable to local damage from creasing. Investigations, both analytical and empirical, have shown that creasing folds will generate biaxial tensile stresses of high magnitude unless the material can relieve itself by substantial elongation. Based on these observations, it is reasonable to assume that biaxial tensile strength and elongation are important physical properties of a film in relation to its durability.

Intuition tells us that the flexibility of a film affects the pressure loads necessary to collapse the bladder to the point of complete propellant expulsion. If this is true, then the flexural modulus must be important also.

Undoubtedly there are other physical properties that should be evaluated but at this time their relationship to bladder film performance is not clear.

Perhaps the one characteristic of bladder films which has received the most attention is permeability; like compatibility, this can be checked easily with small patches of film. The net rate at which a permeant passes through a film is proportional to the concentration gradient, all other factors remaining constant. This rule, known as Fick's Law, means that the most accurate comparisons of the relative permeability of films are made on the basis of data taken at, or reduced to, the same concentration gradient across the film. These data must be for steady-state conditions unless the projected duty cycle for the bladder is about the same as the film saturation time.[22]

Ideally, the film should transmit neither propellant nor pressurant but essentially all purely polymeric materials are permeable to both. There is a considerable difference in rate, however, between different materials and, with a given film, between different permeants.

The last characteristic of special significance to be discussed below is the nature of the response of the film material to the various fabrication processes and the inherent problems which arise during the making of a seamless bladder.

TFE Teflon is made available by the E. I. du Pont de Nemours & Co. in two forms but only the dispersion is of interest here. Their Teflon 30 dispersion contains particles ranging in size from 0.05 to 0.5 μ; Dilectrix personnel say the average size is 0.2 μ. Each of these particles contains millions of polymer chains of various lengths with the average molecular weight falling somewhere between 1×10^6 and 3×10^6.

Sprayed and sintered films of TFE made from this dispersion will not be absolutely pure $(CF_2CF_2)_n$ but it is believed that the contamination level can be kept quite low so that compatibility problems, at least with *earth-storable* propellants, will not be severe. Presuming that the bladders are thoroughly cleaned after fabrication is complete, there appear to be only about four sources of impurities:

1. Trace impurities in the raw materials
2. Residue from the *volatile* substances
3. Markings deliberately put into the film
4. Contamination during processing

[22]The saturation time is the period between initial contact and establishment of steady-state flow, for constant concentration gradient cases, or until the inflection point on the curve of rate vs time is reached, for cases where accumulation of permeant on the downstream side of the film changes the gradient.

The raw materials presently used to make TFE bladders consist of the dispersion, the primer, and the water. du Pont's Teflon 30 dispersion consists of the resin particles, Rohm and Haas Triton X-100 wetting agent, a slight amount of ammonium hydroxide and water. Information on the absolute chemical purity of the resin has not been received as of this writing but it is believed that it is essentially free of foreign substances. Information from Rohm and Haas indicates that their Triton X-100 surfactant is a branch chain octyl phenoxy polyethoxy ethanol containing an average of 10 moles of ethylene oxide. It is not a single species of molecules, for not only will the ethylene oxide chain vary somewhat in length, but it is possible that some of the octyl phenol hydrophobe is actually a dioctyl phenol. Recent analyses indicate that there is approximately 1.5% polyethylene glycol present. Also, about 0.1% is a mixture of sodium dihydrogen phosphate and disodium hydrogen phosphate. Metal ions such as iron, copper, nickel and magnesium were not found; apparently these are not present above a level of 1 ppm. No data were obtained on the sodium hydroxide. du Pont uses deionized water for their carrier.

du Pont's No. 850-202 primer for aluminum surfaces is a proprietary formula containing Teflon 30 dispersion, chromic acid, phosphoric acid, and other unspecified ingredients. While the exact composition has not been revealed, it is understood that a variety of substances are present; some of these yield sodium sulphate in the sintered film. The question of trace impurities has little meaning in connection with a mixture whose standard composition is unknown.

The water added to the dispersion at the fabricator's plant, can also be a source of subtle contamination. It is known that Dilectrix, for example, uses deionized water, not triple distilled or similarly purified water. Data on the compatibility of the complexes remaining after the ion exchange process are not available but Dilectrix personnel do not feel that any problem exists in this regard.

Actually the total amount of substances finding their way into the film as trace impurities is probably a minor problem compared to that created by the residual wetting agent, phosphoric acid, and chromic acid left in the film after sintering. While it has been tacitly assumed that these fluids volatilize completely, common sense tells us that even the 20 min sintering period, approximately 2½ times the minimum recommended by du Pont, does not really drive off all of these undesirable ingredients. Furthermore, very slight amounts of the mandrel etching fluid and the cleaning fluids may permeate into the film.

Besides the unintentional addition of impurities, at least one deliberate form of contamination, the markings, is introduced. Chromic oxide letters are sprayed onto one of the intermediate layers when the customer requires identification markings. This compound is probably compatible with oxidizers but less than completely inert with amine fuels.

Finally, random contamination may occur by accident during the mixing of the dispersions and fabrication of the bladders. Particulate contamination and its control are discussed in Appendix B. The exact degree of contamination is variable but normally held to low levels as substantial efforts are being made to eliminate this source of foreign inclusions. The particles themselves are likely to be reasonably compatible if metallic and somewhat reactive if non-metallic.

No detailed reports on the compatibility of TFE Teflon bladder film with propellant were located. Dilectrix personnel mentioned that some early bladders in which hydrazine was stored for 1 yr developed blisters; apparently the exact cause was not determined. It might be speculated that permeating hydrazine within the bladder wall decomposed to gas. Some hydrazine decomposition will occur regardless of the compatibility of the bladder but it would seem ordinarily that the gaseous products would permeate out of the wall rapidly enough to prevent blisters from forming. This line of reasoning might lead to a tentative conclusion that an accelerated decomposition rate was initiated by some contaminating substance (such as residual wetting agent, etc.). Tests at JPL in which nitrogen tetroxide was stored at ambient temperature for more than 1 yr resulted in no obvious damage to the bladder material (a laminate of TFE and FEP). A sample from this same type of bladder was submitted to an independent chemical laboratory for a spectographic analysis of the material. The weight of the ash was 0.07% of the weight of the original specimen. These remains consisted primarily of the oxides of chromium, sodium and potassium. Apparently these elements were introduced in the primer and wetting agent. A complete list of the results is shown in Table A-1.

To sum up, the present TFE bladder material appears to be reasonably compatible with both fuels and oxidizers. Residue from the non-TFE substances used and particulate contamination are believed to be the most likely sources of trouble if it occurs.

Table A-1. Results of a spectrographic analysis of a TFE-FEP laminate film

Substance (as oxide)	Percent (by weight)
Chromium	31.0
Sodium	21.0
Potassium	11.0
Tin	3.0
Lead	1.5
Iron	1.2
Aluminum	1.1
Calcium	0.95
Cobalt	0.56
Magnesium	0.56
Nickel	0.56
Copper	0.19
Silicon	0.15
Strontium	0.069
Titanium	0.042
Silver	0.037
Manganese	0.024
Boron	0.021
Other elements	nil

Most of the damage sustained by TFE bladder material comes, not from reactions of contamination with propellants, but rather as a result of the mechanical properties of TFE which make it susceptible to creasing damage from the folding and unfolding the bladder undergoes during installation, filling, vibration and expulsion. As mentioned above, the three parameters of special interest which are a measure of the ability of the film to perform with minimum damage are the tensile strength, elongation, and flexural modulus. An optimum film would have a high tensile strength, great elongation, and a low flexural modulus.

Unfortunately the basic factors which determine the magnitudes of these three parameters do not allow the best attainable values of all three to be available simultaneously in the same film. For example, when the average molecular weight, crystallinity, and void content are adjusted to yield the best available tensile strength, the elongation is less than maximum. Table A-2 summarizes the gross relationships between these three basic factors and properties of TFE Teflon.

Table A-2. Relationships between three basic factors and the mechanical properties of TFE Teflon

This factor → must be → to give	Average molecular weight	Crystallinity	Void content
High tensile strength	high	low	low
Great elongation	low	high	low
Low flexural modulus	(not applicable)	low	high

Tensile strength is affected by all three of the basic factors previously mentioned: average molecular weight, crystallinity, and void content. Tensile strength increases with increasing molecular weight. The molecular weight in the film cannot be increased over that originally present in the dispersion but it can be decreased unless thermal degradation is avoided. Sintering temperatures above approximately +734°F may result in degrading the film by the successive removal of monomers CF_2CF_2 from the ends of the chains.

Tensile strength is best at low levels of crystallinity. Low crystallinity is achieved by quick quenching after sintering. Dilectrix usually produces films with 50–55% crystallinity.

Low void content makes for good tensile strength. Void content is not very controllable since it is largely a function of the size, shape and porosity of the particles in the dispersion; careful control over the sintering temperature will, however, help to avoid unnecessary increases in void content.

It can be seen from the above that the tensile strength of the film produced from a given dispersion is maximized if the proper sintering temperature is carefully maintained and then the film is rapidly quenched. This process results in a film with high average molecular weight, low crystallinity, and low void content.

While high average molecular weight is desirable in that it yields high tensile strengths, the elongation of the film is less than maximum at this condition. Shorter Teflon chains give better elongation. To a degree, the same dilemma is faced in the choice of crystallinity objectives because higher crystallinity, up to 85%, results in greater elongation as opposed to the need for lower crystallinity for best tensile strength. A low void content gives both extra elongation and extra strength to the film.

Optimizing TFE film becomes even more complicated, however, when a low flexural modulus is desired. Average molecular weight doesn't seem to have much effect but crystallinity should be low, as with tensile strength, and void content should be high, contrary to the need for low void content to get high tensile strength and great elongation. To illustrate the sensitivity of flexural modulus to crystallinity, fast quenching to keep crystallinity low may yield a film with a modulus as low as 55,000 psi while slow annealing may increase the crystallinity enough to raise the modulus to 90,000 psi.

Based on experience, Dilectrix has found that films with a high average molecular weight and low crystallinity are the best compromise to achieve durability. This seems to imply that tensile strength and flexural modulus are more important than elongation. This is corroborated somewhat by the fact that du Pont reports that *flex life* is increased by adjusting the basic factors in the same way as required to increase tensile strength. The average ultimate tensile strength of Dilectrix TFE film is approximately 4,700 psi although some films rated acceptable by certain customers may have strengths as low as 4,000 psi. Ultimate elongation ranges from 400 to 600%. Flexural modulus usually falls between 55,000 and 65,000 psi but customer specifications may allow values as high as 75,000 psi.[23]

The choice of optimum void content was not mentioned above since, in most cases, the demand for low permeability creates an overriding consideration. Permeability of the film to most fluids used in rocket systems is strongly a function of the void content—less void giving less permeation. To a certain degree permeability is affected by the crystallinity (decreasing permeability with increasing crystallinity) but average molecular weight seems to be insignificant in connection with permeability. Film permeability varies over quite a range but a typical value, based on measurements made by Dilectrix on their own TFE film, indicates N_2O_4 permeates at a rate of approximately 1×10^{-4} psi/hr/mil when the downstream concentration is zero and the temperature is 70°F.[24]

[23]Of course, the measured values of all three of these parameters depend upon the rate of strain and certain other factors.

[24]When converting to thicker sections, divide by the thickness in mils.

TFE film with the properties outlined above can be made into spheres, hemispheres, cylinders and other shapes by the process described in the body of this report; however, certain problems do arise as a result of the nature of TFE Teflon. The shrinkage of the film upon cooling, the inability of TFE to heal over cracks when heated, and the variability of its molecular weight and crystallinity with the sintering and quenching conditions are examples of these inherent characteristics which must be taken into account.

Compared with TFE, FEP Teflon is much easier to describe, at least to the depth attempted herein. It also is available from du Pont in several forms but only the films cast from dispersion, Teflon 120, will be discussed.

The question of the compatibility of FEP films revolves around the same unknowns as with TFE; the same sources of contamination exist. In most cases it is probable that FEP film retains more of the wetting agents because FEP is less permeable than TFE so driving them off through volatilization is more difficult. Pure FEP films are seldom used alone but rather FEP layers are added onto a TFE substrate in most cases. However, where only FEP is used, the primer layer can be made of the normal dispersion instead of the primer containing phosphoric and chromic acids which is used for TFE. Essentially all other compatibility problems are identical with those for TFE.

The structural nature of FEP is more definite because the average crystallinity of FEP which has not been thermally degraded is essentially independent of variations in processing. In other words, crystallinity will be between 40 and 57% regardless of the cool down rate after sintering. The average molecular weight is unchanged from that in the dispersion unless excessive sintering temperatures are reached. Dilectrix reports that their FEP film has an average tensile strength of 3300 psi, an elongation of 350% and a modulus of 70,000 to 80,000 psi. These values are substantially less good than for TFE film with the result that FEP is noticeably more prone to *pinholing*, an occurance of small fractures due to folding, than TFE. FEP is also more subject to *cold flow* than TFE. On the other hand, FEP retains its flexibility better at low temperatures than does TFE.

As mentioned previously, FEP film is substantially less permeable than TFE. A typical rate of N_2O_4 permeability is 2×10^{-5} psi/hr/mil at 70°F; this is about one-fifth the rate for TFE. Mainly because of this property FEP layers are laminated to TFE so that the permeability of the bladder will be reduced.

Fabricating FEP is considerably easier than TFE because it melts and flows. This means, for one thing, that mud cracking is less of a problem. Also, fast quenching is not important.

In comparing the two films, TFE and FEP, it is evident that neither is superior in all ways but, instead, each has its own advantages and disadvantages. TFE is the more durable but subject more to mud-cracking and greater permeation than FEP.

Several attempts have been made to secure a film combining the advantages of both TFE and FEP. The first major step in this direction was the creation of the so-called *laminate film* which has become the conventional form of Teflon bladder material. This kind of film is a composite consisting of discrete layers of TFE and FEP; usually the inside of the bladder is made of a few mils of TFE and the outside is a few mils of FEP, although more complex constructions are possible.[25] Such laminate films do, to a certain extent, combine the good features of the individual constituents. They have less permeability than TFE and more durability than FEP. But the inner layers of TFE are still prone to mud-cracking and severe *crease rolling* can cause delamination between the TFE and FEP.

Dilectrix personnel say that the physical properties of the laminate films can be closely approximated by a proportionate interpolation between the properties of the individual constituents. Figure A-2, a graph based on this assumption, shows the tensile strength, elongation, and modulus of laminate films as a function of the composition.[26] Figure 2, in the Report, is a cross-section view of a typical laminate film built up of a number of layers of TFE, visible in the picture, plus several layers of FEP.

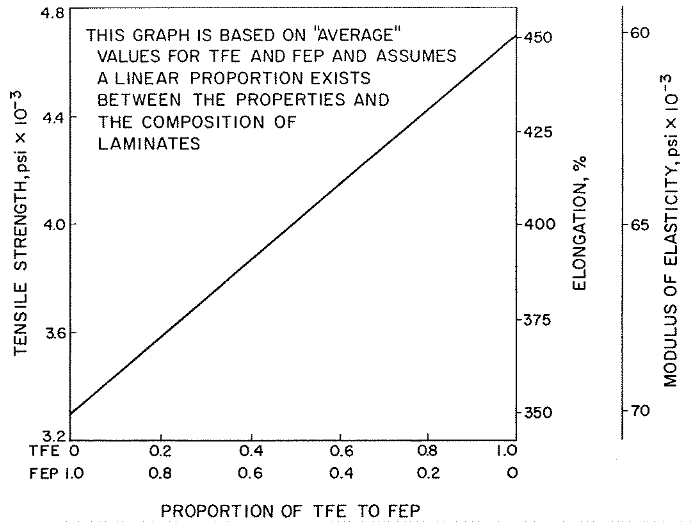


Fig. A-2. Physical properties of Teflon films

While the laminate films represented an advancement over the pure films, further improvements in film properties were still highly desirable, so experimentation continued. One of the better experimental films produced by Dilectrix is called a *codispersion.* Codispersions are mixtures of TFE and FEP that are sprayed and sintered in the same manner as the pure films. Optimum proportions of the two constituents are not established at this time for all applications but most of the more successful compositions tested to date have had less than 20% FEP. Samples containing 10% FEP have shown remarkable resistance to crease rolling damage compared to the conventional laminate film, Ref. 7. Unfortunately, the permeation rate through the codispersion is not noticeably better than for TFE film.

Still further attempts are being made to develop superior bladder films of Teflon but most of these contain foreign substances, for various reasons, and so are beyond the scope of this discussion; Ref. 1 and 2 describe some of these newer materials.

[25]The TFE is usually on the inside for the reasons explained in Section IV of this Report.

[26]Dilectrix personnel recommend that laminate films be no less than 50% TFE in order to attain reasonable durability.

APPENDIX B

Inspection and Quality Control

Careful inspection and quality control must be maintained throughout the entire fabrication process if high quality, defect-free bladders are to be produced. All materials, all processes, and all methods of measurements should be controlled by specification. Adherence to these specifications should be guaranteed by records and logs. At Dilectrix, a log sheet accompanies each bladder so that the operators and inspectors certify satisfactory completion of each step according to the listed formal specification. The following is a digest of the typical sequence of quality control measures.

Raw materials are procured by specification, not trade name. This can be an important factor in assuring consistency. For example, the average particle size in the dispersion affects the critical thickness of the film—smaller particles make for thinner critical thicknesses. Particle size also is one of the parameters determining the void content in the finished solid and void content, in turn, has a radical affect on the physical properties of the bladder.

The process of combining the raw materials into the spraying dispersion must be carefully controlled to assure exact attainment of the specified "blend". As mentioned in a previous section of this report, the optimum blend for a given type of application is determined by trial and error. Experimental blends are tried until one is found that yields a film with the desired tensile strength, elongation and flexural modulus. To do this, various blends are formulated with differing percentages of dispersion, wetting agents, water, etc.; each of these dispersions is sprayed and sintered into simple right cylinders, and then these test "pipes" are cut into specimens for the physical properties measurements. The bladder fabricator does not need to find a new blend formulation for each and every bladder order since, in most cases, he already knows from past experience that one of his "standard" blends will be suitable. In any case, whether a standard blend or a new blend is specified, each and every batch mixed for a given bladder order should be precisely identical in composition.

Batch to batch consistency is assured by accurate measurement of the amount, by weight, of each ingredient used and by checking the specific gravity and viscosity of the mixture. The practice at Dilectrix is to constrain the specific gravity within ± 0.001 and the viscosity within ± 5 cp of the blend specification values. As a further guarantee of batch-to-batch consistency, test samples of film, in the form of pipes, are made simultaneously from the new and current batches; these film samples are subjected to physical properties tests that must demonstrate a close similarity between the films before the new batch is released for production of bladders.

In addition to testing and filtering the ingredients and the mixed batch lot of dispersion, the dispersion is tested (for specific gravity and viscosity) and filtered again as the spraying pots are filled. The filtering is accomplished at Dilectrix by straining the dispersion through a glass fiber element rated at five microns. The chance of the dispersion becoming coagulated or contaminated in the spraying pot is very low since the pots are filled just before starting to coat the mandrel.

As mentioned before, the mandrel itself is subjected to close dimensional and surface finish control. The chief thing to be avoided is imperfections, in the surfaces to be Teflon coated, which would cause flaws to occur in the bladder. Pits or roughness in the weld seams may be caused by porosity or inclusions. Cracks are also of concern but proper design of the mandrel and handling of the welder should avoid this problem. Joints which obviate radical differences in adjacent cross-sections should be used. Also the use of aluminum with its high thermal conductivity minimizes the likelihood of hot spots developing which in turn lowers the chance of distortion. The inert gas (Heliarc or similar) welding process can produce weld beads of very high quality if the gas is kept very dry and the welding speed is carefully maintained.

Scratches and pits in the remaining areas of the mandrel must be avoided by inspection of the raw stock and careful handling at all times. Very shallow scratches can be buffed out but deeper marks may force scrapping the mandrel.

After the mandrel has been given a uniformly good finish, it must be thoroughly cleaned so that the dispersion film will coat it evenly. Such normally innocuous contamination as the oil in fingerprints must be removed;

a water-break test or ultra-violet light test can be used to detect oily film. After cleaning, the mandrels are handled with gloves, by the inside surface, with a fixture fitted into the neck, or in a protective polyethylene bag. Cleaned mandrels are kept in polyethylene bags, to prevent the accumulation of dust, until ready to be coated.

Three major factors are of special concern during the coating process: cleanliness, film thickness, and temperature. The first of these, the need for cleanliness, is primarily a matter of avoiding the inclusion of any foreign matter in the coating. Air-borne particles are likely to be organic substances which, if they settle on the mandrel or film, probably will be carbonized during the sintering. While no direct evidence is known at this writing which proves that small-carbon inclusions will be detrimental to the bladder's integrity, it is probably wise to avoid them.[27] At best, the inclusion may cause a void; at worst, the residual contamination may react with permeating propellant to generate heat and gas. Investigations currently under way at Bell Aerosystems Company for NASA under contract NASw-1317 may reveal whether or not these inclusions are the nucleation sites for local irregularities in the film.

Metal particles are definitely classed as troublesome. It is believed that they cause pinholes and cracks in the film; at this time the relationship between the size of metal inclusions and the severity of the resulting defects in the film is unknown.

A controlled environment and rigidly maintained operating procedures are the methods used to avoid contamination in the coating, drying and sintering areas. Dilectrix has combined these three areas into one facility which is environmentally controlled. Positive pressurization with filtered air, the wearing of *white* suits by the operators, and periodic house-cleaning are standard procedure. The room is of dustless construction. All of the sintering ovens are stainless steel lined and electrically heated.

Detection of inclusions within the film is by visual inspection. This inspection, which can also locate sizeable voids, is performed after each layer is sintered.

[27]Dilectrix has, in fact, produced a special Teflon film containing finely divided carbon. In their *Redundant* construction, the presence of layers of this film apparently contributed to the superior crease resistant properties of the laminate structure. See Ref. 7 for details of the construction, and test results.

Some of the techniques employed to control the thickness of the coating sprayed onto the mandrel were briefly mentioned in Section IV of this Report. That discussion emphasized the need to keep the coating thinner than the critical thickness in order to avoid mud cracking. This particular defect is thought to be a serious problem because of the evidence that many bladder failures occur in areas where the film's integrity is degraded by mud cracking.[28] Mud cracking is usually a localized condition which tends to occur where it is difficult to spray on an even coating; typically it is found on curved surfaces such as the ends and the neck. At this time, the quality control procedure for detecting mud cracked surfaces is a visual inspection after each coating is sintered.

Still another justification for using great care in controlling the evenness (or proper taper, in some instances) of the coating is the desire to obtain repeatable structural characteristics. While most Teflon bladders do fold in a random pattern, reproducibility of the structural characteristics of the wall from bladder to bladder does help minimize the scatter in such performance parameters as the differential pressure required to obtain a given degree of expulsion.

Checking the wall thickness is an "after-the-fact" matter; that is, after each coating has been sintered, the total wall thickness is measured at selected spots. The exact locations on the bladder surface where the thickness is measured is usually specified by the customer. Dilectrix is presently using a Dermitron instrument[29] for this purpose which works on the principle of inducing an eddy current in the mandrel. When the probe is placed on the film, the strength of the eddy current is proportional to the isolation between the probe and the mandrel produced by the intervening Teflon film. This device is calibrated prior to the measurement of each bladder wall; Dilectrix personnel estimated that it is accurate to within 1/10th of the dimension being measured. Figure B-1 shows the Dermitron being used to measure the wall thickness of a bladder.

The primary parameter to be controlled during the sintering process is the film temperature. It must be great enough to coalesce the particles into a strong film but low enough to avoid thermal degradation. Actual film

[28]Mud cracking is *not* believed to be the same phenomenon as orange peel which, as far as is known, is not connected with bladder failures.

[29]Manufactured by Unit Process Assemblies, Long Island, N. Y.

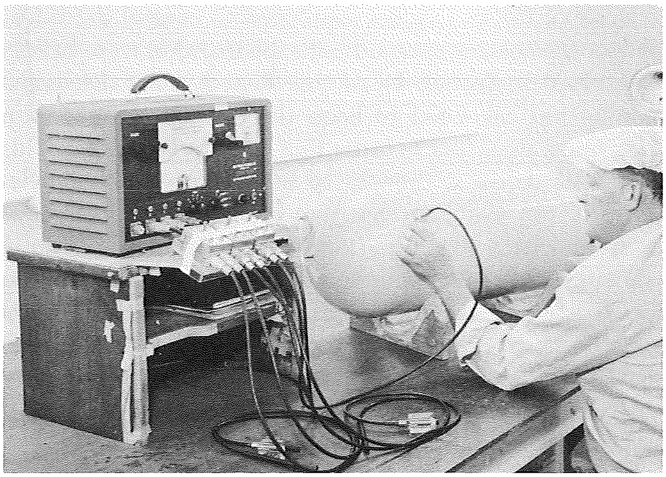


Fig. B-1. Checking the wall thickness of a bladder (photo courtesy Dilectrix Corp.)

temperature is not measured but, rather, several temperatures within the oven are monitored. Dilectrix has 14 thermocouples distributed within each of their ovens. These thermocouples are periodically calibrated to assure the accuracy of the readout. With these data, they can confirm that the temperatures throughout the ovens are within 20°F of the nominal value. The signal from a "nominal" thermocouple is recorded during each sintering operation to provide a permanent record of the temperature history of the bladders that are sintered. Accidental over-heating in case of a malfunction of an oven controller is avoided by having a thermocouple output connected to a automatic override switch which is set to turn off the electric power if the temperature reaches 720°F.

If any of the processes go awry[30] the coating is stripped from the mandrel. Dilectrix finds it necessary to strip about 25% of the mandrels during the spraying and sintering operations. After stripping, any mandrel found to be flawless can be recoated.

The most careful inspection naturally occurs after the bladder has been completed. At this time the entire surface is very thoroughly inspected for flaws and the final wall thicknesses are recorded. The external dimensions of the badder can be checked several ways but no definitive procedure is accepted by all customers at this time. One method is to inflate the bladder to a specified pressure and match its contour to templates. Another procedure calls for the bladder to be inflated inside a special tank made to the same dimensions as the propellant tank into which the bladder will eventually be installed; inspection holes in the special tank's walls allow a visual check to be made of how closely the bladder matches the internal contour of the tank.

Perhaps the most important check is the leak test. Two methods are currently in use. The first is the traditional method for testing automobile inner tubes—immersion in water. This is a manual operation in which the slightly inflated bladder is rotated by hand so as to bring all parts of the bladder successively beneath the surface of the water, which has a wetting agent added, while the operator looks for the telltale train of bubbles. Figure B-2 shows a bladder being leak tested by immersion in water; the transparent sides of the tank allow the inspector to see the submerged underside of the bladder. The second leak test method involves the use of a tracer gas (helium, Freon, etc.) to inflate the bladder and a detector, a mass spectrometer. Each square inch of surface is carefully scanned with the detector probe, a *sniffer*; when properly calibrated, the detector will audibly signal if any tracer gas concentration exceeding the selected limit is found. The equipment for performing this type of leak test is shown in Fig. B-3. Dilectrix reports that the water immersion method has found every leak located with the detector, with bladders pressurized to 0.5 psig with helium gas in all cases.

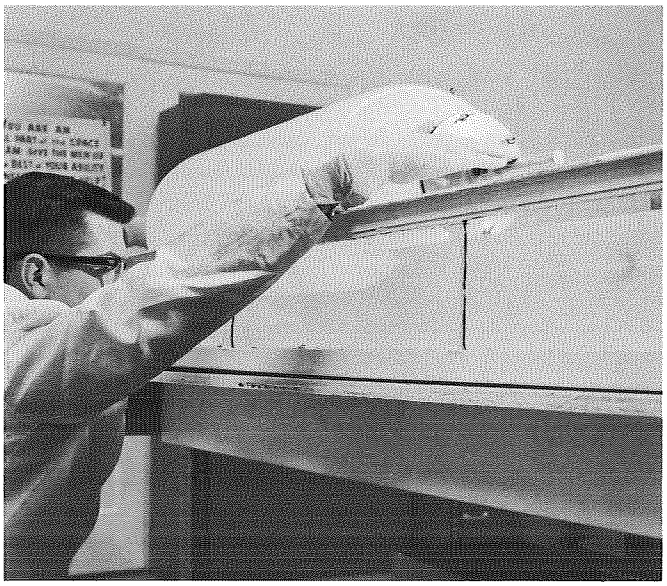


Fig. B-2. Leak testing a bladder by immersion in water (photo courtesy Dilectrix Corp.)

[30]If an inclusion is found, the thickness is found to be out of tolerance, the sintering temperature history is wrong, or if any other defect is found at this stage.

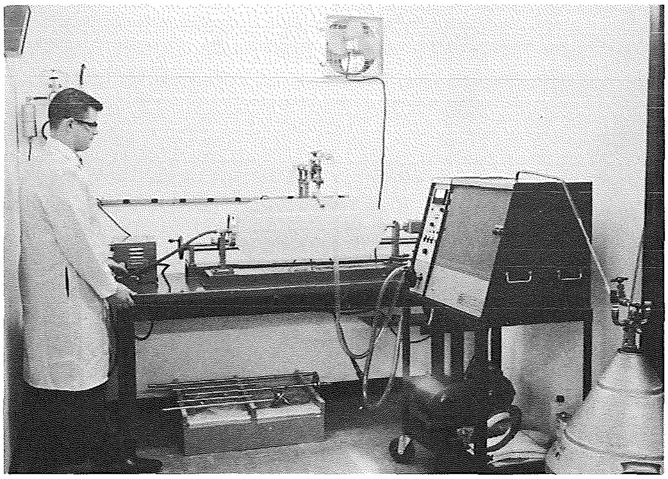


Fig. B-3. Mass spectrometer being used to locate leaks (photo courtesy Dilectrix Corp.)

Improved means of checking bladders for leaks are being investigated. One method suggested by Dilectrix would involve putting the bladder in a complete tank, inflating it, and measuring the total leakage *and permeation* through the bladder wall. As yet, there are no recognized procedures for measuring leaks at very low rates or calibrating the permeation through bladder walls.[31]

The finished bladder can not be thoroughly checked for physical properties using existing techniques since such tests are inherently destructive. For this reason an expendable *pipe* of Teflon film is fabricated simultaneously with each bladder. To assure exact duplication of the bladder's properties, these pipes are sprayed with the same pot of dispersion, dried side-by-side with the bladder, sintered beside the bladder, and have their mandrels etched out as the bladder mandrel is etched. When completed, the pipe is cut into strips lengthwise, along the circumferential direction; the strips are then subjected to test. It is assumed that the measured properties of the pipe film are close to if not identical with the properties of the bladder. This assumption has been proven correct by comparing test data based on strips cut from rejected bladders with data from the pipes that were made at the same time; the properties of the pipe film were essentially the same as those of the bladder film.

In the usual quality control operation, only three properties need to be measured to monitor film quality: density, tensile strength, and elongation. While density is not an important parameter, *per se*, it is an indicator of the molecular weight, crystallinity and void content of the film. The density measurements can be made easily by simply dropping a small piece of film into a transparent vertical cylinder which is filled with a graduated-density liquid. In this calibrated density-gradient column the sample will settle until it reaches the level where the liquid density is exactly the same as the film density; its specific gravity[32] can be read on an external scale by visual inspection.[33] Dilectrix is satisfied if the specific gravity of the sample measured by this technique is between 2.14 and 2.16.

Tensile strength and elongation can be measured on tensile test machines. Among others, the Instron Engineering Corporation, Canton, Massachusetts, makes a line of testers which are used for the precise measurement of the properties of thin films; this company issues many reprints of reports dealing with the finer points in securing accurate measurements of tensile strength, tensile modulus, elongation, etc. The acceptable range of values of these parameters is listed in the customer's procurement specification.[34]

Usually the last step in the quality control program at Dilectrix is the check to assure compliance with the customer's standard for the cleanliness of the finished bladder. Then as each bladder is packed for shipment, a copy of the inspection record is placed in an envelope in the shipping container.

While the current procedures provide considerable assurance of nearly uniform quality bladders, the industry is developing newer methods and tools in the hope that still better inspection and control can provide a stronger guarantee of highest quality. In addition to some of the shortcomings already mentioned, there are, for example, no recognized standards for checking surface smoothness, limiting the allowable degree of mud cracking, fixing the exact chemical composition of the film, etc. One attempt towards producing tighter controls in some of these areas is a cooperative venture between Dilectrix and the Bell Aerosystems Company. This particular effort was not far enough along at the time of the writing of this Report to include specific details here but it is understood that either photographs or actual film samples illustrating various defects are to be used.

[31] Bell Aerosystems and others are making such measurements but the procedures are still under development.

[32] Referenced to water.

[33] Ref. 8 and ASTM D 1505-57T.

[34] These and other properties of the sprayed and sintered film are discussed in Appendix A.

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ACKNOWLEDGMENT

The writer is very appreciative of the help he received from many sources in compiling the information contained in this Report. Personnel of Dilectrix Corporation and Bell Aerosystems Company were particularly generous in disclosing processes and data, supplying photographs, answering a multitude of questions and in reviewing the first version of the manuscript. Product data were contributed by the E. I. du Pont de Nemours Company and the Rohm and Haas Company. Several specialists at the Jet Propulsion Laboratory rendered considerable aid by getting tests performed, clarifying some of the technical aspects of polymer chemistry, and reviewing the manuscript.

The writer assumes responsibility for any errors which may have crept into the Report since time did not allow the final, revised manuscript to be rechecked by those who commented on the first version. Also, the rapid advancements in this field may have outdated several of the detailed descriptions of processes by the time of publication.