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Some Design Considerations, Large Expulsion Bladders for Nitrogen Tetroxide and Hydrazine

A. J. Bauman

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ABSTRACT

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The problems of chemical compatibility, permeation and folding of bladders are discussed in the context of the requirements of the Advanced Liquid Propulsion Systems (ALPS). An extensive review of the literature on subjects pertinent to these problems is summarized. Several experiments are described in which bladder materials were permeated by the fuel and oxidizer, and the meaning of the results discussed. Folded paper models illustrating some attempts to find a scheme for collapsing bladders in a controlled manner are shown; none were found suitable for the ALPS application. Three appendixes review the status of knowledge concerning oxidization resistance and permeation of polymers and the nature of Teflon. A lengthy bibliography and list of references are included.

*Author***I. INTRODUCTION**

This Report is a general discussion of certain ideas and problems involved in the design of large expulsion bladders for long-term use with nitrogen tetroxide and hydrazine. This Report is meant to serve as a basis for discussion, because the problem is not yet solved, and to provide a bibliography for future work. The point of view is generally that of an eclectic-minded materials engineer. Appendixes on polymer systems, permeation and Teflon, with associated bibliographies are included.

II. THE ALPS BLADDER PROBLEM

The ALPS¹ concept, (Ref. 1 and 2), includes propellant storage in two large hemispherical bladders placed back to back within a common pressure envelope. The bags are to be filled with N₂O₄ and hydrazine respectively and made to expel their contents into the combustion chamber by means of external pressure applied by gases generated in a separate catalytic reactor. The bags should withstand exposure to the fuel and oxidizer for a year at 20 to 50°C without degrading or causing the propellant to degrade. They should stand cycling without failure through at least ten expulsion/filling cycles of at least 99% expulsion efficiency. By implication, the bag material should be very thin, yet impermeable to the fuel and oxidizer.

¹Advanced Liquid Propulsion System.

III. N_2O_4 COMPATIBILITY

The basic design problem is that of the oxidizer N_2O_4 which destroys or weakens materials other than aluminum and the noble metals which come in contact with it (Ref. 3). Hydrazine is "compatible" with many polymer systems and is not a great problem in this sense. Propellant grade N_2O_4 often contains small amounts of water and nitrosyl chloride (Ref. 4) so that it is in effect *aqua regia* dispersed in anhydrous N_2O_4 . These traces are probably effective in loosening noble metals plated on materials, e.g., Teflon, in contact with it. "Compatible" polymers such as the fluorocarbons are all swelled and softened by contact with the oxidizer (Ref. 5 and 6) and no elastomers known are useful in it other than as mechanically confined parts such as O-rings (Ref. 7 and 8). Silastic LS-53, for example, swells about 300 vol. % in N_2O_4 . A recent report (Ref. 9) indicates that a cross-linked nitroso rubber does not swell much, but it would still make a very NO_2 permeable membrane.

These facts mean that we must design collapsible thin-walled rigid bags, not elastomeric bladders. There are theoretical reasons for thinking that no elastomer will ever be chemically suitable for use as an "impermeable" N_2O_4 bladder. This point will be discussed in the Appendix on polymers and N_2O_4 compatibility.

Now consider Fig. 1 which shows the appearance of an 18-in.-D Teflon-TFE test bladder which has been folded by external gas pressure. The fold pattern is made up of random three-cornered folds which tend to repeat themselves when the bladder is cycled. Such folds are regions of extreme shear stress and are therefore likely sites of failure. The particular bladder shown held only water throughout its test cycle but had it been filled with N_2O_4 its tensile strength would have been lowered by about 40% and its walls would have been swelled about 5 vol. % (Ref. 7). The permeability of a polymer membrane which is swelled by a permeant (gaseous or liquid) is often many orders of magnitude higher than that of one not solvated by permeant (Ref. 10). The bladder would have become very permeable to N_2O_4 , therefore. The fact that Teflon-TFE is swelled by N_2O_4 means that the polymer net is actually solvated by the N_2O_4 . This swelling phenomenon may be a principal reason for the failure of metallic platings on Teflon to act as permeation barriers to N_2O_4 when the Teflon side is exposed to the N_2O_4 . Otherwise integral coats may be torn by the swelling of the substrate. The effect of this swelling is no doubt enhanced by the markedly anomalous coefficient of linear thermal expansion of Teflon which undergoes a 5-fold increase between 106 and 160°C and then returns again to its former value at the 171°C mark (Ref. 11).

IV. PROPERTIES OF FUEL AND OXIDIZER

Let us now briefly summarize some of the properties of oxidizer and fuel so that we may later discuss the subject of compatibility.

Anhydrous N_2O_4 melts at $-11.2^\circ C$ and boils at $21.2^\circ C$. At $25^\circ C$ the equilibrium mixture is about 20% NO_2 which exerts a pressure above the $N_2O_4 \rightleftharpoons NO_2$ system of 1.2 atm (17.7 psia). About $140^\circ C$ the mixture is entirely NO_2 which with further rise in temperature decomposes to NO and oxygen, a process complete above $620^\circ C$ (Ref. 12). NO_2 reacts with unsaturated compounds to yield nitro alkyl nitriles and *vic*-dinitro alkanes (Ref. 13). It is a general oxidizing and nitrating agent strong enough to nitrate even paraffins. Commercial N_2O_4 contains up to 0.1 wt. % of water and up to 0.08 wt. % Cl as $NOCl$ (Ref. 4). One would imagine that polar surfaces (e.g., metals, glasses) immersed in this material would tend to adsorb a relatively concentrated surface coating of what is in effect dilute *aqua regia*. There are some indications that noble metal/Teflon laminates break down because of this phenomenon.

In theory anhydrous N_2O_4 should be an excellent general solvent. One may calculate its Hildebrand solubility parameter, δ_2 to be about 12 at $20^\circ C$ (Ref. 14). This parameter is in the range of 7-9 (cal/mol/cm³)^{1/2} for most solvents. Hildebrand lists only a few solvents (e.g., Br_2 , I_2 , SnI_4 , OsO_4 , $CHBr_3$, CH_2I_2) with δ_2 -values in this range. This solubility parameter is not perfectly related to the solvent power of the polar liquid and the values for ketones, alcohols, etc., are useless, as noted by Hildebrand. In general, if the δ -values for a polymer and a solvent are the same, the solvent will be an excellent one

for the polymer. One may estimate that the δ_2 value for Teflon is 5 or 6 units. Teflon is swelled by Freon 113 with a δ_2 of 7.2 and dissolves in perfluoroisooctane with $\delta = 6.0$.

N_2O_4 has a surface tension at $20^\circ C$ of 26.5 dynes/cm, a value closely approximate to that of most organic solvents. At $25^\circ C$ the material has a density of 1.4310 gm/cm³. The gas-phase NO_2 molecule is triangular in shape with a bond length of 1.20 Å and a bond angle of 130.4° (Ref. 12).

Hydrazine is an associated ionizing liquid which melts at $2^\circ C$ and boils at $113.5^\circ C$ (Ref. 15). It is miscible in water, which it physically resembles, in all proportions and its surface tension is 66.7 dynes/cm at $25^\circ C$. Aqueous solutions of hydrazine are quite unstable in the presence of catalytic metals such as silver, lead, copper in particular, molybdenum, or iron. Aqueous solutions of hydrazine are corrosive to aluminum alloys which otherwise are unharmed by the anhydrous base (Ref. 16). The methylhydrazines (e.g., MMH and UDHM) are reported to be more stable than hydrazine and compatible with many more materials, though they too are quite corrosive when wet. Anhydrous hydrazine is a good solvent for many inorganic salts, particularly the halides and nitrates. It has frequently been used as a plasticizer for rubber goods. Its Hildebrand solubility parameter is about 12, like that of N_2O_4 . The substance is both a reducing and oxidizing agent, depending on circumstances. It is compatible with a number of elastomers (Ref. 17) provided that common inorganic compounds such as zinc or cupric oxides are not used as fillers. Such metallic oxides induce autocatalytic decomposition of hydrazine (Ref. 15).

V. THE STANFORD-VANGO EXPERIMENT

With these properties of fuel and oxidizer in mind let us now consider the experiment of Stanford and Vango (Ref. 18), also with reference to the appearance of Fig. 1. Stanford and Vango interposed a Teflon membrane between the liquids N_2O_4 and N_2H_4 and found that it was quickly destroyed by a progressive blistering action within the membrane. A similar action was seen when NO_2 gas alone opposed a membrane in contact with N_2H_4 on one side. We carried out a number of such experiments and observed that blisters formed only on the NO_2 side of the membrane and worked their way through to the N_2H_4 side. Photomicrography of cross-sections of attacked Teflon film, Fig. 2, showed that the membrane failed at its edges where clamped. Evidently shear stress was greatest at that site and the swollen membrane tore mechanically. Evidently the Teflon-skived tape has a complex porous structure which readily imbibes N_2O_4 me-

chanically then weakens as the individual polymer particles sorb N_2O_4 molecularly. It is of some interest to note that published engineering data supports the idea that N_2O_4 is imbibed first within the pores of such "cast films," swelling the material in rough approximation to the pore volume. The N_2O_4 -wet membrane likely has a diffusion "constant" which is a function of its degree of solvent saturation. The phenomenon is best described in terms of the structure of Teflon cast dispersion which is discussed in Appendix C, on Teflon. The work of Crank and of Roughton appears to be pertinent to this phenomenon (Ref. 19 and 20).

Now consider the ALPS original design where a pair of hypergolic liquids are enclosed in collapsible thin-walled bags within a common pressure vessel. System failure is implicit in the paper-thin walls of the bags whose walls must be very thin if they are to have good expulsion properties. The Stanford-Vango experiment suggests that if the bladders were to be made of Teflon, blistering would result followed by sure system failure. Because all polymeric membranes are permeable to all liquids and gases to some extent, this conclusion applies to all polymer membranes. We will justify this conclusion further in the appendixes on compatibility and permeability (Appendixes A and B).

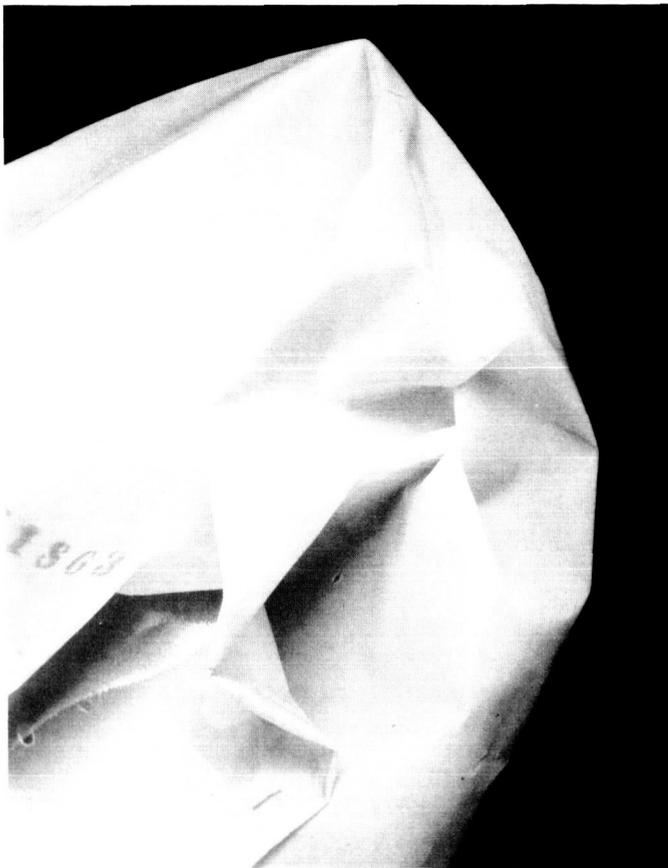


Fig. 1. Prototype ALPS bladder deformed by external gas pressure

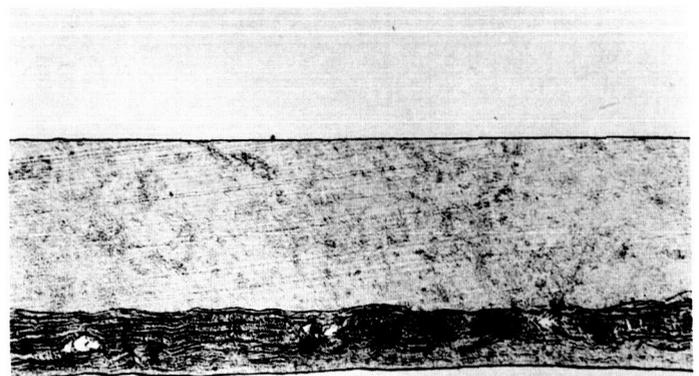


Fig. 2. Photomicrograph (300 \times) of Teflon-TFE cast film which has been sectioned normal to the axis of N_2O_4 penetration into N_2H_4

VI. CRITICAL HYPERGOLICITY LIMITS

A problem basic to the ALPS expulsion bladder program is that of the prediction of miscibility limits for hydrazine and N_2O_4 vapors below which spontaneous ignition will not occur. These limits have been defined for a situation in which a slug of N_2O_4 is quickly injected into a volume of hydrazine vapor (Ref. 21 and 22). If "enough" oxidizer is present, "instantaneous" ignition of the vapor mixture occurs. However, no studies appear to have been made on the situation where very slow mixing of dilute N_2O_4 and hydrazine vapors occurs. Such a condition might be met with if N_2O_4 vapor were to leak very slowly through a faulty valve or porous membrane into a space which held N_2H_4 vapor. As has been seen, the condition where N_2O_4 vapor diffuses through polymeric bladder walls into an N_2H_4 vapor-filled space does not occur in fact in the ALPS design. The Stanford-Vango experiments have shown that NO_2 vapor or condensed N_2O_4 liquid reacts within the (probably) hydrazine-wet membrane. No vapor/vapor contact appears to occur and the membrane is destroyed by the progressively-moving gas blisters described.

In the work done at the Bureau of Mines the interaction of N_2O_4 and N_2H_4 vapors below the spontaneous ignition values results in formation of "white solids." It seems likely that this material is a mixture of various nitrates of ammonia and hydrazine (Ref. 23). There seems no reason why such a mixing process should not proceed indefinitely, provided that the "white solids" do not themselves spontaneously ignite or explode. As long as the spontaneous ignition concentration is not met with or exceeded one would expect a slow leak of NO_2 into N_2H_4 to produce "white solids." The Bureau of Mines Reports also noted the formation of liquids and gases such as water, N_2O , N_2 and ammonia.

If the fuel-oxidizer mixture were saturated with inert gas at high pressure this would probably influence the spontaneous ignition levels. Furno (Ref. 24), et al., have noted that the addition of hydrocarbons to hydrazine vapor inhibits its flame propagation rate. It is possible that further work in this direction may suggest some way to raise the spontaneous ignition values of NO_2 and hydrazine. Perlee, et al., have observed that vapor/vapor hypergolicity occurs between NO_2 and N_2H_4 (Ref. 22). But at $25^\circ C$ in air there must be at least 9 vol % (or 2 mole %) of N_2H_4 present before spontaneous ignition occurs. The $NO_2 \rightleftharpoons N_2H_4$ reaction has been studied extensively and

inconclusively by Skinner, et al. (Ref. 25), whose spontaneous explosion data agreed qualitatively with those of Perlee. They noted that the reaction mechanism is extremely complex and is of the thermal type rather than of the chain branch explosive type. Under dilute conditions in argon below 2 mole % of each reactant, a pre-ignition reaction was observed which yielded principally ammonium nitrate and nitrous oxide. At 3 mole % of each reactant and above, the major gaseous products were nitrogen and nitric oxide with small amounts of nitrogen oxide and ammonia. At 5 mole % and above, spontaneous ignition occurred. Skinner also noted the presence of free hydrogen in the gaseous products. Hydrogen increased from 0.022 mole % for the 2 mole % reactant level to 0.91 mole % at the 4.0% reactant level. Skinner also found that high concentrations of several hydrocarbons inhibited the NO_2/N_2H_4 vapor reaction rate very slightly. Perhaps some sort of chemical means might be found which would suppress this reaction.

Considering these studies in the ALPS operational design context it is not clear what effect long term "sub-critical" leakage might have. One would assume that so long as the NO_2 and N_2H_4 concentration remained below 2 vol % only a slow accretion of ammonium nitrate or "white solids" in the ullage would take place. Perhaps the small amount of nascent elemental hydrogen formed would ultimately cause embrittlement of thin metal membranes or of structural elements. Yet Perlee's experimental conditions are not those to be met with in the ALPS design situation. The Stanford-Vango experiments showed that, for the case of polymeric bags, damage must be expected at a level much below that of vapor/vapor hypergolicity. It may be concluded that the Bureau of Mines work will be found pertinent to ALPS only in a clearly specified engineering situation. But it is not otherwise of much value in making general predictions.

Before it is concluded that the Stanford-Vango findings absolutely interdict the use of simple polymeric membranes for ALPS bladders, consider the general means of reducing permeation through polymer films. This will be discussed at some length in the appendix but, briefly: the polymer can be made crystalline, fillers can be added, or the polymer can be cross-linked. An attractive idea is that of adding flat impermeable filler particles in sufficient amount to retain overall mechanical flexibility yet to block permeation (Ref. 26).

VII. LEAFING PIGMENTS AND FILLED MEMBRANES

Aluminum paint owes its value as a corrosion-resistant film to the presence in the film of fine aluminum flakes oriented roughly parallel to each other. The parallel orientation of the flake is called "leafing" and it is made to take place by treating metal powders with a stearic acid solution in the process of their manufacture into flakes. The pigments fail to leaf at temperatures in excess of 150°F, the melting point of aluminum stearate. It may safely be assumed that "leafing" is a phenomenon related to the flotation behavior of surfactant-treated minerals (Ref. 27). The stearic acid chains adlineate as a monolayer and thus present a non-wettable CH_3 surface to the dispersing medium, or "vehicle." Depending on many little-understood conditions, the aluminum flakes "float" to the surface of the freshly painted film where they orient roughly parallel to each other like shingles on a roof. Paint films made with such leafing pigment are good water vapor barriers.

If Teflon films could be filled with "leafing" aluminum, it would be expected that their permeation behavior would be somewhat reduced (in the absence of swelling). Some pigment was made² which was coated with perfluorooctanoic acid, but it failed to leaf in the lowest-melting perfluoro-carbon polymer available, Vydax. Zisman (Ref. 28) has noted that the lowest-energy surface possible is that made up of ordered CF_3 groups (13 dynes/cm) and it was reasoned that perfluorooctanoic acid might adlineate well enough to give such a surface not easily wet by Teflon melt. In view of the high melting

temperature (250–300°C) and melt viscosity (10^8 – 10^{14} poise) (Ref. 29) of currently available fluorocarbon polymers, it does not now seem that this rationale was at all realistic.

On the basis of surface similarity to the polymer, fluorophlogopite water-ground mica was tested, as was a form of alumina which has been reported to form an "electrostatic bond" with Teflon (Ref. 30). However, on the basis of paint technology reports and a few others, it is not likely that one would reduce gas permeation of polymer membranes by more than 30% at most by the introduction of leafing pigments into their structure (Ref. 26). In view of the N_2O_4 -swelling of Teflon, this estimate for Teflon is probably optimistic.

We may fairly conclude that polymeric membranes alone are not suitable for ALPS program requirements, at least not for the design originally proposed. If an absolute permeation barrier were to be interposed between the bladders so that each would now occupy its own pressure vessel, these conclusions would not apply. Clearly, under a changed design like this the "Stanford-Vango" effect cannot occur and the possibility of vapor/vapor hypergolicity is prevented. Continuing with the original design in mind, however, the ALPS requirements apparently dictate a collapsible stiff-walled "bag" of some sort. If the bag leaks slowly or tears slightly, published work alone does not permit a failure prediction. Two ideas pertain to the problem: how shall we minimize the number of folds (stress points) in the bag and how shall we keep the concentration of vapors in the free system below hypergolic levels? The latter point will be considered first.

²Very kindly provided by Mr. D. R. French of Metals Disintegrating Company, Elizabeth, N. J.

VIII. REMOVAL SYSTEMS

In a sense, chemical removal systems for preventing the NO_2 permeation of Teflon have already been tried. Schuerch and Wituki (Ref. 31) made a quilted sandwich structure of Teflon film which enclosed NO_2 absorbents such as powdered charcoal. The test "membranes" were unhandily thick and the design did not eliminate the possibility of the N_2O_4 eventually saturating the "sandwich packing," even if it did not react (probably) explosively (Ref. 32 and 33) with it.

An efficient NO_2 removal system would permit one to use thin (useful) membranes for ALPS bladders by keeping NO_2 levels below even the "Stanford-Vango effect" level. If it were feasible to allow the damage to the Teflon, the hydrazine-backed Teflon membrane of the fuel bag would be a superb NO_2 -removal system. If one wanted to use such permeable material it would be necessary to consider the competition between the removal system and the "Stanford-Vango effect." Let us suggest a few ideas for the design of NO_2 -removal systems as a basis for discussion:

1. Magnetically cooled trapping (N_2O_4 melts at -11.2°C) would physically remove the gas.
2. Chemical gas-washing, e.g., by strong alkali solution such as KOH, would remove NO_2 . A glass trap containing concentrated aqueous KOH would be sparged by the recirculated gas stream which would vent through a microporous Teflon water barrier.
3. Catalytic conversion of NO_2 or N_2H_4 to light gases. Wikstrom and Nobe convert NO_2 to N_2 and O_2 by means of an alumina/cupric oxide catalyst (Ref. 34). The light gases formed could either be vented through the system's hull or tied up chemically as perhaps CuO or calcium cyanamide.

Filled membranes such as aluminum-filled Teflon have greatly improved tear resistance but are still quite NO_2 permeable. Evidently some composite metal-polymer or tear-resistant metal membrane is needed to satisfy the original ALPS design requirements. Only metals have nearly zero permeability to gases and liquids but thin metal foils tear easily. Let us consider a few methods of making flexible, impermeable membranes.

1. Aluminum sheet is treated by the Cahne method (Ref. 35) which leaves its surface etched with narrow-necked pores. Teflon dispersion sintered on such a surface is rooted mechanically in the pores

and is not affected by immersion in N_2O_4 . However, the Cahne process is not applicable at present to membranes less than about 1 mil thick. Such Teflon/aluminum membrane at present is thick and inflexible. Other reported Teflon coating methods (Ref. 36-38) do not produce coatings which resist N_2O_4 .

2. Etched Teflon is plated by various processes then treated to yield a lead or lead-indium composite (Ref. 39 and 40). The product is completely impermeable to anhydrous N_2O_4 liquid in a very long term static test. However, the stiff and rather thick material poses a difficult fabrication problem for bladder applications. The effects of long term exposure particularly of indium to commercial (wet) N_2O_4 have yet to be studied. If these objections can be overcome the "Vango-Krasinsky" process may eventually produce a suitable N_2O_4 bladder material. One could easily use a butyl-rubber bladder for the N_2H_4 which would otherwise be adversely affected by the catalytic effect of the lead.
3. Schonhorn's "molecular adhesive" process (Ref. 41) has been used successfully to fabricate strong aluminum/polyethylene bonds. Because extremely thin aluminum and polyethylene may be bonded by this means it may be of value to attempt the fabrication of multi-walled structures of this type. A structure made up of very many thin membranes should have excellent tear resistance (Ref. 42 and 43). Polyethylene is completely destroyed by long-term exposure to N_2O_4 , but this would only occur at pinhole sites in the aluminum. With very many very-thin metal membranes the probability of overall failure would be reduced, particularly with the polyethylene used as "bulking" between them (Ref. 42).
4. It is feasible to make thin flexible metal textiles (Ref. 44) such as those used for reentry drogues. Such textiles are currently in production. It should be feasible to use such a textile as a support for thin metal, e.g., stainless steel or aluminum, membranes by contact welding the two together by means of electron-beam welding.
5. It may be possible to fabricate a thin self-sealing membrane of a rather complex design. For example, consider the space between two thin aluminum membranes to be filled with tiny, highly magnetized

metal microspheres (alnico) mixed with a proper number of gelatin microcapsules which contain a special liquid metal alloy. The magnetic microspheres would, in a sense, constitute a thixotropic binder for the gelatin microspheres. The membrane could easily be deformed and, if quilted properly, would return to its former configuration. If N_2O_4 were to enter it at a pinhole, it would quickly attack the gelatin microcapsules and release their contents. The liquid alloy would wet the alnico microsphere "binder," thus sealing off the penetration. A bionic example of such a phenomenon is that of blood clotting round a puncture wound. Rather than magnetic powder, very fine silver wire could be used. This would amalgamate with an encapsulated liquid, e.g., mercury-thallium alloy.

6. The liquid leakage problem may be avoided by devising some sort of slurry monopropellant. Both N_2O_4 and N_2H_4 have been gelled by the addition of large amounts (8-12%) of colloidal silica and it may be possible to encapsulate N_2H_4 and disperse

it in gelled N_2O_4 . Unfortunately, impulse would be reduced and disaster ever imminent.

Prins and Hermans have shown that gas flux through the pinholes of metal-polymer laminates is proportional to the perimeter of the holes, rather than to their total area (Ref. 45). Evidently any sort of metal membrane design must take this into account and production quality control must emphasize membrane integrity.

In summary, thus far the ALPS design problem may be broken down for study into three operational areas.

- a. The interaction of the bladder material and the fuel or oxidizer.
- b. The vapor/vapor interaction of fuel and oxidizer within the bladder membrane or outside of it.
- c. The mechanical folding design of the bladder structure so as to minimize the number of folds and thus the probability of system failure.

IX. BAG FOLDING

The design of flat-folding thin-walled structures so as to minimize the number of folds is somewhat outside the scope of this discussion. However, it is a key element of the overall design problem and merits at least some cursory attention here. The subject has been reviewed by Forbes (Ref. 46) and recently from the ALPS viewpoint by Porter and Stanford (Ref. 18). The problem does not seem to be a popular one with mathematicians. Michael Goldberg³ has considered the general case of a flat-folding closed surface and noted that as the volume efficiency increases to 100% this requires the number of folds to increase exponentially towards infinity. His

designs (Fig. 3) resemble the familiar Japanese lantern. The straight-sided model buckles inward at 48 folds while the curved-sided model does this at 18 folds. Goldberg feels that stiff-walled manifolds like this probably can be made to collapse with not much more than 90% volume efficiency. Arthur H. Stone⁴ has very kindly provided the "screw prism" design shown in Fig. 4 which folds to collapse with 9 folds per segment. Possibly such a design might be used in some sort of ganged array. The problem of designing of such structure merits more attention. Numerous empirical examples of "solutions" to the problem exist in the patent literature; U.S. Patent 2,815,883 is typical (Ref. 47).

³Personal communication.

⁴Personal communication.

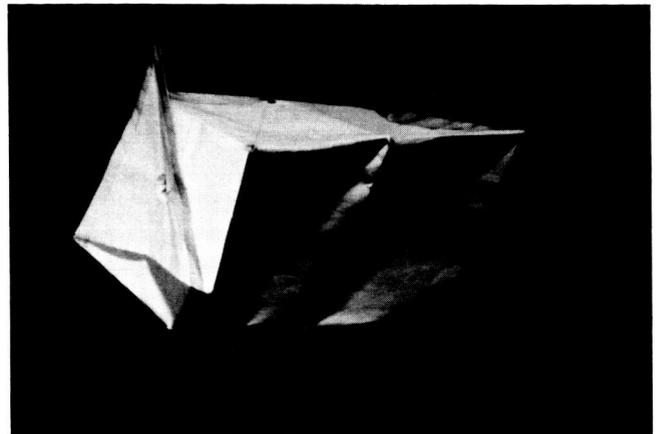
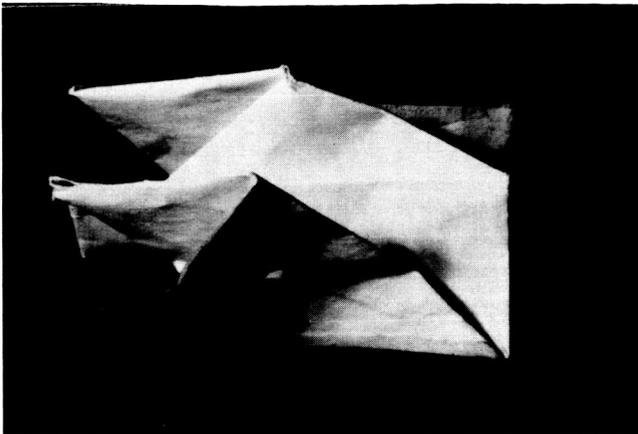


Fig. 3. "Goldberg's morningstars" idealized flat-folding structures with minimal fold numbers

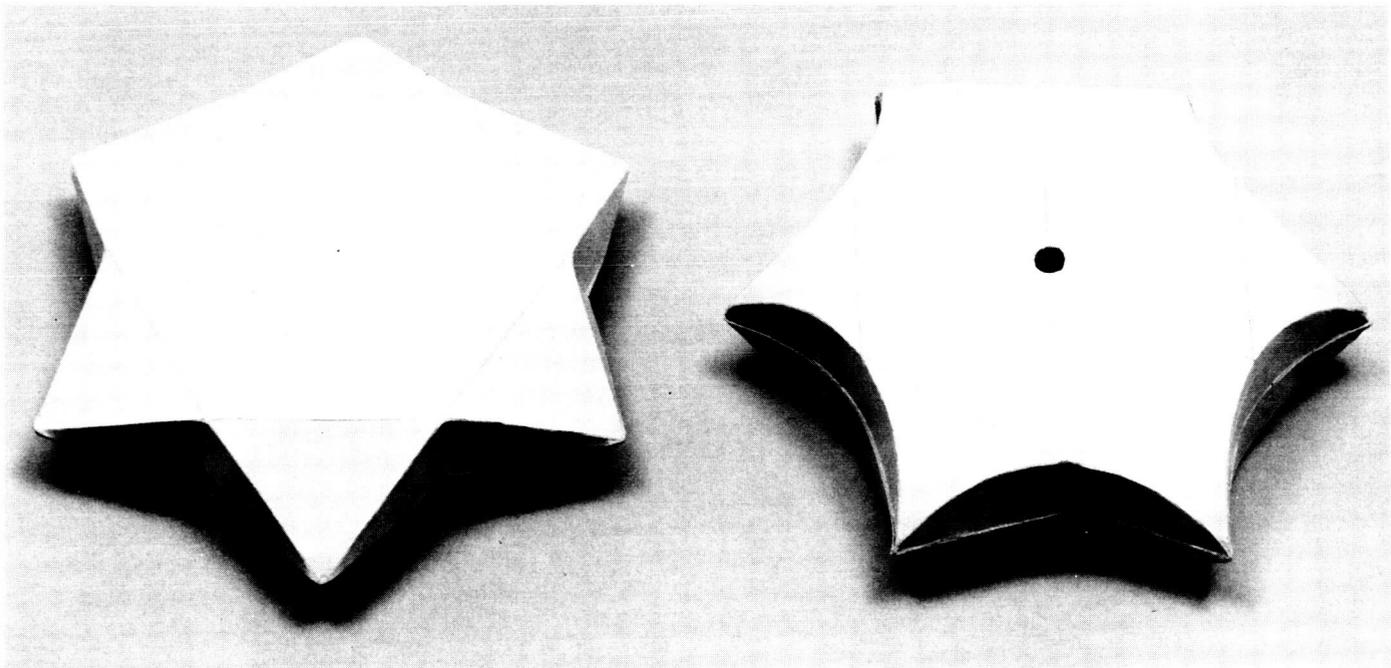


Fig. 4. "Stone's screw-prism" partially flattened and expanded views of a flat-folding structure with only 9 folds per segment

X. AN ADVANTAGEOUS DESIGN MODIFICATION

Vango⁵ has pointed out that a porous N_2O_4 -filled bag at zero g would, in a short time, become coated with a film of liquid N_2O_4 ; in effect there would be a large drop of N_2O_4 liquid which incidentally would include some membrane. The process would stop at this stage. In a gravitational field, of course, the liquid would leak out till the hydrostatic pressure in the bladder equalled that in the surrounding pressure vessel. This suggests that an improved ALPS design would include a permeation barrier between the two bladders.

⁵Personal communication.

XI. CONCLUSIONS

If the original ALPS design is to be kept, no polymeric membrane alone will be satisfactory. Only tear-resistant completely integral metal composite membranes will be satisfactory. The design should include a system, chemical or physical, to remove NO_2 from the ullage. If the original ALPS system is modified to include a permeation barrier between the fuel and oxidizer bladders, all danger of vapor/vapor hypergolicity will be removed. At zero g only a small N_2O_4 loss from the expulsion bladder would occur with the modified design and polymer membranes alone could be used. A number of designs of impermeable flexible membranes are suggested.

APPENDIX A

The Chemical Stability of High Polymers Toward Oxidizing Agents

Much of the literature on the oxidative degradation of polymers is summarized in Ref. 48 and 49 but very little is known of the process, relative to that of thermal degradation. One may make the general statement that at a given temperature the oxidative degradation of any material is always rapid compared with that of pure thermal degradation.

In the context of the general phenomenon of polymeric thermal degradation it may be mentioned that decomposition characteristics are the result of a competition between a "zip" (depolymerization) process and a transfer process. Simha (Ref. 50) has pointed out that oxygen acts as an additional source of free radicals by initiation and transfer and hence decreases the importance of the "zip" step. Other gases may produce catalysis or inhibition but generally, active atmospheres or solvents will randomize the chain process if it was not so to begin with.

The oxidation of complex molecules such as polymers is a very involved process but there is evidence that many of the direct oxidation reactions of small molecules also occur in reactions of polymers (Ref. 51). Hence, the discussion which follows applies at least in part to some of the features of monomer thermal degradation.

Although oxidative degradation occurs with either unsaturated or saturated polymers (or monomers) it is much more important in those that are unsaturated. The oxidation of an unsaturated molecule usually involves two phases—the peroxidation of the molecules followed by subsequent decomposition of the peroxides to give a multitude of decomposition products (Ref. 52). Often the overall rate depends upon the stability of the peroxides formed. The formation of the hydroperoxide groups is a chain reaction which leaves the unsaturation of the molecule unimpaired as long as no secondary decomposition reactions of the hydroperoxide groups take place. The double bond activates the methylene group in the β position and this group then serves as a point of attack for the oxidation. Groups such as methyl groups make adjacent methylene groups still more reactive. The methyl end groups also may be activated by adjacent aromatic substituents, in which case oxidation occurs at the tertiary carbons. Systems that are conjugated differ in that they do not usually form hydroperoxides even with methylene

groups in favorable positions. Instead, the trend is for the addition of oxygen at the ends of a diene segment, resulting in an oxygen bridge to give either transannular or polymeric peroxides. The hydroperoxides formed first in oxidizing systems decompose appreciably early in the reaction and the products may be still further oxidized. The overall products may then be enormously complex. The absorption of oxygen by unsaturated compounds generally is autocatalytic and it is usually accelerated by heavy metal impurities, such as iron or copper.

The oxidation of unsaturated polymers is accompanied by a deterioration of the mechanical properties of the polymer. For example, it usually becomes brittle as a consequence of the rapid increase in molecular weight. This shows that chain scission and crosslinking reactions either accompany or are a part of the oxidation process. It is believed that the reactions are brought about by oxidation of the double bond, followed by chain scission. Crosslinking is probably a consequence of the scission.

Saturated polymers are much less reactive toward oxidation than the unsaturated ones and their physical properties do not break down so markedly. Aromatic substituents have a strong activating effect on the β methylene groups, as in unsaturated systems, and peroxidation occurs at this point.

Hinshelwood (Ref. 48) has summarized the effects of the structure of saturated hydrocarbons on their oxidizability by considering the maximum rates attained by many compounds under similar conditions. His conclusions are as follows:

1. The rate of oxidation is greatly decreased by the introduction of extra methyl groups into a hydrocarbon. The mode of initial attack by oxygen which leads to the peroxide most effective in chain branching (auto-oxidation) is that made on a methylene group as remote as possible from methyl.
2. If there is no place to attack except a methyl group, there is a greatly reduced oxidation rate relative to that of a corresponding compound with a methylene group.
3. The substitution of chlorine increases the rate and acts by destroying the symmetry of any methyl

group into which the substituent enters, and by a direct inductive effect of the chlorine atom.

4. Carbonyl groups and amino groups increase oxidizability.
5. Ethers oxidize faster than paraffins.
6. For unsubstituted hydrocarbons, chloro compounds, amino compounds, and ketones, the rate increases greatly as the chain is lengthened. But with ethers,

the increase from ethyl ether to higher ethers is relatively small.

Overall, the rate of oxidation usually depends on the stability of the hydroperoxide formed. Electron-attracting substituents (e.g., carbonyl, halogen) increase the rate while the opposite is true for electron-repelling substituents such as methyl. In this context it is interesting that several halocarbons have recently been reported to explode in contact with N_2O_4 (Ref. 32 and 33).

I. SUMMARY

An ideal polymer system for use with N_2O_4 should be saturated and should have pendant methyl groups along the chain. It should contain no aromatic systems or other unsaturation nor any halogen other than fluorine.

II. THE FLUOROPOLYMERS

Systems which have exactly this design are the fluorocarbons, such as Teflon, which are marketed under many names: Table A-1 lists some typical chemical structures and Table A-2 lists some typical physical properties. These compounds can be liquids, greases, thermoplastics or elastomers. Although pure hydrocarbon polymers such as polyethylene are structured in agreement with our model, they do not promise long-time compatibility with N_2O_4 . Some branched polyethylenes are reported to have excellent short time N_2O_4 compatibility (Ref. 49), but only the fluorocarbons look good for long-term compati-

bility. Table A-3 lists some compatibility properties of typical fluoropolymer systems with various chemical solvents.

Polytetrafluoroethylene (Teflon) and polychlorotrifluoroethylene (Kel-F) were the first fluoropolymers exploited commercially and Teflon is to be given a separate section later in this report series because of its importance.

The next advance was the development of the fluoroelastomers (Silastics) to replace silicone rubbers in ap-

Table A-1. Chemical structures and trade names of fluoropolymers

Name	Mer	Trade name	Type
Polytetrafluoroethylene (TFE)	$-(CF_2CF_2)_n-$	Teflon, ^a Fluon ^b Fluon GP 1 ^b Algoflon D 60 ^c Soreflon D 119 ^d Fluoroplast-4 ^e	Thermoplastic
Polychlorotrifluoroethylene	$-(CF_2CFCl)_n-$	Kel-F, ^f Fluorothene ^g Polyfluoron Hostafflon ^h Genetron ⁱ Plastic HL ⁱ Halon ⁱ	Thermoplastic
Polyvinylidene fluoride	$-(CH_2CF_2)_n-$	RC-2525, ^j Kynar ^j	Thermoplastic
Polyvinyl fluoride	$-(CH_2CHF)_n-$	Teslar, ^b Tedlar ^a	Thermoplastic
Tetrafluoroethylene-hexafluoropropylene copolymer	$-(CF_2CF_2CF_2CF \cdot CF_3)_n-$	Teflon 100-X ^a Teflon FEP ^a	
Vinylidene fluoride-chlorotrifluoroethylene copolymer	$-(CH_2CF_2CF_2CFCl)_n-$	Kel-F Elastomer ^k Kel-F 500, ^k Kel-F 800 ^k Kel-F 820, ^k Kel-F 3700 ^k Kel-F 5500 ^k	Thermoplastic resins and elastomers
Vinylidene fluoride-hexafluoropropylene copolymer	$-(CH_2CF_2CF_2CF \cdot CF_3)_n-$	Viton A, ^a Viton B, ^a Viton A-HV, ^a Fluorel ^k Kel-F 214 elastomer ^l Fluorel K, ^k Fluorel 2141 ^k Fluorel KX, 2141 ^k	Elastomers

^aE. I. du Pont de Nemours & Co., Inc.
^bImperial Chemical Industries, Ltd. (England)
^cMontecatini (Italy)
^dSociete des Resines Fluorees (France)
^eRussian
^fAcme Resin Corp.
^gUnion Carbide & Carbon Corp.
^hFarbwerke Hoechst A. G. (Germany)
ⁱAllied Chemical & Dye Corp., General Chemical Division
^jPennsalt Chemicals Corp.
^kMinnesota Mining & Manufacturing Co.
^lM. W. Kellogg Co.

Table A-2. Typical physical properties of fluoropolymers

Property	Teflon TFE	Teflon FEP	Kel-F	Kynar	Tedlar
Structure	$-(CF_2-CF_2)-$	$-(CF_2CF_2CF_2CF_2CF_2)-$	(CF_2CFCl)	$-(CH_2CF_2)-$	$-(CH_2CHF)_n-$
Appearance and color	Translucent to opaque; white to blue-gray	Translucent to trans- parent; colorless	Transparent to translucent	Transparent to translucent	Transparent
Transition point, °C	327	285-295	216	171	
Max working temp, °C	250-300	225	200	—	204
Fabrication temp, °C	350-400	382-400	250-350	204-288	—
Preferred working range, °C	-80-250	-85-200	—	-70-150	-73-106
Viscosity of melt, poise	10 ²²	3-10 × 10 ⁴	10 ⁶	—	—
Elongation at break, %	50-400	250-330	20-80	300	110-260
Tensile strength, lb/in. ²	2000	2700-3100	5700	7000	9600-19000
Coefficient linear thermal expansion/°C	9.9 × 10 ⁻⁵ (25-100°C)	8.30-10.52 × 10 ⁻⁵ (-70-70°C)	7 × 10 ⁻⁵	15.3 × 10 ⁻⁵	5 × 10 ⁻⁵
Hardness, durometer D	55-70	55	75-80	80	—
Specific gravity	2.1-2.3	2.15-2.17	2.1-2.15	1.76	1.38-1.57
Refractive index	1.36	—	1.43	1.42	1.46
Volume resistivity, Ω/cm	10 ¹⁹	2 × 10 ¹⁸	10 ¹⁸	2 × 10 ⁻¹⁴	10 ¹⁶ -10 ¹⁸
Dielectric constant, 60 cps	2.0	2.2	2.65	8.4	6.8 (1 kc)

those with carbon-carbon backbones; those with semi-inorganic backbones; and those with inorganic backbones. In the first group are found the vinyl, the fluoro-aromatic and the perfluoroalkylamidine systems. In the second group are the semi-inorganic perfluoronitroso polymers

having NOCC or CNCN backbones, and in the last category are the silicones (Si-O-Si-O), the polysiloxanes (RSiO_{1-6}) and the polyfluoronitrides (NPF_2). These categories will be surveyed briefly in the order given. Table A-4 lists a few of their structures.

III. VINYL POLYMERS WITH A CARBON BACKBONE

Many aliphatic fluoro-carbon olefins have been made, polymerized and co-polymerized and the general rule, as we have seen, is that polymer stability, both thermal and chemical, is greatest in proportion to the amount of fluorine in the system; any extraneous abstractable hydrogen present lessens this stability. The stability of perfluoro-compounds is due to the high dissociation

energy of the carbon-fluoride bond and to the shielding effect and electronegativity of the fluorine atoms. Fluorine is slightly larger than hydrogen (0.64 Å vs 0.61 Å) and the C-C bond in fluorocarbons is probably a little shorter (Ref. 53) than that in hydrocarbon systems. Thus, the fluorine atoms form a compact sheath around the carbon chain to protect it from attack.

IV. THERMOPLASTICS

Polytetrafluoroethylene (Teflon)⁶ the most stable vinyl fluoro-polymer has a working range which extends to 300°C. It is attacked only by molten alkali metals, and at high temperature (300°C) by the tetrachlorides of the silicon group. It is swollen slightly (1-3%) by certain polychlorotrifluoro oils (Fluorolubes) and by the polyhalogenated ethane refrigerants (Freons). It is slightly soluble in perfluorinated solvents, from which it has been crystallized. Although Teflon is technically a thermoplastic, it cannot be fabricated by conventional techniques since its melt viscosity is about 10^{12} poise at 350°C, the working temperature (Ref. 54).

The copolymer of tetrafluoroethylene with hexafluoropropylene (FEP) was designed to be a low-melting elastomeric Teflon. Its melting temperature is about 290°C as compared to that of Teflon's 327°C and it can be processed by normal means.

Polychlorotrifluoroethylene (Kel-F) also has a low-melt viscosity and melting temperature due to the presence of the bulky (0.99 Å) chlorine atoms in the chain. The chlorine also makes Kel-F less stable to thermal and chemical degradation (Ref. 49) and it is swollen by some aromatic and halogenated organics. Less than a week of exposure to N_2O_4 causes Kel-F to lose 60% of its initial

⁶See Tables A-1-4 for trade names and structures of the mers.

tensile strength and 90% of its initial flexural modulus (Ref. 55). It also has a high thermal degradation rate at fabrication temperatures.

Polyvinylidene fluoride (Kynar) is degraded by fuming sulfuric acid and dissolved by acetone, dimethyl sulfoxide and dimethyl acetamide. It loses about 10% of its tensile strength in N_2O_4 , but swelling data is not available at this time. Kynar reacts with primary amines such as

n-butyl amine (and probably hydrazine) to form dark, brittle products. Its melting temperature ($171^\circ C$) is lower than that of either Teflon or FEP but it is good indefinitely at $150^\circ C$ and for short times at $260^\circ C$.

Polyvinyl fluoride (Tedlar) is an unknown quantity at this writing, but it is likely to have even poorer solvent resistance than Kynar in view of the presence of H atoms on the chain.

V. FLUORO-ELASTOMERS

The chemical structures of the fluoro-elastomers developed thus far are summarized in Table A-4. The copolymer of vinylidene fluoride with hexafluoropropylene (Vitons, Fluorel) is available in several grades which are produced by varying the polymerization conditions and monomer ratios. The elastomeric character of these copolymers is due to the marked asymmetry produced in the chain by the pendant trifluoromethyl groups, as well as to the flexibility introduced by the methylene groups. These materials may be cross-linked at the methylene sites by means of β -radiation, peroxides or

polyfunctional amines. They swell as much as 300% in N_2O_4 at room temperature (Ref. 49) but quickly lose the N_2O_4 imbibed when removed and recover their physical properties almost completely.

The copolymer of vinylidene fluoride with chlorotrifluoroethylene (Kel-F Elastomer) is also sold in several grades based on the proportions of monomers used. Some of these such as Kel-F 5500 have good short-time resistance to N_2O_4 ; incidentally, this material detonates in the presence of chlorine trifluoride (Ref. 53).

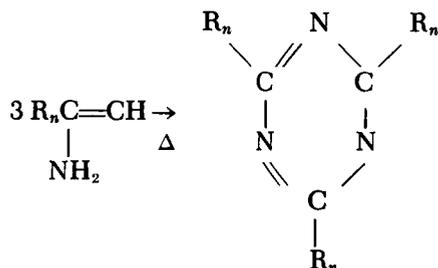
VI. POLYFLUORO-AROMATIC SYSTEMS

Many prospective monomers based on more-or-less fluorinated aromatic systems have been prepared but no polymers based on them are commercially available. Such polymers show great promise theoretically of having

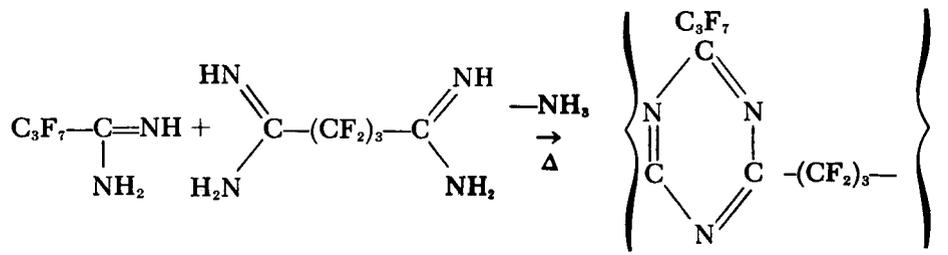
extreme thermal stability. It would be necessary to perfluorinate them, however, if they were to be even slightly compatible with N_2O_4 and even then the aromatic bonds would be sites of attack, thus ruling them out.

VII. PERFLUOROALKYLAMIDINE SYSTEMS

Perfluoroalkylamidines, $R_nC (:NH) NH_2$, where $R_n = CF_3$, etc., are prepared by the addition of ammonia to perfluoroalkyl cyanides. They trimerize when heated to yield the 1,3,5-tris-(perfluoroalkyl)-triazines (Ref. 56).



The reaction extended to diamidines yields condensation polymers which are said to have good thermal and probably good chemical stability. The pyrolysis of perfluoroglutarodiamidine or perfluoroadipodiamidine yields materials said to be resistant to strong oxidizing agents and stable in air at 350° for long periods. Condensation of these diamidines with heptafluorobutyroamidine yields elastomers, with the probable structure below (Ref. 57 and 58).

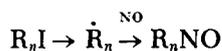


VIII. POLYMERS WITH SEMI-ORGANIC BACKBONES OF THE -N-O-C-C- OR -C-N-C-N- TYPES

A new type of polymer system has resulted from the copolymerization of fluoroalkyl nitroso-compounds with olefins. The —N=O group acts like a —C=C— group so that the polymer repeating unit is usually

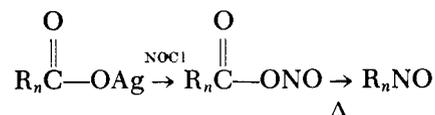


The fluoroalkyl nitroso monomers (such as trifluoro-nitrosomethane) are easily prepared by photochemical reaction of the fluoroalkyl iodide with nitric oxide (Ref. 59):

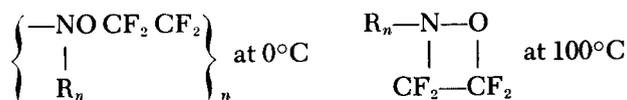


The iodine produced is taken up in mercury.

Recently (Ref. 60) an even cheaper route:



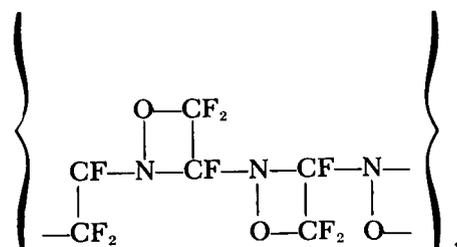
has been developed. Perfluoroalkylnitroso monomers react with olefins, such as tetrafluoroethylene, to yield a 1:1 copolymer and an oxazetidine (Ref. 61).



IX. POLYMERS WITH INORGANIC BACKBONES CONTAINING SILICON

The polymers are either oils, waxes or elastomers depending on the olefin used and the exact conditions. Their resistance to oxidizing agents is said to be good but the trifluoronitrosomethane-tetrafluoro-ethylene compound 1:1 is quickly degraded by N₂O₄ at room temperature (Ref. 49). This copolymer is a white, opaque elastomer stable to prolonged heating in air at 180°. Since the olefin or nitroso compound can be of any type, this reaction is quite general and such elastomers made from other perfluorinated compounds may be promising. Vango (Ref. 62) has recently noted that a proprietary cross-linked TENME elastomer has little swell in N₂O₄. A British Patent (789,254, January 15, 1958) was taken out by ICI, but apparently the commercial production of these materials is not attractive. Another polymer system

in this group is that formed from the homopolymerization of a nitroso-compound which is unsaturated, for example CF₂:CF N:O. This compound forms a polymer via oxazetidine ring formation which has a C—N—C—N—C— structure.



The inorganic polymer systems in use at this writing are chiefly the silicones and the polysiloxanes. They have good thermal stability but poor resistance to solvents, especially at elevated temperatures. For that reason, as mentioned, the fluoro-silicon rubbers (Silastics) were developed in an effort to improve matters.

The precursors of the silicones $(R_2SiO)_n$ and the polysiloxanes $(RSiO_{1-6})_n$ are the halides, R_2SiCl_3 and $RSiCl_3$, respectively. The polyfluoroalkyl silicon chlorides can be prepared from the halides by a free radical route to yield compounds with the fluorine either α , β or γ to the silicon

atom in the $\overset{\gamma}{C}-\overset{\beta}{C}-\overset{\alpha}{C}-S_1$ system (Ref. 61). Only the compounds which have the α or β fluorines are hydrolyzed by bases presumably by nucleophilic attack on the silicon which is activated by the attached electronegative fluoroalkyl group. Silastic LS-53 is a polymer prepared from a gamma-fluorine monomer and it has excellent thermal and chemical resistance. It swells up to 300% in N_2O_4 but, like the Vitons, quickly returns to normal in every way when removed (Ref. 49). For that reason, LS-53 is widely used as an O-ring material for applications in contact with N_2O_4 . The silicone rubbers disintegrate quickly in contact with hydrazine.

X. INORGANIC POLYMERS, OTHER THAN SILICONES

For some time there has been an extremely active research effort directed towards the synthesis of inorganic polymers for high temperature applications. However, such systems exhibit, generally speaking, poor resistance to hydrolytic attack. They do not look at all promising at present for use with N_2O_4 .

APPENDIX B

Permeation Through Membranes

Permeation of gases and liquids through membranes has been studied extensively and several excellent reviews and books have been published (Ref. 63-65). Gaseous permeation through polymeric membranes has received the major share of attention, though liquid permeation studies (e.g., water desalinization) (Ref. 66) are becoming more popular. Recent reviews cover most of the liquid permeation literature (Ref. 67 and 68). If liquid N_2O_4 contacts a Teflon membrane, it quickly swells it and the "saturated" membrane likely offers little resistance to permeation. This is liquid/liquid diffusion. The situation is like that of "self diffusion" in the liquid. The liquid permeation rate through a polymer membrane is independent of inert gas pressure over the liquid and of hydrostatic liquid pressure. The rate increases linearly with temperature and decreases inversely with membrane thickness. In comparison, gas permeation through membranes obeys an Arrhenius temperature-rate law and is directly proportional to the differential gas pressure across the membrane. Van Amerongen's classic paper (Ref. 69) describes the influence of polymeric membrane molecular structure on gaseous diffusion rates. Briefly, any obstacle to the gaseous molecular diffusion, e.g., cross-linking, crystallinity, fillers, decrease diffusion rate. Plas-

ticization, whether "built in" or added by solvation, e.g., water vapor swelling of cellophane, increases the diffusion rate. One may not predict the permeation behavior of a polymer membrane from a knowledge of its chemical nature alone.

The reader should consult the reviews noted, especially that of Muraca, for a more complete understanding of the polymer permeation phenomenon. This phenomenon is of only peripheral importance to the overall ALPS design problem because metal membranes are very nearly completely impervious both to gases and to liquids, and this, of course, fulfills the ALPS requirements. If, as Vango has pointed out,⁷ the basic ALPS design is changed so that a metal barrier separates the bladders, then permeation will stop at zero-g when a "skin" of permeant covers the bladder surface.

The appended Bibliography is fairly complete through 1963 and some of 1964. The few references published thus far on Teflon permeation behavior will be found in Appendix C, on Teflon.

⁷Personal communication, S. P. Vango.

APPENDIX C

Teflon

Teflon particles are made by the emulsion polymerization of monomer in the presence of (usually) a non-ionic wetting agent. The particles resemble striated peanuts when viewed by the electron microscope and they are about 200 $m\mu$ in diameter (Ref. 70, 71). The polymer is uniquely entirely crystalline (Ref. 72) and that prepared from melt exhibits a typical metallic fracture surface (Ref. 73-75). If an aqueous dispersion of particles is sprayed onto a surface it may subsequently be baked to sinter the particles into a contiguous coating (Ref. 76, 77). It is unlikely that the particles sinter other than at touching asperities (Ref. 78) in view of the remarkable viscosity of the melt (Ref. 79). Teflon melts at 327°C but must be raised to 380°C in order to form a true homogeneous melt (Ref. 72). During the sintering coating operation the wetting agent system stabilizer pyrolyzes to give the coat a brown color. The process has been applied to the manufacture of propellant bladders, protective and anti-slip coatings and capacitor foil, to mention only a few applications. The beginner in the field of Teflon coating should expect little advice or help from any organization now in the propellant bladder field. The overall technology is described roughly in typical Ref. 80, but actual practice can be made

successful only by trial-and-error. Because each successive Teflon coat is placed on the one beneath it the maximum practical thickness possible is about 30 mils because of thermal degradation of the first layers applied. Mud-cracking and holidays are the sure result if much more than ¼- to ½-mil thick coats are applied (Ref. 81).

The long term permeation of N_2O_4 through Teflon sheet has been described (Ref. 82). The results suggest that a three-stage process occurs: initial mechanical (Knudsen) flow; swelling and blocking of pores; and final molecular diffusion.

Few studies of Teflon *per se* permeation behavior have been reported (Ref. 83). The copolymer of tetrafluoroethylene/hexafluoropropylene melts at 285°C to a true melt of 10^8 poise and has been treated by conventional molding techniques.

JPL Search No. 370 covers the literature on Teflon through October 1961; Search 369 covers Kel-F, similarly. The annual R&D conference proceedings, sponsored by the Office of Naval Research, summarizes technological applications.

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