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CHAPTER 15

Microbial Deterioration of Polyurethane Systems

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The susceptibility to microbial deterioration of polyurethane formulations used in rigid foams, as coating for fabrics in ponchos and in bladders for storage of hydrocarbon fuels, as insulation for electric cable, and as a rubber have been studied. Techniques used in evaluating the formulations for different uses are noted. The fallacy of attempting a meaningful evaluation of systems where exact formulation ingredients and their chemical nature are not known is emphasized along with the need for establishing the susceptibility or resistance to microbial attack of each component of the formulation. As a first choice toward definition of component susceptibility, polyurethane polymers have been synthesized and studied in an unformulated state. Selected diisocyanates have been reacted with a number of polyols representing four classes of polyethers and one class of polyesters. These have been evaluated in culture tests to determine their ability to sustain fungal growth. Some of the findings are discussed to illustrate the requirement for the proper choice of the polymer itself in providing fungal resistant polyurethane materials. Detailed relationships between structure of the polymer and microbial susceptibility which form the basis for this choice will be reported elsewhere. The need for incorporation of fungicides in the formulation is discussed.

Polyurethanes have found widespread acceptance for a variety of applications both in the civilian economy and the military system. Dombrow (1965) estimated the civilian market for flexible and semiflexible urethanes to be 144 million pounds in 1963, and predicted 269 million pounds consumption for 1968. The corresponding figures for rigid urethane foams were 32 million pounds for 1963 and 88 million pounds for 1968. He classified uses according to industry including the furniture, bedding, textile, rug and floor underlay, automotive, packaging, refrigeration, construction, and container industries. No similar figures were given for polyurethanes used in rubbers, adhesives, coatings, and fibers. In military application, polyurethanes may be used for such diverse purposes as an internal coating for aircraft fuel tanks, insulation for electric wires, in coated fabric for a ground cover or lightweight poncho, as a component for a 5000-barrel capacity flexible fuel tank bladder, as a disposable air drop container for water, as a building material for temporary shelters, as a potting compound for electronic components, in various rubber configurations as components of missile and ordnance systems, and as a coating to provide a moisture vapor barrier for electronic panels.

This versatility is a reflection of the chemistry and technology of urethanes. Dombrow (1965) defines polyurethanes as polymers produced by addition reactions between polyisocyanates (difunctional or higher) and hydroxyl-rich compounds (at least two hydroxyls per molecule) such as glycols, polyesters, polyethers or castor oil. Saunders and Frisch (1962) note that polyurethane polymers contain a significant number of urethane groups but may contain, in addition, aliphatic and aromatic hydrocarbon,

ester, ether, amide, and urea groups. Urethanes are esters of the unstable carbamic

acid or amide esters of carbonic acid: $\text{>N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$. The urethane group is represented

as: $\text{>N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$. The urethane linkage results most readily through the reaction of the isocyanate function $-\text{N}=\text{C}=\text{O}$, with an alcohol group ($-\text{OH}$). The simplest form, a linear polyurethane derived from a dihydroxy compound, $\text{HO}-\text{R}-\text{OH}$ and a

diisocyanate, $\text{OCN}-\text{R}'-\text{NCO}$, is represented by the general formula: $(-\text{R}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-$

$\text{NH}-\text{R}'-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-)_n$. The general formula indicates that the hydroxyl-containing component as well as the isocyanate can be changed in a variety of ways to bring about polymers of different characteristics. Hydroxyl-containing compounds used include adipate esters of diols and triols, polyether adducts derived from propylene oxide and diols, triols or higher functional alcohols, castor oil and its derivatives. Isocyanates may include aliphatic or aromatic diisocyanates with tolylene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI), 3,3'-dimethyl-4,4'-biphenyl diisocyanate (TODI) and 1,5-naphthalene diisocyanate (NDI) among those encountered. By increasing the functionality of the reactants, or altering the chemical groups between the urethane linkages, for example, many possible polymers can be tailored to meet differing physical requirements. Saunders and Frisch (1962) note that the polyurethanes are almost unique in that cross linking, chain flexibility, and intermolecular forces can be varied widely and almost independently. Depending on the type of urethanes, in addition to the diisocyanates and hydroxy-containing compounds, one may find in formulations such additives as blowing agents and cell-size regulators, catalysts, surfactants, pigments, fillers, plasticizers, fire retardants, and releasing compounds.

Application or fabrication technology of polyurethanes also provides additional versatility to the production of materials in different forms. Each of the applications has its own technology that can be manipulated to produce desired characteristics. Prepolymers, semi-prepolymers, and "one-shot" methods are employed; "milleable gums" or casting systems may be used to process rubbers; foams may be produced by adding water or by employment of blowing agents; characteristics of coatings may be altered by varying proportions of reactants or varying timing of application or sequence of formulation ingredients.

We could continue on and on listing the almost innumerable facets affecting the nature of polyurethanes. It should be clear however, that the polyurethanes represent an extremely complex, everchanging, and almost infinite number of formulations. Patent literature alone gives ample evidence of this with literally hundreds of patents issued in the United States (Saunders and Frisch, 1964).

Microbial deterioration of materials, once a vague subject to most materials engineers, today almost routinely receives consideration from those who have been educated by the hard and economically damaging lesson taught when its role has been ignored. Concern for microbial degradation of urethanes for civilian use was shown by Wyandotte Chemicals Corp. (1962) in an evaluation of polyether sealing compounds for clay or concrete

sewer pipe, drain pipe, or other underground service. Five polyether urethanes were formulated using dibutyltin dilaurate, stannous octoate, or tertiary amine groups as catalysts. The polyols included a triol, diol, glycol, and a tetrol containing tertiary amine groups. These varied in molecular weight from 4000 to 500 and were reacted with 80/20; 2,4/2,6 TDI. Cast test specimens were subjected to a number of biological test procedures including incubation in a broth medium and soil burial for 3-4 weeks. The tests presumptively indicated resistance of these formulae to microbial degradation.

Testroet (1963) and Ossefort and Testroet (1966) studied the performance of polyester and polyether rubbers in high humidity environments for military applications. The study was prompted by the failure of polyester urethane items in this country and abroad. Its purpose was to determine the cause of the decomposition of the rubbers to a tar-like consistency in a very short time. The study indicated that two factors were involved in the observed polyester failures: 1) water and moisture vapor induced hydrolysis consisting of scission of main chain ester groups resulting in reversion of rubber, and 2) breakdown of the polymer through fungal activity. Polyethers showed greater resistance to the humid environment than polyesters although the use of additives such as diisocyanates, fungicides, and carbodiimides (carboxylic acid scavengers) improved "hydrolytic" stability under certain conditions. These authors attributed initial fine cracking in the rubbers to fungal activity. They supported their case by a number of observations but no detailed data were presented to prove the point conclusively. Nevertheless, the supposition that fungi could be responsible was a logical one and they must be given credit for recognizing the possible involvement of microorganisms. They noted that sulfur-cured systems tended to be more resistant to fine cracking than peroxide-cured systems and they also indicated that they had evaluated a number of fungicides and had found pentachlorophenol, 0.5-3.0 pph rubber, to be the most effective although it was detrimental to the rubber. These adverse effects on physical properties tended to obscure absolute clearcut judgment in using a fungicide to prove the role of microorganisms.

Kanavel et al. (1966) studied the resistance to fungal attack of sulfur- and peroxide-cured polyether and polyester millable polyurethanes. The measurement of resistance was the extent of growth or inhibition of growth of *Aspergillus niger* ATCC 9642 in a 7-day plate test. Ingredients in the formulation, as with the previous study of Testroet (1963) and Ossefort and Testroet (1966), were commercial preparations with no identification of the chemical nature of some of the ingredients, particularly a number of fungicides. The authors found that sulfur-cured polyether and polyester millable urethanes, as tested, inherently possessed some fungal inertness. The peroxide-cured polyether and polyester millable urethanes did not inherently provide fungal inertness. They concluded that fungicides were required in both sulfur- and peroxide-cured polyether and polyester formulations to provide optimum fungal resistant properties. None of the fungicidal compounds tested retained its fungicidal properties after exposure at 100 C for 3 days, and most of the fungicides had adverse effects on the formulations. The fact that sulfur-cured formulations showed some resistance is understandable since such sulfur containing compounds as the zinc salt of 2-mercaptobenzothiazole, mercaptobenzothiazole disulfide, and mercaptobenzothiazole were included in the formulations, in addition to sulfur alone. As the authors point out, their results should be considered only as a screening test and fungal growth alone is not sufficient evidence of breakdown of the formulation. It is significant, however, that they did note growth on polyether urethanes and that they recognized the need for physical testing after extended exposure to the activity of fungi.

Concurrently with the studies cited, our own laboratory established a broad program to determine to what extent microorganism attack should concern us when polyurethanes were being used. The program developed progressively and broadly as polyurethanes were increasingly considered for end item use.

In 1960, during the development by the Natick Laboratories of new concepts in shelters, rigid foamed polyurethane was being evaluated for use as a construction material (Fig. 1). Among other factors, its ability to withstand microbial damage was considered. A prototype foam, having the composition given in Table 1, was evaluated in the laboratory as a poured sample. The blowing agent in this instance was CO₂ formed in the reaction between water and TDI. The shelter illustrated in Figure 1 was constructed from a foam applied with a spray gun as a two component system with freon

TABLE 1. *Composition of rigid foamed polyurethane^a*

Part A	
Quadrol (N,N' tetrakis-2-hydroxypropyl-ethylenediamine)	27.24 Kg (60 lb)
Castor Oil AA	18.16 Kg (40 lb)
Diallyl phthalate	9.08 Kg (20 lb)
Silicone L-520	5 g
N-methylmorpholine	4 g
Water	25 g
Part B	
Toluene diisocyanate (80/20; 2,4/2,6) (TDI)	
Parts A & B mixed in a ratio of 80:69	

^a Formulation data provided by Dr. George Murray.

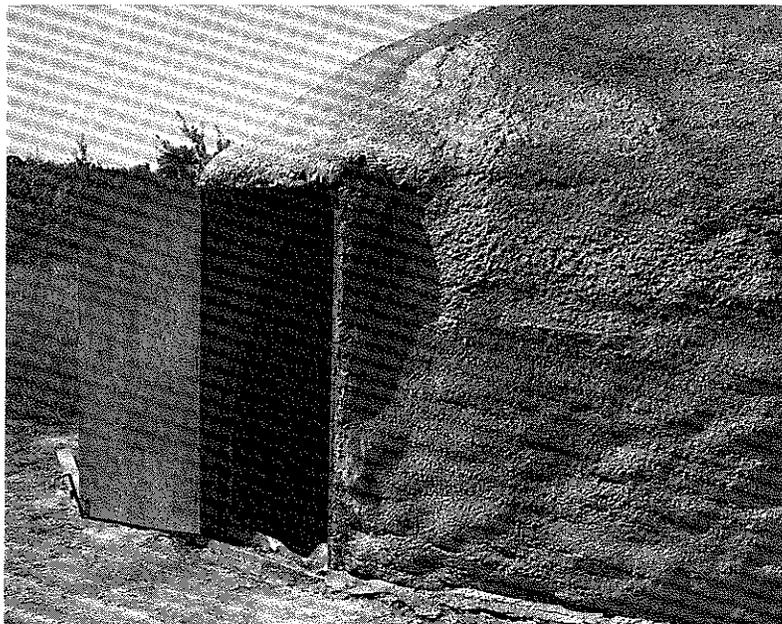


FIG. 1. Rigid foam polyurethane used in shelter construction.

as a blowing agent. This material was judged to be resistant to microbial damage after being held in a tropical chamber, 30 C, 85-95% relative humidity, for one year. In fact, the foam has not been damaged by either microorganisms or high humidity after 7-years' exposure in the chamber, nor has the prototype shelter shown any structural degradation after 7-years' outdoor weathering at Maynard, Mass. Obviously, the one ingredient of prime concern, castor oil, had completely reacted to form a nonsusceptible polyurethane with no unreacted castor oil residuals available to support growth.

This study gave rise to no concern because of the excellent performance of the material. However, the report by Testroet (1963) raising the question of susceptibility of polyurethane rubbers did interest us. Through the cooperation of Rock Island Arsenal, we were provided representative samples of some of these rubbers in sheet form and studied them to determine their ability to support fungal growth.

The formulations for the samples are listed in Table 2. The samples were washed in a lukewarm detergent solution, rinsed thoroughly, immersed in 95% ethyl alcohol, drained, dipped in acetone, and air dried over clean white tissue. All handling of the samples after the detergent wash was done with forceps. Separate samples were sterilized by exposure to a mixture of 85% ethylene oxide and 15% inert gas at 60 C for 180 minutes or by autoclaving at 121 C for 15 minutes. Nonsterilized controls as well as the sterilized samples were subjected to ASTM D1924-63 (1963) plate test at 30 C for 3 weeks.

All of the test samples supported growth, with growth increasing steadily during the incubation period. However, Figures 2 and 3 show that there were obvious differences in the amount of growth on different samples. The polyether (Code Z51C) was significantly less susceptible than the polyester formulations. The polycarbodiimide hydrolysis inhibitor did not affect fungal growth. Pentachlorophenol slowed the rate of growth but did not prevent the growth from being judged as heavy. Both ethylene oxide and autoclaving procedures had some effect on initially retarding growth, but differences in growth rate between sterilized and unsterilized samples disappeared at the end of the incubation period.

Conclusions that could be drawn from this study were not extensive and could be applied only to the specific formulations themselves. No physical testing was carried out on the 2 x 2-inch samples after plate test so that we could not state absolutely that

TABLE 2. *Formulations of polyether and polyester urethane vulcanizates^a*

Compounding Ingredients	Z51C	Z129	Z129G	Z129M17
Adiprene C (polyether urethane elastomer) ^b	100			
Genthane S (polyester urethane elastomer)		100	100	100
Stearic acid		0.2	0.2	0.2
Di Cup 40C (dicumyl peroxide, 40% active)	2.5	5	5	5
Philblack O (carbon black)	30			
Philblack A (carbon black)		35	35	35
PCD ^c			4	
Pentachlorophenol				1
Cure time (minutes) and temperature (°C)	45 min/154°	30 min/160°	30 min/160°	30 min/160°

^a Samples and formulations provided by Z. T. Ossefort, Rock Island Arsenal.

^b See Saunders and Frisch (1964), Appendix F, for commercial sources.

^c PCD is a polycarbodiimide hydrolysis stabilizer that is not identified chemically by its manufacturer.

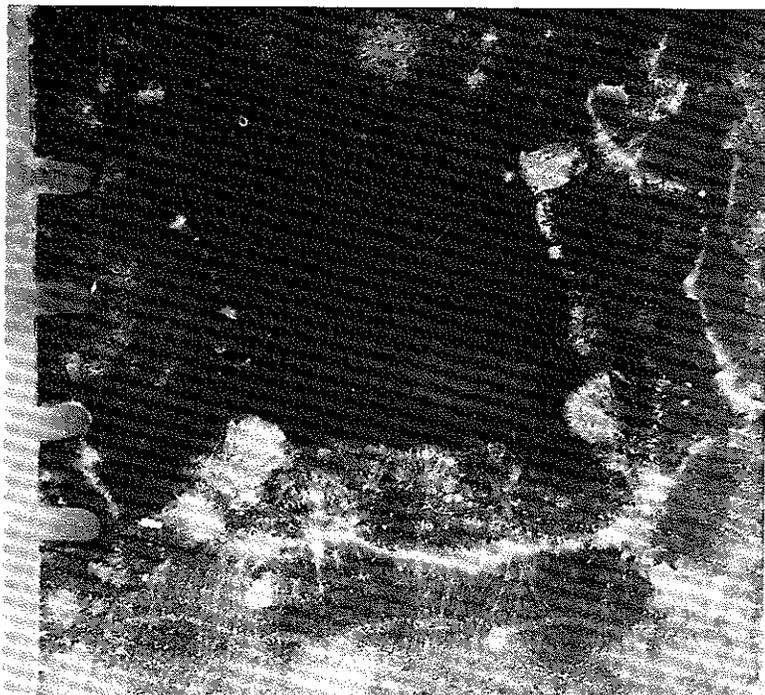


FIG. 2. Fungal growth on polyether elastomer (Code Z51C).

fungi degraded the vulcanizates. Nor could we say that polyethers are more resistant than polyesters, since the polyether formulation omitted stearic acid as an ingredient and the difference in growth between the respective formulations could be related to this rather than to the polymer. Although Testroet (1963) and Ossefort and Testroet (1966) indicated that pentachlorophenol prevented fungal deterioration, it would appear from our results that this fungicide may not be truly effective in the concentrations used. Thus, this particular study did not shed much light on the question of fungal deterioration of the polyurethane systems except to indicate that they all supported growth and therefore might be damaged by fungi. The study merely bolstered the implication made by Testroet (1963) and Ossefort and Testroet (1966) without any unequivocal proof.

However, other studies were being made of a number of different commercial thermoplastic urethane elastomers being considered as insulating materials for tropical electrical cables. These studies shed additional light on the role of fungal deterioration of elastomers. As is generally the case with commercial formulations, exact information was not available concerning the chemical identity of the formulation ingredients. The elastomers were generally identified as polyethers or polyesters with some containing a

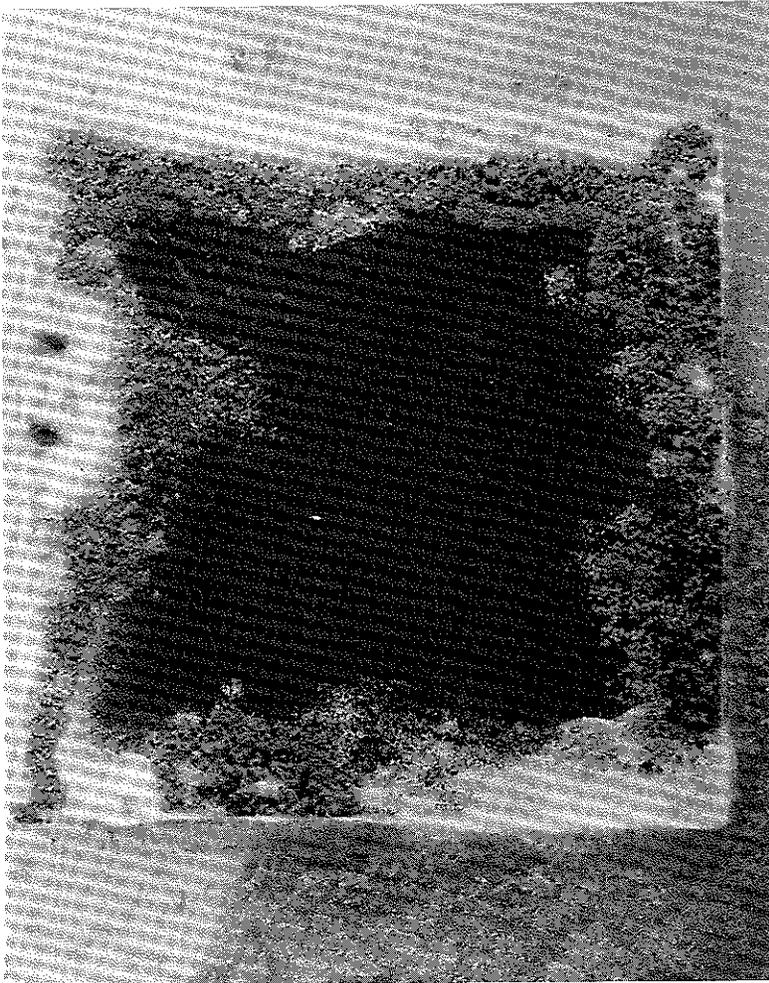


FIG. 3. Fungal growth on polyester elastomer (Code Z129).

fungicide, ultraviolet inhibitor, and an hydrolysis inhibitor. Depending on the formulation, it was determined that the ultraviolet inhibitors were either carbon black or 2,5-dihydroxy-4,4'-dimethoxybenzophenone, the fungicide for one formulation was an ester of 3,5-dimethyl-4-chlorophenol and the hydrolysis inhibitor a polycarbodiimide. Unsterilized specimens, subjected to the plate test previously described, showed moderate growth after 2 weeks' incubation with no significant difference between any of the formulations. Duplicate sets of specimens were subjected to soil burial for periods up to 3 months following Method 5762 of Federal Specification CCC-T-191b (1953). Tensile, ultimate elongation, 100% and 300% modulus, and Shore A hardness measurements were made on triplicate samples for each burial period using ASTM methods (1964) and are listed in Table 3. Physical testing following soil burial revealed practically no change in the polyether formulations, C and D, while the polyesters, A, B

TABLE 3. *Physical properties of polyurethane elastomers before and after soil burial*

Material ^a	Property	Original	After Soil Burial for:		
			1 Month	2 Months	3 Months
A. Polyester, No additives (avg. thick: 0.086 inch)	Tensile, PSI	3200	2100	1850	2250
	Elong, ult, %	650	580	550	500
	100% mod, PSI	500	450	500	600
	300% mod, PSI	900	850	900	1050
	Shore A hard.	79	77	77	80
B. Polyester + polycarbo- diimide & 2,2-dihydroxy 4,4-dimethoxy- benzophenone (avg. thick: 0.099 inch)	Tensile, PSI	4400	2350	2150	2400
	Elong, ult, %	570	500	480	490
	100% mod, PSI	750	650	750	800
	300% mod, PSI	1100	1000	1000	1200
	Shore A hard.	79	77	87	89
C. Polyether + 5 phr ^b carbon black (avg. thick: 0.056 inch)	Tensile, PSI	4950	4800	4300	4900
	Elong, ult, %	800	810	740	780
	100% mod, PSI	850	900	900	950
	300% mod, PSI	1450	1500	1500	1600
	Shore A hard.	89	86	86	88
D. Polyether + carbon black (avg. thick: 0.078 inch)	Tensile, PSI	3300	3000	3000	3300
	Elong, ult, %	770	750	790	740
	100% mod, PSI	600	600	600	600
	300% mod, PSI	900	950	950	1000
	Shore A hard.	84	84	83	84
E. Polyester + 1 phr of an ester of 3,5-dimethyl-4- chlorophenol, 1.4 phr carbodiimide 0.5 phr carbon black (avg. thick: 0.082 inch)	Tensile, PSI	3900	2450	1500	1700
	Elong, ult, %	540	490	410	410
	100% mod, PSI	650	650	600	700
	300% mod, PSI	1100	1100	1050	1200
	Shore A hard.	86	86	86	88

^a Materials and formulations were provided by D. Lichtenstein, Fort Monmouth, N. J.

^b phr = parts per hundred rubber.

and E, showed significant changes in tensile strength and ultimate elongation after 3 months.

It may be assumed that three degrading phenomena can occur during soil burial: hydrolysis, oxidation, and microbiological breakdown. Ossefort and Testroet (1966) demonstrated that a polycarbodiimide could stabilize polyester vulcanizates against hydrolytic effects. Table 3 shows that including a hydrolytic stabilizer in the polyester formulations did not prevent physical changes. Assuming that the stabilizer was used at a proper concentration, hydrolysis as one of the principal degrading factors of the polyesters can probably be eliminated. Dombrow (1965), Saunders and Frisch (1962; 1964), and Ossefort and Testroet (1966) note that urethane elastomers have excellent resistance to oxidation. Saunders and Frisch (1964, p. 42) state that incorporating the ether oxygen in the backbone of a polyether aliphatic polymer lowers its oxidative and thermal stability but that polyethers may be protected against oxidative degradation by stabilization with alkylated phenols, phenothiazine or aromatic amines. They further state (p. 48) that oxidation of polyester chains is usually not significant. It seems improbable therefore, that oxidation was a factor in causing physical changes in the systems studied. Thus, by process of elimination it appears that microbial activity was a prime factor in causing physical changes in the elastomer during soil burial. The fact that changes occurred in the presence of a fungicide does not alter this conclusion since the plate tests showed that the fungicide did not inhibit fungal growth.

The search for definitive identification of microbial activity as a causative factor in the breakdown of a polyurethane system was carried on further during the development

of a very lightweight, 3 oz/yd² polyurethane-coated nylon ground cover for use by the individual soldier. The item was loosely identified as a rip stop nylon coated on one side with a polyester polyurethane, composition unknown. The material supported moderate fungal growth after a plate test of 2 weeks. Soil burial studies followed by hydrostatic pressure measurements, Method 5512, CCC-T-191b (1953) were made to determine functional damage to the system. Samples of the coated fabric were sterilized with ethylene oxide as described earlier and then buried in 1.5-liter Fernbach flasks half filled with soil. One flask with its soil had been autoclaved for 3 hours at 121 C while the other flask was used without sterilization. After 2 weeks incubation at 30 C, 95% relative humidity, samples from the autoclaved soil showed no change in hydrostatic pressure while those in the unautoclaved soil showed a drop from 80 lb/inch² to 0-15 lb/inch². Tests of the ethylene oxide treated control samples (without soil burial) showed no change in hydrostatic resistance indicating that the physical change was not due to ethylene oxide treatment. Samples of the fabric exposed to 71 C and 100% relative humidity in a humidity chamber dropped to 70 lb/inch² after 5 days and to 40 lb/inch² after 12 days.

Therefore, it was concluded that the polyurethane coating could be damaged by microbial or hydrolytic activity. Hydrolytic damage was judged not to have occurred during soil burial. Were hydrolytic activity a factor during soil burial, a drop of hydrostatic values should have been observed for the samples buried in autoclaved soil as well as for those in the unautoclaved soil. It was also noted that hydrolytic effects, as evidenced by decreased hydrostatic test values, were not observed at the lower temperature encountered during soil burial, 30 C. This is similar to the observation of Ossefort and Testroet (1966) who noted no short term hydrolytic softening changes in their elastomers at 10 C, 27 C and 38 C. At these temperatures they observed what they considered to be biologically-caused cracking which did not occur with sulfur-cured compounds or when pentachlorophenol was added to the formulation. Cracking of the compounds did not occur at temperatures in excess of 49 C.

It has been argued that autoclaving the soil also altered its chemistry and that changes in the polyurethane coating were therefore unrelated to microbial activity. Samples of a similar coated fabric subjected to plate tests and incubated at 30 C for 3 weeks showed a 65% loss in hydrostatic test values, from 100 lb/inch² to 35/inch² while showing slight to moderate growth. This loss cannot be ascribed to chemical effects of soil because there is no soil present in a culture test. Neither can the loss be attributed to hydrolysis since hydrolytic activity has not been observed at 30 C in a short time interval. Therefore the change must be due to microbial activity alone. This was confirmed when a duplicate set of samples was sterilized with ethylene oxide and incubated under sterile conditions in the plate test, omitting the test organisms. Hydrostatic pressures under these conditions showed no significant change, from 100 lb/inch² to 96 lb/inch² definitely proving that the change was due to microbial activity.

Resistance to microbial breakdown can also be a function of handling or processing procedures. As has been shown, the polyester urethane-coated nylon ground cover supported fungal growth and showed no resistance to microbial attack as determined by loss in hydrostatic pressure after plate and soil burial tests. However, change in processing conditions resulted in a different situation.

A urethane prepolymer was milled with pigments and mold release compounds, hard paraffin or stearic acid, on a 2-roll rubber mill by a commercial coater. The pigmented mass was dissolved in a suitable organic solvent to proper consistency and applied by

conventional floating knife technique to one side of a nylon fabric. In an effort to increase the abrasion resistance of the fabric the usual procedure was modified by "surface isocyanating" of additional samples of the coated fabric; this was done by adding to the solvent treated pigmented mass 20% MDI and knife coating another layer of this preparation to the coated fabric. The addition of isocyanate in definite proportions to the mix caused cross linking which increased abrasion resistance, due to a harder surface, without affecting flexibility. When these samples were tested after incubation for 3 weeks in a plate test and after soil burial for 2 weeks significant improvement in retention of hydrostatic pressure was noted for the "surface isocyanated" sample (Table 4). Substituting a one-coat thermoset cross linked polyester polyurethane for the 2-coat system also resulted in resistance (Table 4). In this system, 0.7% copper 8-quinolinolate, incorporated in the formulation as the dry powder, inhibited surface growth. This is a commonly observed example of the fact that the presence of surface growth does not necessarily mean functional damage to the system. The foregoing study, coupled with the study showing resistance to microbial activity of the cross linked, rigid foamed polyurethane used in the shelter discussed earlier, points to the possibility that cross linking plays a role in providing resistance to functional damage by microorganisms.

In the case of a coated fabric, the occurrence of surface growth per se may not be of primary concern to the materials engineer. In other instances, such as electronic circuitry, surface growth is not desired and military requirements are becoming more rigid and demanding in their insistence on systems that do not support fungal growth. It is a common practice to apply a coating to electronic components to provide moisture vapor protection to the circuits to prevent moisture shorting and corrosion of the system. The coatings must not support fungal growth. Among coatings that have been used is a clear modification of a polyester polyurethane formulation coating MIL-C-27227A (1965) specified by the Air Force for use on external surfaces of aircraft. The coating is applied from a spray gun after the polyester component is mixed with a TDI component. Pigments, ultraviolet absorbers, solvents, silicone preparations, stearated aluminum silicate, and cellulose acetate butyrate are among the ingredients that may be included in the formulation, depending on use. In addition, the specification notes that grinding and dispersion of pigment in the "resin" solution is improved by the addition of soya lecithin. Figure 4 illustrates fungal growth and corrosion on an electronic com-

TABLE 4. *Resistance of polyurethane coated nylon to microbial activity*

Coating	Surface Growth	Average Hydrostatic Pressure		
	Culture Test ^a	Original	Culture Test ^a	Soil Burial
Thermoplastic polyester	Light	100	35	35 ^b
Thermoplastic polyester "Surface isocyanated"	Light	100	87	73 ^b
Thermoset cross linked polyester	Light	100	100	97 ^c
Thermoset cross linked polyester + 0.7% copper 8-quinolinolate	None	100	95	98 ^c

^a 3-weeks' incubation, 30 C.

^b 2-weeks' incubation, 30 C.

^c 6-weeks' incubation, 30 C.

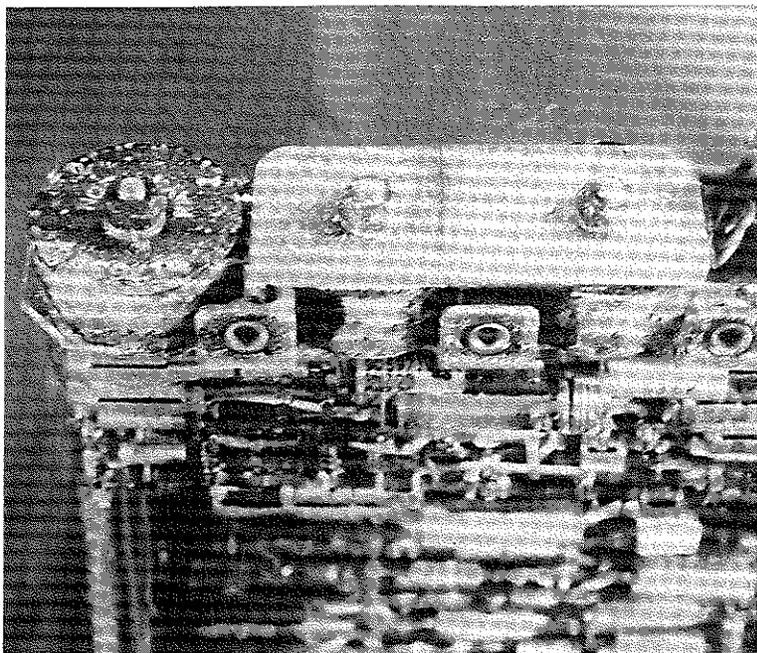


FIG. 4. Fungal growth and corrosion on polyurethane-coated electronic module.

ponent returned from field use that was coated with this polyester formulation. Subsequent testing of the coating freshly applied to aluminum strips in plate and tropical chamber exposure confirmed that the coating supported fungal growth. In this instance the coating should have been suspect since ability to support growth and be affected by such growth in a liquid hydrocarbon fuel/water environment has been reported for a somewhat similar coating by Miller et al. (1964), Cooper et al. (1965), Reynolds et al. (1967), and Crum et al. (1967).

There are other applications of polyurethanes in fuel handling equipment in addition to the use of a polyurethane as an integral aircraft fuel tank coating. Nylon, coated on both sides with a heavy coating of polyurethanes, is being used in the fabrication of 1250-5000 barrel capacity collapsible liquid fuel storage tanks and reservoirs (Fig. 5), and polyurethane-coated Dacron has been studied as a material for lightweight fuel delivery hoses. The microbial concerns here involve exposure of the outside coating to soil contact and the interior coating to a fuel/water environment. Accepting the thesis that polyether polyurethanes are more resistant to environmental effects, including microorganisms, and polyester polyurethanes are resistant to liquid fuels, end item engineers fabricated a system for study where the inner coating of the material was a polyester formulation and the outer coating was a polyether formulation. After 6-months' soil burial, the polyester side showed cracks and delamination of the coating from the fabric. The polyether side showed no change. The system was further evaluated using a modified ASTM Method D814 (1955) test apparatus to simulate the use condition. Material specimens were mounted in the test cells as illustrated in Figure 6. The jars were filled with 200 ml jet fuel, 2 ml of a mineral salts solution described by Knecht

et al. (1965) and inoculated separately with one drop of a suspension of *Pseudomonas* sp. or of *Cladosporium resinae* (QM7998) spores. The specimens were secured to the jar with the polyether side on the outside and the polyester side on the inside. The jars were inverted in soil and incubated for a 10-month period in the tropical chamber. During this period no fuel leakage through the system was observed. Fungal growth occurred on the polyester side in contact with the fuel and slight amount of water, while the jars inoculated with the pseudomonad showed some turbidity and yellowing in the

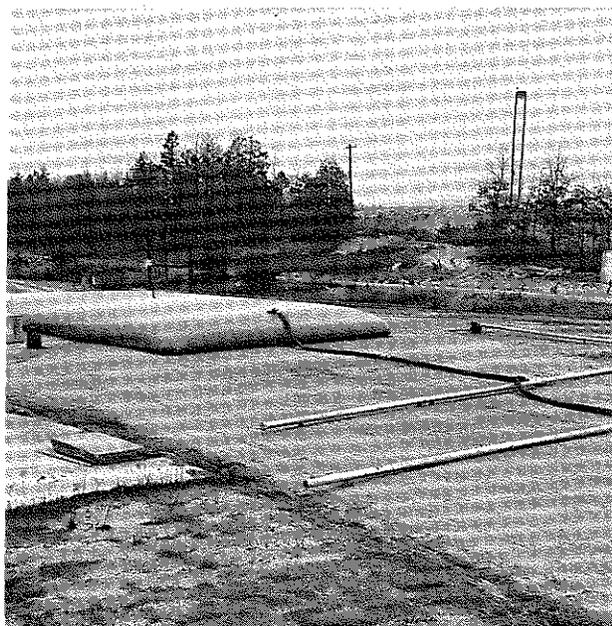


FIG. 5. Polyurethane-coated fabric fuel storage tank.



FIG. 6. Test cells used for evaluation of polyurethane-coated Dacron for fuel hose.

aqueous phase of the fuel/water system. Physical testing of both sides by such procedures as tear strength, permeability, and abrasion did not demonstrate any significant changes over the original properties. Additional studies with the polyether side immersed in a fuel/mineral salts medium showed heavy fungal growth after 2 months.

Broad conclusions cannot be drawn comparing the merits of polyethers and polyesters since we had no details on the chemical elements going into the formulations. It becomes apparent again, however, that in itself visual observation of growth has limited value in judging functional attack. Breakdown of the polyester formulation during soil burial could be caused by either hydrolysis or microbial activity; but no softening or cracking was observed on the polyester side that had been in contact with the aqueous mineral salts medium in the test cell systems simulating a use situation.

The above studies clearly illustrate problems posed by polyurethane systems. The question that arises now is the solution. It becomes obvious that very little can be done to provide a rational base if one works with commercial formulations or for that matter with laboratory formulations using chemically unidentified reactants and additives. We have amply demonstrated that information obtained for any system at this point is applicable only to that particular system at the time it is being investigated. The nuances of the influence of the various components and handling procedures make it almost impossible to establish a set of working principles that could serve as guides for judgments of microbial susceptibility in the absence of exact chemical identification of every component of a formulation and knowledge of the attendant technology in using the formulation. The problem becomes much more formidable for the polyurethanes because of the almost limitless types of polymers that can be synthesized and the equally diverse number of additives and handling procedures employed depending on the use to which the polyurethane is put. These facts however, should not prevent a systematic study of polyurethane systems in order to at least begin to provide the means for making a rational choice of ingredients and procedures for resistant systems. Such a study has been undertaken in our laboratory.

As a first step toward definition of component susceptibility certain selected unformulated polyurethane polymers have been chosen by our laboratory for study using the ASTM (1963) plate procedure modified to include *Chaetomium globosum* QM459 in the mixed culture with a 3-week incubation period. Four groups of diols were reacted with four types of isocyanates to yield over 100 individual polymers. Particular care was taken to have the reagents chemically pure. The diisocyanates used are listed in Figure 7. The diols were chosen from a group of polyethylene glycols, polyoxypropylene glycols, alkane diols and bisphenols. Both polyethers and polyesters were synthesized. The polyesters were based on the reaction products of certain diols with adipic acid. Objectives of the study were to determine the growth supporting properties of the reagents and the resulting polymers and to relate chemical structure of the polymers to biological response, i.e., growth supporting, growth inhibiting or inert. Figure 8 shows the response to 2,5-hexanediol and 2,3-butanediol as contrasted to a cottonseed oil control. The hexanediol by itself inhibited growth while the butanediol stimulated growth. None of the polyurethanes formed by reacting the hexanediol with the various isocyanates supported growth. The polymer formed by reacting the butanediol with TDI supported moderate growth but the polymers formed with MDI, TODI and HDI showed no growth. To illustrate further the difference in polymers, ethylene glycol polyethers showed no growth-supporting properties when reacted with the isocyanates. Ethylene glycol adipic acid esters generally showed heavy growth when reacted with the isocyanates. Figure 9 shows the type of growth encountered with a

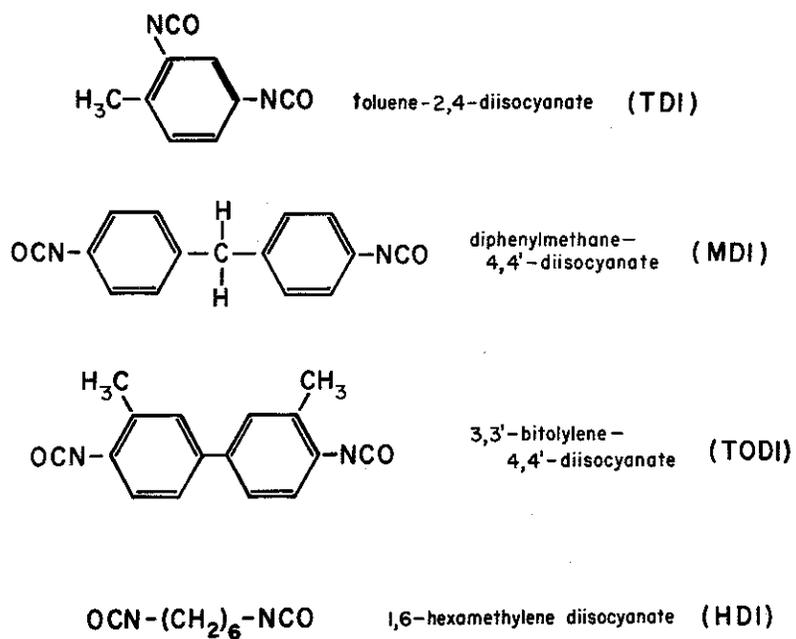


FIG. 7. Diisocyanates used in polyurethane study.

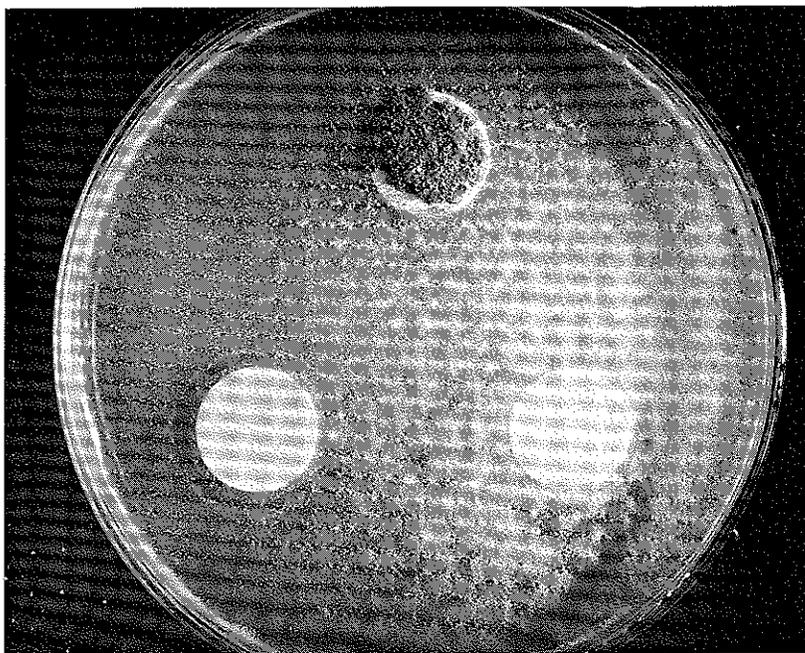


FIG. 8. Fungal growth on fiber glass filter paper disks impregnated with 2,5 hexanediol (lower left) 2,3-butanediol (lower right) and cottonseed oil control (top).

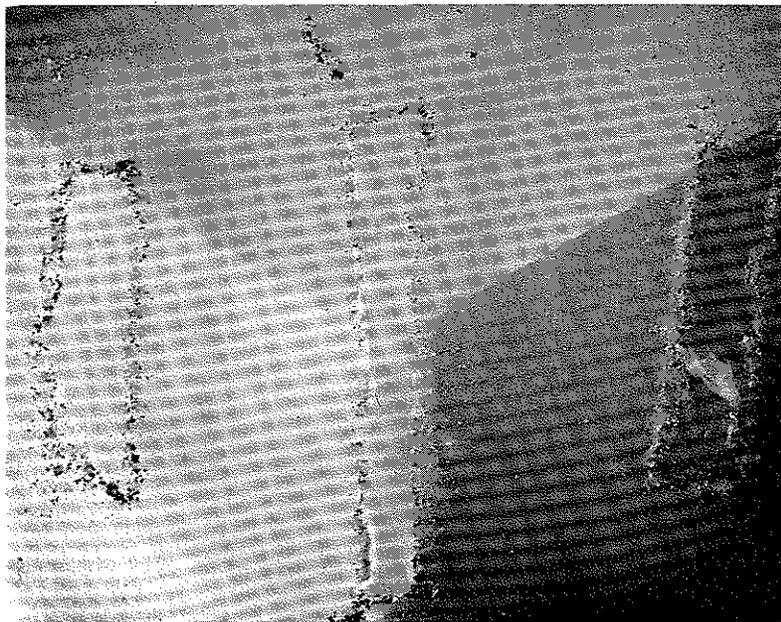


FIG. 9. Fungal growth on polyether polymer of pentaethylene glycol reacted with TDI. Three pieces of the polymer, in sheet form, photographed against white, gray, and black backgrounds to emphasize growth patterns.

polyether, pentaethylene glycol reacted with TDI, and Figure 10 shows growth on polyesters, 1,3-propanediol-adipic acid reacted with MDI, TDI, and TODI.

The full structure-biological response relationship developed in this study is being reported elsewhere and no conclusions concerning this relationship are presented here. The foregoing examples taken from the study, however, demonstrate the point that is pertinent to this discussion. This is that the polyurethane polymer, exclusive of other ingredients in a formulation, provides a direct contribution toward overall resistance or susceptibility of the formulation. Polyurethanes are therefore unique in this respect as compared with other resin systems where the polymer per se does not serve as a fungal nutrient but other elements of the formulation do. Thus, vinyl resins per se do not support growth but vegetable oil derived plasticizers used in vinyl formulations do. Similarly, polyethylenes, nylons, Dacron, and polypropylene—to name a few—do not support fungal growth as polymers but various finishes or additives used for processing purposes may provide a substrate for microbial growth.

Polyurethanes therefore pose a particular problem if prevention of microbial growth and damage is of concern. From the present discussion it becomes clear that it is unlikely that a commercial polyurethane preparation can be guaranteed resistant to microbial damage or growth unless the characteristics of every component and processing technique are known and specified in detail. It is improbable that this can be done in practice. Therefore, if microbial activity is a consideration in a particular application where conditions cannot be controlled, it appears at this point that incorporation of a fungicide in the formulation is required to insure full functionality of the system. Choice of a fungicide must be made with caution, however, since compatibility of the fungicide



FIG. 10. Fungal growth on polyester of 1,3-propanediol-adipic acid (upper left) and polymers of the ester reacted with MDI (lower left), TDI (upper right) and TODI (lower right).

with the formulation appears to be more a problem with polyurethanes than with other polymeric systems. Work in our laboratory indicates that no blanket endorsement can be given to any specific fungicide. Each system must be evaluated individually to make certain that the fungicide employed is active and compatible under use conditions, corroborating the observations of Ossefort and Testroet (1966) and Kanavel et al. (1966).

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