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Introduction

Various coatings and coating processes were evaluated in a program aimed at improving the hydrolytic stability of reticulated polyurethane baffle material [1]. This material is used in fuel tanks of aircraft and ground vehicles such as racing cars to prevent sloshing of fuel and thereby reduce explosion hazards. The most commonly used foam of this type is hydrolytically unstable and, depending on the environment in which it is used, gradually degrades over a 1 to 3 year period.

Potential moisture barrier coatings which were evaluated include Parylene, epoxy-polysulfide, polyether-based polyurethanes, polysulfides, polyolefin rubbers, and several other materials. The greatest improvement in hydrolytic stability was provided by Parylene coatings of 0.2 mil (5×10^{-4} cm) or greater thickness, and the second best coating, in terms of hydrolytic stability, was Astrocoat 8000, a polyether-based polyurethane.

Discussion

Parylene—Two types of Parylene (Types N and C) were examined during the course of this program, but only one (Parylene C) [2, 3, 4] received extensive evaluation. The polymers are deposited from the gaseous state by heating dichloro-p-cyclophane (Type C) or p-cyclophane (Type N), both products of Union Carbide Corp. to 680°C in a heated zone of a vacuum chamber at a pressure of about 100 μm. Gaseous molecular fragments generated in this pyrolysis subsequently deposit and spontaneously polymerize on all objects in the chamber. Because these fragments are gaseous, they penetrate deeply into the interstices and pores of the baffle material structure, thus providing virtually pore-free coated surfaces.

To evaluate the Parylene-C-coated foam, tensile test specimens were coated to various thicknesses between 1×10^{-4} cm and 10×10^{-4} cm. The specimens were subsequently placed in a humidity chamber at 185°F (85°C) and 95% relative humidity (R.H.). At periodic intervals (approximately 3 days), triplicate samples of the tensile test specimens were removed and tested for tensile strength and elongation. The results of these tensile tests are illustrated in Figure 1. It is readily seen from this illustration that marked improvement in hydrolytic stability is achieved with the 5×10^{-4} and 10×10^{-4} cm coatings. The 1×10^{-4} cm coating provided no protection since these thinly coated specimens were essentially equivalent to uncoated foam specimens. Elongation test results are shown in Figure 2.

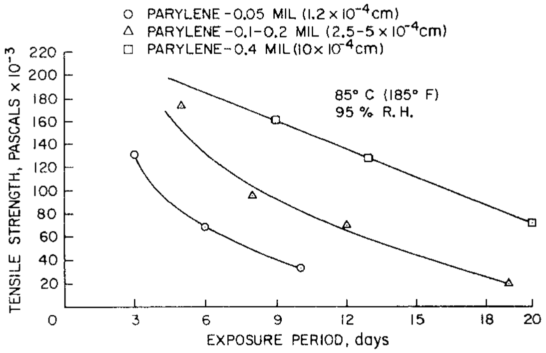

Figure 1. Results of hydrolytic stability tests on Parylene-C-coated foams:

Hydrolytic stability tests were also performed at 160°F (71°C) and 95% R.H. In these tests, the

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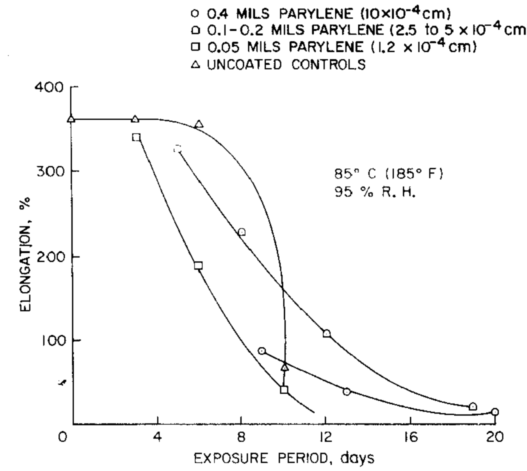

Figure 2. Elongation of Parylene-C-coated foams after humidity exposure.

baffle material samples had a 0.2 mil (5 X 10^{-4} cm) Parylene-C coating. Here also the superior performance of the coated foams is evident. Results of these tests are shown in Figure 3.

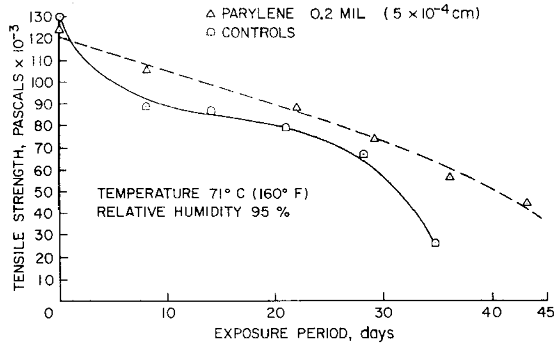

Figure 3. Results of hydrolytic stability tests on Parylene-C-coated foam at 160° F (71° C).

After demonstrating that improved stability was provided by the Parylene-C coatings, several large cylindrical foam sections (20 cm diam X 20 cm high) were coated and the coating thickness was determined in various portions of the cylinders. In one of these, it was found that the coating thickness varied from 1 to 2 X 10^{-4} cm, with the thinner coating in the center of the cylinder, whereas in the second cylinder the thickness varied from 5 to 12 X 10^{-4} cm. This was determined by weight difference and microscopic examination. Neither variation was considered excessive and thus the coating process was deemed satisfactory for commercial practice.

Subsequently, physical property measurements and fluid compatibility tests were made in accordance with Military Specification MIL-B-83054. The specimens examined had 6.3 ± 1.2 X 10^{-4} cm of Parylene-C (~10% by weight) and the results of these tests are shown in Table 1.

Compressive modulus tests were also performed on the Parylene-C-coated baffle material; these results are shown in Table 2. The added rigidity provided by the coatings is considerably greater than that desired. For example, at a 65% deflection load, the modulus increase was 123% compared to the allowable 50% increase.

It is evident from these data, as well as the data in Table 1, that Parylene-C-coated foams can meet all of the military specification requirements except the target modulus requirement. Other applications could, of course, utilize the higher modulus foams without specification changes. It is also to be noted that the entrained solids test showed that the coated foam had an excessive amount of entrained solids; however, there is little doubt that this could be remedied if the foam were rinsed prior to and/or after coating. This extraneous matter could be rinsed with suitable solvent and then dry air blown through the foam.

As pointed out in the subsequent discussion, Parylene-N-coatings were effective at lower thicknesses where the modulus increase was very much reduced.

Tests on Parylene-N-coated baffle material were limited to one set of humidity exposure tests. The results (Figure 4) were extremely promising, even though the baffle material had only 0.06–0.08 mil (1.5–2.0 X 10^{-4} cm) coating, its ultimate strength after 20 days in the humidity cabinet was equivalent to that of the 0.4 mil (10 X 10^{-4} cm) Parylene-C-coated foam. The Parylene-N-thus warrants further and extensive study.

Polyurethane Coatings—Baffle material currently in use is produced from polyester-based polyurethane, and it is because of this that its hydrolytic stability is relatively poor. Polyether-based polyurethanes generally have better hydrolytic stability, and thus it was apparent that the evaluation of such coatings was warranted. In addition, "aliphatic" polyurethanes derived from hexamethylenediisocyanate are also more resistant to hydrolysis, and thus a coating of this type also was selected for evaluation.

The two polyether-based polyurethanes studied were Astrocoat 8000 [5], a rain-erosion coating from Olin Corp., and Churchill 1600H from Churchill Chemical Co., whereas the "aliphatic" polyurethane studied was Alpha 841 from Baker Chemical Co. Humidity exposure tests (at 85°C, 95% R.H.) on baffle material coated with these polyurethanes showed that Astrocoat 8000 was the best of these.

These results (Figure 5) made it quite evident that the Astrocoat coatings were very effective, but not as effective as Parylene. Furthermore, the Astrocoat thickness was 5–10 times as great as the required Parylene coating thickness. In this study, the

Table 1. Results of Fluid Compatibility Tests and Physical Properties of Parylene-C-Coated Foams

Test	TEST PARAGRAPH, in MIL-B-83054	Foam Specifications	RESULTS Parylene-C-Coated Foam
Density	4.7.2	50.4 kg/m^3 maximum	33.1 kg/m^3
Tensile strength	4.7.2	103 X 10^3 pascals	> 200 X 10^3 pascals
Elongation at break	4.7.4	250% minimum	> 300%
Compressive modulus	4.7.7	50% maximum increase over uncoated foam	See Table 2
Fluid displacement	4.7.8	4.5% maximum	1.9%
Fluid retention	4.7.9		
a. JP-5		4.5% maximum	1.3%
b. H_2O		4.5% maximum	0.8%
Extractable material	4.7.11	3.0% maximum	1.5% ave. weight gain
Volume swell	4.7.14	5.0% maximum	0
Entrained solids	4.7.17	396 mg/m^3 maximum	630 mg/m^3

Table 2. Results of Compressive Modulus Tests on Parylene-C-Coated Foam

	25% DEFLECTION LOAD		65% DEFLECTION LOAD		80% DEFLECTION LOAD	
Material	g/cm^2 (ave. of 2)	Increase, %	g/cm^2 (ave. of 3)	Increase, %	g/cm^2 (ave. of 3)	Increase, %
Uncoated	86	—	177	—	536	
Parylene-C Coated	127	47	395	123	1791	235

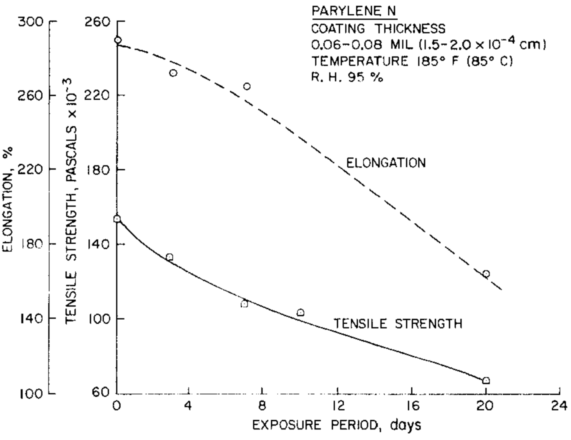

Figure 4. Humidity tests on Parylene-N coated baffle material.

first Astrocoat curing agent evaluated was "MOCA" [methylene-2, 2′-bis(chloroaniline)], a product of DuPont; however, due to its reported carcinogenic activity, work on MOCA was terminated and a new Olin catalyst was evaluated. This new catalyst

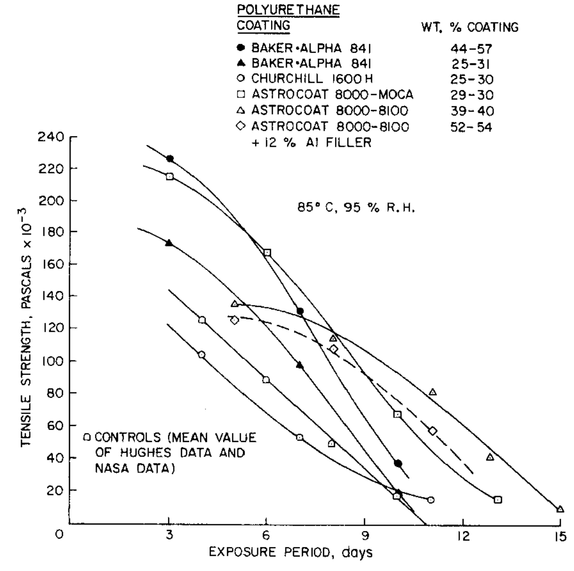

Figure 5. Results of humidity exposure tests on polyurethane-coated foams.

(8100) also provided coatings with superior hydrolytic stability and, consequently, the substitution appeared to be quite acceptable for this application.

After passing these initial hydrolytic stability tests, the physical properties of Astrocoat-coated baffle material (bearing 42% by weight of coating) were measured and the results were compared to Military Specification MIL-B-83054 requirements. The comparisons are shown in Tables 3 and 4.

Table 3. Physical Properties of Astrocoat-Coated Foam

TEST	FOAM SPECIFICATIONS*	ASTROCOAT 8000 WITH 8100 CURING AGENT, 42% BY WEIGHT
Density	50.4 kg/m^3 maximum	49.5 kg/m^3
Tensile strength	103 X 10^3 pascals minimum	> 180 X 10^3 pascals
Elongation at break	250% minimum	> 300%
Compressive modulus	50% maximum increase allowed over uncoated foam	See Table 4
Fluid displacement	4.5% maximum	2.2%
Fluid retention		
JP-5 fluid	4.5% maximum	1.1%
H_2O	4.5% maximum	1.8%
Extractable materials	3.0% maximum	1.5%
Volume swell	5% maximum	0
Entrained solids	396 mg/m^3 maximum	823 mg/m^3

*For specific Military specification paragraph references, see Table 1.

Table 4. Compression Modulus Data on Astrocoat-Coated Baffle Material

	25% DEFLECTION LOAD		65% DEFLECTION LOAD		80% DEFLECTION LOAD	
Material	g/cm^2 (ave. of 3)	Increase, %	g/cm^2 (ave. of 3)	Increase, %	g/cm^2 (ave. of 2)	Increase, %
Uncoated	86.2	–	77	–	536	–
Astrocoat-coated	114	32	218	23	779	45

Results of these tests showed that all of the requirements of the military specification could be met by the Astrocoat-coated baffle material. Thus, although such coatings are inferior to Parylene coatings as far as hydrolytic stability is concerned, they are less rigid and do not create a need for the relaxation of the low modulus requirement.

Rubber-Based Coatings—Various other coatings were also evaluated in the course of this investigation. These included carboxyl-terminated and mercaptan-terminated butadiene acrylonitrile rubbers, butadiene acrylonitrile latex, polysulfides, and epoxy-polysulfides. The mercaptan- and carboxyl-terminated butadiene acrylonitrile rubbers of greatest interest were those which contained the greatest proportion of acrylonitrile, since the acrylonitrile provides the needed fuel resistance. Thus, both of the curable liquid copolymers (Hycar from B. F. Goodrich) and the rubber latex (Chemigum 248 from Goodyear Corp.) were copolymers with 27% acrylonitrile.

Hycar liquid rubbers, or more specifically mercaptan-terminated butadiene acrylonitrile (MTBN) and carboxyl-terminated butadiene acrylonitrile (CTBN), received extensive evaluation. In one series of experiments, the rubbers were copolymerized with Epon 828 epoxy resin (Shell Chemical Co.) using amine catalysts [6, 7 & 8]; however, coatings of this type provided no protection. Air-cured MTBN coatings in which the cure was catalyzed by organometallic catalysts also provided no protection. A minor degree of moisture protection was provided by Epon 828 CTBN formulations which were catalyzed by a chromium dimethylsalicylate catalyst, but the margin of improvement was not great enough to be of any consequence.

Results of these rubber-based coating studies were obviously unsatisfactory, and thus studies of these materials were terminated.

Efforts made to utilize the rubber latex were unsatisfactory because of the numerous coats which were required. When the concentrated latex (containing 56% solids) was used, it frothed badly and closed the pores of the foam structure. Frothing was prevented when dilute latexes were used (~ 10% rubber), but then it became necessary to apply 6 to 10 coats, with drying after each application. Not only was this too repetitive and cumbersome, but also the coated foams made by the process showed no improvement in hydrolytic stability.

Polysulfides—Polysulfides were evaluated in various ways. In some experiments they were oxidatively (air) cured on the reticulated foam after the addition of an organometallic catalyst, such as tin octoate, in various concentrations. Although excellent uniform coatings of this type could be made and applied from toluene varnishes, the coated foams invariably were less hydrolytically stable than uncoated foams. Similar problems were encountered when the polysulfides were cured with MnO_2, or MnO_2 + dinitrobenzene. In both cases, the coated foams proved to be more hydrolytically unstable than uncoated foams.

For these studies, polysulfides of various molecular weights were examined, as shown in Table 5.

Table 5. Properties of Polysulfides

POLYMER	M.W.	MERCAPTAN CONTENT, %	CROSS-LINKING AGENT, %
LP-3	1000	6.6	2.0
LP-12	4000	1.75	0.1
LP-32	4000	1.75	0.5
LP-31	8000	1.1	0.5

The higher molecular weight polymers were of interest because it was anticipated that they would cure faster and with less catalyst; this proved to be the case.

The organometallic catalysts utilized in the study, except for the Nuocure 28 from Metal & Thermite co., were paint driers produced by Cincinnati. Milacron Inc. and included the following:

1. Advadry (12% Co)
2. Advadry (9% Mn)
3. Advadry (36% Pb)
4. Nuocure (28% Sn)
5. Lead Octoate (24% Pb)
6. Manganese Octoate (6% Mn)
7. Cobalt Octoate (6% Co)
8. Zirco drier (12% Zr)

Of these, the Advadry (12% Co naphthenate) and Nuocure 28 proved to be most effective in the concentration range of 2% to 5% and, when activated by 1,10-phenanthroline, tack-free films were obtained after the coatings set in air for about 2 hours at ambient temperature.

Polysulfide-TDI—Copolymerizable polysulfide tolylenediisocyanate (TDI) mixtures were also evaluated using very low concentrations of tin octoate to promote cure (0.5% Nuocure 28 = 0.14% active catalyst). In these cases, water in the air was the effective curing agent. Here again excellent coatings could be produced from varnishes, but again the coated foams were *more* hydrolytically unstable than was the uncoated foam. Catalyst concentrations up to 1% Nuocure were studied, and concentrations below 0.5% were found to be insufficient to promote cure. Both LP-12 and LP-31 were cured in this manner and both provided void-free coatings when 5%–20% theoretical excess of tolylenediisocyanate was used.

Epoxy-Polysulfides—Coatings were also prepared from epoxy-polysulfide mixtures, and the copolymerizations were catalyzed by amines such as benzyl-dimethylamine and tris(dimethylaminomethyl) phenol. Uniform coatings of this type were applied very effectively from toluene-butanone varnishes, but these coated foams also had *reduced* hydrolytic stability. In this case, the increased rate of degradation was attributed to amine-catalyzed hydrolysis of the foam substrate. This conclusion was supported by the observation that the more basic the amine the more rapid was the degradation.

Conclusions

It was concluded from these studies that vapor-deposited Parylene coatings and Astrocoat 8000 coatings could effectively increase the life expectancy of reticulated polyester-based polyurethane baffle material, and coatings of these types thus warranted consideration as potential solutions to the degradation problem. Curves showing the results of hydrolytic stability tests on the best materials are shown in Figure 6. Also included in this graph is a plot of uncoated-foam data.

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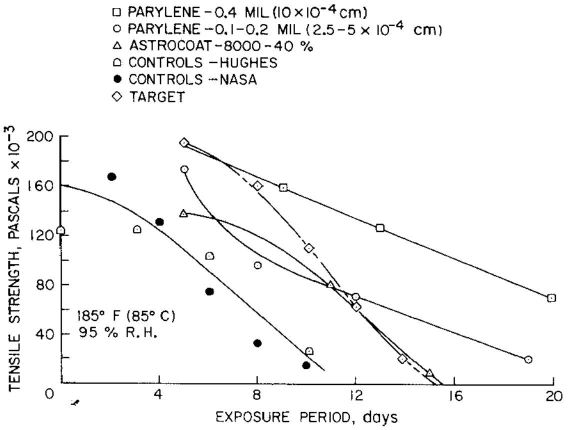

Figure 6. Results of hydrolytic stability tests on best materials.

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Dr. Bilow received his B. S. degree in Chemistry in 1949 from Roosevelt University, Chicago, Illinois, and his M. S. and Ph.D. in 1952 and 1956, respectively, from the University of Chicago. He is the author of 14 scientific papers, inventor on 27 patents, and author of numerous corporation and U. S. Government Contract Research Reports dealing with high temperature plastics, electrical insulation, polyimides, lubricants, ablative materials, polyphenylenes, and various other subjects. After working as a research chemist for Dow Chemical Company from 1949–1952, he joined the Hughes Aircraft Company where he has remained for the last 15 years. During much of this time he was Head of the polymer, physical, and analytical chemistry section. Currently he is the Senior Scientist of the Advanced Materials Laboratory. He is a former member of the New York Academy of Sciences, a current Fellow of the American Institute of Chemists, a past president of Sigma Xi, and a member of the American Chemical Society. His biography has appeared in the Dictionary of International Biography (1969–70), Who's Who in the West (1969–1970), American Men of Science (1968–) and Two Thousand Men of Achievement (1971). He was the recipient of the Industrial Research Magazine "IR-100" award in 1970 and 1974. The former was for his work on ultra high temperature wire insulation and the latter for the development of a family of thermosetting, high temperature, addition curable polyimides.

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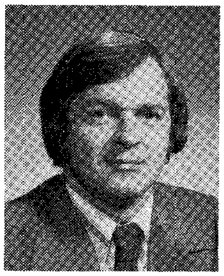

Paul M. Sawko is currently involved in research and development studies of high temperature polymers, fire retardant materials, intumescent coatings, foams, and adhesives. He has authored technical papers on these topics and is the inventor on patents relating to intumescent coatings as well as a patent filed on a transparent, fire resistant, polymer system. He received his undergraduate degree in Chemistry from St. Francis College, Loretto, Pennsylvania, and conducted graduate studies at Duquesne University, Pittsburgh, Pennsylvania. Before joining NASA-Ames Research Center, he was on the staff of the National Cash Register Company and Benjamin Moore and Company with responsibilities for specialty coatings. He is a member of the American Chemical Society, the Golden Gate Society for Coatings Technology, and a member of ASTM F7.08. He has received several awards for his work with intumescent coatings.