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DEVELOPMENT OF FUEL HOSE FOR USE IN THE ARCTIC

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Final Report
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Belvoir Research and Development Center
Fort Belvoir, VA 22060

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20. Abstract (continued)

→ similar hoses from fluorosilicone elastomers were unsuccessful due to problems in processing and end item integrity. ←

Preface

This report describes work performed and results obtained under Contract DAAK70-80-C-0137, for the Belvoir Research and Development Center, Ft. Belvoir, VA, 22060. Mr. Paul E. Gatzka, of the Rubber and Coated Fabrics Research Group, Materials, Fuels and Lubricants Laboratory, was the Contracting Officer's Representative. Appreciation is extended to him and other Belvoir Research and Development Laboratory personnel, who provided technical guidance and assistance in materials selection, compound testing and end item evaluation.

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FORNERS THE BLACK-OUT FILM

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Introduction

Currently used military fuel hose becomes stiff and embrittles at a temperature of about -25°F . Normal winter temperatures in the Arctic fall as low as -60°F , while -40°F is a common occurrence. The Belvoir R&D Center wanted to develop suction and discharge hose which could be used at these low temperatures and, ideally, would remain flexible enough to be reeled and deployed at -60°F . These hoses will subsequently be evaluated as components of Arctic refueling systems currently under development.

Previous attempts to develop a fuel hose for Arctic use had shown that certain elastomers, such as ECO, polychloroprene, nitrile, and polyacrylate were unsuitable. Indeed, few polymers remain flexible at -60°F . However, it was requested that a search for a suitable candidate be made among the polyurethane, fluorosilicone, fluorocarbon, polysulfide, fluorophosphazene and polyester (Hytrel) elastomers.

Other desired properties of the Arctic hose are listed in Table 1. These include, most importantly, excellent fuel and water resistance both in the original state and after a period of use simulated by retention of a substantial fraction of those original properties after exposure to fuel, water, and after solvent extraction.

Equally important was the requirement that the compound selected be suitable for manufacturing hose using conventional techniques, which were developed for, and are based on, standard rubber processing characteristics. This proved to be one of the most difficult requirements to meet.

Albany International Research Co. undertook the task of developing a suitable elastomeric compound. The actual manufacture of hose was to be done initially by American Biltrite Rubber Co. However, due to shifting of corporate priorities they could not continue as subcontractor, and the hose was eventually made by Durodyne, Inc. of Tucson, Arizona.

Hose Manufacturing Technology

Hose of the type called for in this contract is conventionally built on steel mandrels in lengths up to 100 feet. Calendered strips of the green elastomer are wound helically on the mandrel to form the liner. This is then covered with a layer of braided reinforcement, with or without wire, depending on the type of hose being made. Another layer of elastomer is wound on, followed by another layer of braided reinforcement, and a final layer of elastomer to form the cover. The hose is then wound with a nylon

Table 1

Desired Properties of Tube and Cover for Arctic Hoses

Initial	Tube	Cover	Test Method
•Tensile Strength, psi (min)	1500	1500	ASTM D-412
•Stress (100% elongation), psi	record	record	ASTM D-412
•Ultimate Elongation, % (min)	150	150	ASTM D-412
•Hardness Shore A, points	record	record	ASTM D-2240
•Tear Strength, lb/inch	record	record	ASTM D-624, Die C
Immersed in Reference Fuel B at 73.4°F + 3.6°F for:	94 hrs ± 0.5 hr	94 hrs ± 0.5 hr	ASTM D-471
•Tensile Strength Retained, % (min)	60	40	ASTM D-471
•Stress (100% elongation) Retained, %	record	record	ASTM D-471
•Ultimate Elongation Retained, % (min)	85	80	ASTM D-471
•Volume Increase, % (max)	40	70	ASTM D-471
Immersed in Distilled Water, (pH of 7.0) at 160°F + 2°F for:	14 days ± 2 hrs	14 days ± 2 hrs	ASTM D-471
•Tensile Strength Retained, % (min)	80	80	ASTM D-471
•Stress (100% elongation) Retained, %	record	record	ASTM D-471
•Ultimate Elongation Retained, % (min)	80	80	ASTM D-471
•Volume Increase, % (min)	15	15	ASTM D-471
After Accelerated Weathering, 500 hours:			
•Tensile Strength Retained, % (min)	--	85	ASTM D-412, D-750 & 4.3.5 ⁽¹⁾
•Ultimate Elongation Retained, % (min)			ASTM D-412, D-750 & 4.3.5 ⁽¹⁾
•After Ozone Exposure	--	no cracking	4.3.6 ⁽¹⁾
•Existent Gum			4.3.7 ⁽¹⁾ & D:38
Unwashed, mg/100 ml (max)	20	--	19.1-9.6
Washed, mg/100 ml (max)	5	--	19.8-9.1
As Received (specimens conditioned for 4 days):			4.3.3.2 ⁽¹⁾ at -60°F
•Tension Recovery, % (min)	record	record	4.3.3.3 ⁽¹⁾
•Brittleness	no cracking	no cracking	ASTM D-746 & 4.3.3.4 ⁽¹⁾ & ASTM C-509 Appendix
•Torsional Stiffness Ratio (max)	10	10	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•Twist at Room Temp	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•Twist at Low Temp	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•G Modulus of Rigidity, 10,000	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•Torsion Constant of Wire Used	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
After Immersion in Reference Fuel B at 73.4°F for 94 hrs & drying: (specimens conditioned at -60°F for 4 Days)			ASTM D-471 & 4.3.4 ⁽¹⁾
•Torsional Stiffness Ratio (max)	10	10	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•Twist at Room Temperature	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•G Modulus of Rigidity, 10,000	record	record	4.3.3.2 ⁽¹⁾ & ASTM D-1053
•Torsion Constant of Wire Used	record	record	4.3.3.3 ⁽¹⁾
•Tension Recovery, % (min)	record	record	4.3.3.3 ⁽¹⁾
•Brittleness	no cracking	no cracking	4.3.3.4 ⁽¹⁾ , ASTM D-746
•Brittleness	no cracking	no cracking	4.3.3.4 ⁽¹⁾ , ASTM C-509 Appendix

Note: Percent retention of tensile strength and 100% stress after fuel immersion is based on swollen cross-sectional area (see 4.8 of Federal Test Method Standard 601 - Method 611).

tape under tension to provide some pressure to promote the flow between wraps and between layers of the elastomer needed to obtain a fully integrated and impregnated structure. Finally, the mandrel carrying the built-up hose assembly is inserted into a tube oven which is usually filled with steam at pressures not more than 50 psi, corresponding to temperatures not over 300°F. After an appropriate cure time the mandrel is removed from the oven, the nylon tape unwrapped, and the finished hose length blown off the mandrel.

Three aspects of this procedure are critical to the selection of the elastomeric compound:

1. The compound must be suitable for calendaring into a sheet.
2. The compound must be capable of flowing under the relatively low pressures provided by the nylon tape wrapping.
3. The compound must exhibit good adhesion to the braided reinforcement.
4. The compound must flow and cure at a temperature of about 290°F or lower.

The upper temperature limit eliminates most elastomeric systems, which require curing temperatures close to 350°F. Thus, this becomes a critical factor in selecting a candidate elastomer.

Elastomer Selection

Here we review all compounds considered during the course of the work and explain why they were rejected or accepted. Property value measurements are summarized in Table 2. A glossary of compound additives is given in Table 3.

1. Fluorophosphazene

Previous experience with hose manufacture using polyphosphazene convinced MERADCOM that processing problems were too difficult with this compound. Consequently, it was decided not to investigate it further.

2. Polysulfide

Polysulfides have the advantage of a relatively low cost, excellent fuel resistance and low fuel diffusion rate. However, strength is marginal and the polysulfides are known to have a rather sharp, brittle point near -60°F; and low temperature stiffness can be a problem. The following laboratory formulations were made for screening purposes.

2642-4-1 - Formulation based on Thiokol ST

Thiokol ST	100 parts
Zinc Oxide	5
Stearic Acid	1
CaOH	1
SRF Black	60

Table 2

Property Value Measurements for Candidate Elastomeric Compounds

Property	Condition	Target Value	2642-4-1 Thiokol ST	2642-4-3 ST/Hydrin	2642-6-1 Thiokol FA	2642-10-1 ST/Nitrile	2642-7-1 DC LS-40	2642-7-2A DC LSQ4	2642-7-2 DC LSQ4	2642-7-2B GE FSR	2642-7-2C GE FSR	2642-7-2D GE FSR	2642-8-1 Viton GLT	2642-11-1 Adiprene CM	2642-11-1A Adiprene CM	2642-11-2 Adiprene CM	4056 Hyrel	2101-80A Upjohn PU	58300-80A Estane PU	Stevens PU
Tensile Strength psi & retained	A 1500	1125	790	1350	730	480	980	520	1360	1315	1205	2100	3200	4250	2275	4790	2065	3990	7440	
	B tube 60 cover 40	84	89	76	---	---	66	---	80	---	---	52	64	52	24	100	68	75	60	
	C 80	34	33	42	---	---	98	---	89	---	---	116	95	52	---	79	61	68	---	
Elongation, % & retained	A 150	320	220	310	410	375	280	245	450	350	320	150	520	595	670	710	475	700	520	
	B tube 85 cover 80	69	100	90	---	---	92	---	90	---	---	100	95	75	99	105	96	92	---	
	C 80	43	64	74	---	---	103	---	98	---	---	72	95	---	---	115	118	108	100	
Stress at 100% psi & retained	A ----	425	334	488	---	---	190	---	185	---	---	1354	248	84	80	1047	613	496	106	
	B ----	139	110	90	---	---	112	---	111	---	---	73	84	85	61	89	112	89	85	
	C ----	50	45	25	---	---	120	---	150	---	---	52	85	---	---	112	69	70	---	
Tear Strength lb	A ----	138	87	---	---	---	118	---	85	150	134	185	172	172	128	---	523	336	396	
Hardness Shore A	A ----	70	65	70	59	62	70	40	62	64	64	74	54	60	59	90	85	79	85	
	B tube 40 cover 70	8.1	10.7	9.6	---	---	7.8	---	11.6	---	---	30	6.1	15.9	16.0	37.0	15.4	11.3	34	
	C 15	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
Existent gum, mg/100 ml	D 20	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
E 5	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
F 10	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
Torsional Stiffness Ratio	F 10	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
G Modulus of Rigidity kpsi	F ----	10.7	30.2	---	---	---	0.3	---	0.9	---	0.6	12.9	28.0	33.0	30.9	18.0	68.1	29.7	63.9	
Brittleness	F no fracture	2	2	1	1	1	5	5	5	5	5	5	4	4	4	4	4	4	4	
	Condition	A - original																		Brittleness
	B - after fuel immersion, 23°C, 94 hr																			2 - very stiff
	C - after water immersion, 160°F, 14 days																			3 - stiff
	D - unwashed																			4 - flexible
	E - washed																			5 - very flexible
	F - -60°F, 4 days																			

Table 3

Compound Additive Glossary

<u>Name</u>	<u>Description</u>	<u>Supplier</u>
Amberol ST	plasticizer and resin	Rohm & Haas
Aranox	antioxidant	Uniroyal
Benzoflex 9-885G	plasticizer	Velsicol Chemical
Cab-O-Sil MS-7	fumed silica	Cabot Corp.
Cardox TS-50	peroxide catalyst	Noury Chemical
Caytur 4	accelerator	Du Pont
DC-HT-1 modifier	silicon resin	Dow Corning
Diak #1	vulcanizing agent	Du Pont
Diak #7	vulcanizing agent	Du Pont
DOP	plasticizer	Monsanto
DPG	accelerator	American Cyanamid
GE-SE-464	silicon modifier resin	General Electric
Luperco CST	peroxide catalyst	Pennwalt
Luperco 101XL	peroxide catalyst	Pennwalt
MBT	accelerator	Vanderbilt
MBTS	retarder	Vanderbilt
Neozone D	antioxidant	Du Pont
Octomine	antioxidant	Uniroyal
Sulfur	vulcanizing agent	
SRF Black	carbon black	
3M Fluoro PPA 790	fluoro elastomer resin	3M
Cadmium Stearate	co-activator	Vanderbilt

2642-4-3 - An 80/20 blend of Thiokol ST/Hydrin 200
 2642-4-1 80 parts
 2642-4-2 20

2642-4-2 - Formulation based on Hydrin 200
 Hydrin 200 100 parts
 Zinc Stearate 1
 Lead Carbonate 5
 Aranox 1
 SRF Black 30
 DOP 7
 Diak #1 0.75

2642-6-1 - Formulation of Thiokol FA
 Thiokol FA 100 parts
 Neoprene W Master Batch* 29
 Zinc Oxide 10
 Stearic Acid 0.5
 SRF Black 60
 Diak #1 0.5
 MBTS 0.4
 DPG 0.1

*Neoprene W Master Batch.
 Neoprene W 100 parts
 Magnesium Oxide 4
 Octamine 2
 SRF Black 55
 Stearic Acid 0.5
 Zinc Oxide 5

2642-10-1 - Formulation based on 80/20 blend of Thiokol ST
 (2642-4-1) and Hycar Nitrile 1001*

*Hycar Nitrile 1001 Formulation.
 Hycar 1001 100 parts
 Zinc Oxide 4
 CaOH 1
 SRF Black 55
 Neozone D 1
 Stearic Acid 1

Simple screening tests of these formulations indicated that the basic Thiokol ST (2642-4-1) was flexible (although stiff), at -60°F, but deficient in strength. Thiokol FA (2642-6-1) has fair strength but was brittle at -60°F. The blends did not improve strength or brittleness to any significant degree. Also the water resistance of these polysulfides was also found to be poor to fair at best.

The polysulfides were dropped from further evaluations and are not recommended for use in Arctic Fuel Hose Systems.

3. Fluorocarbon

One fluorocarbon, Viton GLT, made by DuPont specifically to achieve low temperature flexibility, was evaluated primarily because it had the lowest brittle point temperature of all the available fluorocarbons.

Formulation 2642-8-1

Viton GLT	100 parts
3M Fluoro PPA 790	4
Diak #7	4
CaOH	4
SRF Black	20
Luperco 101XL	8

Although this material did not crack or fracture at -60°F , it was stiff. Moreover, it was very difficult to process and a cure temperature in excess of 302°F is necessary. Present hose processing techniques are considered inadequate for this polymer system.

The use of a plasticizer might well help the stiffness; but because of cost and processing difficulties, fluorocarbons are not recommended for the present hose system.

4. Polyester Elastomer

DuPont's Hytrel 4050 polyester is strong and has excellent fuel and water resistance. However, Hytrel is a material that cannot be fabricated into a flexible suction or discharge hose using present hose processing technology. Hytrel requires a plastic processing extruder that achieves temperatures in excess of 450°F . It was decided not to investigate the use of Hytrel further.

5. Fluorosilicone

A series of fluorosilicone elastomers were evaluated. The major advantage of the fluorosilicones is their superior very low temperature flexibility, with good fuel and water resistance. Strength is a serious limitation and is definitely lower than desired. However, the extremely good flexibility of this material makes it a prime candidate.

The following formulations were made and evaluated.

<u>2642-7-1</u>		<u>2682-7-2</u>	
Dow Corning LS-AO	100 parts	Dow Corning LSQ4-2860	100 parts
DC-HT-1 Modifier	1	DC-HT-1	1
Cab-O-Sil MS-7	7	Cab-O-Sil MS-7	7
Luperco CST	1.5	Luperco CST	1.5

Cure 5 minutes at 240°F and post cure 4 hours at 392°F .

Both formulations above were very sticky and could not be calendered into sheet form for further processing into hose.

2642-7-2A

Dow Corning LSQ-4-2860	100 parts
DC-HT-1 Modifier	1
Cab-O-Sil MS-7	7
Luperco 101XL	0.8

2642-7-2B

GE FSE 2620U	100 parts
DC-HT-1 Modifier	1
Cab-O-Sil MS-7	7
Luperco 101XL	0.8

The above formulations required a cure at 350°F and yielded better physical properties than the previous formulations. However, both materials still could not be calendered into suitable sheet form.

2642-7-2C

GE FSE 2620U	100 parts
GE SE 464	5
Cab-O-Sil MS-7	7
Luperco 101XL	0.8

Cured at 350°F. This formulation yielded reasonable physicals and could be calendered; however process temperatures were too high for hose processing. The following was the best in terms of overall properties and processability.

2642-7-2D

GE FSE 2620U	100 parts
GE FE 404	5
Cab-O-Sil MS-7	7
Cadox TS-50	1.6
(or Luperco CST)	

The above system was cured at 240°F for 10 minutes, and optimum physicals were obtained after a post cure at 400°F. A 1200 psi tensile strength was obtained, and this compound was considered suitable for a prototype hose-building trial.

c. Polyurethane

The availability of a number of polyurethanes having low temperature capabilities and at a reasonable cost have made polyurethanes suitable candidate materials for low temperature hose.

Their strength, abrasion resistance, and low temperature capabilities are fairly well known but the major limitations appears to be processability and fuel resistance.

First a series of thermoplastic polyurethanes were screened and evaluated:

- | | |
|---------------------------|--------------------|
| (a) Roylar E-9 (Uniroyal) | - polyether |
| (b) Estane 58300 (BFG) | - polyether |
| (c) Betathane (Essex) | - polycaprolactone |
| (d) 680AC (Thiokol) | - polycaprolactone |
| (e) 680A (Thiokol) | - polyester |
| (f) Upjohn 2363 | - polyether. |

Only the polyether materials had any degree of flexibility at -60°F , but these also had poor fuel resistance. A series of blends with Upjohn 2363 polyether did yield flexibility at -60°F , but the materials were very difficult to process. Over-all extrusion temperature of 400°F or higher were necessary and therefore none of these systems would be usable with present hose processing technology.

Three other polyurethanes were also checked. Upjohn 2101-80A, a Stevens formulation, and a new Estane 58300-80A. They all have good physicals with the Estane 58300-80A having a good balance and the best low temperature flexibility. However, processing temperature requirements again were the limiting factor, and this could not be considered a candidate material.

A millable polyurethane (polyether type) made by DuPont was evaluated.

Formulation 2642-11-1

Adiprene CM	100 parts
Cadmium Stearate	0.5
Caytur 4	0.35
SRF Black	30
Amberol ST	5
DOP	10
MBTS	4
MBT	1
Sulfur	0.7

This formulation was processed using the low temperature and pressure dictated by present hose technology and the test samples were quite successful. The extractables were somewhat high and actual hose stiffness at -60°F was excessive. A different plasticizer system was required.

Formulation 2642-11-1A

Adiprene CM	100 parts
Cadmium Stearate	0.5
Caytur 4	0.35
SRF Black	30
Benzoflex 9-88SG	15
MBTS	4
MBT	1
Sulfur	0.75

Formulation 2642-11-2

Adiprene CM	100 parts
Cadmium Stearate	0.5
Caytur 4	0.35
SRF Black	25
Benzoflex 9-88SG	20
MBTS	4
MBT	1
Sulfur	0.75

The plasticizing system was changed in the above two formulations and a marked improvement in flexibility was achieved. Also the extractables were significantly reduced in 2642-11-1A. Formulation 2642-11-2 did show a slight improvement in low temperature flexibility, but there was also a large reduction in strength and a significant increase in extractables.

Formulation 2642-11-1A, based on 15 parts of plasticizer (Benzoflex 9-88SG), was chosen for further work.

A length of discharge hose, manufactured using a commercial process, proved to be outstanding in many of the hose properties. The flexibility at -60°F was less than desired, although the material was not brittle at this temperature. With a modulus of rigidity at -60°F of more than 30,000 psi, stiffness was considered excessive. However, at -40°F flexibility was very good. The main reason why this polyether-type polyurethane has better fuel and water resistance than other polyether polyurethanes is that the polyether prepolymer has crosslinking sites and the prepolymer is fully reacted, leaving no unreacted NCO. At this point the material is both a thermoplastic and rubber-like. When either a sulfur or peroxide cure reaction is employed, a unique polyether urethane, having crosslinked bridges between random polyether-urethane molecules, is formed.

Prototype Hose Manufacture

1. Urethane Compound

The Adiprene formulation which had been accepted by the Belvoir R&D Center as a suitable candidate prototype for hose manufacture was milled and compounded by the R. E. Darling Co., Tucson, Arizona, an affiliate of Durodyne, Inc. who was to build the hose. Small samples of each milled batch were cured for 20 minutes at 330°F to determine physical properties of the sheet. Results for 3 batches were as follows:

Tensile strength, psi	3035, 3105, 3309	average 3150
Elongation, %	630, 620, 630	average 627
Shore A hardness	55, 57, 56	average 56
Specific gravity	1.19, 1.22, 1.20	average 1.20
Thickness, mil	76, 76, 80	average 0.077".

Desired minimum values for tensile strength and elongation were 1500 psi and 150%. Clearly this compound exceeded these minimum requirements, and was suitable for processing into hose.

Construction of the suction and discharge hose was as follows:

	<u>Suction Hose</u>	<u>Discharge Hose</u>
Tube	2 plies 0.030" spiral wrap	2 plies 0.020" spiral wrap
First braid*	36 carrier, 3.6 per inch	48 carrier, 4.9 per inch
Helix wire	3/8 inch spacing	none
Tie gum	lay up one ply 0.030"	lay up one ply 0.020"
Second braid*	36 carrier, 3.2 per inch	36 carrier, 3.5 per inch
Cover	2 plies 0.030" spiral wrap	2 plies 0.030" spiral wrap.

*Primed rayon cord.

The hoses were constructed in 15-foot lengths according to normal hose manufacturing procedures. No problems were encountered. The urethane handled and processed as easily as conventional rubber systems. Curing was easily accomplished, and release from the mandrel was simple.

Properties of the resultant hose were as follows:

	<u>Suction Hose</u>	<u>Discharge Hose</u>
Inside diameter	2"	2"
Dimensional change		
0 psi	15'	15'
65 psi	15', 4-1/8"	14', 10-1/4"
100 psi	15', 4-1/2"	14', 9-3/4"
Twist under pressure	none	none
Minimum bend radius at 65 psi	12" to 13"	12" to 13"
Burst, psig	500	425
Resistance to vacuum	no delamination	----
20" Hg 30 sec, then 15" Hg 15 min	no defects	----
Weight per foot	337.5 gm	294.5 gm
Adhesion	impossible to strip rubber from base without breaking	
Appearance	excellent	excellent.

These properties all exceed the desired values. Sections of both hose types approximately 6 feet long were exposed in a cold room at the Belvoir R&D Center. At -40°F, it was judged that the hoses could be reeled. At -60°F, the hoses were judged to be too stiff for reeling, but there was no embrittlement.

Although the flexibility fell somewhat short of what was desired, the hose was an obvious improvement in the state of the art and so satisfactory in other respects that it was considered a desirable candidate for Arctic trials.

2. Fluorosilicone Compound

The GE fluorosilicone formulation, 2642-7-2D, was used in attempt to build suction and discharge hose. Although a section of discharge hose was made, the difficulties encountered were so serious that no attempt was made to build suction hose. These problems were:

- (1) The uncured compound was so soft that it was hard to handle, and braiding tensions had to be reduced so as to minimize penetration of the yarns into the compound.
- (2) There was no bond between layers.
- (3) There was no bond to the reinforcing yarns.
- (4) Flaw and knit lines were excessive.
- (5) The cured state was poor, resulting in a soft compound.

A check into the cause of these problems revealed that the oven used for curing this hose sample was contaminated, causing inhibition of the cure reaction. Consequently, it was decided to repeat the hose-building trial, using an oven devoted solely to the curing of silicones for the final cure.

This second trial was carried out, with only a marginal improvement in the final product. It was decided that:

- (1) Nothing could be done about the softness of the uncured compound. This is the hardest fluorosilicone available for the purpose.
- (2) The poor bond between layers was the result of inadequate normal pressure from the nylon wrapping. Trials in a laboratory press showed excellent inter-layer bonding. All that could be done, therefore, would be to increase the wrapping tension of the nylon tape as much as possible.
- (3) The lack of bond to the yarn might have been because RFL coated yarn had been used, as was customary in Durodyne's operation. This problem needs to be studied in the laboratory.
- (4) Flaw and knit lines were also the result of inadequate normal pressure during curing.
- (5) Removal of the source of contamination during curing resulted in a good cure.

Tests carried out in the laboratory indicated that adhesion to an uncoated rayon yarn was no better than to the RFL-treated yarn. A study was undertaken, therefore, to determine whether a tie-coat could be found which would improve the adhesion between the fluorosilicone compound and the yarn reinforcement.

Tie Coat Investigation

Several suppliers of adhesives were contacted for advice and potential candidates, as well as General Electric Co., Dow Corning, and Engineered Yarns, Inc.

None of our attempts with adhesives, primarily of the Chemlok type, were effective in increasing adhesion to the yarn by a significant amount.

The General Electric Co. tried a variety of primers and additives, the best of which (a one-component, fluorosilicone adhesive), FRV-1106, resulted only in a 5 to 10% cohesive bond (the remainder-adhesive failure), too little to be of any value.

Engineered Yarns, Inc. submitted samples of the rayon cord with Dow Corning DC A-4040 silicone primer and a proprietary adhesive coating which laboratory trials showed gave no significant improvement in the fluorosilicone/rayon cord adhesion. They also supplied samples of polyvinyl alcohol tire cord which proved to be no easier to bond to than the rayon cord.

After considerable effort to achieve fluorosilicone/cord adhesion we concluded that we shall have to be satisfied with ensuring good penetration and encapsulation of the cord structure to hold the hose together. This can only be achieved if the compound flows during curing, which was not the case with GE's FSE2620U fluorosilicone.

A New Fluorosilicone

At this point in the investigation, General Electric submitted a new fluorosilicone compound, FSE7140, for our evaluation. In addition, Dow Corning's compound LSQ2860, tested previously in formulations 2642-40-2 and 2A, was retested in a new formulation which included different additives.

The two formulations were:

	<u>2642-40-1</u>	<u>2642-40-2</u>
DC LSQ2860	100	
GE FSE7140		100
GE SE484	5	5
DC HA-1	0.7	0.7
MS7 Fumed Silica	7	7
Luperco CST	1.5	1.5

Cured under low pressure 30 minutes at 250°F; post cure 1 hour at 400°F.

Both formulations gave improved interlaminar flow and encapsulation of the reinforcing yarns compared to formulation 2642-7-20 which was based on GE FSE2620U. No yarn adhesion was obtained using the LSQ2860 formulation, while FSE7140 gave slight but detectable yarn adhesion and significantly increased ply adhesion. The physical properties of a cured film of 2640-40-2 were:

Tensile Strength: 1275 psi
Elongation: 54%
Shore A Hardness: 49.

Fuel resistance and low temperature stiffness were the same as for the FSE2620U formulation, which had been deemed to be adequate. It was therefore recommended that an attempt be made to make a test length of 2-inch discharge hose using formulation 2640-40-2.

Durodyne, Inc. attempted to make a 15-foot length of fluorosilicone hose, using FSE7140 from General Electric, compounded according to formulation 2642-40-2. Representatives of AI Research Co. were present to observe the procedure.

This was milled and calendered to a 50 mil sheet by the staff at the R. E. Darling Co. in Tucson before we arrived, and had been slit to strips about 7" wide, ready for the manufacture of 2" hose at Durodyne, Inc.

The manufacturing steps are shown in the enclosed photographs:

In Figure 1, a fifteen foot long, 2" diameter steel mandrel has been laid on a 7" wide calendered strip of uncured fluorosilicone rubber, which is then wrapped manually around the mandrel. The sheet is sufficiently tacky to stick to itself, and an overlap seam is formed as shown in Figure 2. After covering the mandrel, any slits which have developed are covered by pressing on a patch of the fluorosilicone sheet.

Figures 3 and 4 show the first layer of braid being added by a 48-carrier braider. Then, in Figure 5, a second wrap of fluorosilicone is being added manually as the mandrel moves through the machines. A second layer of braid is being added in Figure 6 by a 32-carrier braider. In Figure 7 a layer of sheet plastic is being wrapped around the mandrel in order to prevent possible contamination from contact with moving "caterpillar-type" jaws which draw the mandrel through the braiders. In Figures 8 and 9 a final helical wrap of the fluorosilicone sheet is added to form the outer cover. Finally, in Figure 10, two wraps of nylon tape, saturated with a soapy water-silica dispersion, are being applied to provide some normal pressure to promote interlaminar flow when the resin is cured.

After wrapping, the hose on its mandrel was taken to the R. E. Darling Co., to be cured in their vulcanizer (autoclave) which is used only for silicone hose. It was left in the autoclave at 60 psi steam pressure (307°F) for 30 minutes. Upon removal, an examination of the end of the hose seemed to indicate good flow between wrapped layers of fluorosilicone. It was given a 4-hour post cure at 360°F in an air oven the following day.

After cooling, the tape was removed and an unsuccessful attempt made to remove the hose from the mandrel. This is done by blowing high pressure air between the hose and the mandrel. Unfortunately, the inner wrap of fluorosilicone was sufficiently stuck to the steel mandrel that removal was impossible. This had happened in previous attempts to make fluorosilicone hose, and was overcome by covering the mandrel with soap before wrapping. Presumably, therefore, this problem could be overcome.

A much more distressing problem was that the fluorosilicone did not cure properly. It was too soft (Shore A 30 instead of 50) and too weak. This could only be due to contamination, since fluorosilicone curing is unusually sensitive to the inhibiting effects of small amounts of sulfur or other contaminating elements. We were satisfied that Durodyne had taken all reasonable precautions to avoid contamination during hose manufacture. We therefore pursued this question with the staff who prepared the compound at R. E. Darling.

Darling had run a small preliminary trial in which small quantities of unpigmented fluorosilicone had been processed on a small laboratory mill and calendered on a small laboratory calender. This had cured satisfactorily, and gave physicals which were essentially the same as we had obtained in our own laboratory. On the basis of this trial, they did not anticipate any problems with processing the larger batch of fluorosilicone. The only difference between the batches was that the large batch was to contain an olive drab pigment, and was to be run on their normal plant equipment.

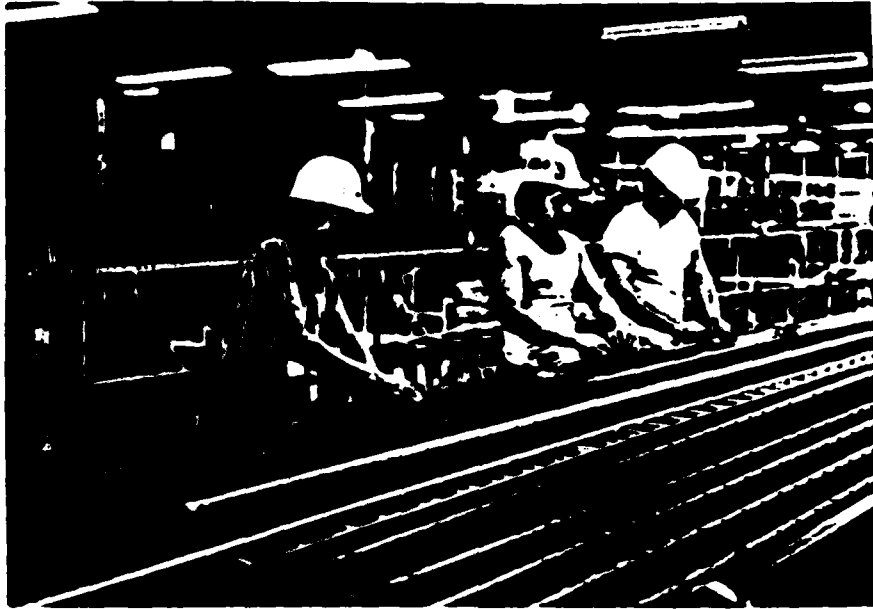


Figure 1. Wrapping Liner on Mandrel

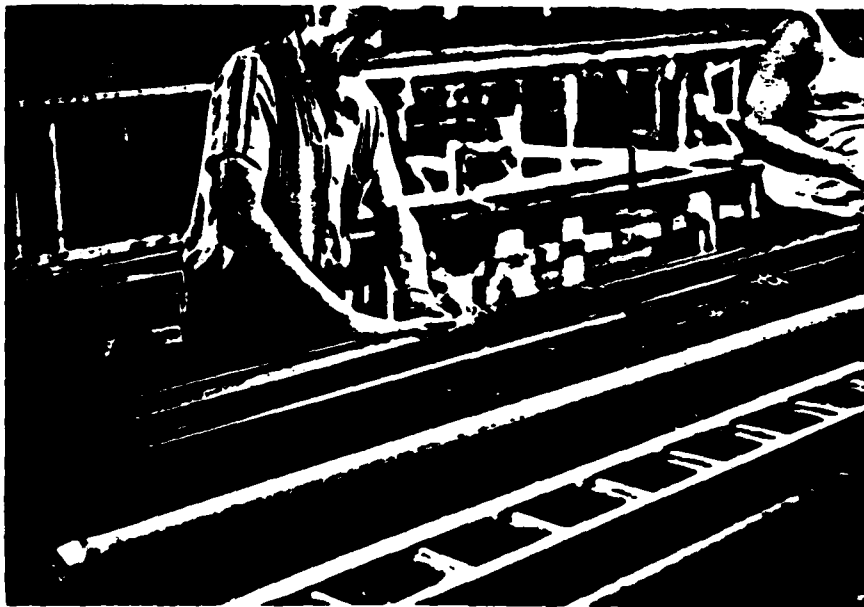


Figure 2. Wrapping Liner on Mandrel



Figure 3. First Layer of Braid

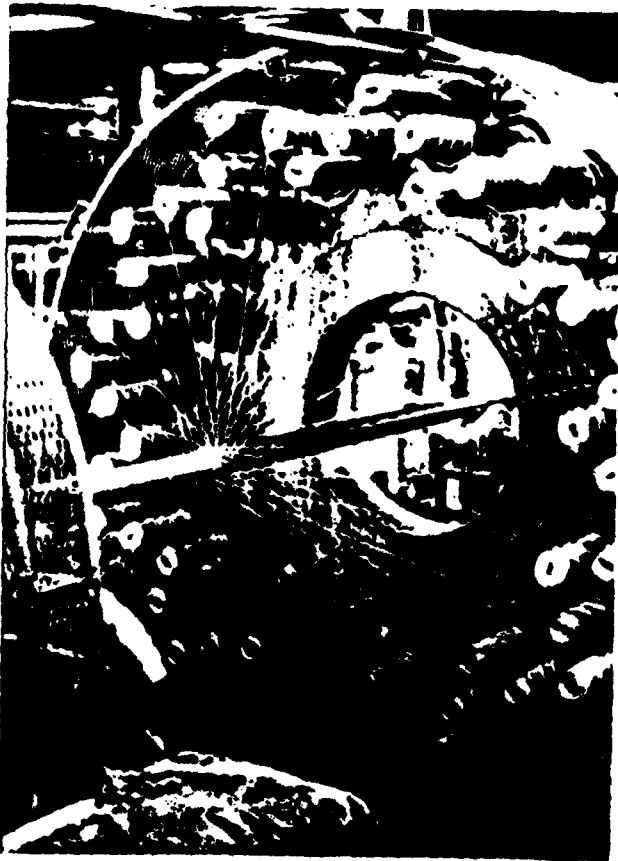


Figure 4. First Layer
of Braid



Figure 5. Second Layer of Fluorosilane



Figure 6. Second Layer of Braid



Figure 7. Protective Wrap for Passage Through Pulling Jaws



Figure 8. Starting Cover Wrap

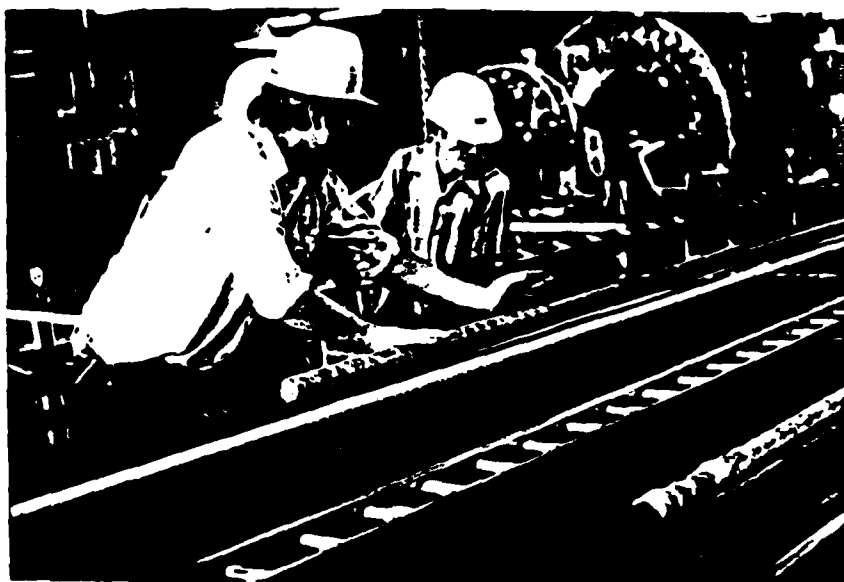


Figure 9. Cover Wrap



Figure 10. Nylon Tape Cover

During the laboratory calendering of the small batch, slight edge discoloration had been observed and immediately cut off. This was assumed to be the pickup of small amounts of bearing grease from the calender rolls. In processing the large batch, no edge discoloration could be seen because of the presence of the green pigment. Although the edges were trimmed, it is now assumed that some residual grease remained in the fluorosilicone, and that it was sulfur in this grease which contaminated the mix and inhibited the cure.

After careful consideration, we have now concluded jointly with Durodyne that, even though the GE FSE7140 fluorosilicone seems to be suitable for manufacturing acceptable hose, its extreme sensitivity to contamination makes it an impractical compound to be used in the conditions found in a normal, well-run plant. We believe that the conditions in both the Darling and the Durodyne plants reflect good commercial practice, and that the care taken to process the fluorosilicone was at least as good as would be found in other hose manufacturing plants. Fluorosilicone processing, however, requires that the equipment used be kept scrupulously clean and isolated from the rest of the plant. Such an operation, though possible, would require a commitment which would only be feasible for much larger scale production than is contemplated in this contract or, for that matter, in any near-term future procurements which, because of the high cost of fluorosilicone hose, would probably be modest in scope. We recommended, therefore, that manufacture of fluorosilicone hose be dropped from the contract. Belvoir R&D Center agreed with this recommendation.

Hose Manufacture

The original contract requirements called for delivery of four 25' hose lengths of 2", 4" and 6" diameter discharge fuel hose, and four 10' hose lengths of 2", 4" and 6" diameter suction fuel hose to be made from each of two compounds suitable for use in Arctic conditions. In Phase I, the two compounds which were selected were the urethane Adiprene CM and the fluorosilicone FSE7140. For reasons already explained, it became necessary to drop the manufacture of fluorosilicone hose from the contract. Consequently we were asked to make 8 hose lengths of each type from Adiprene CM.

These prototype hose lengths were manufactured by Durodyne, Inc. without any problems. The compound processed well, was easy to handle, and responded well to conventional hose manufacturing techniques. The resulting hose passed the required tests for proof pressure, minimum burst and crack resistance. Initial tests at Fort Greely, Alaska late in the winter of 1981-82 showed that the hose remained flexible and was easy to handle down to -40°F. Below that temperature it stiffened, so that at -50°F it was too stiff to handle, but it did not become brittle, and the original flexibility was regained when the temperature rose again.

As a consequence of this initial success, a contract modification was issued to make an additional twenty 50' lengths of 2" diameter discharge hose, and twenty 10' lengths of 3" suction hose from Adiprene CM. The 2" discharge hose lengths were made by Durodyne, Inc. without difficulty. A problem arose, however, in manufacturing the 3" suction hose lengths. About one-half of these pieces could not be removed from the steel mandrel on which they were formed. In a second attempt only 3 of 13 pieces could be removed from the mandrel.

The problem with the 3" suction hose was finally traced to mandrel contamination resulting from their previous use in manufacturing hose from epichlorhydrin. After thoroughly cleaning the mandrels, the remaining hose lengths were made without difficulty. All hose sections passed the required tests for proof pressure, minimum burst and crush resistance.

Adiprene CM has proved to be adaptable to standard hose manufacturing procedures with no problems, provided clean mandrels are used. Mandrels which have contaminated surfaces to which the urethane can adhere make it impossible to remove the formed hose from the mandrel without damaging it.

Hose Gaskets

We were also required to make fluorosilicone coupling gaskets for the 20 lengths each of 2" discharge and 3" suction hose made under contract modification. The formulation which was specified was:

Fluorosilicone LS-422	100.0 parts
Luperco 101-XL	1.2 parts.

Press cure for 15 minutes at 340°F; no post cure.

The gasket dimensions were given in drawing MS27030 as follows:

<u>Nominal Size</u>	<u>External Diameter (inches)</u>	<u>Internal Diameter (inches)</u>	<u>Thickness (inch)</u>
2"	2-5/8	2	0.250
3"	3-22/32	3	0.250

tolerance $\pm 1/64$ inch; ± 0.005 inch,
allow for setting shrinkage of 2-1/2%.

A steel mold was made in which the 2" and 3" gaskets were made concentrically in one operation. The compound was milled into sheets approximately 1/4" thick. Cut strips of the milled compound were laid into the grooves of the mold, and curing was done in a heated platen press. No problems were encountered in making the required gaskets, which were shipped to Fort Greely, Alaska.

Summary

Fuel hose for Arctic use has been successfully made from a urethane compound, Adiprene CM, which is suitable for use in a standard hose manufacturing operation. A fluorosilicone compound, FSE7140, was also found to be potentially suitable for hose manufacture, but was deemed impractical for commercial use because of its extreme sensitivity to contamination, which would require unusual precautions to ensure complete cleanliness.

Preliminary tests on the urethane hose in the Arctic indicate that it remains sufficiently flexible for easy handling down to -40°F. Below that, while some stiffening will occur, the compound will not become brittle, making this the best hose yet developed for Arctic use. Flexibility at lower temperatures could be provided by the fluorosilicone compound, if sufficient care were taken in the manufacturing operation to ensure total lack of contamination.

The following lengths were made, tested, and shipped to Fort Greely, Alaska, for service tests:

<u>Type</u>	<u>Diameter</u>	<u>Length</u>	<u>No. of Pieces</u>
Discharge	2"	25'	8
	2"	50'	20
	4"	25'	8
	6"	25'	8
Suction	2"	10'	8
	3"	10'	20
	4"	10'	8
	6"	10'	8