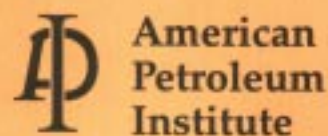


HEALTH AND
ENVIRONMENTAL
AFFAIRS
DEPARTMENT

API PUBLICATION
NUMBER 328

JANUARY 1995

Laboratory Evaluation of Candidate Liners for Secondary Containment of Petroleum Products





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- ❖ To commit to reduce overall emission and waste generation.
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- ❖ To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

Laboratory Evaluation of Candidate Liners for Secondary Containment of Petroleum Products

Health and Environmental Affairs Department

API PUBLICATION NUMBER 328

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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

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ABSTRACT

An earlier investigation of tankfield dike lining geosynthetic materials and methods for secondary containment of aboveground storage tank (AST) facilities was completed in 1992. At that time, direct comparative data to evaluate the various candidate liners did not exist. A second phase of work was initiated to meet this need. This report documents the Phase II evaluation of chemical resistance of a variety of liner materials. Six geosynthetic membrane liners and two geosynthetic clay liners (GCLs) were tested to determine vapor permeation resistance (membrane liners) and hydraulic conductivity (clay liners), and to measure changes in physical properties after immersion in fuels and blends representative of those stored in AST facilities. The work included four separate tasks that generated comparative data on vapor permeation, chemical resistance, liquid conductivity and other physical properties of geosynthetic membrane liners and GCLs as a function of controlled exposure to the fuels and blends. Project test results were used to rank the various liners in terms of performance in the vapor permeation test and relative changes in properties measured after immersion.

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EXECUTIVE SUMMARY

An earlier investigation of tankfield dike lining geosynthetic materials and methods for secondary containment of aboveground storage tank (AST) facilities was completed in 1992. At that time, direct comparative data to evaluate the various candidate liners did not exist. A second phase of work was initiated to meet this need.

This report documents a laboratory study of geosynthetic liner materials proposed for use for the secondary containment of petroleum fuels and fuel blends in ASTs. Six geosynthetic membrane liners and two geosynthetic clay liners (GCLs) were tested to determine vapor permeation resistance (membrane liners) and hydraulic conductivity (clay liners), and to measure changes in physical properties after immersion in fuels and blends representative of those stored in AST facilities.

The objective of this test program was to provide comparative data on vapor permeation, chemical resistance, liquid conductivity and other physical properties of geosynthetic membrane liners and GCLs as a function of controlled exposure to fuels and blends. The liner materials tested included:

- Polyester elastomer coated woven polyester fabric;
- Ethylene interpolymers alloy (EIA) elastomer coated woven polyester fabric;
- Tri-polymer blend elastomer coated woven polyester fabric;
- Polyurethane elastomer coated woven polyester fabric;
- High density polyethylene (HDPE) sheet;
- Field applied spray-on geotextile coating (polysulfide elastomer on nonwoven needle punched geotextile);
- Two GCLs having different geotextile backings.

The fuel blends tested were:

- 100% unleaded gasoline (winter blend);
- 100% diesel fuel;
- 100% ethanol;
- 100% methyl *tert*-butyl ether (MTBE);
- 10% ethanol/90% gasoline mixture (by volume);
- 15% MTBE/85% gasoline mixture (by volume).

Specifically, the following tasks were undertaken:

- Rates of vapor permeation were determined for six selected geomembranes exposed to six fuels and/or additives. Two of the fuel blends represented high oxygenate formulations. For membrane liners, the mode of transport is vapor permeation or diffusion driven by the concentration gradient which exists across the barrier. Vapor permeation was measured according to ASTM F 739-81 (ASTM, 1981), which is a test method providing direct, analytical determination of permeating vapor with very high sensitivity. The test was specifically designed to measure the vapor permeation resistance of barrier films and coated fabrics exposed to hazardous chemicals.
- The chemical resistance of six geomembranes to fuels and blends was determined by measuring changes in physical properties as a function of one-sided exposures of 72 hours and 30 days duration.
- Liquid conductivity or permeability rates were determined for two fully hydrated geosynthetic/clay liners (GCLs). For GCLs, the mode of transport is hydraulic conductivity or liquid flow driven by the difference in hydraulic head which exists across the barrier. Each of the six fuels and/or additives was used as a permeant in a modified triaxial cell.
- The effects of immersion in fuels and additives on the geotextile backings used in manufacture of GCLs were determined by measuring changes in physical properties of the geotextiles as a function of exposure for 72 hours and 30 days duration.

Tables ES-1, ES-2 and ES-3 summarize the results of this study. Table ES-1 presents vapor permeation results. Ranking was by material and permeant (1 = lowest steady state permeation rate), and summed rankings are listed at the bottom of the table, providing a relative indication of overall permeation resistance against the six fuels and/or additives.

Table ES-1. Ranked permeation results for geomembrane liners

Fuel or Blend	Polyester elastomer coated fabric	EIA coated fabric	Tri-polymer Blend coated fabric	Poly-urethane coated fabric	HDPE	Poly-sulfide spray-on
Gasoline	3	6	5	2	1	4
Diesel	3	5	6	2	1	4
Ethanol	2	5	3	6	1	4
MTBE	1	5	6	4	2	3
Gasoline/MTBE blend	2	4	6	3	1	5
Gasoline/ethanol blend	3	6	2	5	1	4
Summed rankings	14	31	28	22	7	24

Table ES-2 presents results of liquid conductivity testing for GCLs. In Table ES-3, ranking for chemical resistance tests was calculated by determining a grand mean for deviations from 100% of original property retained (1 = lowest mean deviation). This scheme favors those materials which show the least overall change in physical properties.

Table ES-2. Summary of hydraulic conductivity results for GCLs

Permeant	Hydraulic Conductivity (cm/sec x 10 ⁻⁹)			
	GCL #1		GCL #2	
	Water	Fuel permeant	Water	Fuel permeant
Gasoline	1.8	1.5	2.9	2.3
Diesel	1.1	2.2	1.2	2.9
Ethanol	1.4	1.0	2.1	1.9
MTBE	1.4	1.7	1.2	1.4
Gasoline/MTBE	1.5	6.7	1.4	6.9
Gasoline/ethanol	1.5	1.7	1.2	1.9

Table ES-3. Ranked chemical resistance results for geomembrane liners

Fuel or Blend	Polyester elastomer coated fabric	EIA coated fabric	Tri-polymer Blend coated fabric	Poly-urethane coated fabric	HDPE	Poly-sulfide spray on
Gasoline	4	3	1	2	5	6
Diesel	4	2	1	3	4	4
Ethanol	3	2	1	5	2	4
MTBE	5	2	1	3	4	6
Gasoline/MTBE blend	3	2	1	2	4	5
Gasoline/ethanol blend	4	2	1	3	5	6
Summed rankings	23	13	6	18	24	31

With few exceptions, all of the materials tested showed good performance when tested against the six fuels and blends. The following conclusions were drawn from this study:

CHEMICAL RESISTANCE

Ranked by overall performance in the physical tests, the tri-polymer blend clearly showed the least overall change after immersion. It was ranked first against each of the six fuels and/or blends. The next best performing product was EIA coated fabric, followed by polyurethane

coated fabric. HDPE and the polyester elastomer coated fabric showed comparable performance. The polysulfide spray on coated fabric ranked no better than fourth against any fuel or blend.

In terms of physical properties, none of the six geomembrane liners were considered to be severely degraded by immersion in the six fuels. Decreases up to 20% in puncture strength were common for coated fabrics; however, the same materials showed consistent increases in tensile strength after one-sided exposure to fuels. Observed increases in tear strength were not considered significant (see Page 4-3). Observed changes in puncture and tensile strength were not large enough to conclude that serviceability or reliability had been compromised.

When cut edges were exposed, coated fabrics were found to be subject to wicking into the textile fibers, as evidenced by large weight gains. This observation points to the importance of workmanship in seaming and installation. Cut edges can be protected from exposure to fuel by covering seams with a bonded strip.

HDPE showed evidence of slight softening and plasticization as a result of fuel absorption into the polymer matrix. Changes in physical properties of up to 20% were observed, with corresponding increases in weight.

PERMEATION RESISTANCE OF GEOMEMBRANE LINERS

HDPE showed superior overall vapor permeation resistance. The next best performing product was polyester elastomer-coated fabric, followed by polysulfide- and polyurethane-coated fabrics which showed comparable performance. EIA coated fabric was ranked no better than fourth against any fuel or blend. HDPE and polyester elastomer-coated fabric showed superior permeation resistance to neat MTBE. HDPE's resistance to diffusion or permeation of fuels was attributed to the fact that as a film, a much thicker polymer barrier is presented to the permeant than exists with any of the elastomer-coated fabrics that were tested.

LIQUID CONDUCTIVITY OF GCLS

Both GCLs showed very low permeability to both water and fuels. Gasoline/MTBE blend and diesel fuel had higher permeability rates than water did. Rates for gasoline/MTBE blend and diesel fuel were two to five times higher, but still remained in the 10^{-9} cm/sec range.

GCL GEOTEXTILE BACKINGS

Effects on the physical properties of geotextile backings that were exposed to fuels were not considered significant.

PERMEATION TESTING

It was concluded that the analytical vapor permeation test (ASTM F 739-81 (ASTM, 1994)) is highly appropriate for determining diffusion rates for fuel containment applications.

However, poor correlation with the commonly used gravimetric test (ASTM E 96-93 (ASTM, 1993)) was observed. It is strongly recommended that the analytical test, ASTM F 739-81, be considered as the preferred method for measuring diffusion rates and breakthrough times for fuel exposure to geomembranes.

It is also recommended that permeation resistance for synthetic geomembrane liners not be specified in terms of hydraulic conductivity units (cm/sec), since the mode of transfer across the barrier is by vapor diffusion rather than liquid transport.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Further study is recommended to develop design and product selection guidelines for release prevention barrier and dike containment applications. Use of these products for petroleum containment applications is expected to increase, and a comprehensive program to develop design parameters and selection criteria would meet a pressing need that exists in the petroleum industry.

The overall conclusion drawn from this study is that each of these materials can offer good-to-excellent performance in applications where contact with fuels may occur, assuming that proper design practices are used. The user should consider requirements for permeation resistance together with other factors in selecting the liner material which best suits each situation.

Section 1

INTRODUCTION

This report documents a laboratory study of geosynthetic liner materials proposed for use in the secondary containment of petroleum fuels and fuel blends in aboveground storage tanks (ASTs). Six geosynthetic membrane liners and two geosynthetic clay liners were tested to determine vapor permeation resistance (membrane liners) and hydraulic conductivity (clay liners), and to measure changes in physical properties after immersion in fuels and blends representative of those stored in AST facilities.

A previous study completed in 1992 (TRI, 1993) provided an assessment of tankfield dike lining materials and methods for secondary containment of AST facilities. The direct comparative data needed to evaluate the various kinds of synthetic liners available on the market was lacking, and the present study was initiated to meet this need. The resulting performance data would be useful to potential users of synthetic liner products for fuel containment applications, such as release prevention barriers¹ and the lining of dikefields.

The selection of liner products, fuels and blends was made by the API Liner Study Workgroup which provided oversight to the development and execution of the project. The matrix of fuel exposure conditions and testing procedures was recommended by the contractor based on methods used to characterize coated fabrics and films within the geosynthetics and waste containment industry, with approval by the Workgroup. Tests were selected which are designed to be used with each type of material under consideration (e.g., coated fabric vs. thermoplastic film - HDPE).

OBJECTIVES AND PROJECT OVERVIEW

The objective of this test program was to provide comparative data on vapor permeation, chemical resistance, liquid conductivity and other physical properties of geosynthetic membrane liners and GCLs as a function of controlled exposure to fuels and blends.

¹ The term release prevention barrier includes steel bottoms, synthetic materials, clay liners and all other barriers or combinations of barriers placed in the bottom of, or under, an aboveground storage tank, which have the functions of: (1) preventing the escape of contained material, and (2) containing or channeling released material for leak detection.

The liner materials tested included:

- Polyester elastomer coated woven polyester fabric;
- Ethylene interpolymer alloy (EIA) elastomer coated woven polyester fabric;
- Tri-polymer blend elastomer coated woven polyester fabric;
- Polyurethane elastomer coated woven polyester fabric;
- High density polyethylene (HDPE) sheet;
- Field applied spray-on geotextile coating (polysulfide elastomer on nonwoven needle punched geotextile); and
- Two GCLs having different geotextile backings.

The fuel blends tested were:

- 100% unleaded gasoline (winter blend);
- 100% diesel fuel;
- 100% ethanol;
- 100% methyl *tert*-butyl ether (MTBE);
- 10% ethanol/90% gasoline mixture (by volume); and
- 15% MTBE/85% gasoline mixture (by volume).

Specifically, the following tasks were undertaken:

- Rates of vapor permeation were determined for six selected geomembranes exposed to six fuels and/or additives. Two of the fuel blends represented high oxygenate formulations. For membrane liners, the mode of transport is vapor permeation or diffusion driven by the concentration gradient which exists across the barrier. Vapor permeation was measured according to ASTM F 739-81 (ASTM, 1994), which is a test method providing direct, analytical determination of permeating vapor with very high sensitivity. The test was specifically designed to measure the vapor permeation resistance of barrier films and coated fabrics exposed to hazardous chemicals.
- The chemical resistance of six geomembranes to fuels and blends was determined by measuring changes in physical properties as a function of one-sided exposures of 72 hours and 30 days duration.
- Liquid conductivity or permeability rates were determined for two fully hydrated geosynthetic/clay liners (GCLs). For GCLs, the mode of transport is hydraulic conductivity or liquid flow driven by the difference in hydraulic head which exists across the barrier. Each of the six fuels and/or additives was used as a permeant in a modified triaxial cell.
- The effects of immersion in fuels and additives on the geotextile backings used in manufacture of GCLs were determined by measuring changes in physical properties of the geotextiles as a function of exposure for 72 hours and 30 days duration.

The synthetic geomembranes were ranked in terms of performance in the vapor permeation test and relative changes in properties measured after immersion.

SCOPE

The scope of this study was limited to physical characterization of the products when exposed to fuels and blends. Issues surrounding the decision of whether or not to use liners for a particular application, including economic or regulatory considerations, were not addressed.

Section 2

LINER MATERIALS AND PETROLEUM PRODUCTS TESTED

Six flexible geosynthetic liner products were selected representing three types or classifications of materials. These included four elastomer-coated fabrics, one plastic film (HDPE), and one spray on coating applied to geotextile substrate. Two geosynthetic clay liners (GCLs) were also tested, each representing a different manufacturer. The liners were selected by the Liner Study Workgroup to represent products that have been used or proposed for use in secondary containment applications. Table 2-1 describes the materials selected for testing in this program.

Table 2-1. Description of selected liner products

Material Type	Description
Coated Fabric	Polyester elastomer coated fabric; polyester woven fabric base weight 5 oz/sq yd; nominal coated product weight 30 oz/sq yd; nominal thickness 30 mils
	Ethylene interpenetrating polymer alloy (EIA) elastomer coated fabric; polyester woven fabric base weight 7.5 oz/sq yd; coated product weight 38 oz/sq yd; thickness 40 mils
	Tri-polymer blend elastomer coated fabric; polyester woven fabric base weight 7.5 oz/sq yd; nominal coated product weight 30 oz/sq yd; nominal thickness 30 mils
	Polyurethane elastomer coated fabric; polyester woven fabric base weight 13 oz/sq yd; coated product weight 38 oz/sq yd; nominal thickness 40 mils
Unsupported thermoplastic sheet	High density polyethylene; nominal thickness 60 mils
Field-applied spray on geotextile coating	Polysulfide coating applied to nonwoven geotextile base; nominal minimum coating thickness 36-40 mils over primer coat
Geosynthetic/clay liners	GCL #1; bentonite blanket sandwiched between woven geotextile with non-woven geotextile backing; needle-punched
	GCL #2; bentonite blanket sandwiched between two woven geotextiles

The following fuels and blends were selected by the Liner Study Workgroup for testing with the liner products listed above:

- 100% unleaded gasoline (winter blend);
- 100% diesel fuel;
- 100% ethanol;
- 100% methyl *tert*-butyl ether (MTBE);
- 10% ethanol/90% gasoline mixture (by volume); and
- 15% MTBE/85% gasoline mixture (by volume).

Section 3

SUMMARY OF EXPERIMENTAL METHODS

Experimental methods are summarized in this section. Refer also to Appendix A for more detailed information.

CHEMICAL RESISTANCE OF GEOMEMBRANES

Chemical resistance refers to the extent to which the liner materials retain their original physical properties after exposure to fuels and additives. The effects of direct, one-sided exposure to the six fuels, additives and blends were determined for each of the six selected geomembrane liner products. Tensile strength, elongation, puncture strength, tear resistance and hardness of the materials were measured (1) on pristine, unexposed samples, (2) on samples exposed on one side only for 72 hours, and (3) on samples exposed on one side only for 30 days. Weight gain or loss as a function of exposure was also measured.

The 72-hour period was included because proposed revisions to the current SPCC regulations would require a diked area to be sufficiently impermeable to contain a release for 72 hours. The 30-day test period represents longer term exposures. The individual tests listed in Table 3-1 are described in Appendix A.

Table 3-1. Test methods used to characterize geomembrane liners

Property	Material Type	Test Method Standard	Specimen Dimensions	No. of Replicates	
				Baseline	Exposed
Puncture Strength	Coated Fabrics	ASTM D 4833	4" circle	4	2
	HDPE	FTMS 101C Method 2065	1" circle	4	2
Tensile Strength	Coated Fabrics	ASTM D 751 strip method	1" x 6" strip, machine direction	10	5
	HDPE	ASTM D 638	Type IV dumbbell, machine direction	10	5
Tensile Elongation	HDPE	ASTM D 638	Type IV dumbbell, machine direction	10	5
Tear Strength	Coated Fabrics	ASTM D 4533 (modified)	4" x 2.5" specimens, machine direction	10	5
	HDPE	ASTM D 1004	Bent dumbbell, machine direction	10	5
Hardness	Coated Fabrics	ASTM D 2240	Stacked specimens; Duro A scale	6	3
	HDPE		Duro D scale	6	3

PERMEATION RESISTANCE OF GEOMEMBRANES

Vapor permeation rates for the six selected geomembrane liner materials were measured (1) after 72 hours one-sided exposure to each fuel or blend, and (2) after sufficient time had elapsed to verify that steady state, or maximum flow conditions had been reached.

Permeation testing was performed in accordance with ASTM F 739-81 (ASTM, 1994), "Resistance of Protective Clothing Materials to Permeation by Liquids or Gases under Conditions of Continuous Contact." A limited investigation was conducted to assess correlation of this method with ASTM E 96-93 (ASTM, 1993), "Water Vapor Transmission of Materials."

PERMEABILITY OF GEOSYNTHETIC CLAY LINERS

Each of the two selected geosynthetic clay liners (GCLs) were subjected to hydraulic conductivity (permeability) testing with each of the six fuels and blends. The tests were conducted in general accordance with EPA Method 9100 standards using a triaxial pressure cell apparatus.

CHEMICAL RESISTANCE OF GCL BACKING GEOTEXTILES

The two GCL products tested each consisted of a layer of bentonite sandwiched between two geotextiles. Both woven and non-woven geotextiles were used, depending on the manufacturer. The resistance of these geotextiles to exposure to fuels, additives and blends was determined. This was done by fully immersing each geotextile for periods of 72 hours and 30 days, with measurement of physical properties (tear, puncture and tensile strength) before and after exposure.

Section 4 RESULTS

This section presents summaries and discussions of laboratory results. Detailed graphs and tables appear in Appendices B-E.

CHEMICAL RESISTANCE OF GEOMEMBRANES

Table 4-1 indicates baseline results for physical properties tested as manufactured, prior to exposure for coated fabrics and spray on coatings, and Table 4-2 indicates baseline results for HDPE.

Table 4-1. Baseline physical property results for coated fabrics

Material	Puncture strength ASTM D 4833 (lb at rupture)	Tensile strength ASTM D 751 (lb/in width)	Trapezoidal tear strength ASTM D 4533 modified (lb)	Hardness ASTM D 2240 Shore A scale
Hytel coated fabric	178	277	99	83
EIA coated fabric	277	423	97	85
Tripolymer blend coated fabric	277	402	45	95
Polyurethane coated fabric	583	728	163	83
Polysulfide spray-on	83	50	48	46

Table 4-2. Baseline physical property results for HDPE geomembrane liner

Puncture strength FTMS 101C Method 2065 (lb)	Tensile strength ASTM D 638 (lb/in ²)		Tensile elongation ASTM D 638(%)		Tear strength ASTM D 1004 (lb/in thickness)	Hardness ASTM D2240 Shore D scale
	Yield	Break	Yield	Break		
107	2885	4484	17	760	828	59

This test program was designed to compare physical properties of materials before and after fuel exposure, not to directly assess or rank performance of the selected materials and products. Care should be exercised in comparing results from unexposed materials tested in this program with manufacturers' published values. It should be verified that the test procedures were the same, and that the effect of modifications, where used, is understood.

Results of physical tests for exposed geomembranes are presented graphically as Figures B-1 through B-36, Appendix B. Results are expressed in terms of percentage of original property retained, with 100% being the baseline value. Each figure shows the four physical properties tested, with individual bars corresponding to the exposure times and venting conditions. In these figures, "IT" refers to immediate test, or pre-venting; and "DT" refers to delayed test, or post-venting. Please refer to Section 3 for a detailed discussion of test procedures followed.

Weight change data for geomembrane liners are presented graphically in Figures C-1 through C-6, Appendix C. Note, however, that because specimens were fully immersed for weight gain tests, the coated fabrics showed very large changes in weight because of wicking from the exposed edges. Therefore these results should be considered only as a very general index of the tendency for products to support wicking, and not a relative indication of chemical resistance. It is important to note that the standard installation practice for coated fabrics is to prevent contact of exposed edges with areas that could contact contained fuels by means of strip seaming. This practice is followed to prevent wicking.

With coated fabrics, the fabric reinforcement or scrim contributes nearly all of the strength and physical properties to the product. Therefore, changes observed after fuel exposure are mostly attributable to scrim effects rather than effects due to immersion of the polymer barrier. This is in contrast to HDPE which is a homogenous plastic film. Note, however, that the thickness of the polymer barrier presented by HDPE is significantly greater than the thickness of the elastomer coatings used with the coated fabrics tested.

For coated fabrics, large changes in tear strength after immersion were noted in many cases. However, this was not considered to be significant for the following reasons. Fibers exposed to fuels may have absorbed enough of the solvents to become "plasticized." This could have allowed the fibers to stretch more prior to breakage, resulting in more fibers carrying the load and higher loads at rupture. The fact that pre-venting changes in tear strength were consistently larger supports this theory. This effect is considered to be an artifact of the test method and not necessarily a reflection of product performance.

Ranking

Table 4-3 presents a scheme for ranking chemical resistance results in terms of the magnitudes of deviations from 100% of property retained. This scheme favors those materials

that show the least overall change in measured properties as a result of exposure, considering all physical properties and exposure conditions. It provides a relative measure of comparative performance.

The calculations included all tests and exposure conditions, including 72-hour and 30-day tests under pre- and post-venting conditions. Note, however, that because of the considerations discussed above, trapezoidal tear data for the coated fabrics were not included. Weight change data were also not considered for any of the products. In Table 4-3, the first number is the grand mean of the magnitudes of deviations from 100% of property retained. The second number is the ranking for each fuel, with "1" being the lowest grand mean of deviations from 100%.

Table 4-3. Ranked chemical resistance results for geomembrane liners

Fuel or Blend	Polyester elastomer coated fabric	EIA coated fabric	Tri-polymer blend coated fabric	Poly-urethane coated fabric	HDPE	Poly-sulfide spray on
Gasoline	13%/4	10%/3	7%/1	8%/2	14%/5	19%/6
Diesel	12%/4	7%/2	5%/1	9%/3	12%/4	12%/4
Ethanol	14%/3	8%/2	7%/1	19%/5	8%/2	16%/4
MTBE	14%/5	9%/2	6%/1	11%/3	12%/4	17%/6
Gasoline/MTBE blend	12%/3	8%/2	5%/1	8%/2	16%/4	17%/5
Gasoline/ethanol blend	14%/4	8%/2	5%/1	9%/3	15%/5	21%/6
Summed rankings	23	13	6	18	24	31

Ranked in this manner, the tri-polymer blend clearly was the best performer, and was ranked first against each of the six fuels and/or blends. The next best performing product was EIA-coated fabric, followed by polyurethane-coated fabric. HDPE and the polyester elastomer-

coated fabric showed comparable performance. The polysulfide spray on coated fabric ranked no better than fourth against any fuel or blend.

Summary of Individual Product Performance

Polyester Elastomer-coated Fabric: This product showed very good retention of tensile properties; however, a drop of 20% to 40% was noted in puncture resistance. The most marked drops in puncture resistance occurred in the two oxygenate blends. A large increase in trapezoidal tear resistance was noted in pre-venting results. The effect was also observed after venting; however, the effect was consistently less than in pre-venting results.

Significant weight gains were noted after this product was exposed to gasoline, diesel and gasoline/ethanol blends. This indicated extensive wicking into fiber ends. Pre- and post-venting weight losses were noted after exposures to MTBE and ethanol, suggesting that these solvents may have dissolved and extracted components of the polymer.

EIA-coated Fabric: This product showed slight but fairly consistent losses in puncture strength after exposures of 72 hours and 30 days. These losses ranged from 5% to about 20% and were greatest with the oxygenates and blends. Very large increases in tear resistance were observed in pre-venting results, with the property returning to near baseline levels after venting.

Weight gains were noted in pre-venting data, with corresponding losses noted in post-venting data for exposure to all fuels with the exception of diesel. The evidence suggests that the EIA polymer absorbs significant quantities of these fuels, with extraction of polymer components and additives by the fuels.

Tri-polymer Blend Coated Fabric: Tri-polymer blend coated fabric performed in a similar fashion to the EIA-coated fabric, with slight but consistent decreases in puncture strength and large increases in tear strength measured before venting.

Tri-polymer blend coated fabric also showed similar performance to EIA-coated fabric in weight gain studies (see above).

Polyurethane-coated Fabric: This product showed consistent decreases in puncture strength ranging from 10% to 20% in all fuels and blends. A significant decrease in tensile strength was observed in neat ethanol but did not occur in other fuel exposures. The marked increase in pre-venting trapezoidal tear strength, which was observed with other coated fabrics, was not observed here. This suggests that there was less absorption into the textile substrate during the one-sided exposures, as compared with the other coated fabrics.

Weight changes for polyurethane coated fabric were much less significant than those observed for the other coated fabrics, and were generally less than 5%. The same trend of swelling and extraction resulting in weight loss after venting was noted.

HDPE: HDPE results show a significant drop, ranging from 10% to 30% in tensile stress at yield. This was accompanied by a corresponding increase in elongation at yield, which increased with the volatility of the fuel and was especially marked in the oxygenate blends. A consistent drop of up to 20% in puncture strength was also observed, and this decrease was also greater in the oxygenate blends. These effects were caused by fuel absorption into the polymer matrix, resulting in plasticization or softening of the polymer. In most cases, the effect was less significant in tests performed after venting, indicating that the effect is reversible to some extent.

HDPE showed pre-venting weight gains exceeding 5%, with gains after venting in the range of 2%-3% except for ethanol which showed almost no interaction with the polymer. Of the six geomembrane liners tested, HDPE showed the lowest overall weight change as a function of exposure. This was attributed to the fact that HDPE is a film not having a textile substrate, so there are no wicking effects from exposed fiber ends.

Polysulfide Spray-on: This product showed good retention of baseline properties after exposure. There was a slight drop in puncture strength tested before venting, but the property returned to baseline levels after venting in most cases. Tensile properties remained at or well above baseline values after exposure in almost all cases.

Weight losses of up to 10% were noted for all exposures with the exception of diesel fuel. This suggests that the volatile fuels and blends tend to dissolve and extract polysulfide polymer components and additives. Since the coating was on one side only, and the

specimens were fully immersed during the test exposures, extraction of components of geotextile probably occurred also.

PERMEATION RESISTANCE OF GEOMEMBRANES

Each geomembrane liner was tested against each of the six fuels, additives and blends for permeation resistance following ASTM F 739-81 (ASTM, 1994). Results are presented in Table 4-4.

Table 4-4. Permeation results for geomembrane liners

Permeant and Exposure time		Permeation rates (micrograms/cm ² -min)					
		Polyester elastomer coated fabric	EIA coated fabric	Tri-polymer coated fabric	Poly-urethane coated fabric	HDPE	Poly-sulfide spray-on
Gasoline	72 hour	0.062	16	10	0.35	0.035	3.5
	Steady state	0.66	16	10	0.35	0.20	3.4
Diesel	72 hour	0.0020	0.10	1.2	0.0060	NM [1]	1.2
	Steady state	0.13	2.1	3.4	0.066	0.071	1.2
Ethanol	72 hour	0.12	3.2	0.39	18	NM [1]	1.1
	Steady state	0.37	3.2	0.39	18	0.012	1.1
MTBE	72 hour	1.5	8,400	10,000	9.2	NM [1]	710
	Steady state	18	8,400	10,000	3,100	18.3	710
Gas/MTBE	72 hour	0.06	15	24	2.7	NM [1]	17
	Steady state	0.46	15	24	2.7	0.19	17
Gas/Ethanol	72 hour	1.6	25	26	6.8	0.14	4.2
	Steady State	1.6	25	26	6.8	0.14	4.2
[1] Not measured; breakthrough not detected							

Minimum detectable limits were measured for each individual test. The limits of detection were extremely low in all cases, ranging from 0.01 to 0.8 parts per million on individual tests. The time required to reach steady state was not reported, since the test cells were not continuously monitored. However, examination of Table 4-4 shows that steady state was reached within the initial 72-hour exposure period in many cases where relatively high rates of permeation were observed. There were also instances in which the time to reach steady state was as long as eight days. If no breakthrough was observed after 500 hours, the exposures were terminated.

Unit Conversions

Permeation data were measured directly in units of micrograms/cm²-min as reported in Table 4-4. To convert to ounces/sq ft-day, a unit frequently used in the U.S.A. for specifying liner performance, multiply the reported result by 4.71×10^{-2} .

The issue of conversion to permeability in cm/sec units may be raised in evaluating these data. Vapor permeation rates are expressed in terms of mass transfer, and hydraulic conductivity is a volume measurement. Therefore a direct conversion was not made. However, the following equivalency may be helpful. Soil liners having very low permeability are commonly associated with hydraulic conductivity values of 10^{-7} cm/sec or less. This is equivalent to 2.83 ounces/sq ft-day for water, or 60.1 micrograms/cm²-min. By considering the density of each fuel, a conversion could theoretically be made (assuming that all components of the mixtures permeate a given material at the same rate).

Ranking

Table 4-5 shows permeation results ranked by material and permeant (1 = lowest steady state permeation rate). Summed rankings are listed at the bottom of the table, providing a relative indication of overall permeation resistance against the battery of six fuels, additives and blends.

Table 4-5. Ranked permeation results for geomembrane liners

Fuel or Blend	Polyester elastomer coated fabric	EIA coated fabric	Tri-polymer blend coated fabric	Poly-urethane coated fabric	HDPE	Poly-sulfide spray-on
Gasoline	3	6	5	2	1	4
Diesel	3	5	6	2	1	4
Ethanol	2	5	3	6	1	4
MTBE	1	5	6	4	2	3
Gasoline/MTBE blend	2	4	6	3	1	5
Gasoline/ethanol blend	3	6	2	5	1	4
Summed rankings	14	31	28	22	7	24

Ranked in this manner, HDPE clearly was the best performer, with the lowest permeation rate in all but one case. The next best performing product was polyester elastomer-coated fabric,

followed by polysulfide-coated fabric and polyurethane-coated fabric which showed comparable performance. EIA coated fabric ranked no better than fourth against any fuel or blend.

Correlation of ASTM E 96 with ASTM F 739

Table 4-6 shows results of the study performed to compare results from the ASTM E 96-93 (ASTM, 1993) gravimetric permeation test with data produced from ASTM F 739-81 (ASTM, 1994) analytical permeation test.

Table 4-6. Correlation results for permeation testing

Steady state permeation rates (micrograms/cm ² -min)		EIA Coated Fabric	HDPE
Gasoline	ASTM F 739-81	16	0.20
	ASTM E 96-93	5.3	2.1

Good agreement was not found between the two methods in this very limited exercise. The reason for the poor agreement could not immediately be determined. A more extensive study to identify possible sources of bias or error is indicated.

PERMEABILITY OF GCLS

Two GCLs were tested for permeability to six fuels and blends using a triaxial pressure cell apparatus. Procedures were described in Section 3. The results are summarized in Table 4-7, and detailed tables of results appear in Appendix D.

Table 4-7. Summary of hydraulic conductivity results for GCLs

Permeant	Hydraulic Conductivity (cm/sec x 10 ⁻⁹)			
	GCL #1		GCL #2	
	Water	Fuel permeant	Water	Fuel permeant
Gasoline	1.8	1.5	2.9	2.3
Diesel	1.1	2.2	1.2	2.9
Ethanol	1.4	1.0	2.1	1.9
MTBE	1.4	1.7	1.2	1.4
Gasoline/MTBE	1.5	6.7	1.4	6.9
Gasoline/ethanol	1.5	1.7	1.2	1.9

The hydraulic conductivity tests indicated fairly uniform permeation rates during initial permeation of the GCL samples with water. The hydraulic conductivities of GCL #2 with the water permeant ranged from about 1.2×10^{-9} cm/sec to 2.9×10^{-9} cm/sec with an average value near 1.7×10^{-9} . The results for GCL #1 ranged from about 1.1×10^{-9} cm/sec to 1.8×10^{-9} cm/sec with an average value near 1.5×10^{-9} .

Virtually no change in the permeation rates was observed as the two GCLs were permeated with MTBE and when GCL #1 was permeated with the gasoline/ethanol mixture. Only a slight increase was observed when GCL #2 was permeated with the gasoline/ethanol mixture. These minor variations in the recorded permeation rates were not considered significant.

Modest decreases in permeation rates were noted when both GCLs were permeated with gasoline and with ethanol. Also, a modest increase in the permeation rate was observed when GCL #2 was permeated with the gasoline/ethanol mixture. A review of these test results suggests that the permeant did have some minor effects on the hydraulic conductivities of the samples. However, factors affecting the precision of the test procedures could not be ruled out, especially at these very low hydraulic conductivities.

The gasoline/MTBE mixture and, to a lesser degree, the diesel fuel permeant had significant effects on both of the tested GCL materials. A 350% to 500% increase in the liquid conductivity of the GCLs were observed as the gasoline/MTBE mixture was introduced as the permeant and the permeation rate was doubled upon addition of diesel fuel.

CHEMICAL RESISTANCE OF GCL BACKING GEOTEXTILES

The following properties of each of the four backing geotextiles were tested on material removed from the GCL as manufactured, and after exposure to the six fuels and blends:

- Puncture strength (ASTM D 4833-88 (ASTM, 1988));
- Grab tensile strength (ASTM D 4632-91 (ASTM, 1991a)); and
- Trapezoidal tear strength (ASTM D 4533-91 (ASTM, 1991b)).

The results are presented in graphical format in Appendix E. The following observations were made.

For GCL #1, The nonwoven backing geotextile showed consistent drops in grab tensile strengths of 10% to 20% after exposure to each of the six fuels, with the exception of ethanol.

In diesel fuel, tensile and tear strengths dropped by 30% or more. The woven geotextile showed a drop of 40% in puncture strength after exposure to diesel fuel, but effects due to other exposures were not considered significant. The decrease after exposure to diesel fuel was attributed to the fuel's lubricating effect, which allowed some of the fibers to move laterally rather than be broken.

Both nonwoven backing geotextiles from GCL # 2 showed decreases in physical properties generally ranging from 10% to 20%. The only significant change was in puncture strength after exposure to diesel fuel, where decreases of 30% to 50% were observed. This was also attributed to the lubricating effect of the fuel.

Section 5

CONCLUSIONS AND RECOMMENDATIONS

With few exceptions, all of the materials tested showed good performance when tested against the six fuels and blends. The following conclusions were drawn from this study:

CHEMICAL RESISTANCE

Ranked by overall performance in the physical tests, the tri-polymer blend clearly showed the least overall change after immersion. It was ranked first against each of the six fuels and/or blends. The next best performing product was EIA coated fabric, followed by polyurethane coated fabric. HDPE and the polyester elastomer coated fabric showed comparable performance. The polysulfide spray on coated fabric ranked no better than fourth against any fuel or blend.

In terms of physical properties, none of the six geomembrane liners were considered to be severely degraded by immersion in the six fuels. Decreases up to 20% in puncture strength were common for coated fabrics; however, the same materials showed consistent increases in tensile strength after one-sided exposure to fuels. Observed increases in tear strength were not considered significant, and were attributed to anomalies in the test method. Observed changes in puncture and tensile strength were not large enough to conclude that serviceability or reliability had been compromised.

When cut edges were exposed, coated fabrics were found to be subject to wicking into the textile fibers, as evidenced by large weight gains. This observation points to the importance of workmanship in seaming and installation. Cut edges can be protected from exposure to fuel by covering with a bonded strip.

HDPE showed evidence of slight softening and plasticization as a result of fuel absorption into the polymer matrix. Changes in physical properties of up to 20% were observed, with corresponding increases in weight.

PERMEATION RESISTANCE OF GEOMEMBRANE LINERS

HDPE showed superior overall vapor permeation resistance. The next best performing product was polyester elastomer coated fabric, followed by polysulfide- and polyurethane-

coated fabrics which showed comparable performance. EIA-coated fabric was ranked no better than fourth against any fuel or blend. HDPE- and polyester elastomer-coated fabric showed superior permeation resistance to neat MTBE. HDPE's resistance to diffusion or permeation of fuels was attributed to the fact that as a film, a much thicker polymer barrier is presented to the permeant than exists with any of the elastomer coated fabrics that were tested.

LIQUID CONDUCTIVITY OF GCLS

Both GCLs showed very low permeability to both water and fuels. Gasoline/MTBE blend and diesel fuel had higher permeability rates than water did. Rates for gasoline/MTBE blend and diesel fuel were two to five times higher, but still remained in the 10^{-9} cm/sec range.

GCL GEOTEXTILE BACKINGS

Effects on the physical properties of geotextile backings, which were exposed to fuels, were not considered significant.

PERMEATION TESTING

It was concluded from this study that the analytical vapor permeation test (ASTM F 739-81 (ASTM, 1994)) is highly appropriate for determining diffusion rates for fuel containment applications. However, poor correlation with the commonly used gravimetric test (ASTM E 96-93 (ASTM, 1993)) was observed. It is strongly recommended that the analytical test, ASTM F 739-81, be considered as the preferred method for measuring diffusion rates and breakthrough times for fuel exposure to geomembranes.

It is also recommended that permeation resistance for synthetic geomembrane liners not be specified in terms of hydraulic conductivity units (cm/sec), since the mode of transfer across the barrier is by vapor diffusion rather than liquid transport.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Further study is recommended to develop design and product selection guidelines for release prevention barrier and dike containment applications. Use of these products for petroleum containment is expected to increase, and a comprehensive program to develop design parameters and selection criteria would meet a need that exists in the petroleum industry.

The overall conclusion drawn from this study is that each of these materials can offer good-to-excellent performance in applications where contact with fuels may occur, assuming that proper design practices are used. The user should consider requirements for permeation resistance together with other factors in selecting the liner material which best suits each situation.

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APPENDIX A

EXPERIMENTAL PROCEDURES

Appendix A

EXPERIMENTAL PROCEDURES

This Appendix presents additional detail describing procedures and equipment used in this test program.

FUEL EXPOSURES FOR GEOMEMBRANES

To provide some correlation with possible exposures which could occur in the event of a spill in the field, only one side of the materials was exposed to the liquid. A set of exposure fixtures were constructed consisting of 14" square aluminum plates onto which was attached an aluminum "fence" or barrier. This resulted in a 12" square exposure area. The geomembrane to be tested was clamped to the face of the plate under the fence with the side to be exposed facing up. This exposed a relatively large surface area (on one side only) while minimizing the volume of fuel product used. The fixtures were stackable so that multiple exposures could be performed at the same time. A fuel resistant sealant was used to prevent leakage.

For each exposure interval, two sets of material were exposed to fuels. Post-exposure tests were conducted (1) no less than 2 hours, but no greater than 8 hours after removal from one-sided exposure to test properties while the product was wet, and (2) after geomembrane samples are allowed to dry or "vent" for at least 72 hours. Venting was performed in a hood at ambient temperature. The purpose of venting was to drive off absorbed fuels, to determine whether properties returned to their original state. For identification purposes, tests performed before venting are referred to as "immediate test" (IT), and post-venting tests as "delayed test" (DT).

All exposures were at room temperature, and were performed in a large fume hood with metal components grounded for safety reasons.

TESTING PROCEDURES FOR PHYSICAL PROPERTIES

Appropriate tests defined by ASTM or Federal test method standards were selected based on the type of materials under test (ASTM, 1988). Tests were selected which are designed and in common use for the type of material under consideration (e.g., coated fabric vs.

thermoplastic film -- HDPE). For coated fabrics, physical properties are contributed primarily by the scrim or fabric base which serves as a support for the relatively thin polymer coating. Therefore, the testing approach was based on methods used to characterize woven and non-woven textiles, consistent with industry practice. Tests that are sensitive to roll direction (tensile and tear properties) were performed in the machine direction only.²

This test program was designed to compare physical properties of materials before and after fuel exposure, not to directly assess or rank performance of the selected materials and products. Care should be exercised in comparing results from unexposed materials tested in this program with manufacturers' published values. It should be verified that the test procedures were the same, and that the effect of modifications, where used, is understood. Individual tests are described in the following paragraphs.

Tensile strength and elongation

ASTM D 638, "Tensile Properties of Plastics", was the method used to determine tensile strength and elongation for HDPE. This test method covers the determination of the tensile properties of unreinforced and reinforced plastics in the form of standard dumbbell-shaped test specimens. Type IV dumbbell specimens were used, having a reduced area 1.3 inches in length and 0.25 inches wide. The dumbbell shape constrains failure to the reduced area of the specimen, thus eliminating grip breaks. The properties measured were tensile strength at yield and elongation at yield. Although ultimate (breaking) properties were recorded, they were not considered in the analysis of chemical effects since the yield point defines failure. Strength at yield was measured in units of stress (pounds per square inch), the result being the maximum load recorded at the yield point divided by the cross sectional area of the dumbbell's reduced section. Testing was in the machine direction.

Coated fabrics were tested following ASTM D 751 (strip method). Rectangular strip specimens were cut to 6 inches by 1 inch with the long dimension in the machine direction. The tensile strength reported was pounds force at maximum load.

² The term *machine direction* refers to the direction of goods manufacture, or the long direction parallel to the roll edge. Most textiles, coated fabrics and manufactured roll goods such as HDPE show different properties in the machine vs. cross machine directions. However, the objective in this program was to measure changes in strength due to fuel exposure. Cross machine properties were not measured since it was desired to limit the influence of other variables.