

## **Brownfield Vapor Barriers: Chemical Compatibility, Testing, and Advances in Materials Science**

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**ABSTRACT:** A new composite membrane system, Geo-Seal™, has been developed that offers exceptional chemical resistance for use as a vapor barrier at brownfield sites. Data generated in controlled laboratory conditions indicate the composite membrane to have < 0.2X the volatile organic compound partitioning when compared to spray applied latex/asphalt vapor barriers. More importantly, data generated under both liquid and gas permeability tests indicate that the new composite membrane system limits the transmission of volatile organic vapors. Data indicated the Geo-Seal membrane to resist contaminant permeation breakthrough for a period 18X longer than that of simple asphalt/latex membranes and to allow for < 0.16X the rate of VOC permeance of the asphalt/latex membranes.

### **INTRODUCTION**

Brownfield site development often requires the use of a contaminant vapor barrier to inhibit volatile organic contaminants remaining on-site from migrating into the newly constructed buildings, potentially impacting indoor air quality.

Historically plastic sheet materials such as high density polyethylene, known for chemical resistance, have been applied as contaminant vapor barriers. The use of these materials, however, requires labor-intensive cutting and seaming to ensure a continuous and cohesive barrier to vapor migration. This installation process can be intensive, difficult, and costly when applied to construction foundations with multiple penetrations (e.g. piping, electrical conduits).

In recent years “spray applied” latex/asphalt membrane-type waterproofing materials have been widely promoted for brownfield vapor barrier use. While easy to apply and proven to retard water migration through concrete, the use of these latex/asphalt materials for repelling volatile organic constituents (VOCs) such as benzene and chlorinated solvents may be complicated by the affinity of latex/asphalt for VOCs. It is widely recognized that asphalt/latex-based products are, in fact, highly susceptible to partitioning by VOCs, particularly chlorinated dry cleaning- type solvents.

### **BACKGROUND**

**Spray Applied Asphalt/Latex Membranes.** Asphalt/latex membranes are chemically described as bitumen/polystyrene emulsions that are spray-applied in the presence of calcium chloride salt solutions. Simply put, the salt solution “breaks the emulsion” upon mixing when applied forming a continuous layer of bitumen-styrene as the material dries upon a surface. Depending on the exact formulation, the emulsion material may also have clay or calcium carbonate added as a “filler” or “builder” which allows for varying of key characteristics such as viscosity, flexibility, etc.

**Geo-Seal™ Composition.** Geo-Seal™ (Land Science Technologies, San Clemente, CA, USA) is a unique composite membrane (patent pending) that incorporates the ease of application associated with spray applied asphalt/latex membranes with the chemical resistance, low chemical permeability, and mechanical strength of high density polyethylene (HDPE). The Geo-Seal membrane incorporates all the positive aspects of 60 mil asphalt/latex membranes plus the two outer layers of proprietary HDPE.

**Hydrophobic vs Lipophilic.** All asphalt/latex membrane materials are hydrophobic (water repelling) due to the petroleum (bitumen) content. This is why these materials tend to have both low adsorptivity toward water (water does not partition into the membrane itself) and low permeance with regard to water vapors (very little water vapor moves through the membrane). Asphalt/latex membranes make for excellent water-proofing and damp-proofing materials.

Conversely, asphalt/latex membrane materials are lipophilic (oil attracting, or non-polar). When contacted with oils they absorb the oil. In the same fashion, non-polar VOCs like benzene or perchloroethene (PCE) tend to partition into the membrane itself. This is very well documented. In fact, this is why the “dry cleaning” industry has adopted the use of PCE to remove bitumen from clothes...the PCE partitions into the bitumen and extracts it from the fabric. Likewise gasoline is commonly used as a cleaner to remove tar.

## **SOLVENT EXPOSURE TESTING**

Any solvent exposure testing relevant to the use of materials for under-slab VOC contaminant vapor barriers should test or model the true long term exposure of the barrier material to the specific contaminant of concern. In the case of testing latex/asphalt contaminant vapor barrier material for exposure to volatile organic contaminants (e.g. benzene, PCE, trichloroethene (TCE), etc.) the most important factor to consider is the long term adsorption of the contaminant into the membrane itself.

Over time the lipophilic membrane material will continue to absorb contaminant until some point in the future when it reaches equilibrium and/or becomes “saturated”. The period of time required to reach saturation is dependent upon the contaminant type, its concentration in the soil pore gas, temperature, pressure, and its specific partitioning coefficient toward the specific asphalt/latex membrane under testing.

The standard analytical method for solvent exposure testing is generally considered to be ASTM D-543 (ASTM D-543-06). In this test the specific membrane material (latex/asphalt) is exposed to the specific contaminant of concern (e.g. PCE) within the specific medium of concern (air) for a period of 7 days. The amount of weight gained by the membrane is a direct measure of the absorption of the contaminant by the membrane material. When little absorption occurs it can be said that there is little reactivity or change of the membrane with exposure. This test however, will only indicate the absorption (partitioning) which occurs within the 7 day period when the membrane is subjected to the contaminant at the specific concentration tested. It does not indicate the total potential absorption (partitioning) that may occur over the lifespan of the membrane in an actual field application.

In order to understand the long term effects of a membrane’s exposure to solvents one has to either 1) test the membrane under low volatile organic vapor (VOC) concentrations

for an extended period of time- until the partitioning equilibrates (this could be many years depending on how low the vapor concentration is) or 2) run the test at very high concentrations to ensure saturation within the test period. At the point of saturation with VOCs, asphalt/latex membranes show very different characteristics, particularly with regard to VOC permeation, weight, dimensions, and tensile strength.

It is widely known that unprotected asphalt/latex membranes absorb significant contaminant vapors as the VOC partitions into the bitumen fraction of the membrane itself. Eventually this leads to saturation of the membrane, membrane swelling, softness, etc.

**General Asphalt/Latex Solvent Exposure Testing.** In work conducted by an independent laboratory experienced in asphalt/latex membrane formulation, ASTM D-543 was conducted on varying formulations in the presence of hexane vapors. Specific formulations and test results are presented below in Table 1. It is appropriate to note that in all of the varying formulations a weight gain of greater than 10% was observed indicating that asphalt/latex membranes by their very chemical makeup absorb (partition) VOC vapors when properly exposed to the VOC.

**TABLE 1. VOC Solvent Exposure Testing of Various Asphalt/Latex Membranes By ASTM D-543 Employing Hexane Vapors\***

Ingredient	(%)			
Bitumen	72.2	71.7	72.2	66.2
Polystyrene Latex	18.1	17.9	18.1	16.6
CaCl <sub>2</sub>	0.7	1.4	0.7	0.7
CaCO <sub>3</sub>	9.0	9.0	0.0	16.6
Bentonite	0.0	0.0	9.0	0.0
% Weight Gain	15.0	12.5	14.1	10.9

\*Applied Power Concepts Laboratory, Anaheim, CA 2004, USA.

**Comparative Solvent Exposure Testing.** In an effort to confirm that in fact commercially available spray-applied asphalt/latex membranes behave just as other asphalt/latex membranes, a third party laboratory conducted testing upon a sample (60 mil thickness) of a commercially available spray applied asphalt/latex vapor barrier (Liquid Boot®, Santa Ana, California, USA) obtained directly from a manufacturer-certified applicator.. The identical test was conducted employing a sample of the Geo-Seal composite membrane. The method employed was a modified ASTM D-543 using PCE vapors on one side of the membrane and ambient air on the other. Results indicated 2.1% weight gain for Geo-Seal, compared to 10.8% weight gain of the commercially

available asphalt/latex membrane sample. Data derived from this testing is presented in Table 2 below.

	Pre-Test Weight (g)	Post-Test Weight (g)	Weight Gain
Asphalt/Latex <sup>+</sup>	4.24	4.70	10.8%
Geo-Seal™	3.87	3.95	2.1%

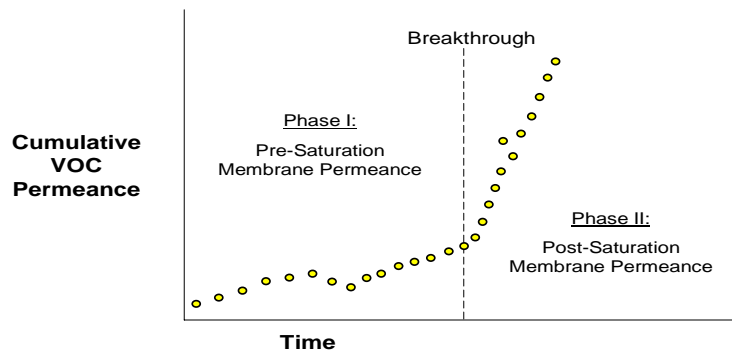
\*Intertek Laboratories, Foxboro Mass. 2008  
<sup>+</sup>Liquid Boot®, Santa Ana, CA, USA

These data clearly indicate that commercially available asphalt/latex is subject to the same weakness as other simple spray applied asphalt/latex membranes- they do not repel VOC vapors. Instead they tend to absorb (partition) vapors. The Geo-Seal composite membrane, on the other hand, incorporates two layers of the very chemical resistant high density polyethylene in addition to the 60 mil spray applied copolymer modified bitumen/polystyrene core layer. These HDPE layers serve to limit exposure of the core layer to VOCs and to ensure mechanical integrity of the membrane.

**PERMEATION TESTING**

Permeation testing measures the rates of transport across membranes. Traditionally this has been conducted by simply placing the challenge gas or liquid on one side of the membrane and, after sealing, measuring the amount of the gas that emerges from the opposing side of the membrane over time. This method is the basis for several standard analytical techniques used in the testing of materials for waterproofing applications. However, this basic approach is flawed in testing VOC permeation through lipophilic membranes such as simple asphalt/latex membranes.

**VOC Partitioning, Break-through and Permeation.** Permeation of VOCs through a lipophilic membrane can be viewed as a three phase process where: 1) VOCs move into the membrane through absorption (partition) with only a fraction passing completely through, 2) partitioning of the VOCs into the membrane continues to the point of equilibrium saturation where break-through of higher concentrations occur, and 3) post saturation where VOCs are moving out of the membrane at significantly increased rates. This process is depicted in Figure 1, below.



**FIGURE 1. Permeation of VOCs through a Lipophilic Membrane**

**Asphalt/Latex Membrane Permeation Testing.** When testing asphalt/latex membranes against VOCs one should not simply measure the flux of low concentrations of VOCs across the membrane as this approach does not take into account the concentration of VOCs absorbed (partitioned) by the membrane itself.

In the ASTM publication “Determination of Volatile Organic Compound Permeation Through Geomembranes” (Park, 1996) the authors state, in reference to the general testing method employed by vendors of asphalt/latex membranes:

“The permeation rate was estimated solely on the amount of VOC that passed through the geomembrane surface area in a unit time. This estimation is incorrect for it does not account for partition and diffusion and assumes a constant concentration above the geomembrane”.

In the permeation testing conducted by a vendor of asphalt/latex membranes (Cetco Liquid Boot, 2008), which was then used to generate a diffusion coefficient, the physical partitioning of the VOCs into the membrane was not taken into account. As noted by Park, et. al. (1996), this method is in error. The membrane in this testing was almost certainly not at the point of saturation after less than one year’s time in contact with vapors from aqueous dissolved VOC. Thus, the testing was conducted under conditions where much of the VOCs were being partitioned into the membrane. Over time, however this lipophilic membrane would become saturated and the rate of VOC permeation would significantly increase.

**Testing Permeation upon Pre-Saturation.** An approach to understanding the capacity of a membrane to act as a long term barrier to VOC permeation is to first saturate the membrane with VOC. Once saturated, the membrane can then be subjected to the VOC in specific concentrations and the associated permeation rate can be measured. In this case, the impact of the VOC absorbance (partitioning) on the measurement of permeation is minimized if not eliminated altogether.

A series of tests were conducted by a third party laboratory in order to gain an understanding of the relative long term performance of the Geo-Seal composite membrane and the commercially available asphalt/latex membrane against VOC permeation.

**Comparative Liquid VOC Challenge Post-Saturation.** In order to understand the chemical permeation of VOCs through the two membrane systems a standard method ASTM F-739 was employed utilizing an open loop system permeation test cell (ASTM F739-07). The membranes were subjected to liquid VOC for 24 hours to ensure saturation followed by an 8 hour test of the materials toward VOC permeation from direct liquid VOC contact.

Results of this test represent “worst case” permeation rates, as it assumes maximum VOC concentration challenge after membrane saturation. Thus, the absolute VOC permeation rate numbers are very high. This test however serves to indicate the relative

capacity for the two membranes to block permeation from the specific VOCs under identical controlled conditions. All tests were performed in triplicate under controlled laboratory conditions.

Barrier Material	VOC Contaminant	Breakthrough Time (minutes)†	Steady-State Perm Rate ( $\mu\text{g}/\text{cm}^2/\text{min}$ )
Asphalt/Latex <sup>+</sup>	PCE	15	12.9
Geo-Seal™	PCE	270	2

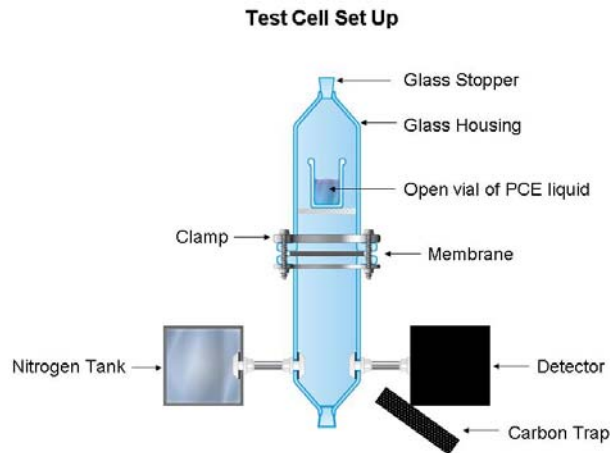
\*Intertek Laboratories, Foxboro MA, USA. 2008

+Liquid Boot®, Santa Ana, CA, USA

† Time when permeation rate reached  $1.0 \mu\text{g}/\text{cm}^2/\text{min}$

As can be seen from the results presented in Table 3, the Geo-Seal barrier after saturation was much more resistant to permeation than the asphalt/latex membrane. Geo-Seal held up breakthrough permeation for an 18X longer period when compared to Liquid Boot. Additionally, once steady state permeation was reached, Liquid Boot allowed for 6.45X the rate of permeation when compared to Geo-Seal. This is not surprising when considering the HDPE composite composition of Geo-Seal compared to the simple commercially available asphalt/latex membrane.

**Comparative VOC Vapor Challenge Post-Saturation.** In order to compare the relative performance of Geo-Seal and commercially available asphalt/latex membranes to act as a long term barrier to VOC vapor permeation, a series of test were conducted by a third party laboratory employing a double compartment apparatus in a modified ASTM-F739 test protocol (see Figure 2). Under this test the membranes were first subjected to the VOC for 24 hours to reach saturation then placed into the apparatus which subjected the membrane to VOC vapors for a period of 8 hours.



**FIGURE 2. Double Compartment Apparatus**

As can be seen from the results presented in Table 4, Geo-Seal did not break-through or allow detectable permeation of the VOC vapors within the testing period even after being saturated with the VOC prior to testing. The simple asphalt/latex membrane however,

under the same conditions, reached break-through after 450 minutes and had reached a steady state permeation rate of 5  $\mu\text{g}/\text{cm}^2/\text{min}$ .

<b>TABLE 4. Results of Comparative Permeation Testing under VOC Vapor Challenge*</b>			
Barrier Material	VOC Contaminant	Breakthrough Time (minutes)	Steady-State Perm Rate ( $\mu\text{g}/\text{cm}^2/\text{min}$ )
Asphalt/Latex+	PCE	450	5
Geo-Seal™	PCE	No Breakthrough	< 0.01

+Liquid Boot®, Santa Ana, CA, USA

## SUMMARY

Membrane materials for use as sub-slab contaminant vapor barriers are evolving. It is now becoming recognized that traditional waterproofing materials such as asphalt/latex membranes, while low in cost and easy to apply, are limited in their ability to block the permeation of volatile organic contaminants. Through recent advancements in membrane science a composite membrane (Geo-Seal™) is now available which encapsulates a spray applied asphalt/latex membrane with chemically resistant high density polyethylene. This technology is shown to have superior characteristics as a vapor barrier to VOC contamination when compared to traditional asphalt/latex membranes.

## REFERENCES

- ASTM D543-06: American Society for Testing and Materials method ASTM S543-06, “Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents” [www.astm.org](http://www.astm.org)
- ASTM F739-07: American Society for Testing and Materials method ASTM F 739, “Standard Test Method for Permeation of Liquids and Gases through Protective Clothing Materials under Conditions of Continuous Contact” [www.astm.org](http://www.astm.org)
- Cetco Liquid Boot. 2008. CETCO Liquid Boot Vapor Intrusion Seminar: Chemical Compatibility of Liquid Boot® Membranes with Respect to Vapor Barrier Application, Workbook April 29,2008.
- Park, J.K., J.P. Sakti, and J.A. Hoopes. 1996. “Determination of Volatile Organic Compound Permeation Through Geomembranes”. *Volatile Organic Compounds in the Environment, ASTM STP 126, W. Wang, J. Schoor, and J. Doi, Eds.*, American Society for Testing and Materials, 1996, pp. 245-258.