

**Final Report to
The Propane Education and Research Council
(PERC)**

on

**An Assessment of the Merit of
Conditioning LP Gas Hoses:**

Volume I: User's Guide

February 2005

**Battelle
Energy and Environment**

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Executive Summary

Technical literature from researchers in France, Japan, and Canada has reported that hydrocarbons like propane (the main constituent of LP Gas) absorb chemicals from hoses and also permeate through the hose wall. In technical literature, the absorption of chemicals is referred to as “leaching” or “extraction,” and the permeation through the hose wall is called “effusion.” The chemicals that are leached are referred to as “contaminants” because they were not intended to be present in the LP Gas. The rate at which leaching or permeation occurs depends on variables such as the composition and construction of the hoses, the time of exposure, the composition of the LP Gas, and the temperature.

Contaminants that were leached from hoses and were deposited in the vaporizer/converter of LP Gas vehicles caused poorer engine performance, or excessive tailpipe emissions, or both. Another potential problem is that excessive permeation could result in significant loss of product, and could trigger failure in a Sealed Housing for Evaporative Determination (SHED) test. The LP Gas market could suffer long-term adverse effects if problems caused by contaminants are not solved.

Battelle, on behalf of the Propane Education and Research Council (PERC), investigated two concerns in particular that have been raised about commercial LP Gas hose.

The first concern is that plasticizers extracted from hoses may foul equipment. This concern could be addressed by conditioning new hose. “Conditioning” means exposing new hose to LP Gas for a certain period of time so that plasticizers and other chemicals released by the hose could be removed; the LP Gas used in this conditioning process would remain suitable for use in applications where the presence of plasticizers is unimportant. The goal of work conducted by Battelle on this aspect of the investigation is to determine whether conditioning the hoses prior to use is beneficial. The term “beneficial” is taken to have three facets: economic, operational, and technical. In economic terms, the conditioning must be inexpensive relative to the benefits. Presumably, the benefits would be realized by acquiring new customers for LP Gas, or charging a premium for conditioned hose, or in some other manner. In operational terms, the conditioning must be simple to execute, must be completed within a reasonable time frame, and must be procedurally simple enough that the associated training is minimal. In technical terms, conditioning must be feasible. This means that after hose is conditioned and stored, if it is re-exposed to LP Gas it should behave as a “depleted” hose and not as a “new” hose. In other words, it must be demonstrated that removal of the plasticizers is a one-time process. To demonstrate technical feasibility, tests were performed to determine the characteristics of the extraction of plasticizers and other chemicals from hoses. An analysis of the test data indicated that it is technically feasible to condition hoses before first use. To demonstrate how the conditioning may be undertaken in practice, we conceptualized, designed, and fabricated a prototype device and procedure.

The second concern is that excessive permeation from LP Gas hose could cause safety concerns, and also lead to unacceptable loss of product. To address this concern, we measured the permeation through typical commercial LP Gas hose, investigated analytical methods to estimate permeation through hose walls, and compared permeation rates allowed by different standards.

This study yielded very practical results. However, some of the methods that were used are technically complex. To satisfy the needs of the practicing LP Gas community, as well as the scientific community, the final report is divided into two volumes. Volume I is a simpler description of the problem, the approach, and the results. Volume II covers the same material but in greater technical detail.

Some specific conclusions from the study are:

- Several chemicals, mainly plasticizers, are leached from hose when in contact with LP Gas.
- The type of chemical, the amount that is leached, and the speed at which it is leached probably depends on the manufacturer and the model of hose.
- Leaching is quickest initially, when new hose is exposed to commercial grade LP Gas. The rate of extraction decreases for a few days and the levels off. The extraction may continue at a low rate for a considerable period.
- Hose that was “depleted” showed much lower rates of extraction for all species the second time it was exposed to LP Gas. This suggests that conditioning of hose is technically feasible.
- If one of the physical properties of a hose, “permeability,” is known, it is possible to estimate how quickly propane will permeate through the hose wall.

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Format of the Report

The study conducted by Battelle on the merits of conditioning LP Gas hoses yielded very practical results. However, some of the methods that were used are technically complex. To satisfy the needs of the practicing LP Gas community, as well as the scientific community, the final report is provided in two volumes. Volume I is a simpler description of the problem, the approach, and the results. Volume II covers the same material but in greater technical detail.

Reasons for this Study

Technical reports received from France, Japan, and Canada have indicated that hydrocarbons like propane (the main constituent of LP Gas) absorb chemicals from hoses and also permeate through the hose wall. The absorption of chemicals is referred to as “leaching” or “extraction.” The permeation through the hose wall is sometimes called “effusion.” The chemicals that are leached are referred to as “contaminants” because they were not intended to be present in the LP Gas. The rate at which leaching or permeation occurs depends on variables such as the composition and construction of the hoses, the time of exposure, the composition of the LP Gas, and the temperature.

Contaminants that were leached from hoses and were deposited in the vaporizer/converter of LP Gas vehicles caused poorer engine performance, or excessive tailpipe emissions, or both. Another potential problem is that excessive permeation could result in significant loss of product, and could also lead to safety issues. The LP Gas market could suffer long-term adverse effects if problems caused by contaminants are not solved.

In order to evaluate the likelihood and magnitude of these potential problems, the Propane Education and Research Council (PERC) commissioned Battelle to measure the amount of leaching and permeation in commercial LP Gas hose for the purpose of assessing the merits of hose conditioning. “Hose conditioning” means exposing new hose to LP Gas for a certain period of time so that the chemicals are removed before the hose is put into service.

Goal

The goal of this work is to measure the extent of leaching and permeation in commercial LP Gas hose in order to assess the merit of conditioning hoses prior to use.

Background

Typical commercial hose for LP Gas consists of a multi-layer construction. Figure 1, which is taken from the website of the manufacturer, shows a three-layer construction. The innermost layer, which is in contact with the LP Gas, should resist the permeation of the LP Gas and should not leach chemicals into the LP Gas. This layer is often made of rubber. The next layer, moving radially outward, is a reinforcing layer consisting of a textile or metallic fiber that is wound or knitted around the innermost layer. The outermost layer is designed to resist handling and abrasion. It also generally contains small pinpricks to enable gases that migrate through the inner layer to escape. This layer is often made of a synthetic rubber.



Figure 1. Cutaway view of a typical commercial LP Gas hose, showing three-layer construction.

The following description of hose manufacture is based on the article “Watson-Marlow Bredel Hose Pumps invests in advanced grinding machinery” in the November 2002 issue of *World Pumps* published by Elsevier Science Ltd., and available on the Internet. The production of hose is a multi-step process. At the beginning of the process, the ingredients for the specific rubber compounds are mixed and some key properties of the rubber compound, such as hardness and density, are verified. Plasticizers are a class of chemicals (often oily liquids) that are routinely added to rubber and polymers to give the materials desirable properties such as increased flexibility, particularly at low temperatures. Many chemicals are used as plasticizers. European manufacturers account for about 1,300,000 tons of various plasticizers each year, over 90% of which belong to a class of chemicals called phthalates. The most common phthalates used as plasticizers are di-(2-ethylhexyl) phthalate, di-isodecyl phthalate, and di-isononyl phthalate. Vendors often package generic plasticizers under their own brand names. To add to the confusion, many plasticizers are known by several names. For example, di-sec-octyl phthalate is also known as 1,2-Benzenedicarboxylic acid bis(2-ethylhexyl) ester, BEHP, DAF 68, DEHP, DOP, Union Carbide Flexol 380, and so on. A manufacturer would typically add plasticizer to the inside and the outside hose layers.

The construction of the hose starts with extruding a homogeneous resilient rubber inner layer upon a mandrel. The composition of the inner layer determines the material that can be transported by the hose. Then the reinforcement layers (made of Nylon or steel cord) are wound around the inner layer. The type and extent of reinforcement determines the maximum operating pressure. The final hose construction step is the extrusion of the outer layer, which is made to resist abrasion and handling. Pinpricks are introduced into the outside layer so that gas that permeates through the inner layers can escape instead of delaminating the outside layer. The hose undergoes additional steps to add printlines and fittings, but there is no further significant change in the wall construction.

Depending on the design and the intended use, additional internal layers may be added for reinforcement or impermeability, as shown in Figure 2 (which is taken from the website of the manufacturer). Because the composition of the hose materials varies with the product line and the manufacturer, and the compositional information is often regarded as proprietary, it is difficult to extrapolate the results from one hose construction to another, except in a general sense.

Some hoses recently made available in the United States (such as Aeroquip CR170 and Parker SS23CG) have an inner lining that is less permeable to LP Gas and less likely to leach than an inner lining made of rubber. These inner linings are made of a polymer such as Nylon. This type of hose was not part of the study. Based on manufacturer’s specifications, one would expect the extraction and permeation of “lined” hose to be much less than that of unlined hose.

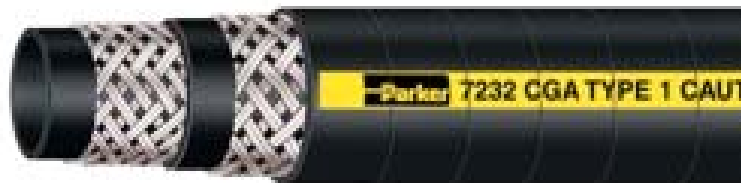


Figure 2. Cutaway view of a commercial LP Gas hose with additional layers provided for reinforcement.

Approach

To determine whether hoses need to be conditioned, we need information on whether leaching occurs, which chemicals are leached, how quickly the leaching takes place, and whether the leaching is reduced when the hose is exposed to LP Gas a second time. We set up a test facility to take measurements to obtain this information. We also set up a test facility to measure permeation.

To make sure that we were performing the testing consistent with previous tests, we reviewed papers on this subject from around the world. A summary of the review findings is presented in the section titled “Information Acquisition and Analysis.”

We designed the test facilities, developed the test methods, and decided on which tests to run. These activities are described in the section titled “Testing.”

Analysis of the test data is discussed in the section titled “Data Analysis.”

The measurements suggested that conditioning new hose was feasible. A prototype device was fabricated to show how commercial LP Gas hose could be conditioned. This is discussed in the section titled “A Prototype Design for Conditioning Hose.”

The results of the study are summarized in the section titled “Conclusions.”

Information Acquisition and Analysis

Information available from various international sources suggests that leaching from LP Gas hose is a matter of widespread concern.

A Japanese study analyzed thirty-one samples of residues, mainly from autogas converters. The residues proved to be complex mixtures containing:

- **Insoluble Materials** (meaning insoluble in chloroform) such as iron, sulfur, copper, zinc, and tin
- **Plasticizers** such as phthalates and adipates
- **Lubricants** such as silicon compounds
- **Reaction products** that were probably not extracted but resulted from reactions
- **Waxes**
- **Glycolic or Miscellaneous Materials** such as glycols and additives.

In addition to the foregoing, trace amounts of about 25 to 80 other materials were found. The presence of so many contaminants is not necessarily a cause for alarm. Many of the contaminants are only detectable using sensitive laboratory instruments, and the significance of a particular contaminant depends on the application. If the presence of a contaminant has no effect on the application, or on the equipment used in the application, it may be irrelevant.

Plasticizers occurred in 98% of the samples. The amount of plasticizer in the four “representative” samples was about 40%, while the amount of plasticizer in the four “special” samples was about 15%. The authors concluded that amides and glycols (used as slip agents in rubber) and dialkylesters (used as plasticizers in rubber) probably occurred as a result of extraction from hoses and from coatings used to line pipes and tanks.

Another Japanese paper found non-volatile residues in LP Gas consisting of oily substances that form a clear liquid, but may appear opaque because of a suspension of iron sulfide and iron oxide particles. The residues had a high boiling point component and a lower boiling point component. The high boiling point component appeared to be relatively harmless. Most of the low boiling point component (about 85%) consisted of plasticizers while the remaining 15% consisted of rubber-based chemicals such as anti-aging agents, and surface reactive agents.

The largest contributor to the plasticizer content is identified as high-pressure hose. The major consequence of the extraction was that the rubber hose increased in hardness. It also showed a minor reduction in elongation, and a negligible effect on tensile strength when exposed to propane.

Measurements on in-service hose showed that the rate of extraction is higher in earlier stages of use, and the bulk is extracted in about a year.

Different standards specify different allowable permeation rates through hose. Further, the units used vary from source to source. Therefore, one should be careful when comparing values from different sources. We shall use typical units used internationally ($\text{cm}^3/\text{m}/\text{hr}$), and also the equivalent in $\text{in}^3/\text{ft}/\text{hr}$. The quantity $\text{in}^3/\text{ft}/\text{hr}$ means the volume of LP Gas (at “standard conditions” which are typically close to atmospheric pressure at sea level and room temperature) that escapes from a foot-long section of hose each hour. For ease of conversion, $1 \text{ cm}^3/\text{m}/\text{hr} = 0.02 \text{ in}^3/\text{ft}/\text{hr}$, and $1 \text{ in}^3/\text{ft}/\text{hr} = 53.76 \text{ cm}^3/\text{m}/\text{hr}$.

The Underwriters Laboratory Standard for LP Gas Hose (UL21) allows a permeation rate of $171 \text{ cm}^3/\text{ft}/\text{hr}$ ($3.2 \text{ in}^3/\text{ft}/\text{hr}$) while the Japanese standard JIS K 6347 allows permeation rates of about $60 \text{ cm}^3/\text{m}/\text{hr}$ ($1.1 \text{ in}^3/\text{ft}/\text{hr}$). For high-pressure hose, the Australian/New Zealand standard requires the permeability to be less than or equal to $25 \text{ cm}^3/\text{m}/\text{hr}$ ($0.5 \text{ in}^3/\text{ft}/\text{hr}$). A Japanese standard requires the maximum permeability of high-pressure hose to be of the order of magnitude of $30 \text{ cm}^3/\text{m}/\text{hr}$ ($0.6 \text{ in}^3/\text{ft}/\text{hr}$).

Testing: Leaching

This section discusses the rationale for the test design and the variables that were selected for parametric testing, and provides a detailed description of the test configuration.

Test Design

These tests were used to measure the rates of extraction from different sizes of hose under different operating conditions.

LP Gas flow through in-service hose varies from less than 0.1 ft/sec to about 35 ft/sec. A pump that could deliver a speed of 2 ft/sec through 1-inch hose was selected as being representative of in-service conditions. It is difficult to extrapolate the results from one hose construction to another, except in a general sense, because the composition of the hose materials varies with the product line and the manufacturer, and the compositional information is often regarded as proprietary. For this reason, a typical commercial LP Gas hose in three diameter sizes (1/4 inch, 3/4 inch, and 1 inch) was used for the tests.

System Description

The system design was based on (1) the need to test commercial hoses of different diameters and lengths safely, at different and controlled flow rates, and with minimal contamination from sources other than the hose, and (2) the ability to obtain samples for compositional testing.

We equipped the system with the following

- A pump to circulate LP Gas
- Stainless steel components to minimize chemical interaction with the LP Gas as much as possible
- A bypass loop so that the flow rate through the hose could be controlled by means of an upstream flow control valve
- A containment section that enclosed the hose so that the LP Gas would not be released in case the hose ruptured
- A method for extracting LP Gas samples when desired
- A flaring system to purge propane vapor that may form.

The plan was to remove samples of the LP Gas at periodic intervals, determine the chemical composition, and thereby find how the concentration changes with time for each contaminant.

The system was a closed system as shown in Figure 3. This ensured that no significant release of LP Gas would occur unless there was an unexpected system overpressure.

The test hose was contained in a two-piece black iron tube (connected by a flange) with an annular clearance between the hose and the tube. The ends of the tube were threaded and capped. The caps had drilled holes and Swagelok fittings through which the stainless steel tubing passed. The space between the hose and the tubing was filled with nitrogen so that the nitrogen could be sampled for hydrocarbons that had permeated through the wall of the hose. A pressure gauge, P_G , was used to ensure that there was no leak and that the pressure in the annular region was slightly above atmospheric. A valve isolated the pressure gauge as needed. A pressure switch, P_{S1} , was designed to trigger an alarm if the pressure in the annular space exceeded a set value. A gas sampling port was located on the black iron tube. The port consisted of a fitting with a rubber plug through which a hypodermic could be inserted to extract a gas sample. An inlet on the black iron tube was used to introduce nitrogen through a valve, V_5 , which was closed after nitrogen was introduced and the air was purged. An outlet on the black iron tube was connected to the inlet by tubing that included a control valve, V_7 , and a circulating device, F_A . The recirculation ensured that the gas in the annular region was well mixed so that the extracted gas sample was representative of the gas mixture. Samples of liquid LP Gas for chemical analysis were removed through valve, V_4 , using a stainless steel sample container (not shown). Pump, P_U , pumped the liquid. Valves, V_2 and V_3 , determined whether the liquid flowed through the test section or the bypass loop. The flow rate was measured by the flow meter, F_L . The LP Gas system tank contained liquid and vapor at ambient temperature. It had sight glasses drilled into the tank so that the level of the LP Gas could be maintained between the two sight glasses. A pressure switch, P_{S2} , on the tank was designed to trigger an alarm when an overpressure situation was detected. If an alarm were to be triggered, both support and

engineering staff would have been notified. Also, if the pressure continued to increase, a pressure relief valve, P_R , was to open to allow vapor to discharge through a vent. The pressure transducer, P , and the valve, V_8 , were used for startup and purging the system. TI is the supply storage tank, and TO is a storage tank to hold LP Gas after use in a test.

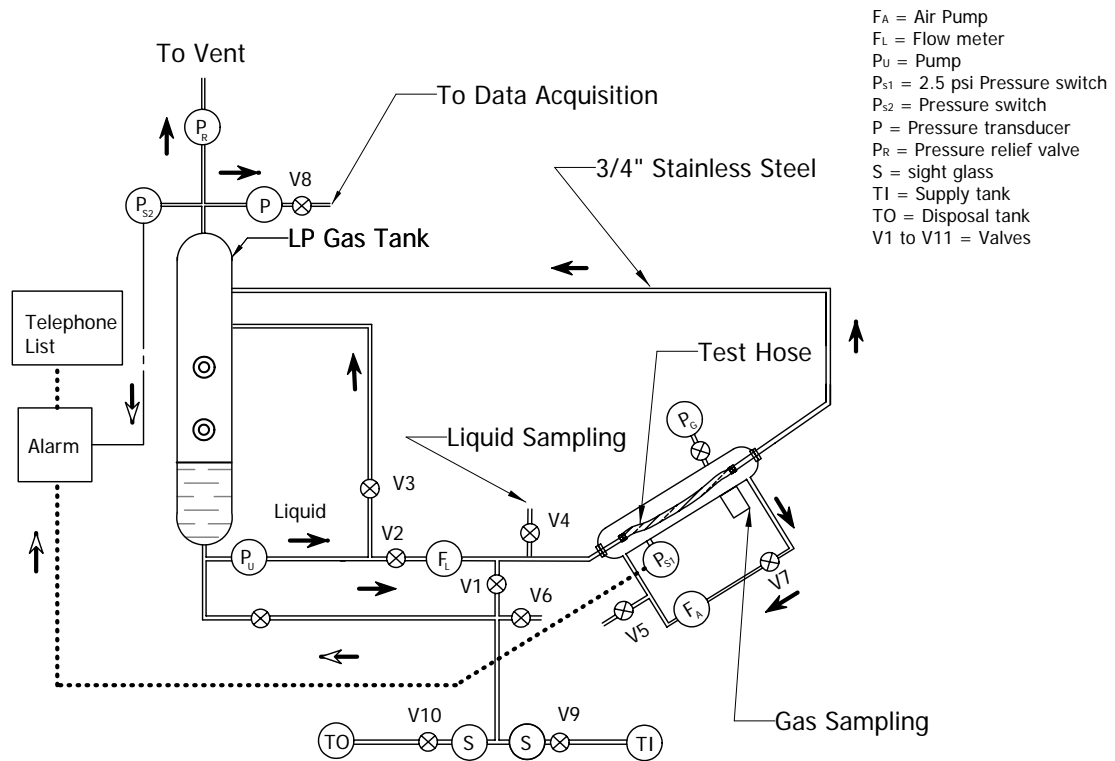


Figure 3. Schematic of test setup for periodic removal of LPG samples from test hose.

Figure 4 shows a composite photograph of the test configuration that was computationally “stitched” together from individual photographs.

Commercial LP Gas from a local supplier was used to charge the system. The pressure and temperature of the system were set by ambient conditions, which were typical of summer conditions in the Midwestern United States. The test variables were:

- Type, size, and length of hose (1/4-inch, 3/4-inch, 1-inch diameters; 2-foot and 4-foot lengths)
- Liquid composition and phase (two suppliers)
- Flow rate (no flow; flow up to 5 gpm)
- Pressure (set by ambient temperature)
- Temperature (ambient).



Figure 4. Composite photo of test configuration.

The following variables were monitored by an automated data acquisition system:

- Flow rate
- System pressure
- Nitrogen jacket pressure.

Two sets of samples were taken at preset intervals:

- Liquid for extracted material
- Gaseous for permeation rate.

When the LP Gas is just contained in the hose and is not flowing with respect to the hose, the tests are termed “static” tests. A separate test facility for static tests was designed and constructed. Hereafter, the flow rig will be referred to as the “dynamic” rig, and the other will be referred to as the “static” rig. The static rig and the sampling and test procedures are discussed next.

Static Testing

Figure 5 shows the test setup to determine extraction of hose materials under static conditions. Liquid LP Gas was introduced through a valve, V1. The level in the reservoir was monitored by a commercial propane level gauge. The intent of noting the liquid level in the reservoir was to ensure that the hose was filled with liquid, and that there was enough volume to supply test samples for the duration of the test. The initial volume of liquid was calculated from the dimensions of the hose and the level of the liquid in the container, or by weighing the apparatus before and after filling LP Gas. The total amount of LP Gas that was withdrawn for sampling was not significant compared to the volume in the test rig so that the weight of the samples was not taken into account in calculating the extraction of chemicals from the hose.

Three separate reservoir systems were built, one for each hose diameter to be tested (1/4 inch, 3/4 inch, and 1 inch). The length of the reservoir is 12 inches for the 1/4-inch hose and 18 inches for the other two sizes. Figure 6 is a photograph of the three static test assemblies.

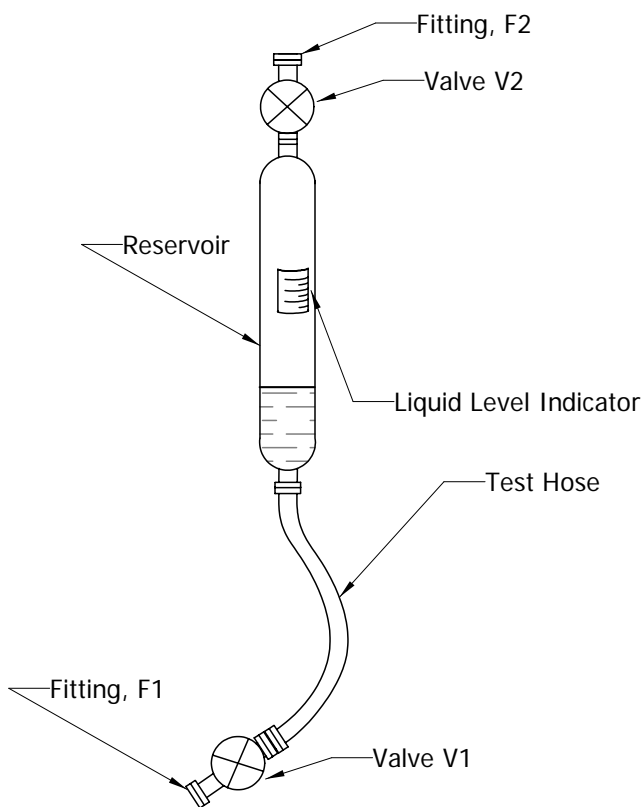


Figure 5. Schematic of static test rig.



Figure 6. Static test assemblies.

The sampling apparatus was made of stainless steel except for the valve seals that were made of Teflon. A strict procedure was followed to calculate the concentration of the contaminants in the sample. The samples were analyzed using gas chromatography and mass spectroscopy (GC/MS).

Species that were monitored

The sample bottles were first rinsed with hexane, and then with acetone. Only trace amounts of contaminants were detected in the acetone rinse as compared to the hexane rinse. Thus, for all subsequent testing only hexane was used as a rinse while acetone was used as a cleaning solvent.

Nine chemicals were identified as frequently occurring in the LP Gas samples:

- Dibutylphthalate (DBP),
- Dibutylsebacate (DBS),
- Dioctyladipate (DOA),
- Phosphoric acid tris (2-ethylhexyl) ester) (TOP),
- Diisooctylphthalate (DIOP),

- Dioctylphthalate isomer #1(DIOP1),
- Dinonylphthalate isomer #2 (DIOP2),
- Dinonylphthalate isomer #3 (DIOP3), and
- An unknown component whose chemical structure was not determined because the additional expense was not warranted.

These are typical of species found in other studies.

It is interesting to note that after each static test was complete, and the LP Gas had been flared, an oily, golden-yellow liquid (shown in Figure 7) was recovered from the hose. The amount of liquid varied from test to test, from less than a teaspoonful to several tablespoonfuls for a 2-foot hose. By analogy, for a 125 ft hose typically used on a bobtail, the amount of residue would be in the cupfuls! An analysis of the liquid showed that it consisted mainly of plasticizers and heavy hydrocarbons. It is also interesting to speculate what happens to such liquids in the LP Gas distribution system. If the residue segregates in tanks, the level of residues probably continues to rise as the tank ages, unless the tank is cleaned out. If the residue is transported to the converter/vaporizer, it may remain there depending on the temperature and other conditions in the vaporizer. This could lead to additional maintenance requirements or operational problems.

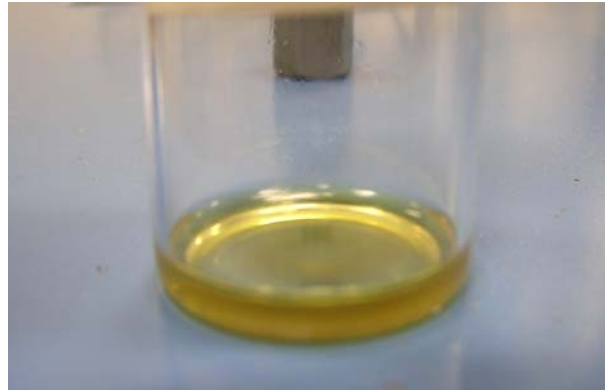


Figure 7. Oily residue recovered from hose after static testing.

Results of Testing

Data were analyzed to determine the effect of flow, hose diameter, LP Gas supplier, hose length, and re-using hose. Allowing for scatter in the data, the typical change in concentration of a contaminant can be schematically displayed as shown in Figure 8. The concentration of the contaminant increases in each successive sample in time. The rate at which the chemical is being leached decreases with each successive sample in time. Thus, Figure 8 shows a graph where the total amount of chemical leached levels off after a few days of continuous contact between the hose and the LP Gas. Another way to present the same information is in terms of the rate at which contaminants are being leached from the hose. Figure 9 shows time along the x-axis and rate of extraction on the y-axis. For example, moving right along the x-axis represents an increasing number of days, while moving up along the y-axis represents amount of contaminants leached from the hose in terms of gm/day. Figures 8 and 9 both show that the rate of extraction is high at the beginning and then levels off in time.

The influence of each test variable is discussed next.

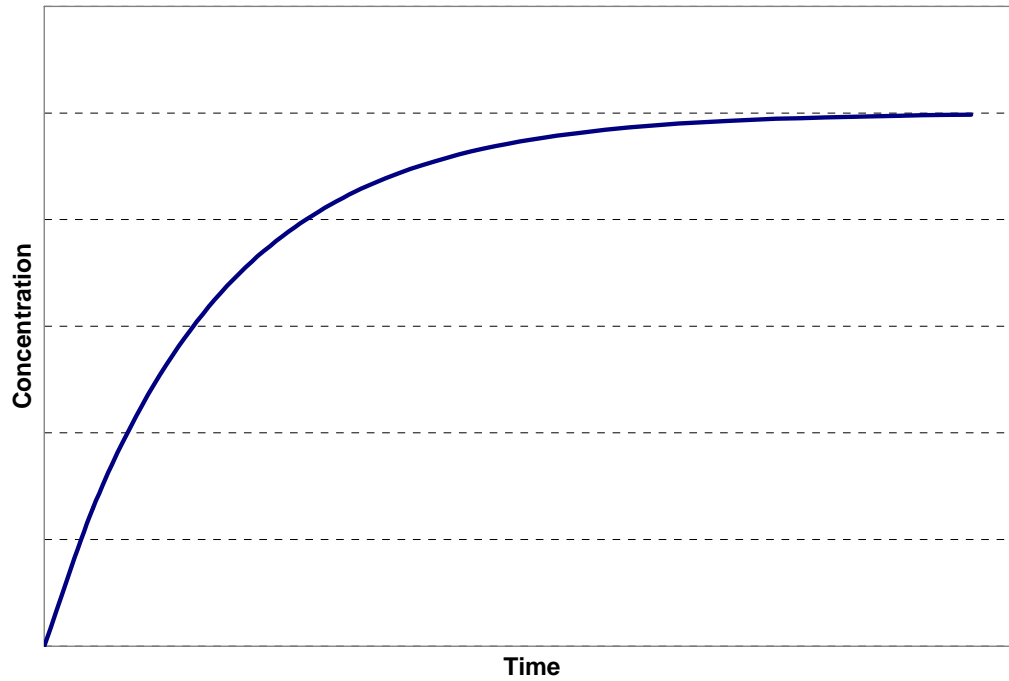


Figure 8. Typical change in concentration over time.

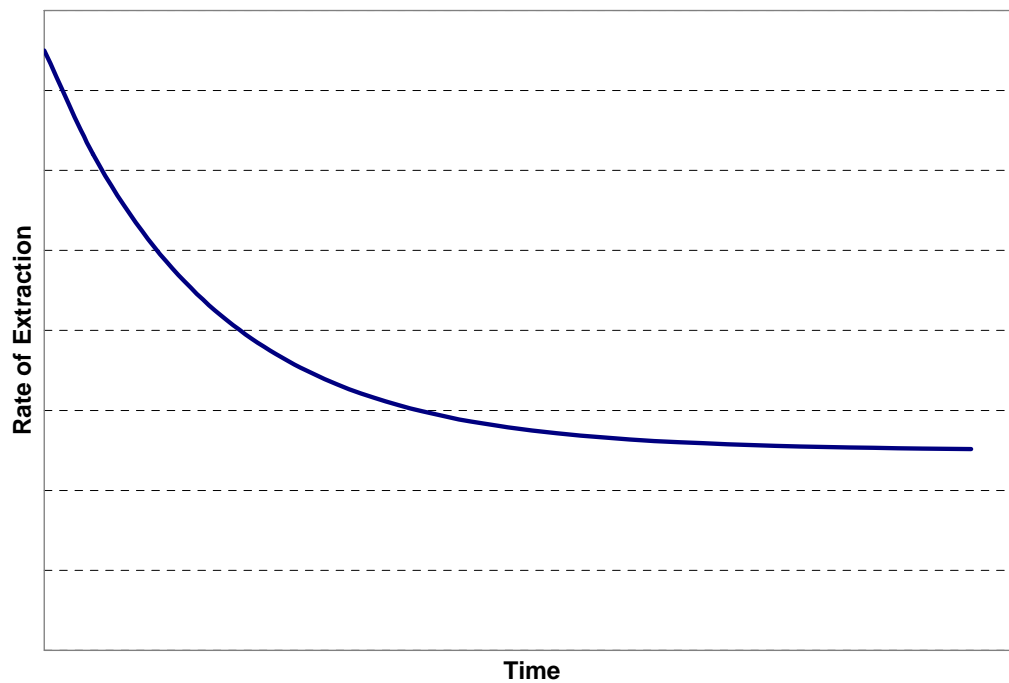


Figure 9. Typical change in rate of extraction over time.

Effect of Flow

Results from the dynamic rig at full pump capacity (5 gpm) were compared with the results from the static rig at identical conditions for a 1-inch diameter, 2-foot section of hose. For some contaminants, the dynamic concentrations were higher, for other contaminants the dynamic concentrations were lower, and for still others there was no significant difference. The summary assessment was that the effect of flow up to 5 gpm did not appear to be significant. As a result, because of the significantly higher cost of running the dynamic rig, the remaining tests were undertaken in static rigs.

The reasons for the different observations with the different species may lie in the detailed extraction and transport mechanisms, which may vary with the species.

Effect of Hose Diameter

Static tests were conducted on 1-inch, 3/4-inch, and 1/4-inch diameter hoses that were two feet long. The overall trend is for the concentrations to be of the same order of magnitude except for a few species. However, these are “raw” values. If the concentration of the contaminant is divided by the area of contact between the LP Gas and the hose, the results depend on the contaminant. This may be explained by the fact that we do not know whether the composition of the different-sized hoses is identical. It is possible that the hoses of different size have internal layers that contain different extractable contaminants.

Effect of LP Gas Supplier

The LP Gas used for the testing was obtained from two different suppliers. To test the effect of different suppliers, three hose sections were tested in the static mode. The hose dimensions were 1 inch, 4 feet; 3/4 inch, 2 feet; and 1/4 inch, 2 feet. The overall conclusion is that the amounts extracted are large compared to the initial variations between suppliers, so that the supplier of the LP Gas does not appear to be of central importance.

Effect of Hose Length

Analysis of the test data shows that the resultant concentration of species in the LP Gas for 2-foot and 4-foot lengths of hose is almost indistinguishable. This suggests that the concentration per unit quantity of LP Gas does not depend on length. Of course, the absolute amount of material that is extracted is proportional to the length of the hose.

Effect of Re-using Hose

Sections of hose, 2-feet long and with nominal diameters of 1 inch, 3/4 inch, and 1/4 inch that were exposed to LP Gas for several weeks, were emptied and air-dried for several days. They were then refilled with LP Gas. Samples of the liquid were withdrawn periodically, uniquely labeled, weighed, and chemically analyzed.

On first exposure, the extraction of materials from the hose is rapid. The rate of extraction progressively lessens, and the concentration of each species tends to level off. A similar behavior is observed when the hose is exposed to LP Gas for the second time. The “leveling off” values for two cases, namely (1) first or virgin exposure, and (2) second exposure, are shown in Figures 10 to 12 for 1-inch, 3/4-inch, and 1/4-inch diameter hose, respectively.

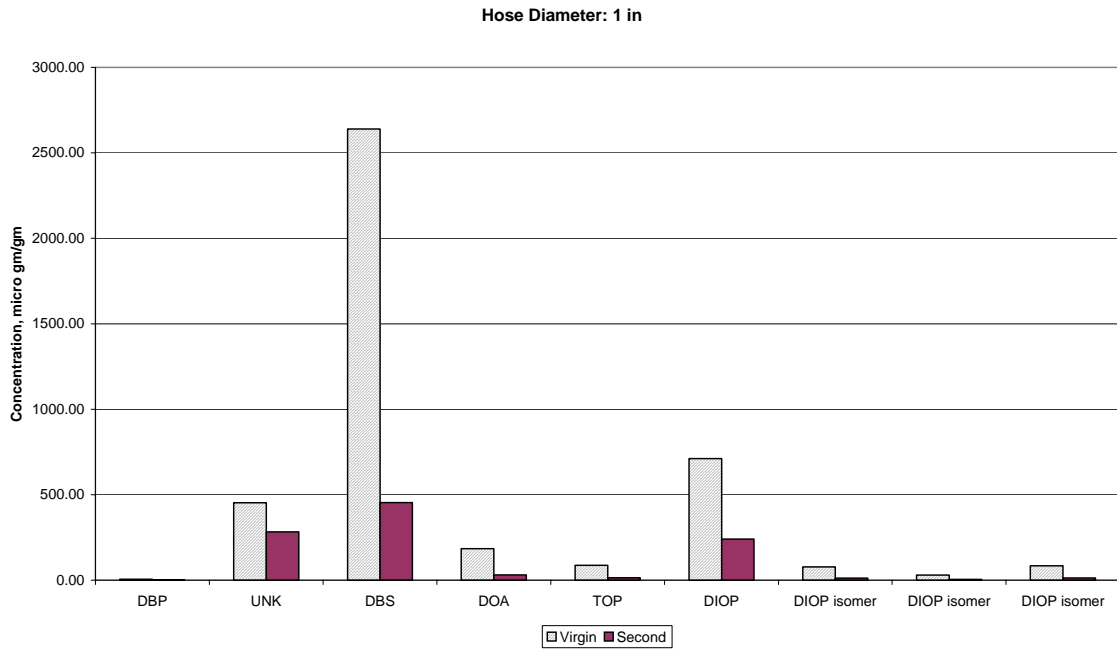


Figure 10. Extraction rates for virgin and second exposure in hose with 1-inch diameter.

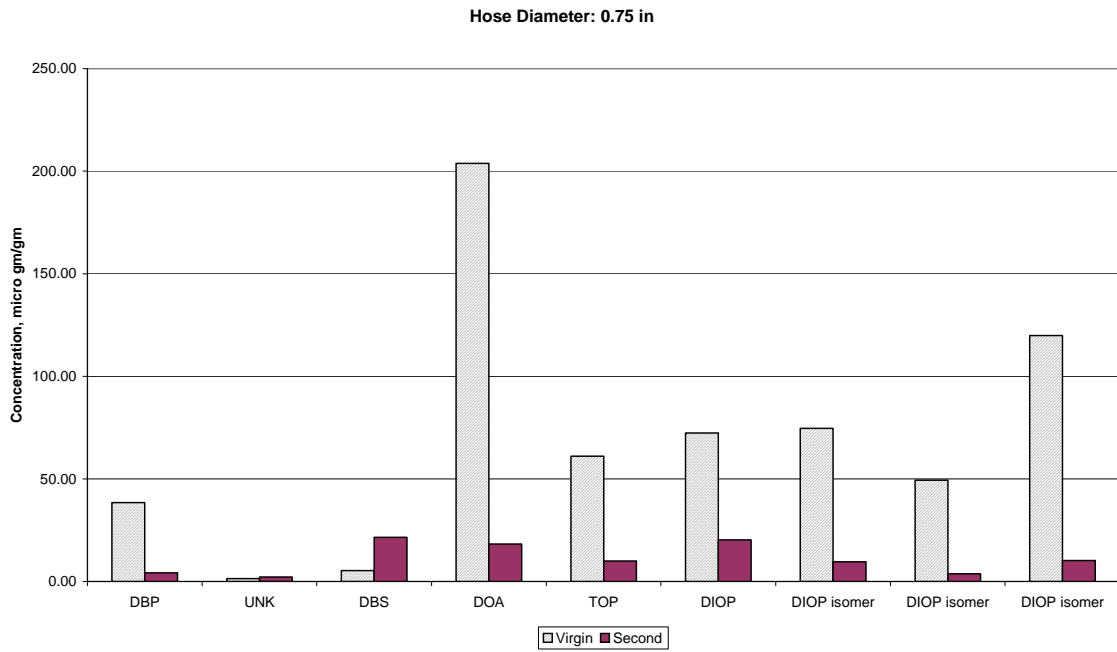


Figure 11. Extraction rates for virgin and second exposure in hose with 3/4-inch diameter.

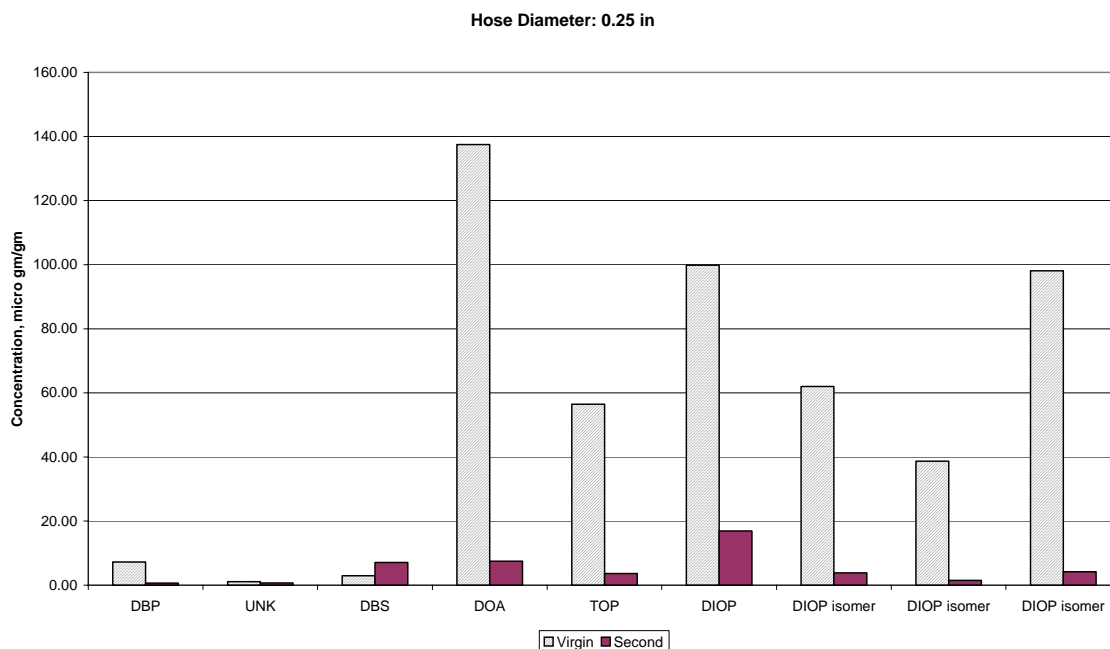


Figure 12. Extraction rates for virgin and second exposure in hose with 1/4-inch diameter.

In all three cases the amount of major species extracted on second exposure is significantly less than the first exposure – by about an order of magnitude.

This suggests that each hose has a limited amount of species that can be extracted. In turn, this implies that conditioning of hoses prior to service is technically feasible.

Testing: Permeation

Dynamic Rig Measurements

In the dynamic rig, the test hose was enclosed in a jacket that was filled with only nitrogen gas at the beginning of the test. As the LP Gas inside the hose permeated through the hose wall, the jacket gas composition showed an increasing amount of propane. Samples of the jacket gas were removed at regular intervals and analyzed by means of gas chromatography. The measured data are shown in Figure 13 with propane concentration along the y-axis and time along the x-axis.

The propane concentration increases linearly for the first six days up to concentration of 65%, and then begins to level off because of the increasing amount of propane in the jacket.

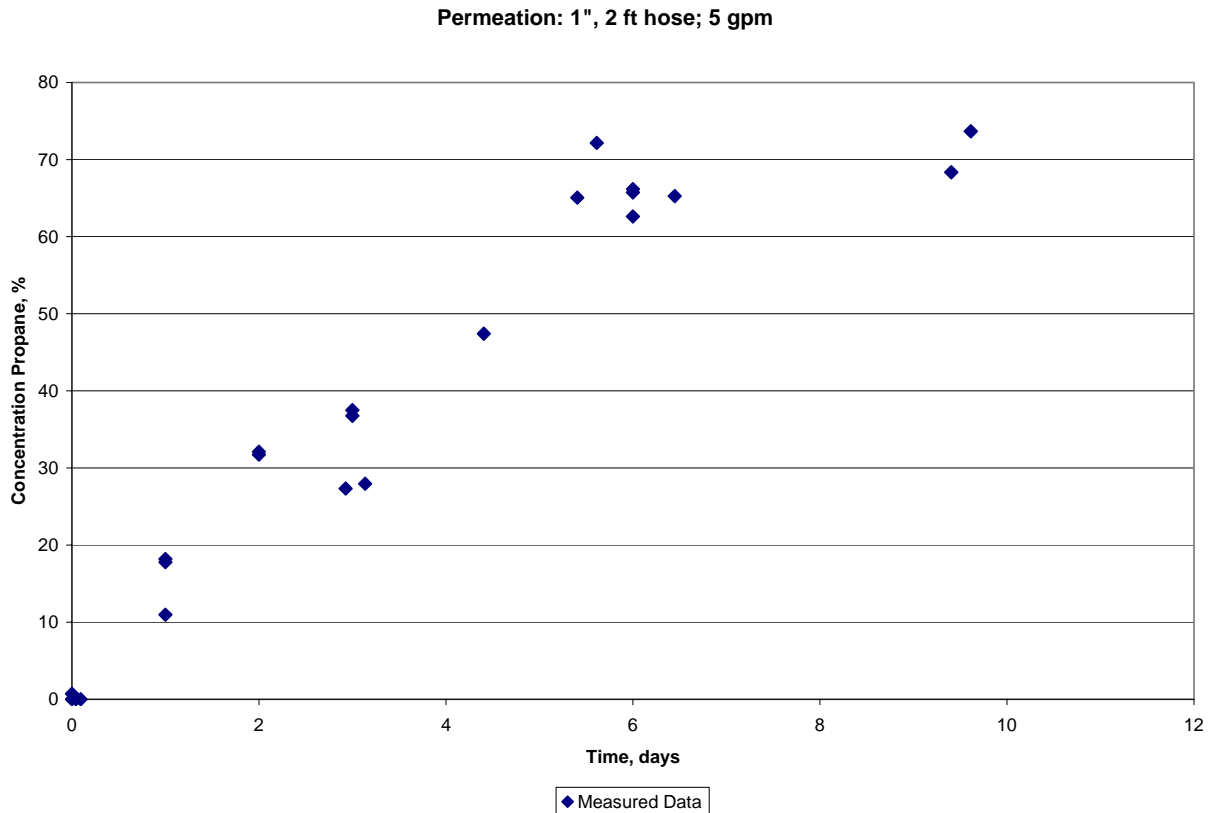


Figure 13. Plot of permeation data from dynamic rig testing on 1-inch diameter, 2-foot hose at 5 gpm and 150 to 200 psi.

Load Cell Measurements

Thus, permeation measurements in the dynamic rig showed that the permeation was constant until high concentrations of propane in the jacket reduced the concentration gradient through the hose wall that drives permeation. Direct measurement of permeation weight loss was attempted in an effort to eliminate the effect of external propane concentration, reduce costs, and confirm the measurements using an alternative technique. The concept was to continually and accurately weigh a hose filled with LP Gas. The weight of the hose/LP Gas combination should decrease as the propane permeates through the hose wall to the atmosphere. The measured rate of weight loss is the rate of permeation (by weight). In this method, the LP Gas escapes to the atmosphere, and there is no back pressure as in the sealed jacket. Therefore, the rate of permeation in this method can be expected to be constant, and not show a leveling off. This method is described next.

A hose was attached to a reservoir, and the hose and part of the reservoir were filled with LP Gas. A pressure gauge was used to monitor the pressure in the hose. The pressure varied only slightly because the hose was in a thermostatically controlled room. The apparatus was suspended from a load cell, which measured the force — in this case the weight of the apparatus. The intent was to measure the weight loss, which was presumably attributable to the loss of LP Gas through permeation. The test setup is shown in Figure 14.

The test on hose with a diameter of 1 inch and a length of 2 feet showed the average daily loss of LP Gas to be about 0.8 gm/day. The test was repeated with a 1/4-inch, 2-foot hose. In this instance, the average weight loss per day was about 1.25 g.

Thus, the 1/4-inch hose lost about 50% more propane by permeation than the 1-inch hose. The surface area available for permeation is greater in a 1-inch hose as compared to a 1/4-inch hose of the same length. On this basis, it might appear that the 1-inch hose should lose more propane by permeation than a 1/4-inch hose for the same length and time period. However, this assumes that the materials and construction of the two hoses are identical – this may not be true. Further, some of the difference may be attributable to experimental error.

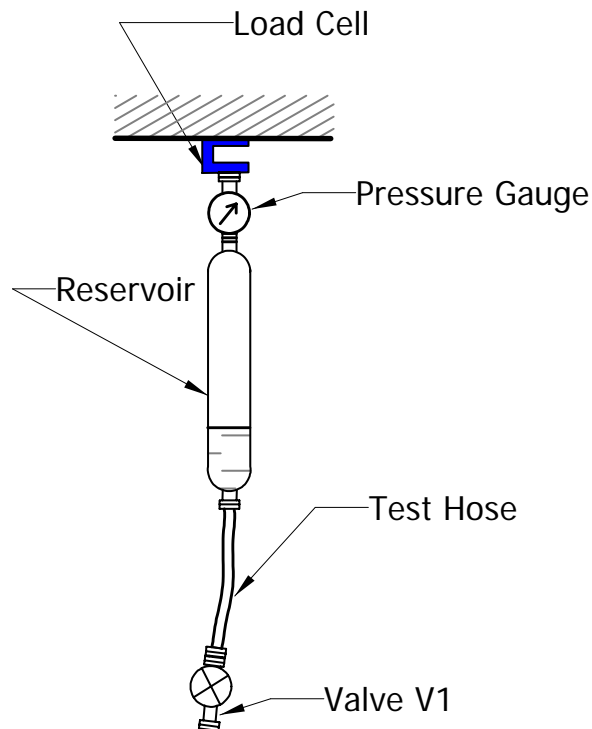


Figure 14. Test setup for load cell measurement.

Analysis and Modeling

If test results can be generalized or otherwise extended by theoretical models, the usefulness of the test results can be enhanced at relatively low cost. For this reason, theoretical modeling of the hose testing was investigated. The intent was not to develop detailed mathematical models or elaborate computer models. The goal was to combine the test data with known operative physical and chemical mechanisms such as rates of reaction associated with typical leaching phenomena, and rates of diffusion associated with permeation through a wall, particularly if similar phenomena had already been studied.

Formulation of a permeation model proved to be a formidable task because of the lack of previous work, and the complexity of the physics and the chemistry. Therefore, no further attempts were made to theoretically model extraction of chemicals from hoses. Modeling the permeation of LP Gas through hose proved to be more successful.

A mathematical model was formulated for loss of propane through the hose wall into a sealed jacket containing nitrogen gas. The only “unknown” input parameter was the value of the permeability, which is a measure of how easily a particular substance (in this case, propane) can permeate through the wall. For typical test conditions, the mathematical model was used to estimate the loss of LP gas by permeation. The permeability, P , is unknown for the hose under test. When the permeability was adjusted to a constant value between measured limits, good agreement between theory and experiment resulted. Figure 15 shows the measured propane permeation (shown previously on Figure 13) and the model calculation. These results suggest that classic permeability theory can be used to compute product loss once the permeability of the hose is measured or computed.

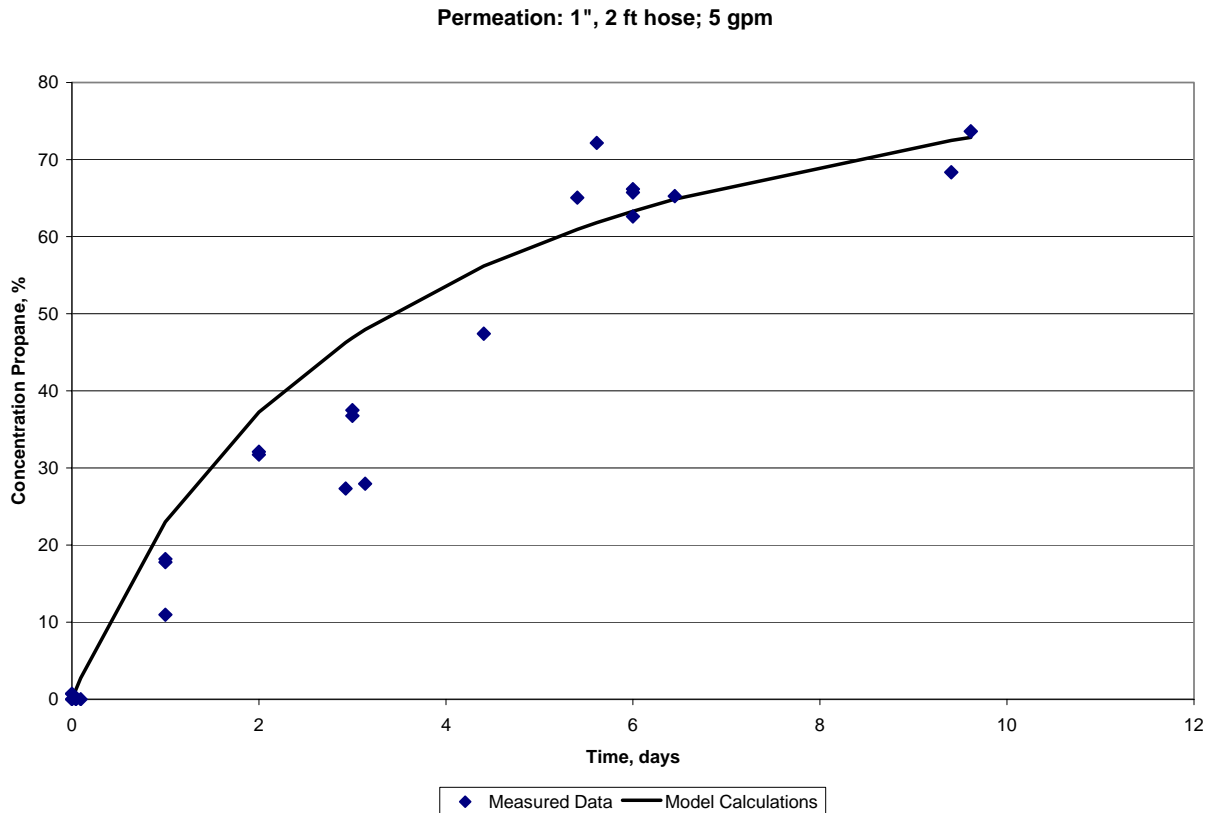


Figure 15. Measured propane permeability for samples taken with plastic and glass syringes and model calculation (solid line).

For example, the model shows that a 1-inch, 2-ft hose would lose about 1 gm/day of propane. For a 1-inch, 125-ft hose, this would lead to a loss of about 2 oz of LP gas each day. Similar calculations can be undertaken prior to SHED (Sealed Housing for Evaporative Determination) testing to assess whether problems may be encountered, assuming that the permeability of the hose is known, or can be estimated.

A Prototype Design for Conditioning Hose

We designed and fabricated a prototype to demonstrate how the information from this study could be put to practical use. We assumed that the following were important:

- Ease of operation (thereby minimizing training)
- Cost
- Speed of operation
- Flexibility.

Depending on the manufacturer and the service conditions, many types of plasticizers could be present. The users of the conditioning system are not experts in chemistry or have gas chromatography available. Therefore, these aspects need to be pre-programmed into an on-board computer. The computer would then communicate with the user using a display and an appropriate input device. The type of information

that the user would need to put in would be, e.g., the diameter of the hose. For the prototype we used a STAMP microprocessor, a display, and a two-button input. Because the purpose of the prototype was illustrative, we did not program full functionality into the microprocessor. Instead, when the prototype program is initiated, it displays the appropriate prompts, accepts the information “entered” by the user, and then proceeds with “conditioning” of the hose. After the requested level of conditioning has been reached, the microprocessor displays a suitable message on the display, and also beeps audibly to alert the user.

In order for the microprocessor to determine that the conditioning is complete, it needs to know the desired level of extraction and the time of exposure. The first is specified by the user, and the second is based on a clock maintained by the microprocessor. In addition, for a commercial unit, it is desirable to know the condition of the LP Gas in the hose. Therefore, we also installed a pressure transducer that measures the pressure in the LP Gas and communicates this information to the microprocessor. A schematic of the design (not to scale) is shown in Figure 16.

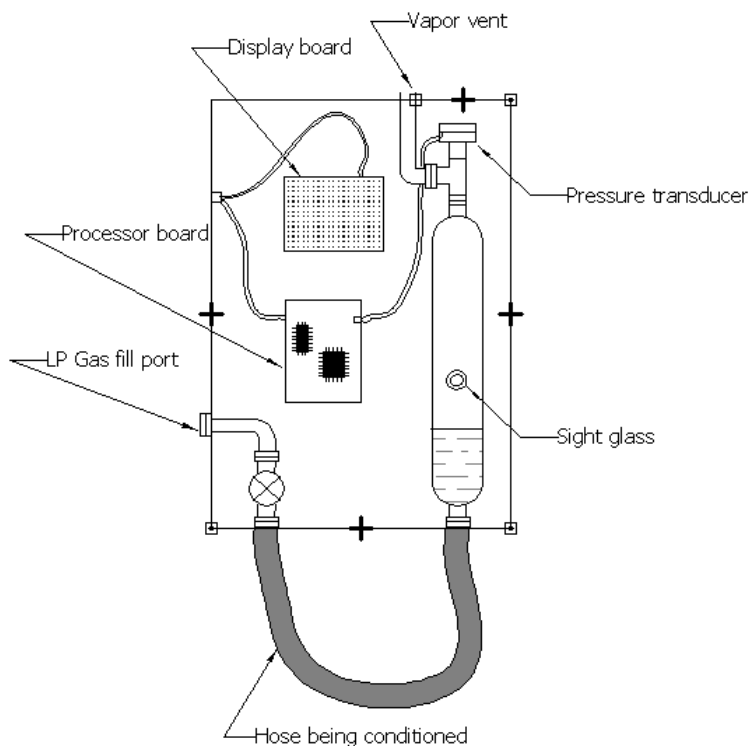


Figure 16. Schematic of design of prototype device for conditioning hose .

All the components are enclosed in a metal enclosure that can be hung on a wall. On the bottom of the enclosure are two standard fittings to which the hose can be quickly connected. On the side of the enclosure is another standard fitting to which the LP Gas supply is connected for filling the hose. After the hose is filled, the excess LP Gas fills a reservoir with a sight glass. When the LP Gas is visible in the sight glass, the filling of the LP Gas is stopped by closing the valve in the filling section. Then, the computer program is activated and the conditioning can be started and stopped under the control of the microprocessor.

Figure 17 is a photograph of the microprocessor and associated hardware. Figure 18 is a photograph of the display. Figure 19 is a photograph of the rear of the prototype.

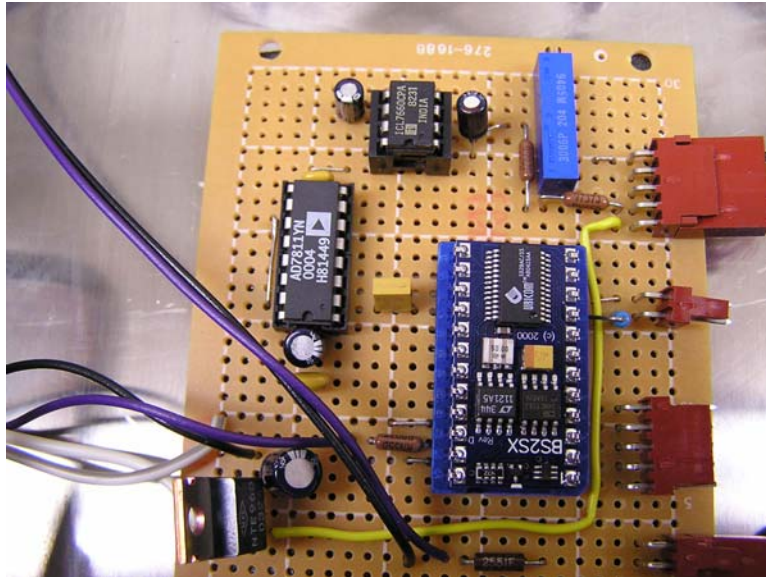


Figure 17. View of microprocessor and associated hardware for prototype hose conditioning device.



Figure 18. Display screen of prototype hose conditioning device.

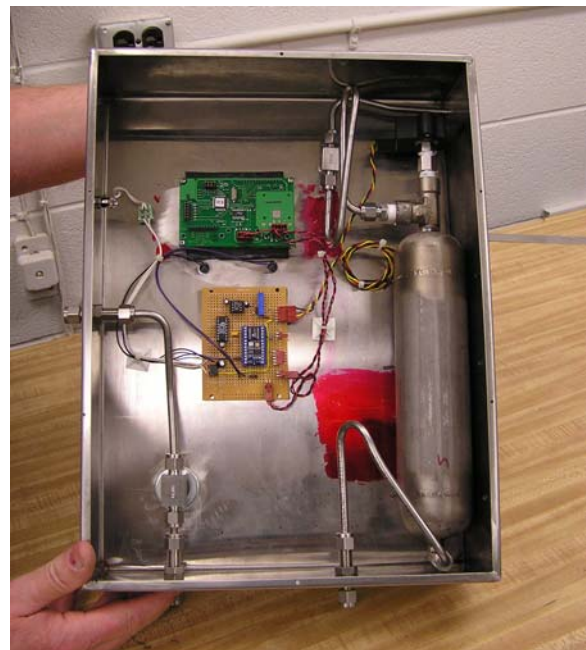


Figure 19. Rear view of prototype hose conditioning device.

In quantities of 100 to 1000 units, the cost of production of such a test unit is estimated to be about \$ 500 as follows:

- \$ 125 for the electronics,
- \$ 225 for the mechanical components (mainly stainless steel valves)
- \$ 50 for miscellaneous materials, and
- \$ 100 for assembly.

The actual costs may vary (up or down) depending on the specific design features implemented, the materials, and the number of units. In addition, there would initial investment for developing a robust, production program for the on-board microprocessor, for laying out the circuit board, and for making the molds for the enclosure.

Conclusions

1. Several chemical species are leached from hose when in contact with LP Gas.
2. The chemical species, their relative rate of extraction, and the relative concentration may depend on the manufacturer and the model of hose.
3. Most of the extracted species appeared to be plasticizers.
4. The rate of extraction is greatest initially, when new hose is exposed to commercial grade LP Gas. The rate of extraction decreases for a few days and the levels off. The extraction may continue at a low rate for a considerable period.
5. There may be an effect of flow rate on extraction, but based on our testing we could not label the difference as significant. This suggests that static testing is a good indicator of extraction.
6. We did not detect a substantial difference in extraction based on the supplier of the LP Gas.
7. We did not see clear trends with respect to hose diameter.
8. The amount of extraction per unit area of the hose is independent of the length of hose, but the total amount extracted is proportional to the length of the hose.
9. Hose that was “depleted” showed much lower rates of extraction for all species the second time it was tested. This suggests that conditioning of hose is technically feasible.
10. In order to gauge the operational feasibility of conditioning hose, a prototype conditioning unit was conceptualized, designed, and fabricated.
11. Measured permeation of LP Gas through the hose walls was consistent with classical estimates of transport of gas through a porous medium.
12. The uncertainty in estimating the amount of LP Gas lost through permeation is related directly to the permeability of the hose. The permeability depends on the hose materials and the hose construction. Measured values of permeability in the published literature vary by an order of magnitude.
13. The measured amount of permeation was about 0.84 g/day to 1.23 g/day for 2-foot hose lengths. This is equivalent to 30 cm³/m/hr (0.6 in³/ft/hr) to 50 cm³/m/hr (0.9 in³/ft/hr). These values are well within Underwriter Laboratories UL21 value of 560 cm³/m/hr (10.4 in³/ft/hr) and the maximum value of 400 cm³/m/hr (7.4 in³/ft/hr) required by ISO 11759:1999(E), “Rubber Hoses and Hose Assemblies for Dispensing Liquefied Petroleum Gases (LPGs) – Specification.” The measured values are comparable to the Japanese standard limits of about 50 cm³/m/hr (0.9 in³/ft/hr), but exceed the Australian suggested limit of 25 cm³/m/hr (0.5 in³/ft/hr).