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Selective Permeation of Solvents through Plastic Bottles

Introduction

Loss of material, whether by spill, leakage, evaporation, etc. translates directly to loss on the bottom line. This was brought home directly to Boeing Defense and Space Group when E-Team members observed collapsing plastic chemical storage bottles. The E-Team is comprised of hourly employees who are cross-trained in many aspects of hazardous materials from storekeeping and regulations to emergency response. On noticing bottles of solvent which had collapsed for no apparent reason, they brought a few to Environmental Engineering and asked why. Although the phenomena had been observed by many, it had not been considered a problem.

A preliminary evaluation indicated that, without apparent degradation of the plastic or contamination of the hydrocarbons, hydrocarbons were permeating through the plastic. Information on the magnitude and range of the problem was not readily available. The objective of a resulting investigation was to evaluate the integrity of readily available storage and dispensing bottles for commonly used solvents by conducting a series of small studies. Preliminary observation indicated that LDPE bottles containing xylene, toluene and d-limonene were collapsing but bottles containing only water, denatured alcohol or MEK were not.

Methods and Materials

A variety of plastic bottles were filled with solvents, capped, weighed and stored on an open rack. These were periodically re-weighed to measure solvent loss. Plastics tested were LDPE, HDPE, HDPE-N, FLEP, FEP, Fluorinated LDPE and Fluorinated HDPE. The following bottle materials were specifically not tested due to known incompatibilities with solvents: ABS, Acrylic, polystyrene, polycarbonate, polyvinyl chloride. The singular solvents tested initially were denatured alcohol, acetone, MEK, water, xylene, and toluene. Naphtha, a petroleum cut similar to kerosene, was also tested as a "singular" solvent because of its wide use.
Solvent blends were similarly tested but were also quantitatively analyzed for selective permeation. A blend of toluene and MEK, and a blend of IPA, MEK, ethyl acetate, and naphtha (a blend in itself) were tested.

Additionally, because many different solvents are often stored in the same cabinet, a test was done to demonstrate the potential for cross contamination through closed bottles due to permeation. A bottle of toluene was placed into a larger, loosely covered container with three bottles of acetone. The acetone was later analyzed for toluene and compared with a control.

Finally, a visual check was made of vendor products supplied in plastic bottles and all chemicals being dispensed from bulk containers and stored, temporarily, in plastic squeeze bottles

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awaiting delivery to a using shop. Chemical constituents were noted from the MSDSs for those on the shelf more than 6 months . Those constituents in collapsed bottles were compared against constituents in non-collapsed bottles in order to better define the range of the problem.

A source was found for fluorinated bottles as a possible solution to the permeation problem. The worst offenders were tested in these bottles.

Results

Three solvents were tested (xylene, toluene, and d-limonene) in five different bottle types; one test for each bottle/solvent pair. A summary of the test results showing a loss of material over the 30 day test period is found in Table 1:

Bottle Material	Xylene	Toluene	d-Limonene
LDPE	81 gm	115 gm	29.5 gm
HDPE	27.4^	39.7^	8.4^
HDPE-N	23^	26.6^	5.7^
FLEP	0.1^	0.3^	-0.3^
FEP	0.3^	NA	0.2^

^ MATERIAL LOSS NORMALIZED BASED ON BOTTLE SURFACE AREA: LDPE = 1.

Table 1

Because LDPE was found to be the worst case and the most prevalent in use, a broader group of solvents was tested in LDPE as a baseline. In addition to the three above, naphtha, IPA, 2 blends, acetone, MEK, denatured alcohol, and water were tested. Permeation of the alcohols, ketones, and water were found to be insignificant. Results for a 56 day test for xylene, toluene, d-limonene, and a blend of 34% MEK with 66% toluene are shown in Figure 1.

An analysis of the 34-66 blend showed that, because toluene permeated through the plastic while the MEK did not, the composition of the blend changed. Figure 2 shows the change. Figure 3 shows the changes in a four part blend made of an alcohol, a ketone, an acetate, and naphtha. These two figures demonstrate that the composition of a mixture may change given the time because of selective permeation.

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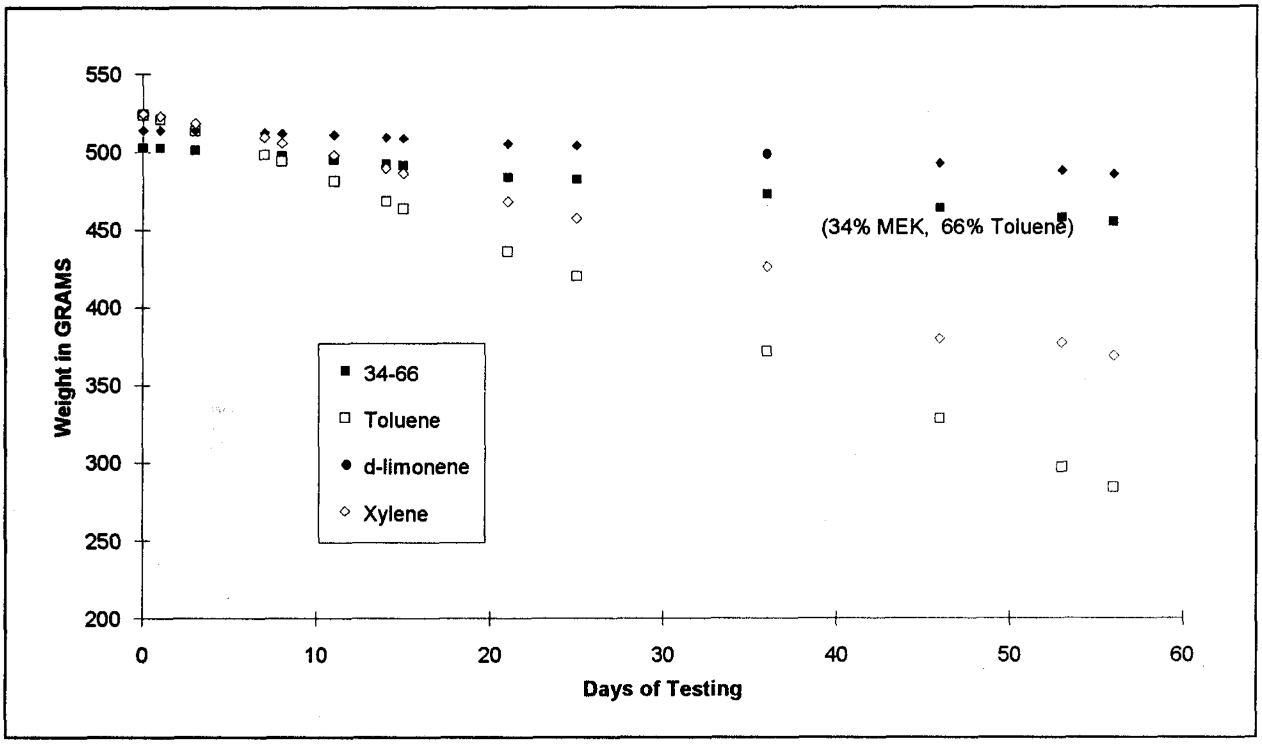

Weight Loss for Solvents, LDPE
Figure 1

Fluorinated bottles were obtained and two of the "big offenders", toluene and naphtha, were tested. The thirty day solvent loss results are shown in table 2. Different levels of treatment were available for standard bottle types.

	Toluene	Naphtha
HDPE level 1	2.4 gms	1.4 gms
LDPE level 1	2.6 gms	1.7 gms
LDPE level 3	1.6 gms	1.0 gm

Solvent Loss in Fluorinated bottles
Table 2

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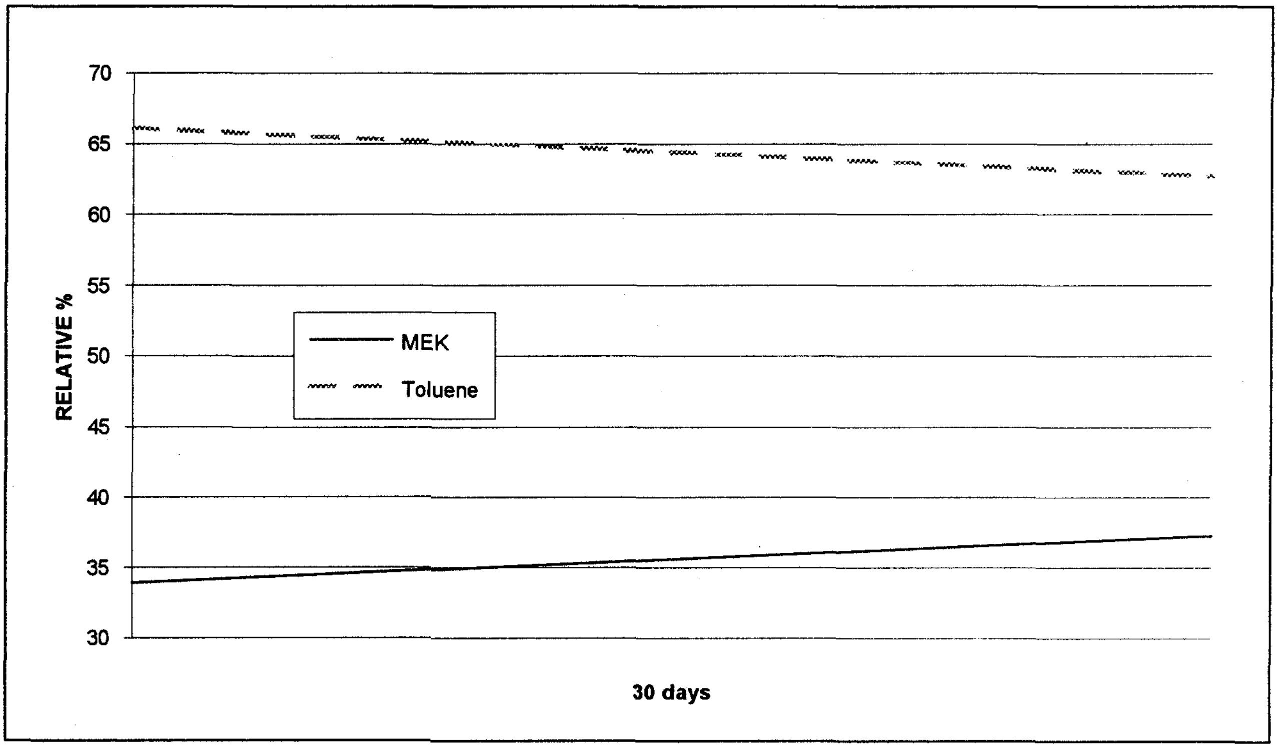

Composition Change of a 34% MEK, 66% Toluene Blend
Figure 2

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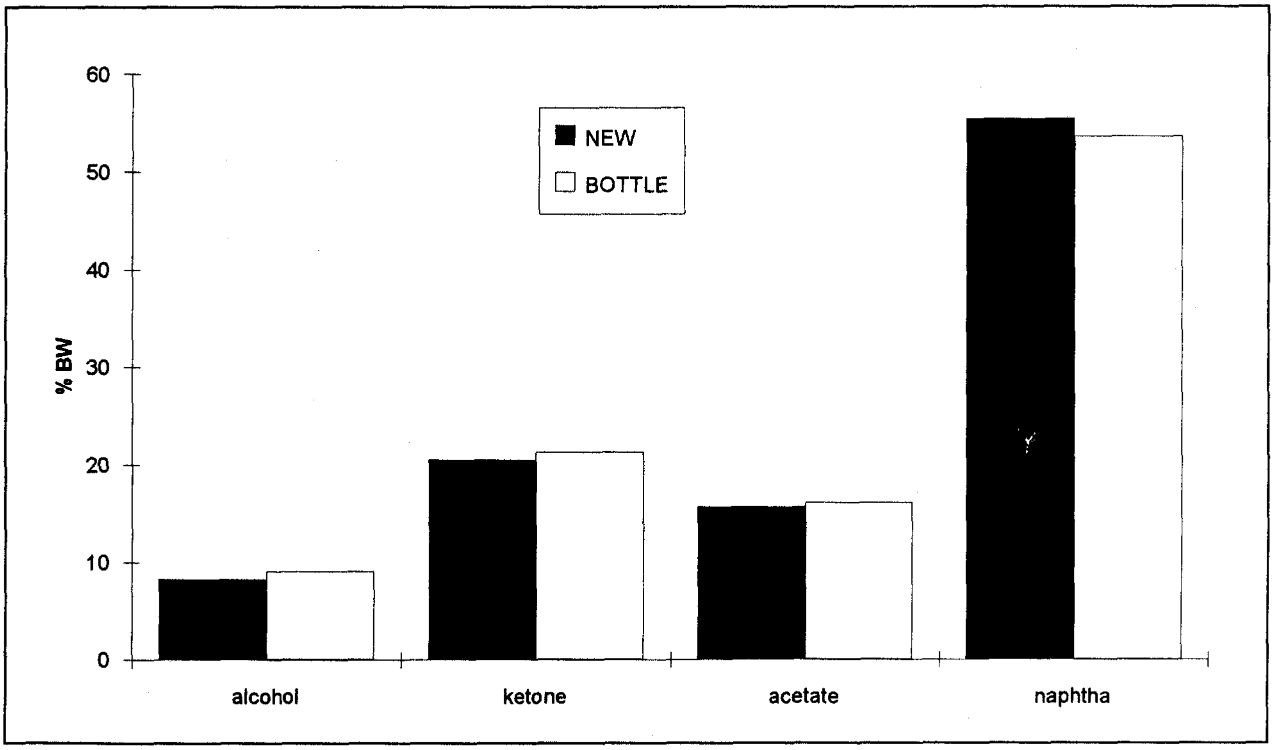

Blend Composition (%) of New Material vs. Material After LDPE Storage
Figure 3

In the attempt to find cross contamination by storing bottles of IPA in a larger container with a bottle of toluene (note: 5 milliliters of toluene were placed in a depression of the larger container to pre-saturate the container volume. This test ran for 32 days.), 56 ppm toluene was found in the IPA at the end of a month storage.

A tabulation of the "results" of the visual inspection of vendor supplied and shop dispensed materials could as easily be placed in the conclusions section because many of the materials on the table were not actually tested. Evidence of bottle collapse, time on the shelf, and constituent make-up based on MSDS information were used to make an educated guess for those materials not actually tested. Materials not tested are indicated with an asterix(*) (see Table 3).

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Additionally, I have set an arbitrary and somewhat fuzzy line at about 2 grams per month for a 16 ounce dispensing bottle as the cut-off for "permeable" for the items tested in this table.

Permeable through LDPE (generally the "non-polar" solvents)	**"Not Permeable" through LDPE** (generally the "polar" solvents)
Common Aliphatic Alkanes	Alcohols
pentane*	ethanol, ethyl alcohol*
hexane*	denatured alcohol
heptane*	isobutyl alcohol*
octane*	IPA, isopropanol, isopropyl alcohol
Aromatic Alkanes	n-butyl alcohol*
toluene	sec-butyl alcohol*
xylene	diacetone alcohol*
benzene*	cyclohexanol*
Light Oils	Ketones
Petroleum Blends	MEK, methyl ethyl ketone, 2-butanone
naphtha	MIBK, methyl isobutyl ketone*
mineral spirits*	MPK*
Stoddard solvent*	acetone
kerosene	cyclohexanone*
gasoline*	Acetates*
paint thinner	Water
Terpene Blends	Detergent/Water*
d-Limonene	
Production Blends containing any of the above in significant quantity	

"Non-Polar" vs. "Polar" Hydrocarbons
Table 3

Conclusions

1) It is advantageous to have a group of shop personnel trained in safety, environmental and material management who have as their work focus the management of hazardous materials and can thus recognize a potential problem when they see it. It is also important that they are empowered to follow a question to its solution.

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2) Significant quantities of organic compounds are escaping plastic containers currently in use. The problem extends beyond the Aerospace industry to a variety of vendor supplied materials, many of which can be found in hardware stores. This problem can be mitigated by a different choice of packaging materials or, to a lesser degree, by instituting "just-in-time" inventory practices.

3) Material composition may change over time due to selective permeation of the non-polar solvents through LDPE and HDPE plastics. This may lead to variable manufacturing results if the blend has been optimized and if the composition is critical. Alternately, a particular solvent blend may be robust from a manufacturing view point, but chancy in other ways. For example, the Aerospace NESHAP has two vapor pressure cut-off limits for hand wipe solvent cleaners: < 7 mm Hg for minimal recordkeeping, and < 45 mm Hg for non-exempt processes. If a formulation were designed to fall just below 45 mm Hg (e.g. about 86% toluene and 14% MEK), it would be fine when initially blended and dispensed. However, if it were dispensed into non-fluorinated LDPE bottles, Figure 2 indicates that there is cause for concern when the shelf life exceeds two weeks.

4) Cross contamination from permeation between bottles stored in proximity was confirmed but at such a low level, under such unlikely conditions, that there should be concern only when ultra pure solvent is required. Ultra pure solvents are usually stored in glass.

5) Other concerns exist due to selective permeation and include:

Safety:	Increased fire or explosion potential;
Health:	Increased employee exposure;
Environmental:	Increased air emissions;
Manufacturing:	Material composition variation (blends);
Cost:	Material lost is money lost.

Recommendations

In order to decrease material loss through permeation, move toward a "just-in-time" inventory for non-polar materials dispensed in non-fluorinated LDPE or HDPE containers. Substitution of fluorinated bottles for non-polar solvents should be investigated; the cost is on the order of 130% to 150% of regular bottles if ordered in quantity.

Use "just-in-time" inventory practices, including FIFO (first in, first out), for suspect vendor products. If a local vendor is manufacturing a blend specifically for your company, you or your purchasing agent may want to work directly with them for more appropriate packaging. Education of national vendors may take a little longer.

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Take a careful look at material blends to determine if small composition changes will result in a negative impact on manufacturing or on environmental compliance.

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