TIP FROM TECHNOLOGY

ExxonMobil Chemical

Comparison of Linear and Crosslink Polyethylenes in Certain Acid and Base Environments

Introduction

Sulphuric acid and sodium hypochlorite are two chemicals often stored in polyethylene tanks. The report documents work carried out by ExxonMobil comparing property performance of non-crosslinked HDPE, LLDPE resins with natural and white crosslinked resins.

Test Protocol

The following specific resins were used in this study:

Grade	LLP8460 (formerly LL 8461)	HDP8660 (formerly HD 8661)	Paxon 7004 Natural	Paxon 7004 White
Type of Resin	LLDPE	HDPE	Natural crosslink HDPE	White compounded crosslink HDPE
Melt Index, dg/min (2.16, 190C)	3.3	2.0	Not Applicable	Not Applicable
Density, gm/cc	0.938	0.942	0.945(1)	0.945(1)

(1) Estimated final molded part base resin density.

Parts were rotationally molded to optimum conditions obtaining good impacts and ductility and used as the basis for all samples outlined in this report. The HDPE and LLDPE samples had no bubbles in the cross-section of the parts but not taken to a point where discoloration had occurred on the inner surface.

Type 1 dogbones were die cut from 1/8" (3mm) thick parts and used to establish the tensile properties. Dogbones were pulled on an Instron tensile tester at room temperature (RT) using a 50 mm. per minute crosshead speed. 1/8" (3mm) rotationally molded samples were also used for bent strip Environmental Stress Crack Resistance (ESCR) testing.

Association of Rotational Molders, (ARM) impact geometry specimens were cut from 1/4" (6 mm) thick parts. Samples were conditioned at -40°C and impacted with a 20 lb. tup on the mold side of the samples following the standard ARM procedure. Ductility was defined as the percentage of samples, which failed in a ductile fashion divided by the total number of failures. If 5 samples out of 25 failed but 4 failed in ductile fashion then the % ductility would be 80%.

All samples were engraved to ensure sample identification was still possible after chemical exposures. The sulphuric acid was 97% minimum assay and was not changed through the test period. The sodium hypochlorite was purchased as greater than 14% and was changed twice weekly to maintain the minimum assay level above 12.5%. Test temperature for the tensile and impact exposures was ambient conditions done in Florida from a February to June period. The estimated average temperature from climatological records was 70°F (21°C).

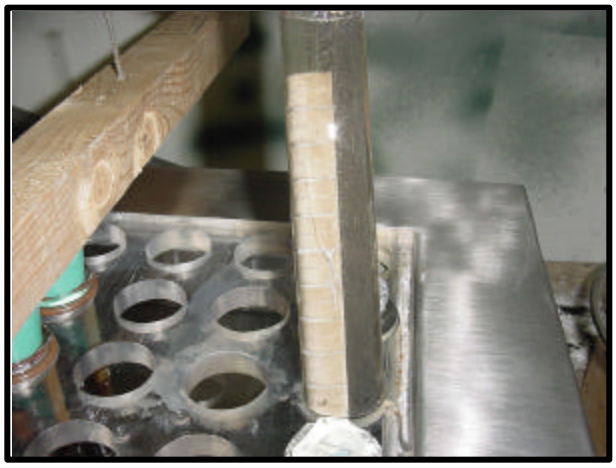
Samples for tensile properties were submersed in the chemicals vertically with small spacers so the chemical could contact the entire specimen except for about 0.5" (12.7mm.) on one end, which was used to hold the sample. This unexposed area would ultimately be in the jaw grip of the tester and thus would not affect the tensile results.

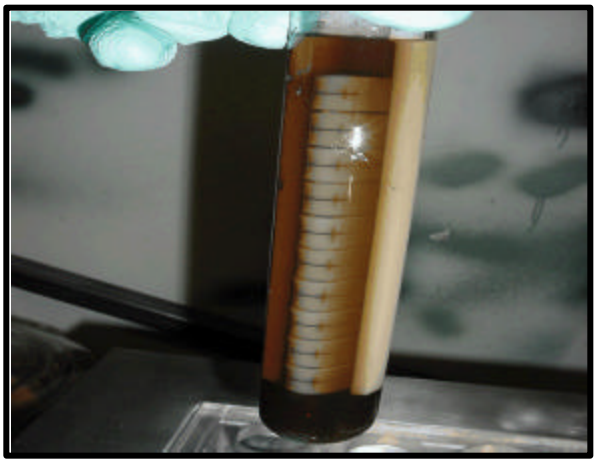
Samples for impact properties were stacked horizontally with small PE spacers placed at the corners of the samples to ensure proper chemical contact. A glass rod was placed through a hole drilled in the corner of the samples was well as the spacers to ensure the stack maintained alignment. This vertical, pancake-like stack was then submerged in the chemical using lead shot in a glass to keep it submerged.

Pyrex glass containers were used to hold the tensile and impact specimens. No extra iron or copper was added to the chemicals to reportedly increase severity of the tests.

Samples were exposed for various hours as outlined in the results. Sets of unexposed samples were also done at the end of the test period to ensure the results were due to chemical exposure and not sample aging.

In addition, bent strip ESCR testing using the same chemicals was also completed. This test was based on ASTM D 1693 Condition A, with slit specimens. Sulphuric acid temperature was 50°C and the acid was left in the tube for the test duration. The sodium hypochlorite was tested at 35°C and changed twice weekly. A 50°C test temperature for the sodium hypochlorite was found to be too high as it resulted in vaporization of the chemical. The figures below show the setup of the bent strip samples in the tubes. The specimen holder was made from brass. Sodium hypochlorite is on the left; sulphuric acid on the right. Note the scale-like deposits on the samples seen during sodium hypochlorite testing which was not evident during sulphuric acid testing.

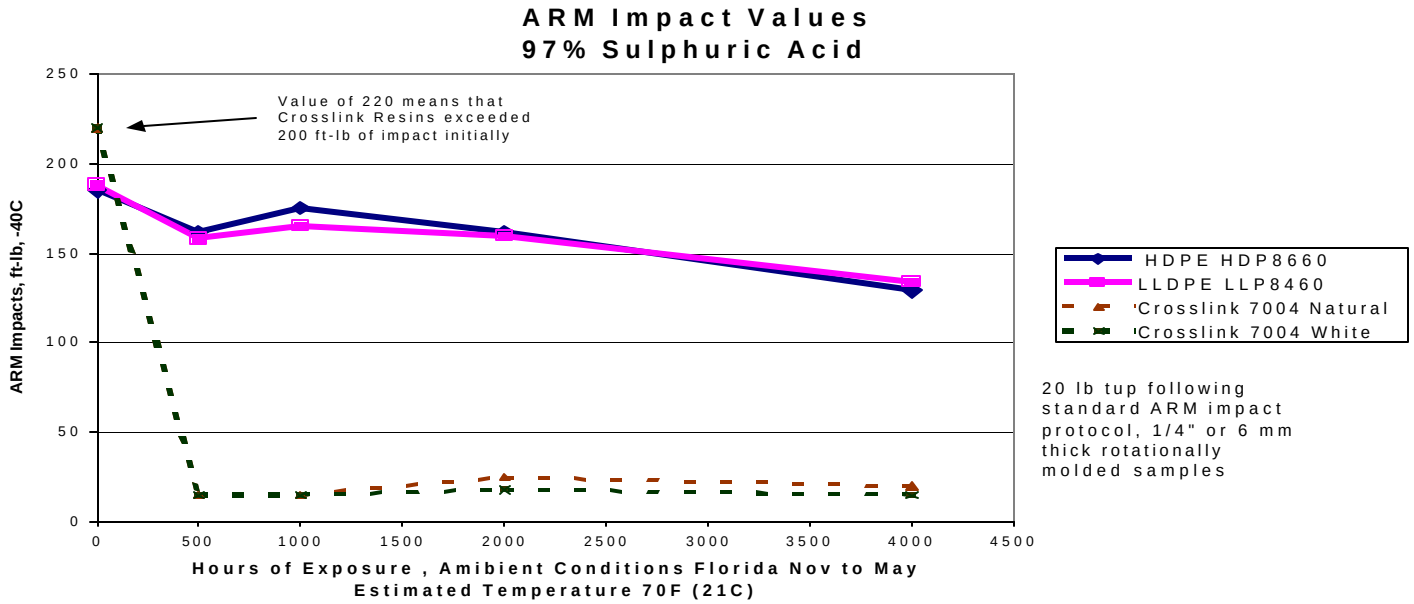


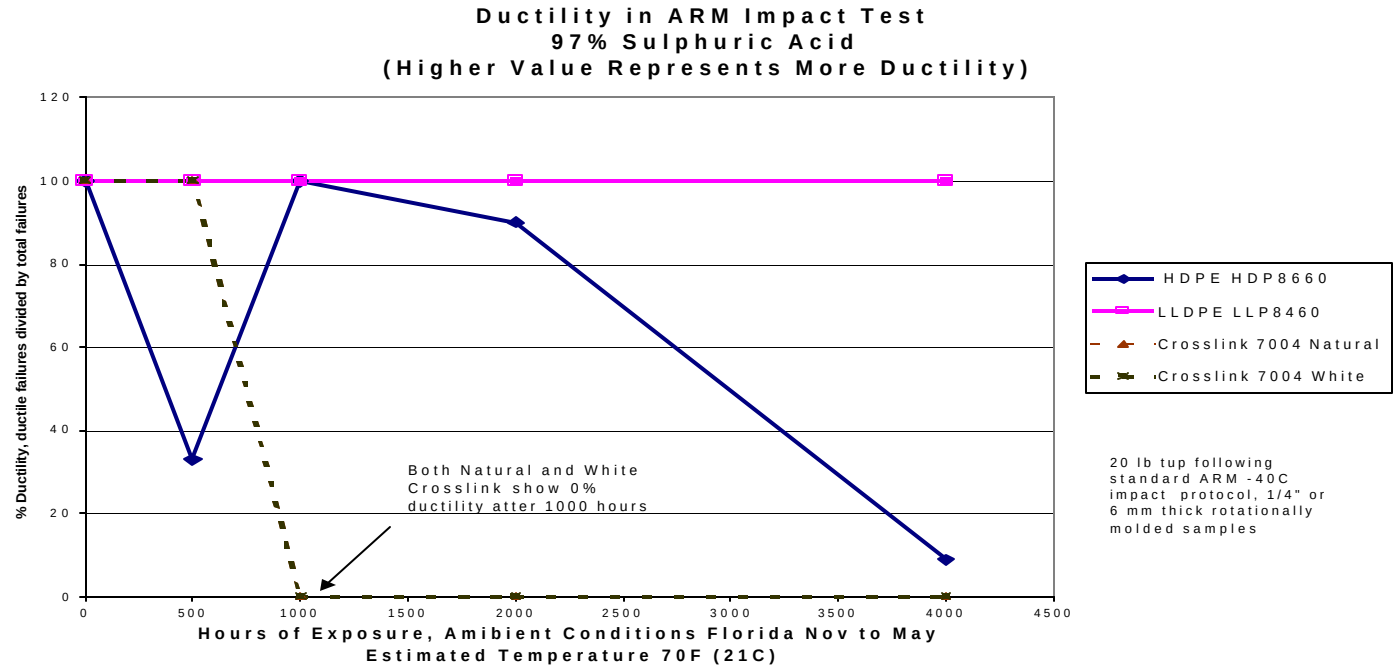


Results

The graphs below outlines the effect of chemical exposures on ARM impacts. Numerical values are detailed in Appendix 1.

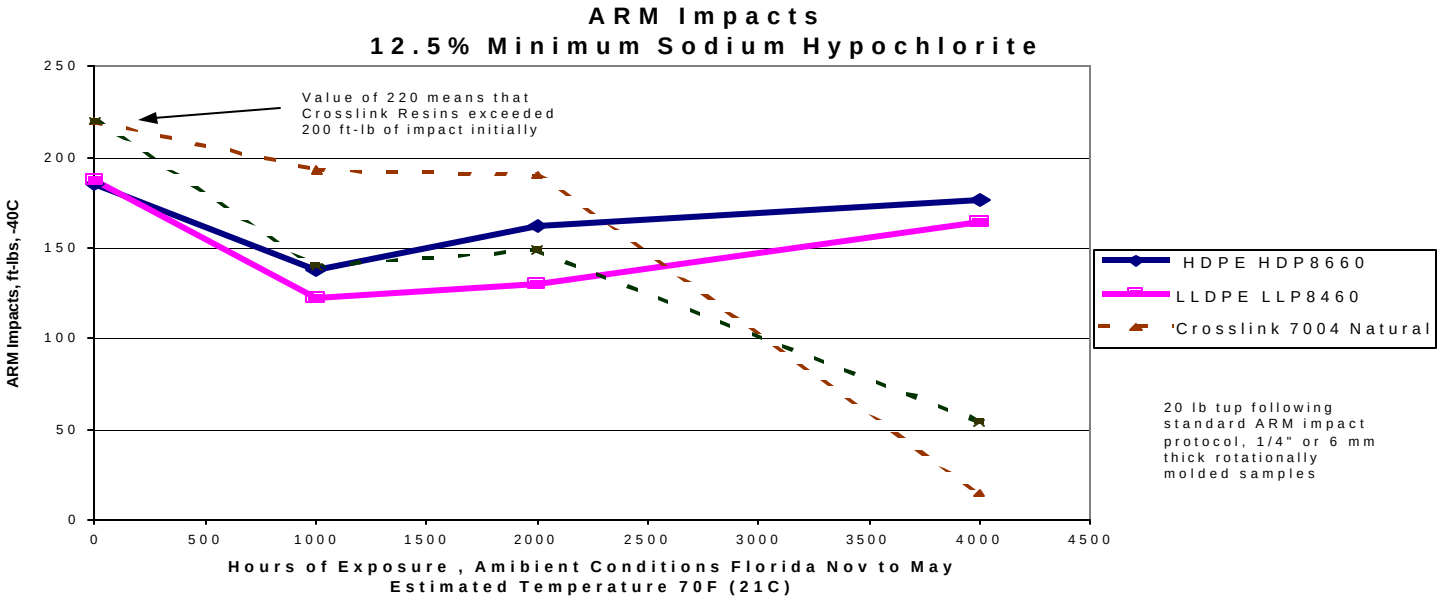
The first two graphs cover sulphuric acid.

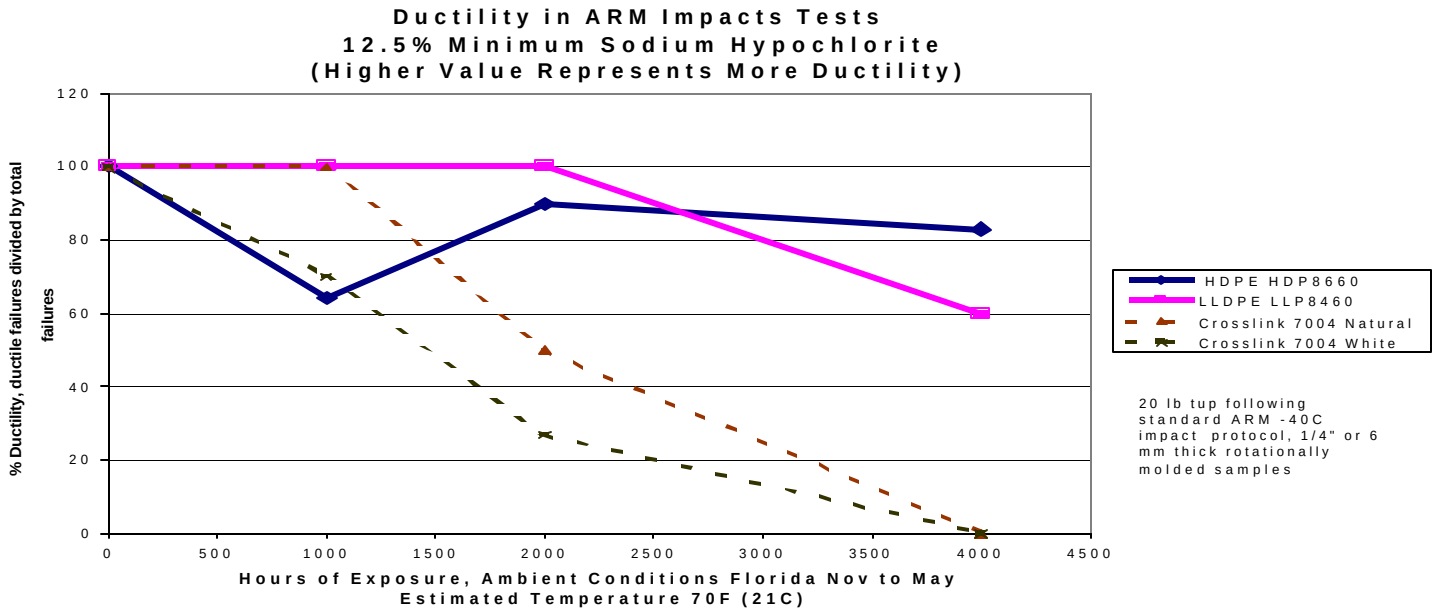




All samples start with good ductility with the crosslink samples having higher impact values than the HDPE or LLDPE. However, the HDPE and LLDPE samples retain more of their initial impact values and ductility after 1000 hours of exposure.

The next 2 graphs illustrate the same type of results for exposures to sodium hypochlorite.

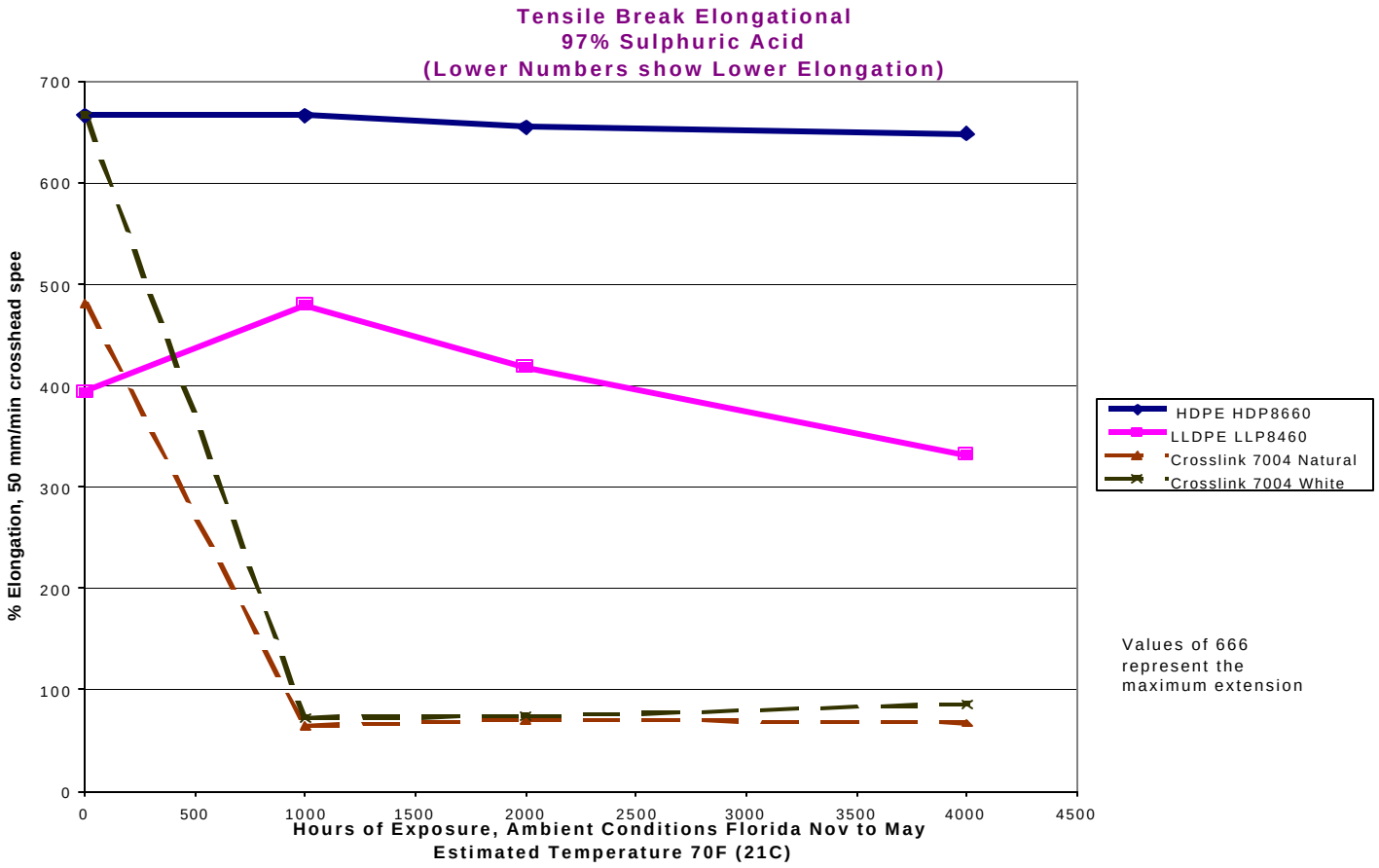




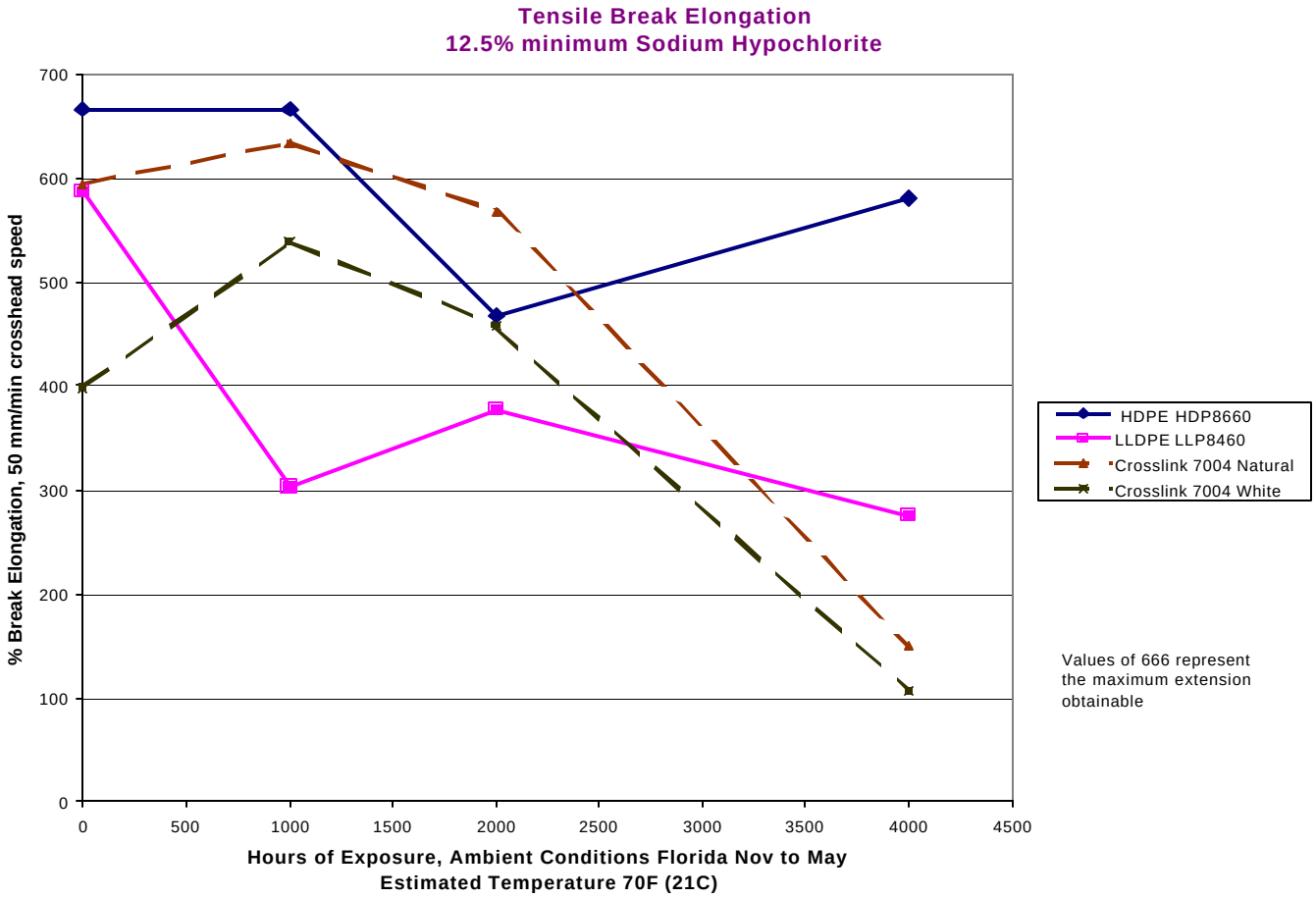
Here it appears that the sodium hypochlorite is not as aggressive as sulphuric acid but that after 2000 hours the crosslink resins trend to lower impact and ductility relative to the HDPE and LLDPE materials.

The next graphs outline the change in tensile properties. Refer to Appendix 1 for the complete set of data. The tensile yield values did not change significantly since the overall density of the resin, which is not substantially changed during chemical exposures, determines this. Thus only the break elongation values are plotted as these did show changes over time. The values are expressed as a % of the original gauge length based on ASTM D638. Decreasing values showing embrittlement of the sample.

Here again, the crosslink resins have reduced tensile break elongation vs. the HDPE and LLDPE resins with HDP8660 showing the least change in values.



The next graph shows the same for sodium hypochlorite.



In this case the elongational decline is more rapid for LLP8460 but again ultimately the LLDPE and HDPE materials maintain their elongational values especially at the 4000 hour exposure point.

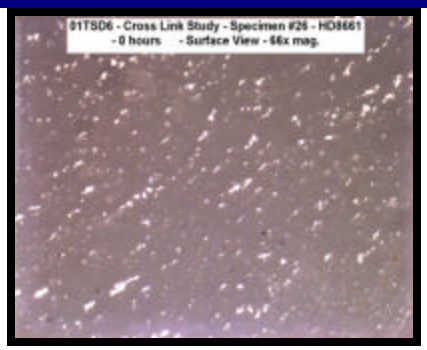
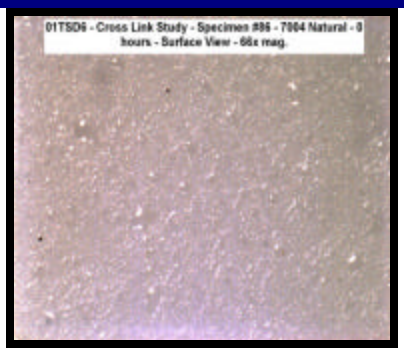
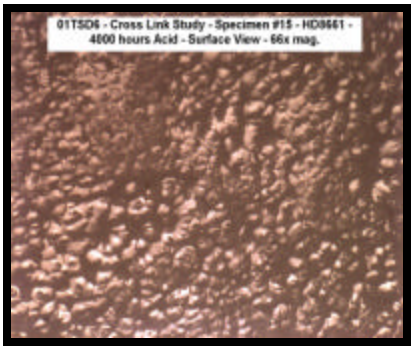
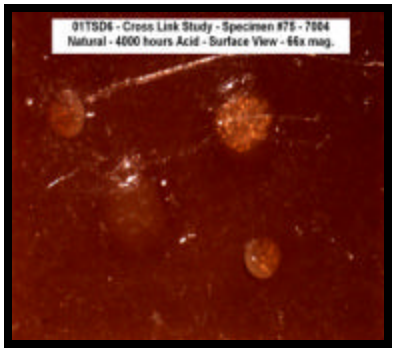
Bent strip ESCR results are shown below. This again supports the conclusion that acid is more severe than sodium hypochlorite with again HDPE and LLDPE showing less change in the sulphuric acid environment. The fact that no failures were observed with sodium hypochlorite for all the resins may be a result of the deposits on the sample surfaces as noted above. Such deposits would tend to reduce surface contact. The ESCR test is usually only done to 1000 hours due to stress relaxation in the samples. However in view of no failures occurring, the sodium hypochlorite the test was extended to 2000 hours.

Grade	LLP8460	HDP8660	Paxon 7004 Natural	Paxon 7004 White
Sulphuric acid, 50°C, Cond A, slit F50 hours	No failures at 1000 hours	No failures at 1000 hours	225	273
Sodium hypochlorite, 35°C Cond A, slit	No failures at 2000 hours	No failures at 2000 hours	No failures at 2000 hours	No failures at 2000 hours

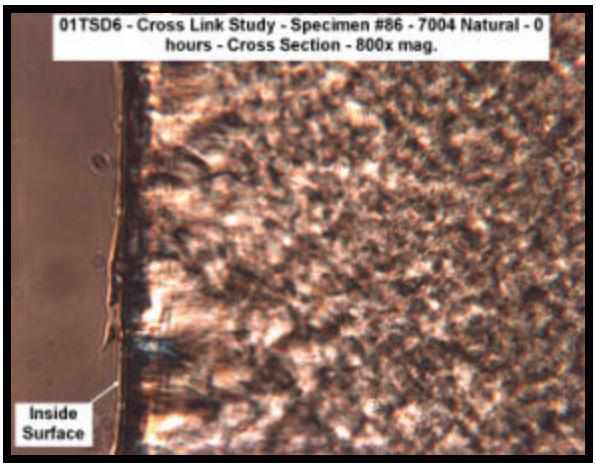
Further Discussion of Results

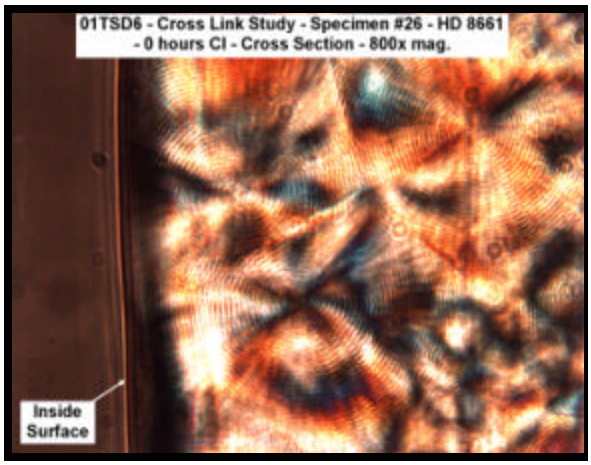
Both sodium hypochlorite and sulphuric acid create oxidative environments, which tend to pull the hydrogen molecules off the polyethylene chains, thereby causing chain scission of the polymer to occur. This creates low molecular weight or high MI material at this surface causing embrittlement of the sample.

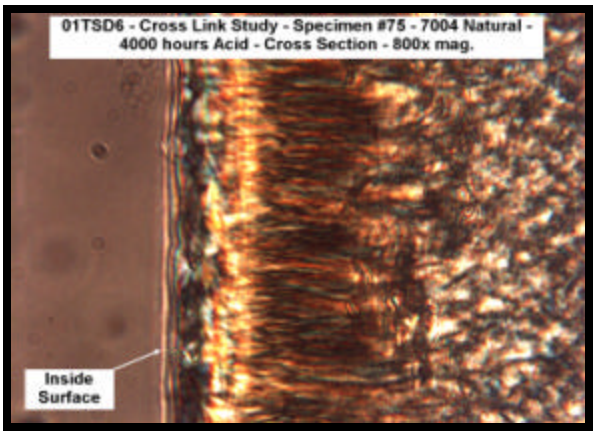
An identification of the rate of oxidative attack can be seen by the discolouration of the sample surfaces. Below is a set of photos showing the discoloration of the inside surface to illustrate the point.

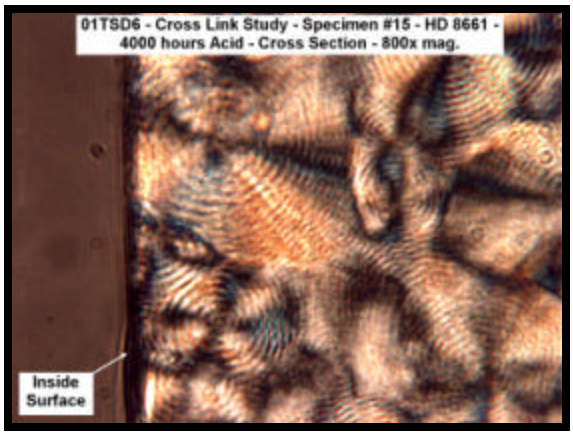
HDP8660	Paxon 7004 Natural	Hours of Exposure in 97% Sulphuric Acid
		**Unexposed Samples**
		**4000 hours**

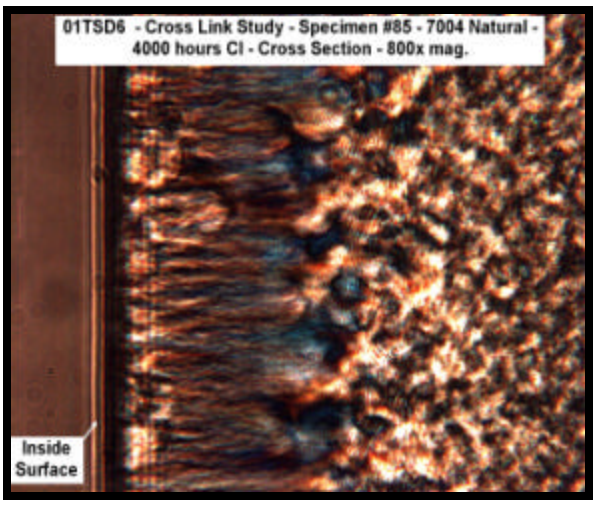
Another way of examining this oxidative attack is to look at the cross-sectional view of the materials taken near the surface of the chemical attack. A set of photos below illustrates that the rate of embrittlement is higher in the 7004 Natural when compared to HDP8660. This can be seen by the formation of column-like structures created on the inside surface of 7004. The depth of the penetration from the sulphuric acid or sodium hypochlorite attack on the 7004 Natural was estimated at 30-60 microns vs.6-15 microns for HDP8660. Similar results where seen when comparing 7004 White with LLP8460.

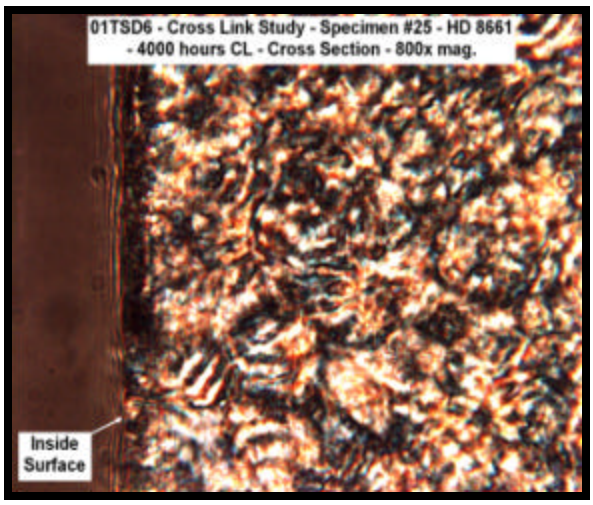












Summary

It is important to understand that general extrapolations to other acid and base chemicals and different protocols cannot be made. The test was designed to specifically address certain concentrations of sulphuric acid and sodium hypochlorite, which is commonly used in the industry. It is our understanding that this represents the most complete side by side testing ever published and hope that the facts contained in this report aids our customers in making their decisions.

Appendix 1

Table 1: ARM Impact Data Shown in Graphs

GT refers to "greater than". 7004NAT is natural Paxon 7004 and 7004WHT is 7004 White. Acid refers to 97% sulphuric acid and the Cl refers to the 12.5% minimum sodium hypochlorite. The number following these symbols is the hours of exposure. For example, Acid 500 is the results of 500 hours of sulphuric acid exposure.

ARM -40C Impacts, ft-lbs, 1/4" thick samples

	HDP8660		*LLP8460*		*7004NAT*		*7004WHT*		
	ARM Ft-lbs	*% Ductile*	*ARM Ft-lbs*	*% Ductile*	*ARM Ft-lbs*	*% Ductile*	*ARM Ft-lbs*	*% Ductile*	
Acid 0	**185**	**100**	**188**	**100**	**GT 200**	**100**	**GT200**	**100**	Acid 0
Acid 500	**162**	**33**	**158**	**100**	**15**	**100**	**15**	**100**	Acid 500
Acid 1000	**175**	**100**	**165**	**100**	**15**	**0**	**15**	**0**	Acid 1000
Acid 2000	**162**	**90**	**160**	**100**	**25**	**0**	**18**	**0**	Acid 2000
Acid 4000	**129**	**9**	**134**	**100**	**20**	**0**	**15**	**0**	Acid 4000
Cl 0	**185**	**100**	**188**	**100**	**GT 200**	**100**	**GT 200**	**100**	Cl 0
Cl 1000	**138**	**64**	**123**	**100**	**193**	**100**	**140**	**70**	Cl 1000
Cl 2000	**162**	**90**	**130**	**100**	**190**	**50**	**149**	**27**	Cl 2000
Cl 4000	**177**	**83**	**164**	**60**	**15**	**0**	**54**	**0**	Cl 4000

Table 2: Tensile Data

YE refers to tensile yield elongation and BE refers to break elongation both expressed as a % of the original gauge length based on ASTM D638. GT refers to "greater than".

Tensiles RT Type 1 at 50 mm/min crosshead pull

	HDP8660		*LLP8460*		*7004NAT*		*7004WHT*		
	YE %	*BE %*	*YE %*	*BE %*	*YE %*	*BE %*	*YE %*	*BE %*	
Acid 0	19.4	GT 666	19.7	394	22.4	481	23.2	GT 666	Acid 0
Acid 1000	21.6	GT 666	21.6	479	21.9	64.1	22.7	72.9	Acid 1000
Acid 2000	21.6	655	21.4	418	22.1	71	23.4	73.6	Acid 2000
Acid 4000	21.6	648	21	332	22.9	67.4	23.5	86.2	Acid 4000
Cl 0	21.5	GT 666	22.5	587	22.1	594	22.8	398	Cl 0
Cl 1000	21.9	GT 666	22.2	303	23.1	634	24	539	Cl 1000
Cl 2000	21.3	468	21.6	377	23	568	24.2	458	Cl 2000
Cl 4000	20.5	580	22.7	275	23.9	150	24.1	106	Cl 4000