Air-Oven Aging of HDPE Geomembranes Containing Different Additives

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ABSTRACT: Even though high density polyethylene is one of the most stable polymers, additives must still be placed in geosynthetic products to ensure long term stability. The types of additives used include phosphites for process stabilization, hindered phenols for long term oxidative stability and carbon black or hindered amines for protection from UV radiation. The effectiveness of additives is often determined by exposure to elevated temperatures in a forced-air oven. The purpose of this study was to evaluate the effect of oven exposure on HDPE geomembranes made with different stabilizers. Samples of geomembranes made with fifteen different additive packages were aged for 500 days at 115°C and some of their properties were monitored. The results showed that the melt flow rate is a test sensitive to the effects of air-oven aging. Additionally, it was shown that hindered amines were the best long term stabilizers and that the addition of carbon black actually reduced the oxidative stability of the products.

1 INTRODUCTION

High density polyethylene (HDPE) is one of the most inert polymers because its chemical structure is very simple and it is semi-crystalline. However, additives are still required to protect HDPE products from oxidation. The different kinds of additives used include heat stabilizers for protecting the sheet during manufacturing, long term anti-oxidants for protection during service, and UV stabilizers to reduce the effects of outdoor exposure. Because of these different requirements, different additives are usually required.

The most common additives used in HDPE geomembranes include phosphites as heat stabilizers, hindered phenols as long term anti-oxidants, and carbon black for UV resistance. A new class of stabilizers that have proven to be effective as long term anti-oxidants and UV stabilizers are hindered amine light stabilizers (HALS). These additives were originally marketed as UV stabilizers, then were shown to be excellent anti-oxidants also.

There have been many different methods reported for evaluating the effectiveness of additives (Gugumus, 1987; Foster, 1990). In general, the method believed to produce the best correlation with the actual service environment is air oven aging. In this test, samples are exposed in a hot oven and samples removed periodically for analysis. Over two dozen different properties have been monitored to show the effects of aging (Foster, 1990). However, the properties most often followed are probably tensile strength and elongation.

The effects of air oven aging on a resin used in HDPE geomembranes was recently reported (Yim, 1993). Samples containing carbon black and several different additives were aged for 12 months at 110°C. Specimens were obtained every two months and melt flow rate, stress and strain at break, and brittleness were measured. The results showed that air-oven aging is an effective way to distinguish different additive packages. Additionally, it was shown that packages containing HALS performed the best.

The purpose of this paper is to report the results of a similar study designed to study the effects of different additives on the oxidative stability in air oven aging tests.

2 EXPERIMENTAL

2.1 Additive Packages

Fifteen (15) different additive packages were used during this study. They were composed of six different additives which are shown in Table 1. Notice that there are three hindered phenol anti-oxidants (AO), one phosphite heat stabilizer (HS), and two HALS.

Table 1 Experimental Additives.

Additive	Commercial Name
AO-1	Irganox 1010
AO-2	Irganox 1076
AO-3	Santowhite Crystals
HALS-1	Tinuvin 622
HALS-2	Chimassorb 944
HS-1	Irgaphos 168

The additives were blended and made into a sheet on a one foot wide flat sheet extruder with a 6.36 cm screw. Two different sets of sample rolls were made. The first set of samples (A-1 through A-6) were made into 2.0 mm sheet and contained the additives shown in Table 1. All the samples contained 2.5% carbon black except samples A-2 and A-5, which did not have any.

Table 2 Experimental Additive Packages - "A" Series.

Sample Number	Additive	Concentration(%)
A-1	AO-1	0.150
	HS-1	0.075
A-2*	AO-1	0.150
	HS-1	0.075
A-3	AO-1	0.300
	HS-1	0.075
A-4	AO-1	0.075
	HALS-1	0.100
	HS-1	0.075
A-5*	AO-1	0.075
	HALS-1	0.100
	HS-1	0.075
A-6	AO-1	0.075
	HALS-1	0.200
	HS-1	0.075

*No carbon black

The second set of experimental geomembranes made (B-1 through B-16) were 1.5 mm thick. In this case, only nine of the packages were studied. These are shown in Table 2.

Table 3 Experimental Additive Packages - "B" Series

Sample	Additive	Concentration(%)
B-1	AO-1	0.100
	AO-3	0.050
	HS-1	0.075
B-2	AO-1	0.100
	HALS-1	0.075
	HS-1	0.075
B-3	AO-1	0.100
	HALS-2	0.075
	HS-1	0.075
B-6	AO-1	0.100
	AO-2	0.100
	HALS-1	0.075
	HS-1	0.075
B-11	AO-1	0.100
B-12	AO-2	0.100
B-13	AO-3	0.100
B-14	HALS-1	0.100
B-15	HALS-2	0.100

2.2 Air-Oven Aging

The exposures were done in a commercial forced-air oven as described previously (Thomas, 1993). All tensile tests were done in accordance with ASTM D638 and the melt flow tests were done according to ASTM D1638.

3 RESULTS

The tensile properties and the melt flow rate under two different conditions for the "A" series are shown in Fig. 1. The melt flow rate is obviously the most sensitive test for following the effects of oven aging. This is reasonable since the melt flow test is more sensitive to molecular weight changes that the tensile properties. However, this may only be true for the

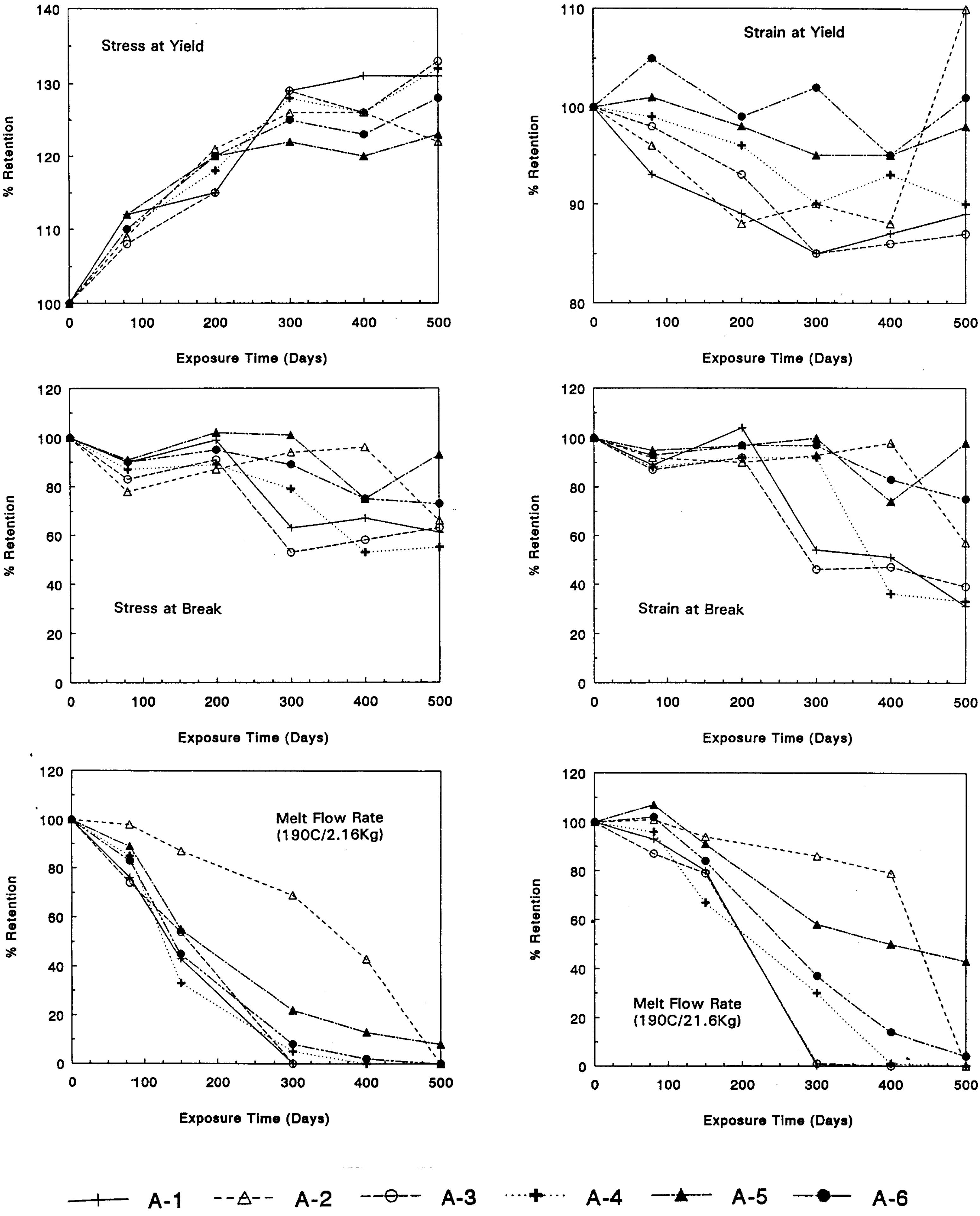

Fig. 1 The Effect of Oven Aging at 115°C on Various Properties

type of resin used in this study. Resins made by different catalyst technologies may behave differently. However, for the resin used in this study, the melt flow rate seems to be a sensitive indicator of the effects of oxidation.

It is interesting to note that the samples without carbon black are the most resistant to the effects of oven aging. This is probably due to the fact that carbon black adsorbs small molecules like additives and therefore effectively removes them from the environment. It was also observed that for the samples containing carbon black, the samples with HALS performed better than those without HALS.

Since the high load melt flow rate was the best indicator of aging for the "A" series, it was the only method used to evaluate the "B" series of samples. These results are shown in Fig. 2.

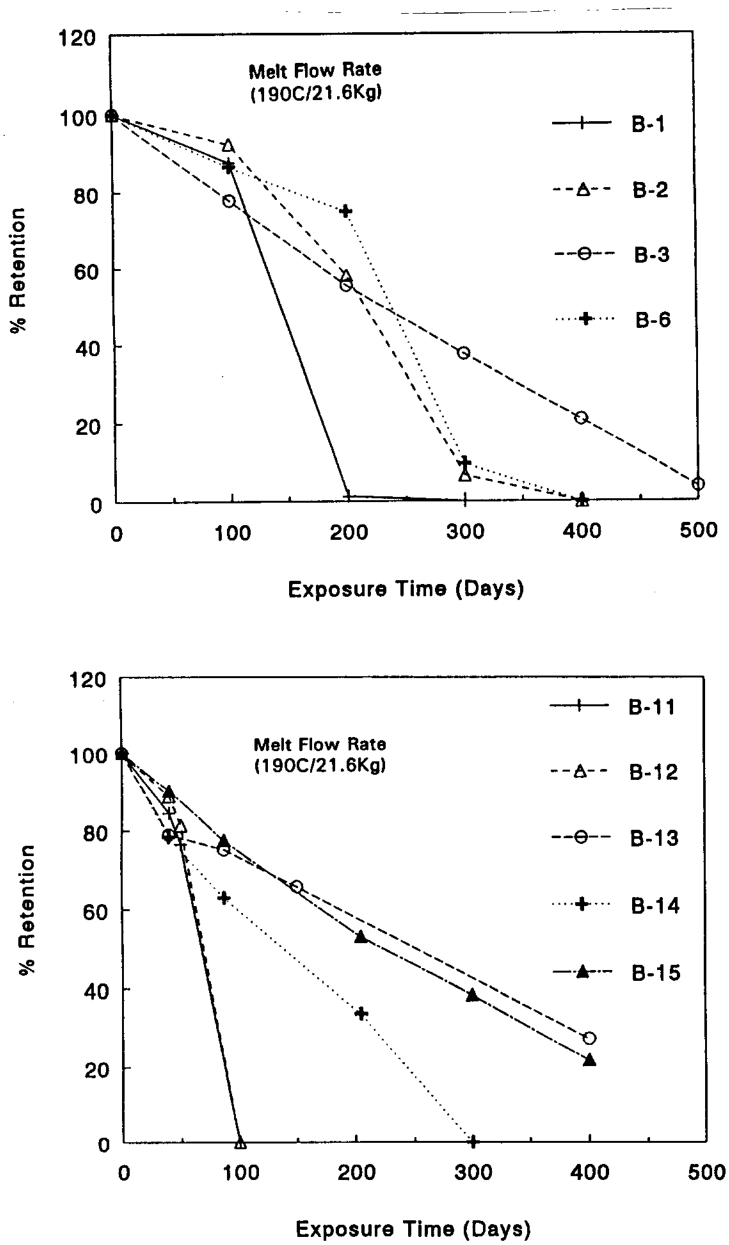

Fig. 2 The Effect of Oven Aging on the "B" Samples

There are several interesting results seen in this figure. First, notice that Santowhite Crystals has excellent oxidative resistance by itself (B-13), but performs poorly in combination with others (B-1). This indicates that it is not compatible with Irganox 1010 and Irgaphos 168. Next, notice that samples containing HALS (B-2, B-3, B-6, B-14, B-15) perform better than those without. Also, samples with Chimassorb 944 (B-3, B-15) perform better than those with Tinuvin 622 (B-2, B-6, B-14). And, finally, notice that Irganox 1010 and Irganox 1076 behave about the same (B-3, B-6, B-11, B-12).

These results are consistent with those reported previously (Yim, 1993).

4 CONCLUSIONS

The results of this study showed that, for the resin used, the high load melt flow rate was a sensitive indicator of degradation during air oven aging. It was also shown that the best additive packages were those containing HALS and that Chimassorb 944 performed better than Tinuvin 622. It is believed that other tests sensitive to molecular weight changes would also be appropriate methods for following the effects of aging. This is because large changes in molecular weight occur before changes in mechanical properties are observed.

5 REFERENCES

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