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Title:

The Influence of Polymer Process Aid (PPA) and Hindered Amine Light Stabilizer (HALS) Combinations in LLDPE Blown Film Applications

Abstract:

Polymer Process Additives (PPA) are used extensively to enhance the extrusion of polyolefins. Hindered Amine Light Stabilizers (HALS) are used to prolong their UV (ultra-violet) stability. The two classes of additives are often used together in LLDPE blown film applications where melt fracture free films with good UV stability are needed; for example, agricultural film applications. The potential for an interference between PPAs and alkaline HALS is known, but not well understood. This paper discusses the potential mechanism for the interference, ranks two commercially available PPAs for their ability to eliminate surface melt fracture in the presence of HALS and gives practical recommendations on how to minimize the interference when it is encountered. In addition, the complementary data set is presented, showing the effect (if any) of PPAs on the ability of HALS to provide UV stability to LLDPE blown films.

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**The Influence of Polymer Process
Aid (PPA) and Hindered Amine
Light Stabilizer (HALS)
Combinations in LLDPE Blown Film
Applications**

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ABSTRACT

Polymer Process Additives (PPA) are used extensively to enhance the extrusion of polyolefins. Hindered Amine Light Stabilizers (HALS) are used to prolong their UV (ultra-violet) stability. The two classes of additives are often used together in LLDPE blown film applications where melt fracture free films with good UV stability are needed; for example, agricultural film applications. The potential for an interference between PPAs and alkaline HALS is known, but not well understood. This paper discusses the potential mechanism for the interference, ranks two commercially available PPAs for their ability to eliminate surface melt fracture in the presence of HALS and gives practical recommendations on how to minimize the interference when it is encountered. In addition, the complementary data set is presented, showing the effect (if any) of PPAs on the ability of HALS to provide UV stability to LLDPE blown films.

INTRODUCTION

Polymer Process Additives were added to LLDPE resins even before their wide spread introduction in the late 1980's. (Ref 1, 2). Around this time, Hindered Amine Light Stabilizers (HALS) were being adopted in LLDPE as a significant step forward in providing light stability to blown and cast film products. Within a few years of the introduction of these two functional classes of additives, it became clear that under certain circumstances, the efficiency of the polymer processing aid could be impacted by the presence of a particular hindered amine light stabilizer. This interaction was investigated and the first work that described this phenomenon was reported soon afterward (Ref. 3,4). In this work, the impact of the interaction was described as being a negative interference in regard to the elimination of melt fracture in LLDPE film blown experiments.

This paper is a practical range-finding study, which further investigates this potential interaction in regard to the nature of the polymer processing aid and the hindered amine. Elimination of melt fracture during blown film experiments as well as UV stability testing were carried out to elucidate the nature of the interaction. Plausible mechanisms for the interactions will be discussed. It will be demonstrated that a careful selection of the additives can address the potential interaction from a practical perspective.

EXPERIMENTAL

Polymers: Various resins were used for the evaluations performed for this study. For ease of understanding, the description of each resin is included with the Figure it pertains to instead of being listed here.

Additives: The final letdown concentrations are identified on each Figure.

PPA- 1 = Dynamar™ FX 9613

PPA-2 = Dynamar FX 5920A

HALS- 1 = Tinuvin® 622

HALS-2 = Chimassorb® 119

HALS-3 = Chimassorb 944

HALS-4 = CGL 116

HALS-5 = Chimassorb 2020

The molecular structures of the HALS are shown in Table 1.

Masterbatches for Blown Film Work: The PPA masterbatches were 3% target concentration in a 2.0 MI LLDPE. The HALS masterbatches were 10% target concentration in a 2.0 MI LLDPE.

Film Fabrication: Slightly different melt temperatures were used for the various evaluations performed in order to collect the data for this study. For ease of understanding, the melt temperatures are included with the appropriate Figures instead of being listed here.

The formulations were blown into film on a Kiefel blown film line. The film line consisted of a 40 mm grooved feed extruder, 24/1 L/D, 18/35/60 mesh screen pack, 40 mm die, 1.2 mm die gap and a single lip air ring. The films manufactured for the light stability testing were the exception where a 2 mm die gap was used to afford a baseline melt fracture free film sample containing no PPA. The output was approximately 30 lbs/hr to give a shear rate of approximately 600 sec⁻¹ with the narrow die gap.

UV Stability Testing: The film samples were tested for stability against ultraviolet (UV) radiation using an Atlas Ci65 Xenon Weatherometer chamber. The specific accelerated weathering and physical property testing conditions were as follows:

Light Flux (Intensity):	0.35 watts/m ² Irradiants
Light Source:	Xenon lamp with borosilicate filters
Black Panel Temperature:	63°C
Exposure Cycle:	Continuous lights; 108 minutes dry; 12 minutes water spray
Mounting Frames:	2.5" x 4" open frames; 1 interval / formulation / frame
Physical Testing:	Instron 4511 Tensile Tester;
Test Specimen:	Type IV tensile bars stamp cut from the exposed films;

Assessment of Chemical Reactivity: Equal amounts of PPA/HALS were mixed at ambient temperature on a two roll mill until a homogeneous blend was obtained. The unmodified raw gum fluoroelastomer found in PPA- 1, without the 10% inorganic partitioning agent, was used for these blends. Two gram samples of the individual additives and of the blends were placed in open glass Petri dishes and exposed to heat in forced air ovens at 232°C and 270°C for 30 minutes. Reactivity was assessed by visual observation. The individual additives and the blends were also tested by TGA. In addition, photoacoustic IR was run on the additives and blends both with and without oven aging.

Capillary Rheometry: Capillary rheometry data were obtained to look at the effects of various conditioning purge materials on PPA performance at different shear rates. This data was collected on an Instron model 4202 at 190°C using a flat entry 20 mil die with L/D of 40.

Table 1. Molecular Structure of Hindered Amine Light Stabilizers

HALS-1	
HALS-2	
HALS-3	
HALS-4	
HALS-5	

TECHNICAL CHALLENGE

Before the data set is presented and discussed, it is important to discuss the nature of the technical challenge this project represents. As stated earlier, there have been observations over the last few years suggesting certain types of alkaline compounds, including but not limited to hindered amines, can have a negative impact on the efficiency of the polymer processing aid in regard to the elimination of melt fracture. This can be an issue for producers of LLDPE films for applications where outdoor stability is a key concern. If both polymer processing aid and alkaline hindered amines are used in the same formulation, there may be a potential for a reduced efficiency of the polymer processing aid. In these infrequent cases, the film producer may sometimes need to add more processing aid to achieve a melt fracture free UV stable film product.

Again, it should be noted that this interaction is certainly not a ubiquitous phenomenon; however, where it is observed it may have an impact on the efficiency of the polymer processing aid. The efficiency can be measured in regard to rate of elimination of melt fracture, or the amount of processing aid necessary to completely eliminate melt fracture. In those few cases where it is observed, there is a straightforward set of remedies, such as: add a little more processing aid or change the processing aid. In cases where the hindered amine has been identified as the source of interference, changing the hindered amine to one that is less alkaline, or changing the hindered amine concentration relative to that of the processing aid can be attempted. While these may be pragmatic solutions to this infrequent observation, it does not address the root cause of the PPA inefficiency. Consequently, the authors felt the responsibility to establish experimental conditions where the phenomenon could be observed, measure the impact of the interaction, and determine what alternatives might be available.

The experiments that were conducted in this initial study included: 1) Evaluations of the chemical reactivity of the polymer processing aids with hindered amines; 2) Blown film experiments to measure the extent of the interaction; and 3) UV weathering studies to determine whether the hindered amine was affected as a light stabilizer for the polymer. The resulting data sets provided a better understanding of the interaction and pointed out future experiments needed in order to refine our current knowledge base.

It will also be useful to describe the nature of potential interaction between processing aids and sources of alkalinity: in this particular study, hindered amine light stabilizers.

Possible Mechanisms: As mentioned above, when certain types of alkaline HALS are added to LLDPE blown film to ensure good UV stability during outdoor applications, additional PPA may be required to eliminate melt fracture. This interference between HALS and PPAs, in regard to rate of elimination of melt fracture or ability to thoroughly eliminate melt fracture, has been observed in both the lab and in the field. At this point, the authors propose two likely mechanisms for this interaction:

- competition of the two different additive chemistries for the metal surface
- a potential for acid / base chemistry between alkaline hindered amines and the fluoropolymer

In regard to competition for the metal surface, additives that strongly compete with the PPA are undesirable as they negatively impact the elimination of melt fracture. This interference can be an issue since one of the primary mechanisms for the processing aid to function is based on establishing and then maintaining a coating of PPA on the metal surface. If other additives prevent or impede the coating process, it will take longer to establish the coating, or take more processing aid to maintain the coating.

One of the primary mechanisms for bonding to the metal surface is thought to be (multiple) hydrogen bonding sites between the various additives and the hydrated oxidized metal surface. Hindered amines, as well as other types of functional additives are theoretically capable of interacting with the metal surface via hydrogen bonding interactions. (See Figure 1.)

While Figure 1 shows potential interactions based on a hydrogen bonding mechanism, it is neither rigorous nor complete. However, it is a useful depiction of the types of interactions with the metal surface that can occur with the various functional additives dispersed in the polymer matrix. The basis of these interactions can be found in numerous textbook references that describe the nature of metal surfaces as well as the principles involved regarding hydrogen bonding interactions.

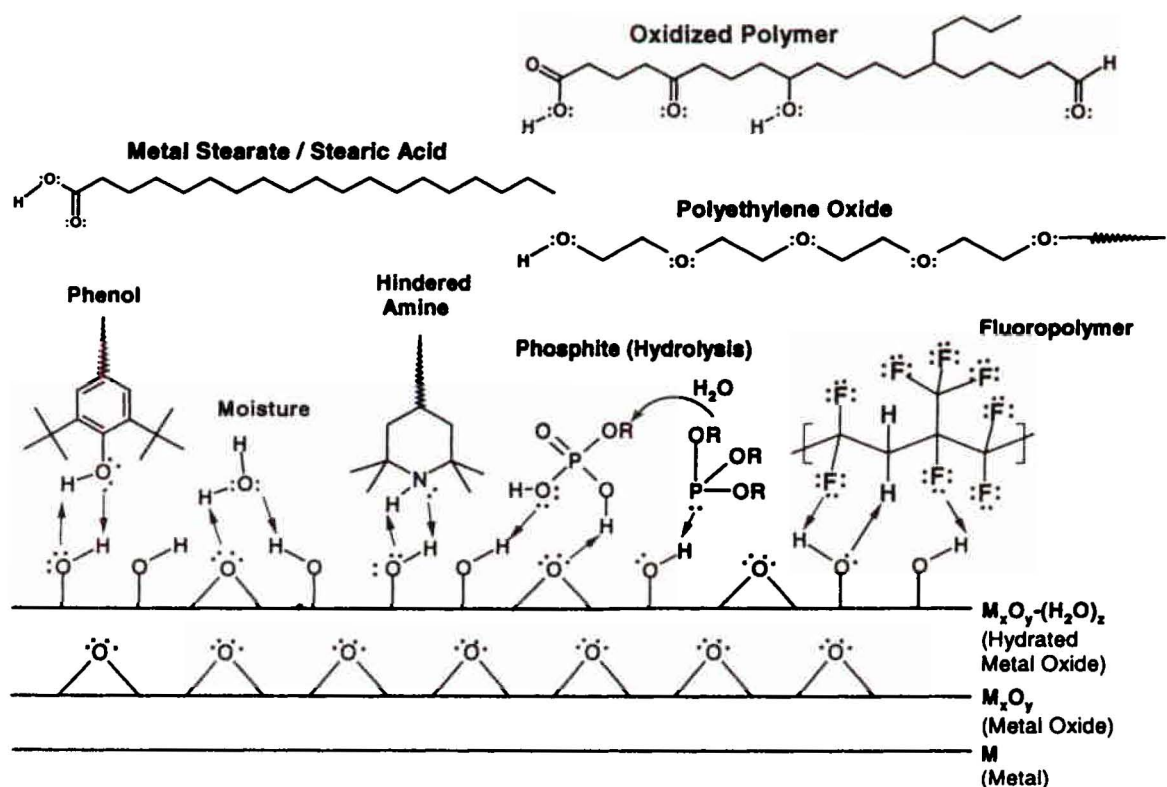


Figure 1 - Potential Interaction via Hydrogen Bonding Mechanism

The premise of the hydrogen bonding interaction is based on the assertion that the metal surface of the processing equipment is actually a partially oxidized metal surface. On top of the partially oxidized metal surface, there is a thin layer of hydration of that oxidized metal surface. The molecular level result of the partially hydrated /oxidized metal surface is a series of -OH bonds and bridging -O- groups that are capable of interacting with other species in the polymer matrix that contain functional groups known to have hydrogen bonding capabilities. Water, H-O-H, either entrained in the polymer matrix or a reaction by product of stabilization, would be the simplest example. Other examples include metal stearates, stearic acid (which is the by-product of the metal stearate reacting with residual HCl (catalyst residue) in the polymer), or even oxidized polymer itself.

The primary role of the fluoropolymer is to coat out on the partially hydrated / oxidized metal surface. As can be seen from the schematic, the primary interaction is between the C-F bonds of the fluoropolymer and the -OH bonds of the partially hydrated / oxidized metal surface. There is also a potential for a hydrogen bonding interaction from the relatively acidic C-H bonds of the fluoropolymer and the -OH of the metal surface. Since there are many C-F and C-H bonds on the fluoropolymer, there are multiple contact points between one fluoropolymer chain and the various -OH

groups and bridging -O- groups of the metal surface. The polyethylene oxide (PEO) is also capable of establishing multiple contact points between the -OH end groups and the bridging oxygens of the PEO chain and the various -OH groups and bridging -O- groups of the metal surface.

As a first example of the interference, let's further examine the reference to oxidized polymer itself. The oxidation of the polymer is a stepwise process that proceeds from alkane, to alcohol, to aldehyde or ketone, to carboxylic acid. Each of these functional groups is quite capable of participating in a hydrogen bonding interaction, and consequently, there is a greater affinity for the oxidized polymer to interact with the metal surface than a non-oxidized polymer chain. This is not a good situation, since prolonged contact of the oxidized polymer will only lead to further oxidation and crosslinking of the polymer. At some point, however, the oxidized and/or partially crosslinked polymer sloughs off of the metal surface and travels out of the extruder. This may be a potential mechanism for the formation of gels that can be observed during blown or cast film extrusion.

Any reagent that could be utilized to prevent the prolonged contact of the oxidized polymer with the heated metal surface should help to inhibit this mechanism for creating gels. The use of fluoropolymers and polymer processing aids has been investigated in this regard, and the results of that work have been reported. [Ref. 5]

As another example, with a phenolic antioxidant, the possibility of a hydrogen bonding interaction exists between the -OH of the phenol group and the -OH of the partially hydrated / oxidized metal surface. This interaction is undesirable, since the polymer typically needs the phenolic antioxidant to be dispersed throughout the matrix to scavenge free radicals, and not be interacting with the metal surface where it cannot perform a similar function. (However, this may deserve further thought, since polymer that is possibly stuck on the metal surface may be in desperate need of some additional stabilization due to prolonged contact times of the polymer with the heated metal surface.)

For the hindered amine group, a hydrogen bonding interaction can be formed between the -NH of the piperidinyl group and the -OH of the partially hydrated / oxidized metal surface. In regard to the hindered amine, even though there is no need for the molecule to become involved in polymer stabilization, since hindered amines are not recognized as melt processing stabilizers, there is no net gain from the molecule interacting with the metal surface either. In fact, if this interaction is strong, it will prevent the fluoropolymer from coating out on the metal surface.

A traditional phosphite does not have much capability for establishing a classic hydrogen bonding interaction with the metal surface. However, if the phosphite is partially hydrolyzed, there now exists a very strong possibility for a hydrogen bonding interaction between the P-OH of the hydrolyzed phosphite, and -OH groups of the partially hydrated / oxidized metal surface. The consequence of partially hydrolyzed phosphite can be significant since the relatively acidic P-OH bond is strongly interactive with the -OH of the metal surface, and is potentially capable of displacing more weakly bound materials. Accordingly, there can often be an association between hydrolyzed phosphites and black specks that come out of the extruder. This phenomenon may in part be due to the partially hydrolyzed phosphite displacing weakly bound charred material from the metal surface of the extruder.

Other representative reagents that can compete for the partially oxidized / hydrated metal surface via a hydrogen bonding mechanism might include other co-additives in the matrix, such as metal stearates, and stearic acid, ethoxylated amines, slip agents and the like. However, the fact that there may be an interaction is not necessarily the key point; ~~this cannot be understated. It should be recognized that it is~~ not only the potential for an interaction, but also the relative strength of that interaction. Further work is currently underway in order to understand not only the nature of the interaction, but also the relative ranking of the interactions as well.

Potential for Chemical Reactivity

In regard to the potential for acid / base chemistry between the relatively acidic fluoropolymer and the relatively alkaline hindered amine. It is useful to understand the source of the acidic sites and the alkaline sites of each reagent. Figure 2 shows a typical fluoropolymer structure with 'acidic hydrogens'. Normally, a fluoropolymer, based on tetrafluoroethylene is not considered to be 'acidic' (i.e., there are no 'acidic hydrogen' atoms). However, with the incorporation of hydrogen atom containing comonomers (as is the case for fluoropolymers commonly used as PPAs), the resulting fluoropolymer now has a different nature. There is certainly less rigidity, since the replacement of fluorines by hydrogens allows for more carbon-carbon bond rotation. In addition, the hydrogen atoms are now sites of relative slight acidity due to the strong electronegativity of the neighboring fluorine atoms.

PPA-1 Structure

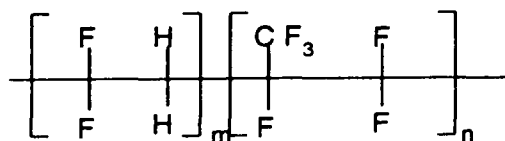


Figure 2 -Structure Concept of PPA-1 Showing 'Acidic' Hydrogens

Figure 3 illustrates the relative alkalinity of various hindered amines. The measurement was made by titration of the conjugate acid of each of the hindered amines. This measurement is not as straightforward as it sounds, since the various hindered amines included in this study have multiple pKa's. Multiple pKa's are observed based on the different types of nitrogen atoms found in the molecular structure of the compound. Consequently, it is important to understand which pKa peak is associated with the backbone or template of the hindered amine molecule, and which pKa peak is associated with the key piperidinyl functional group that provides light stability.

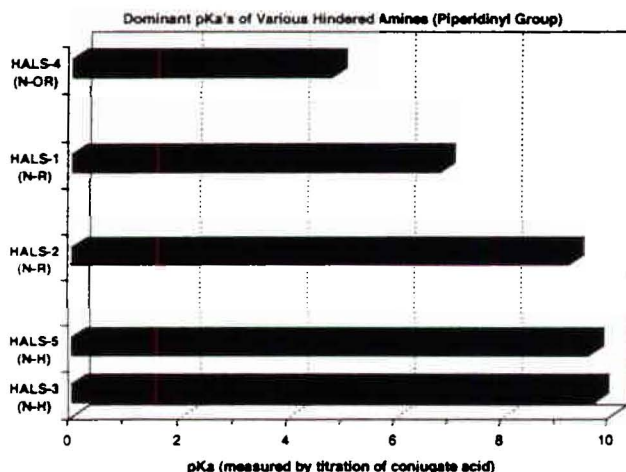


Figure 3 - Relative Alkalinity of HALS

Accordingly, since fluoropolymers can be described as relatively 'acidic' by nature and certain types of hindered amines can be described as relatively 'basic' by nature, it is reasonable to hypothesize that some type of "acid/base chemistry" could play a role in the interaction as well. This type of acid / base chemistry is only a metaphor since these concepts typically only apply to aqueous or polar solvents; however, it is a useful exercise to describe a possible mechanism for the transformation of the polymer processing aid and the hindered amine, if such chemistry does take place. As such, the reactivity of the relatively acidic hydrogen atoms on the fluoropolymer chain can lead to transformation chemistries that do not facilitate a coating of the processing aid on the walls of the processing equipment. As such, these type of transformation chemistries are undesirable in terms of trying to achieve the highest efficiencies relating to the performance of the PPA to eliminate melt fracture.

At this point it is proposed that it is most likely that there is at least a combination of the two proposed mechanisms at play. Depending on the conditions (e.g. shear rate, temperature, particular HALS and/or PPAs in the formulation) one mechanism may play a more dominant role than the other.

RESULTS AND DISCUSSION

The data set collected was composed of three parts: I) a measurement of reactivity of the fluoropolymers with the various additives II) blown film experiments where the amount of melt fracture was measured over time in LLDPE compositions containing combinations of different hindered amines and processing aids and III) UV light stability testing of the blown film samples.

Section 1: Measures Of Chemical Reactivity

TGA (Thermal Gravimetric Analysis) and Visual Oven Aging Data:

The TGA and visual oven data deals with the pure components, not the let down levels seen in blown film applications. It is also important to consider that the temperature and times used are more extreme than blown film applications. Therefore, this data is merely an indicator of the potential for reactivity in blown film applications.

Figure 4 shows the criteria for relative ranking of reactivity by visual observation of the oven aged blends. Table 2 summarizes the visual results. A ranking of 1 indicates slight reactivity, 2 moderate, and 3 extreme. Accordingly, by visual observation, we can rank the HALS in order from slight to extreme potential reactivity as HALS-1 < HALS-2=HALS 5 < HALS-3=HALS-4.

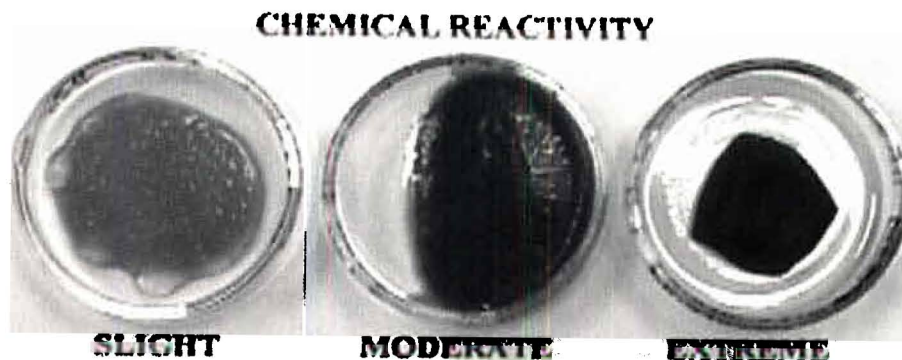


Figure 4. Visual Observation of Oven Treated Blends

Table 2. Visual Ranking Results - Samples were kept at cited temperatures for 30 Minutes
(1=slight, 2=moderate, 3= extreme potential reactivity)

	232°C	270°C
HALS-1 + PPA- I Raw Gum	1	3
HALS-2 + PPA- 1 Raw Gum	2	3
HALS-3 + PPA- I Raw Gum	3	3
HALS-4 + PPA- I Raw Gum	3	3
HALS-5 + PPA- I Raw Gum	2	3

A more quantitative ranking was obtained from the TGA data. (Table 3) An actual/predicted weight loss number greater than one can be an indication of chemical reactivity. By TGA, HALS- 1 and HALS-5 had the smallest increase in actual weight loss for the blends compared to the predicted values based on the individual additives and thus would be expected to be less potentially reactive with PPA- I . HALS-3 ranked the highest in both visual observation and the TGA actual/predicted weight loss and appears to be the HALS that is most potentially reactive with PPA-1. HALS-4 had a large weight loss on its own and doubled that in the blend. However, the actual/predicted weight loss was only slightly more than that of the HALS-1 or HALS-5. It is believed that this extreme weight loss may be more a characteristic of the particular HALS rather than an indication of extreme reactivity.

Table 3
Summary of TGA Weight Loss
30 Minutes in Air @ 275°C

	Actual	Predicted	Actual/Predicted
HALS-1 + PPA Raw Gum	6.6	3.5	1.9
HALS-2 + PPA Raw Gum	4.9	1.9	2.5
HALS-3 + PPA Raw Gum	9.2	1.5	6.1
HALS-4 + PPA Raw Gum	29	14	2.1
HALS-5 + PPA Raw Gum	4.0	2.1	1.9

Analytical Data

Infrared spectra were obtained to look for evidence of a chemical reaction in the heat-treated blends. (A chemical reaction resulting in dehydrofluorination of the PPA would produce double bonds.) The spectra of the blended polymers were visually observed for the presence of any double bond character in the polymers both before and after heating. No significant differences were noted. However, since the sensitivity of this Infrared Spectroscopy method to the detection of these double bonds is unknown at this time we were able to neither confirm nor deny chemical reaction as a possible mechanism.

Capillary Data

It has been shown that the oxidative stability of the resin used for a conditioning purge between runs in capillary studies has an effect on the percent pressure decrease of a 500ppm PPA- I containing resin run immediately after. (Ref. 6) Building on this concept, capillary rheometry was utilized to study the effect of a conditioning purge containing only 10% HALS-3. The PPA containing resin ran as well after the 10% HALS-3 conditioning purge as after a standard well-stabilized resin . This particular test therefore would indicate no evidence of site competition at the die wall. (See Table 4)

When the PPA/HALS-3 conditioning purge was run, we saw no pressure decrease. This is an indication of no performance from the PPA and could indicate either chemical reactivity and/or interference at the die wall preventing the PPA from functioning. A resin containing only 500ppm PPA-1 was run immediately after the PPA/HALS-3 combination purge. This took longer to equilibrate, but the final pressure drops were very similar to those seen after the other purges. The longer equilibration time could indicate material on the die wall interfering with the PPA's conditioning rate. (See Table 4)

Thus, the capillary data gives conflicting support on site competition as a mechanism.

Table 4 - CAPILLARY RHEOMETRY DATA
Data for 500ppm PPA-1 Resin Run After Conditioning Purges

CONDITIONING PURGE	Percent Pressure Decrease @ 100s-1	Percent Pressure Decrease @400s-1	Equilibration Time (min)
Well Stabilized Resin	55	51	20
10% HALS-3	55	48	20
6000ppm HALS-3+500ppm PPA-1	50	46	35

Section 2: Measuring Interferences During Blown Film Experiments

Blown Film Data - Temperature Effects

Figures 5-8 illustrate not only the increase in PPA that is required in the presence of HALS but also a temperature effect that is present with HALS-3, but not HALS-1. The resin requires 300ppm of PPA-2 to clear melt fracture when it is barefoot at both 380°F and 445°F. As expected, when 3000ppm of HALS-1 is added, it requires more PPA-2 (for a total of 500ppm of PPA-2) to clear melt fracture. With HALS-1, the level of PPA-2 required was the same at both the lower and higher temperatures.

When we repeat the same study with HALS-3, we see that although 500ppm of PPA-2 essentially cleared melt fracture at 380°F, even 700ppm of PPA-2 was not successful in eliminating melt fracture at 445°F. So with HALS-3 we do see a temperature effect. In addition, although HALS-3 is widely thought of as superior to HALS-1, depending on your individual application it may or may not offer the best performance as a UV stabilizer in LLDPE blown film. Careful selection of all additives in a formulation is vital for optimum performance.

Temperature Effects

3000ppm HALS-1 and PPA-2 in octene LLDPE
(1.0MI, 0.920) @ 380°F

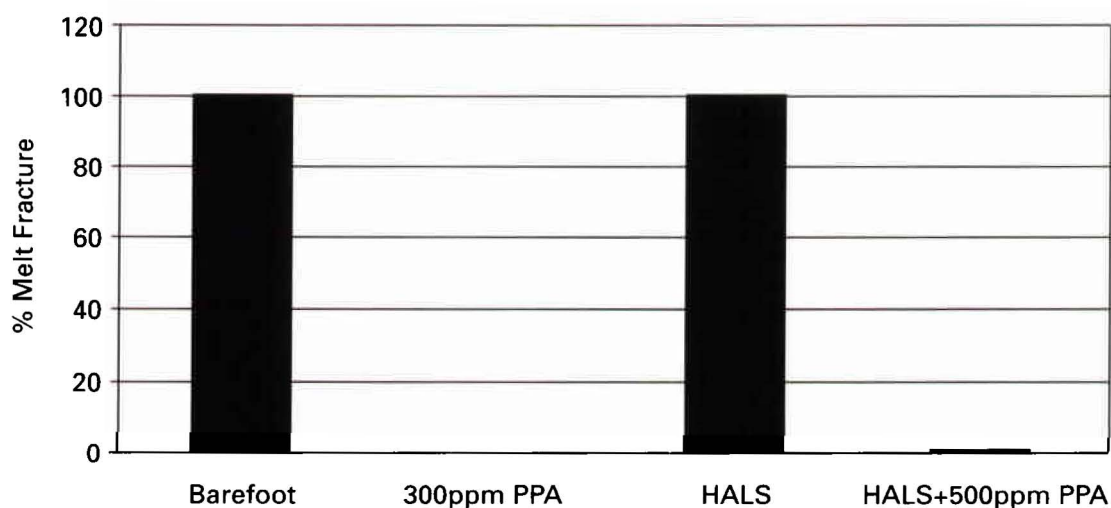


Figure 5.

Temperature Effects
3000ppm HALS-1 and PPA-2 in octene LLDPE
(1.0MI, 0.920) @ 445°F

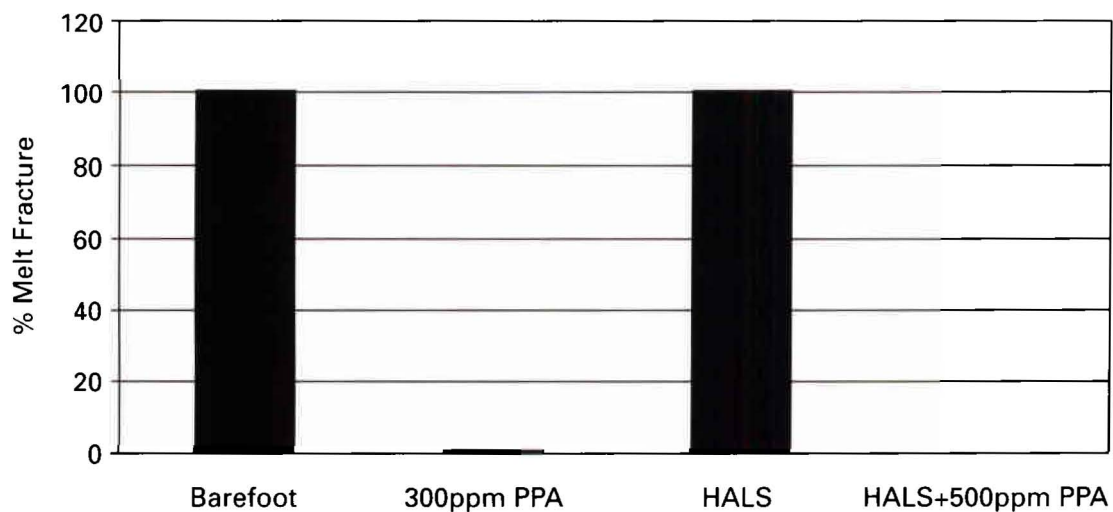


Figure 6.

Temperature Effects
3000ppm HALS-3 and PPA-2 in octene LLDPE
(1.0MI, 0.920) @ 380°F

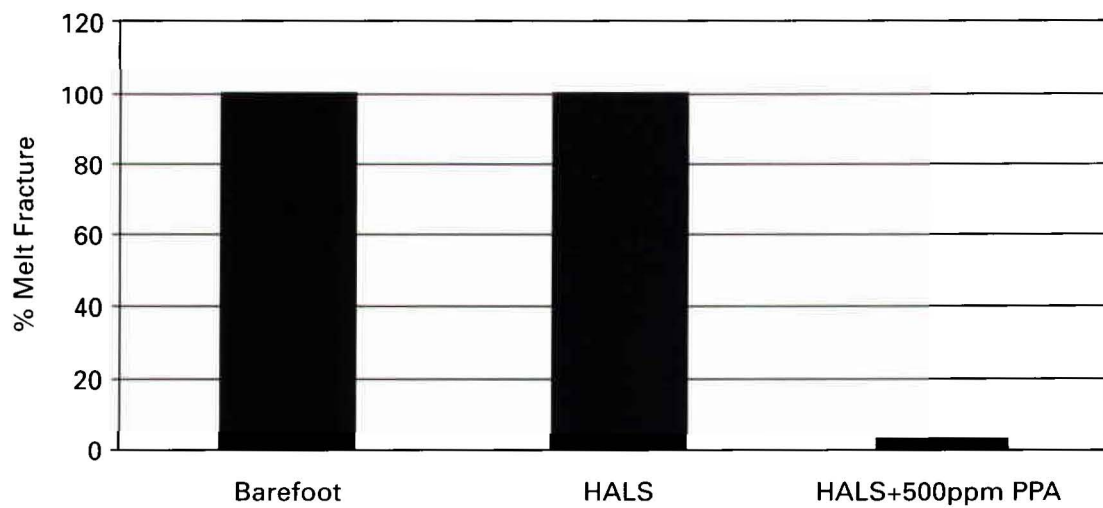


Figure 7.

Temperature Effects

3000ppm HALS-3 and PPA-2 in octene LLDPE

(1.0MI, 0.920) @ 445°F

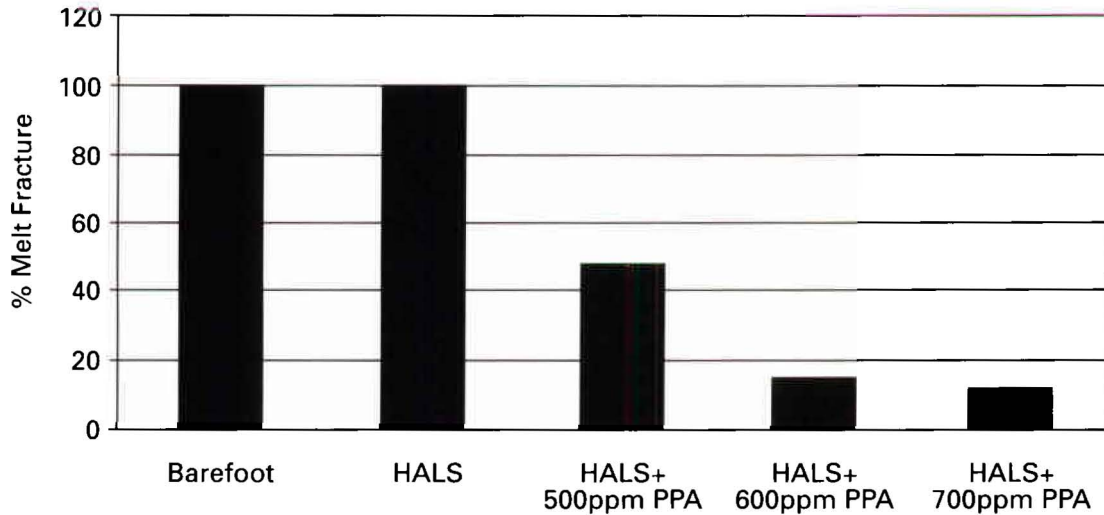


Figure 8.

Blown Film Data - Ranking of HALS with PPA-I

We selected PPA- I to evaluate in the presence of 1500ppm of various HALS. As can be seen in Figure 9, with PPA- 1, the relative ranking of the impact of the different HALS are as follows:

Least: HALS-1 < HALS-2, HALS-4, HALS-5 < HALS-3 :Most

(HALS-2 may have slightly less impact than HALS-4 and HALS-5.)

Ranking of HALS with PPA-1

1500ppm HALS + PPA-1 in Butene LLDPE (1.0, 0.918)

@ 425°F (PPA @ 600ppm 1st hour, 800ppm 2nd hour)

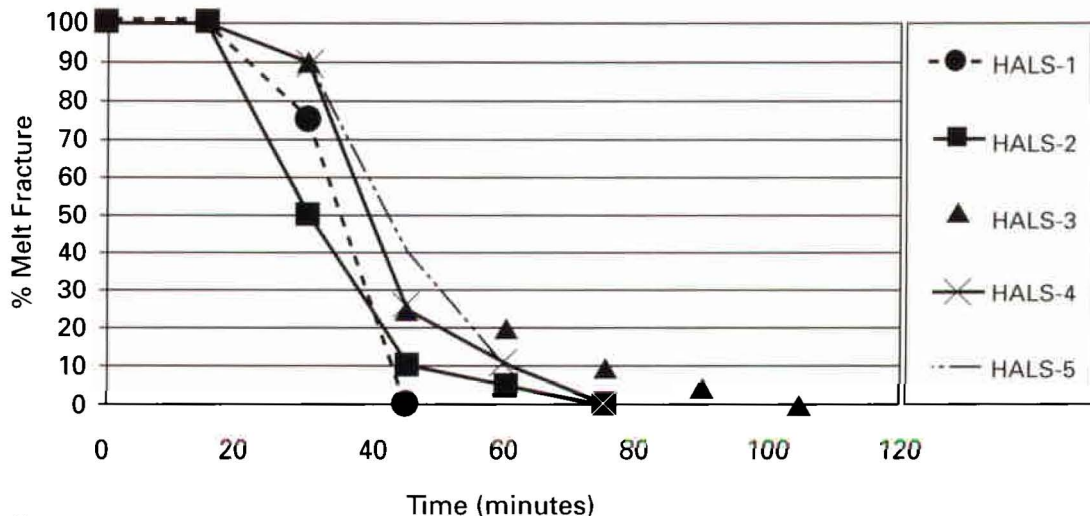


Figure 9.

Blown Film Data - Ranking of PPAs with HALS

Figures 10-14 show two commercial PPA products in the presence of different HALS. As can be seen in these graphs, a relative ranking of the effectiveness of PPA-1 and PPA-2 is observed relative to a particular HALS. In this particular barefoot resin, PPA-2 is the best performer followed by PPA-1. With the presence of HALS-1, HALS-2, and HALS-3 the order of performance switched and PPA-1 outperformed PPA-2.

Ranking of PPAs
Barefoot mLLDPE (0.85, 0.926) @ 430°F

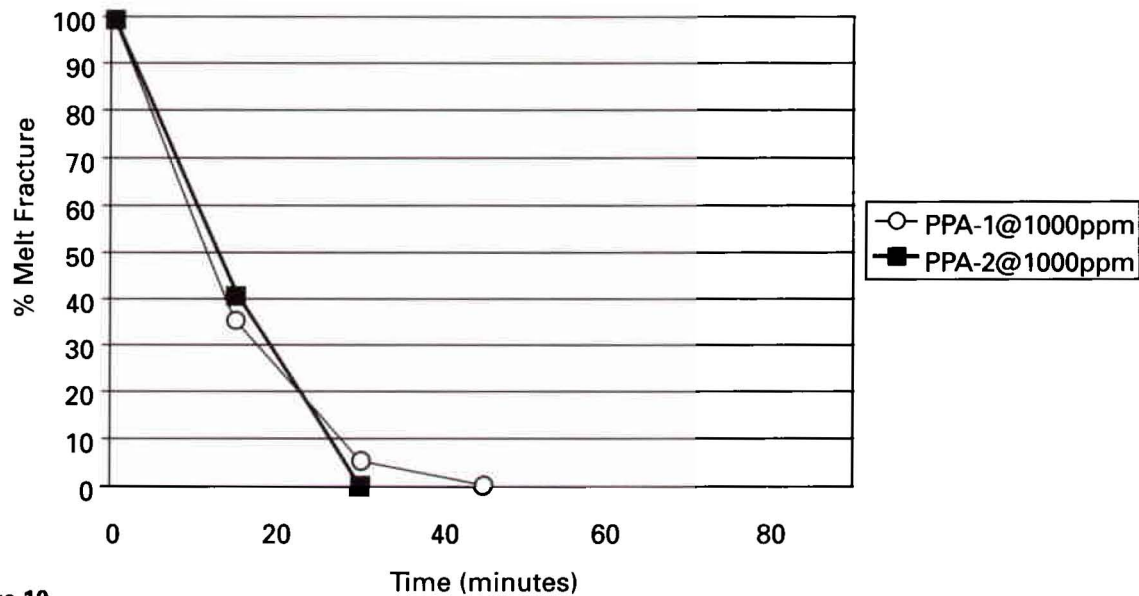


Figure 10.

Ranking of PPAs
HALS-1 @3000ppm in mLLDPE (0.85, 0.926) @ 430°F

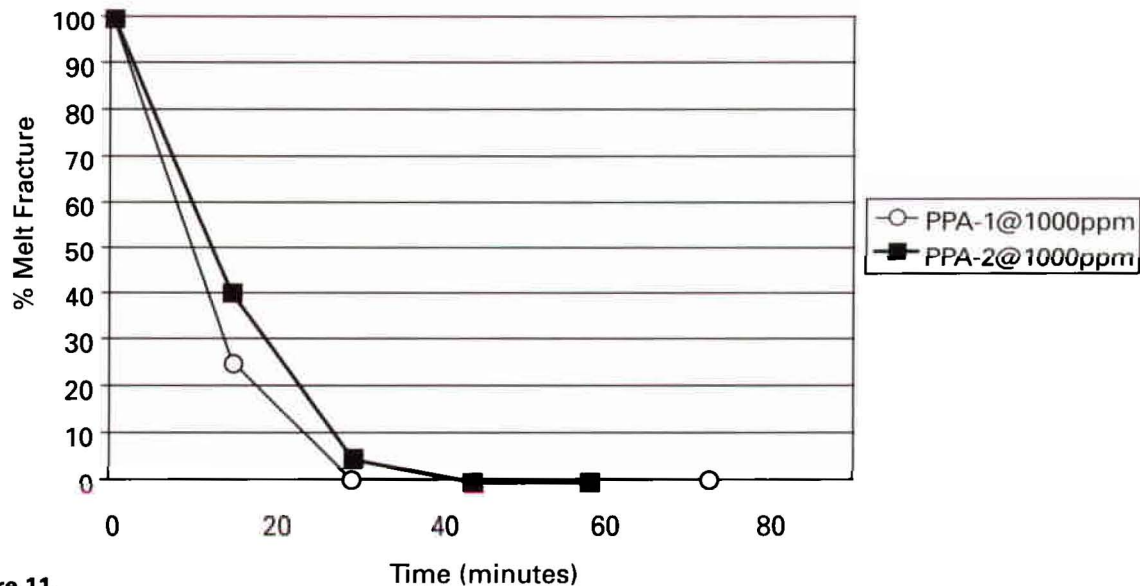


Figure 11.

Ranking of PPAs

HALS-2 @ 3000ppm in mLLDPE (0.85, 0.926) @ 430°F

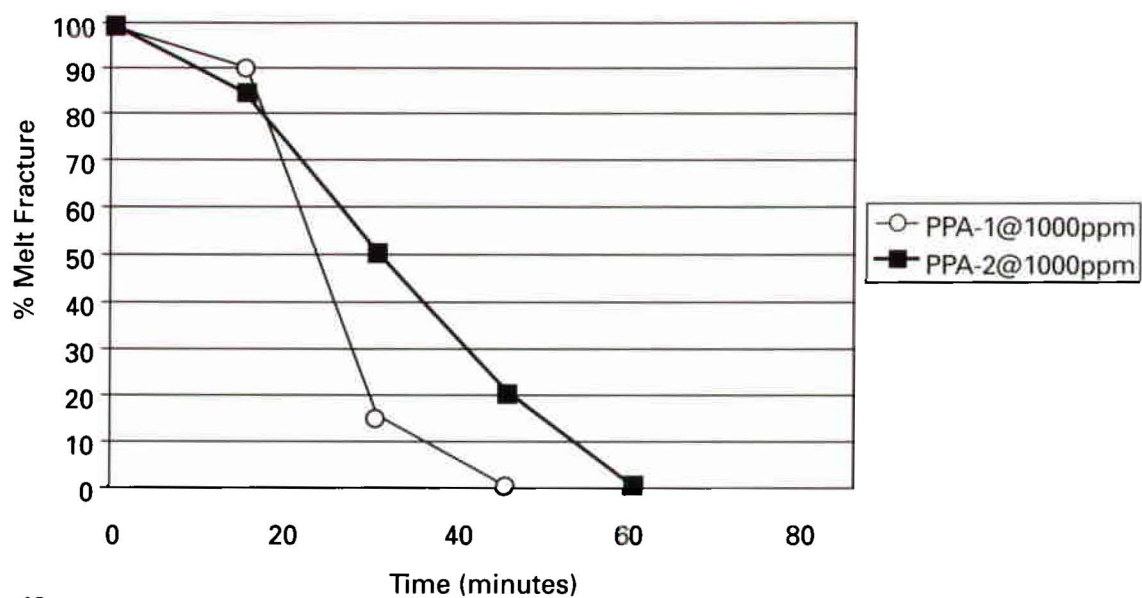


Figure 12.

Ranking of PPAs

HALS-3 @ 3000ppm in mLLDPE (0.85, 0.926) @ 430°F

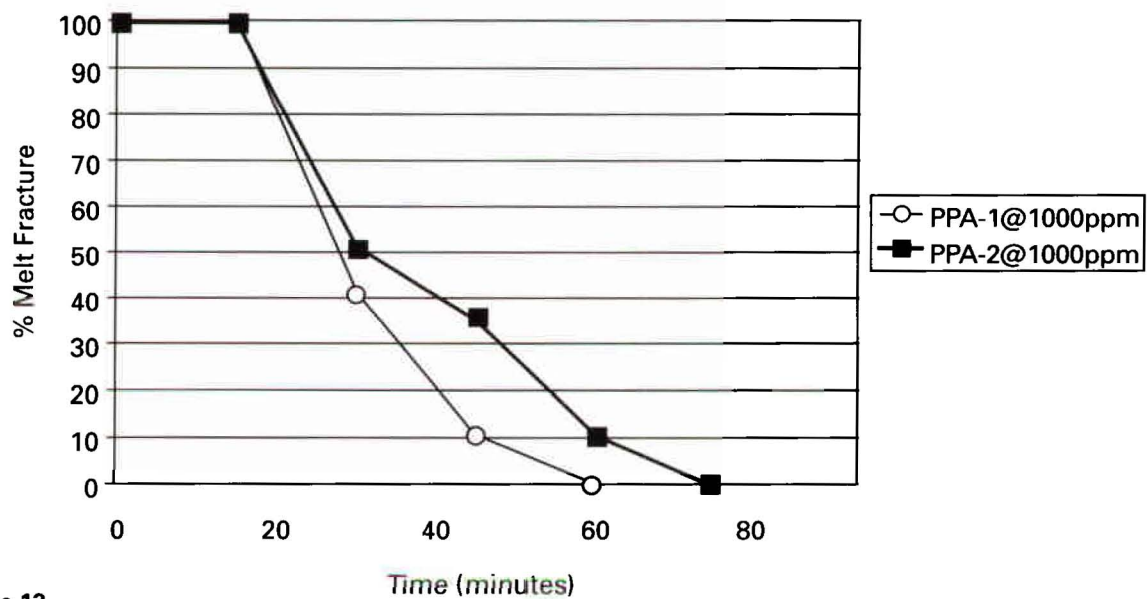


Figure 13.

Ranking of PPAs

HALS-5 @ 3000ppm in mLLDPE (0.85, 0.926) @ 430°F

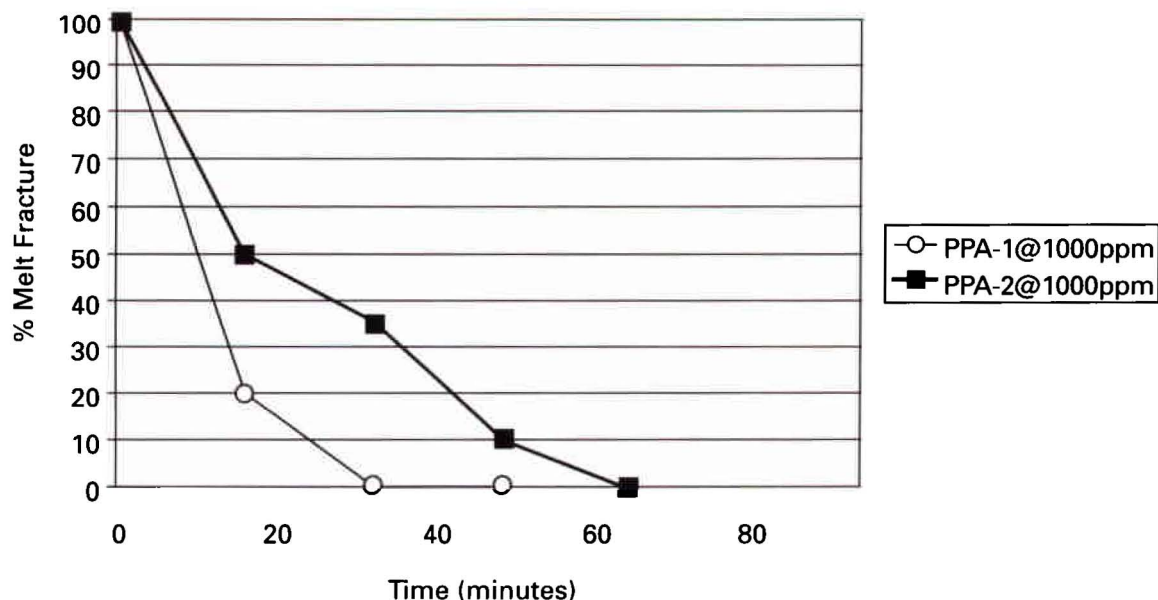


Figure 14.

Section 3: Measuring Interferences During Accelerated Weather Experiments

Influence of PPAs on the Effectiveness of HALS

While the existing data suggest that HALS are potentially reactive/interactive with PPAs the complimentary concern of 'Does the PPA react/interact with the HALS' was not widely asked until recently. Accordingly, it was determined that the best way to measure the impact was to carry out accelerated weathering studies on LLDPE blown film samples containing the various fluoropolymers and the different hindered amines described in the experiments above.

At the time of this paper, the film samples had undergone over 3000 hours of Xenon Weatherometer exposure, which approximately correlates to over two years of natural outdoor weathering. As can be seen in the Graphs 15 - 17 below, there are virtually no significant differences in light stability observed between the various fluoropolymers and the different hindered amines. As can also be seen in the three graphs, the only samples that fail in regard to retention of tensile strength are those not containing a light stabilizer, which is to be expected.

These results clearly demonstrate, at least out to 3000 hours of accelerated weathering, that there is virtually no impact, positive or negative, of the fluoropolymer on the performance of the five different hindered amines. By the time this paper is presented, it is predicted that any performance differences that might be observed will be more of a reflection of the potency of the hindered amine. Please refer to the graphs illustrating these interim results.

Influence of Fluoropolymer Processing Aid on the UV Stability of LLDPE Film

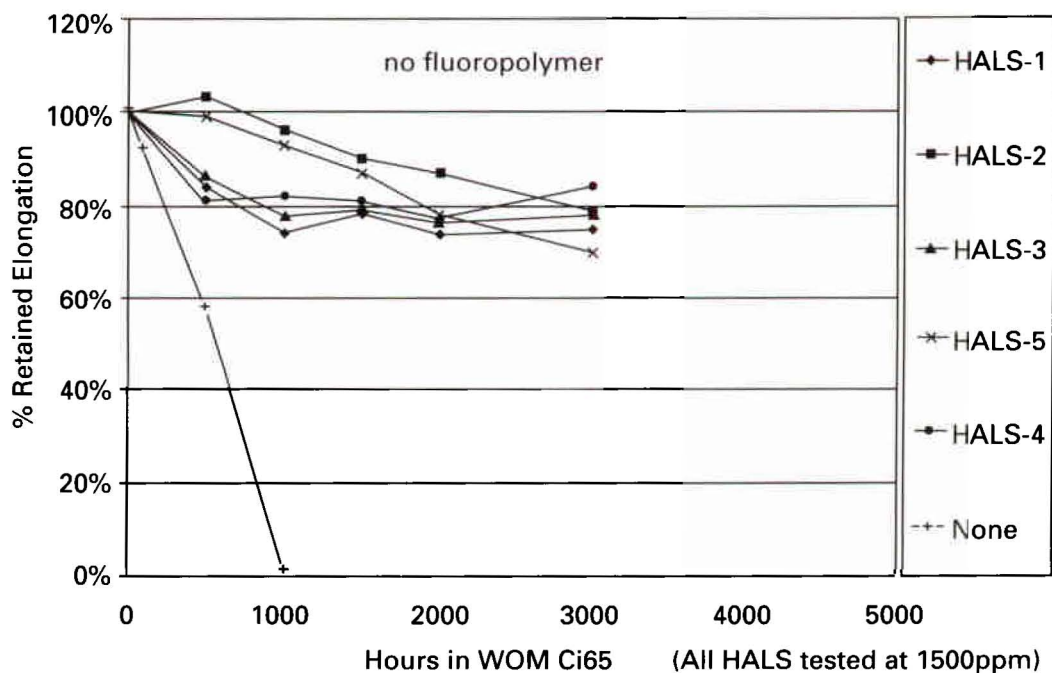


Figure 15.

Influence of Fluoropolymer Processing Aid on the UV Stability of LLDPE Film

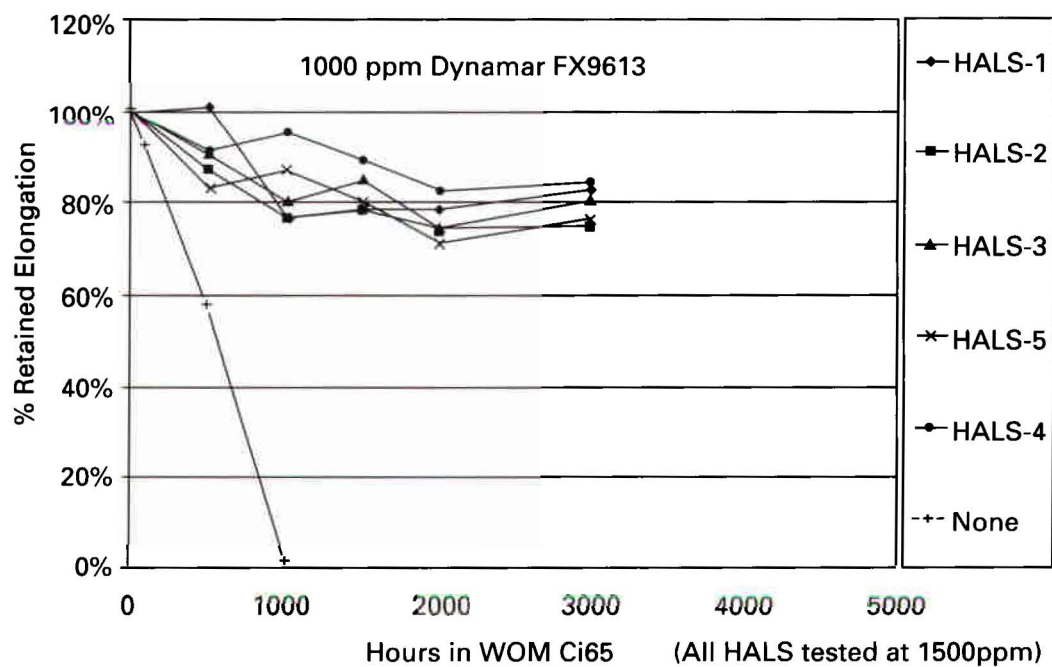


Figure 16.

Influence of Fluoropolymer Processing Aid on the UV Stability of LLDPE Film

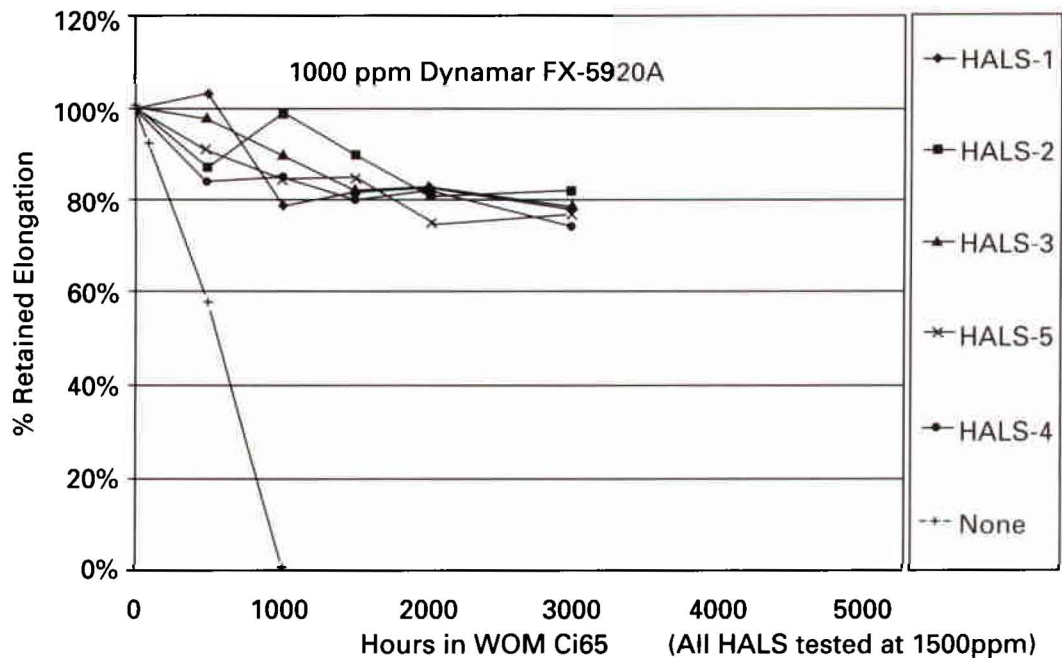


Figure 17.

RECOMMENDATIONS

To summarize, it appears that in those experiments where the HALS-PPA interaction was observed, the interaction most likely is comprised of two components:

- site competition at the polymer / metal interface
- acid / base chemistry between the fluoropolymer and the hindered amine; respectively

Depending on the individual situation one of these may have more influence than the other.

From a practical point of view, the way to handle this interaction situation is as follows:

- keep your temperatures low
- think about your whole additive package:

- order of increasing HALS interference

(HALS- 1 < HALS-2, HALS-4, HALS-5 < HALS 3)

- order of increasing PPA effectiveness in the presence of HALS

(PPA- 1 outperforms PPA-2)

In regard to the impact of the HALS / PPA interaction on the effectiveness of the hindered amines as light stabilizers, we have no data to suggest that there is a positive or negative interaction. Accordingly, the utility of the HALS as reagents for providing stability under the harsh effects of UV radiation remains unaffected. Consequently, the pragmatic recommendations described above outline a path forward for manufacturing melt fracture free LLDPE blown films that should serve a variety of outdoor applications.

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