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Title:

Processing Additives and Acid Neutralizers—Formulation Options in Polyolefins

Intro:

While the advent of higher activity catalysts has reduced the need for extensive de-ashing of most polyolefin resins, the persistence of some residues, even at the parts per million level, can provoke a multitude of post-reactor difficulties. In particular, the chloride associated with some catalysts and cocatalysts can be corrosive to melt processing equipment, and can reduce the thermal and light stability of the polymers in which they are contained. The use of additives, such as metal stearates and alkaline metal oxides, to neutralize these acidic residues has become common, but can lead to additional problems such as color instability, die build-up, and smoking at the die exit. In addition, these neutralizers can cause further complications by interacting with other resin components, such as polymer processing additives (PPAs). The application of fluorocarbon polymers to improve the processing of various polyolefin resins is well known (1), and has become an increasingly significant factor in the design of new resin formulations (2). Careful adjustments of these formulations is desirable to both minimize any undesirable neutralizer sideeffects, and to assure the greatest efficiency of processing additive use. To aid in achieving this goal, the study of chemical and functional additive interactions described in this paper was conducted.

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Processing Additives and Acid Neutralizers— Formulation Options in Polyolefins

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PROCESSING ADDITIVES AND ACID NEUTRALIZERS – FORMULATION OPTIONS IN POLYOLEFINS

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INTRODUCTION

While the advent of higher activity catalysts has reduced the need for extensive de-ashing of most polyolefin resins, the persistence of some residues, even at the parts per million level, can provoke a multitude of post-reactor difficulties. In particular, the chloride associated with some catalysts and cocatalysts can be corrosive to melt processing equipment, and can reduce the thermal and light stability of the polymers in which they are contained.

The use of additives, such as metal stearates and alkaline metal oxides, to neutralize these acidic residues has become common, but can lead to additional problems such as color instability, die build-up, and smoking at the die exit. In addition, these neutralizers can cause further complications by interacting with other resin components, such as polymer processing additives (PPAs).

The application of fluorocarbon polymers to improve the processing of various polyolefin resins is well known (1), and has become an increasingly significant factor in the design of new resin formulations (2). Careful adjustments of these formulations is desirable to both minimize any undesirable neutralizer side-effects, and to assure the greatest efficiency of processing additive use. To aid in achieving this goal, the study of chemical and functional additive interactions described in this paper was conducted.

EXPERIMENTAL

Materials

The fluorocarbon polymer-based processing aid used in this study was a copolymer of vinylidene fluoride and hexafluoropropylene. It was utilized as either a raw fluorocarbon polymer gumstock, or in the form of a 25 mesh free-flowing powder that is commercially available as Dynamar™ FX-9613. In some cases, the fluorocarbon polymer was present as a component of a proprietary formulation designed for specific processing improvements. This product is commercially available as Dynamar™ FX5920. These products will hereafter be referred to as PPA-1 and PPA-2, respectively.

The acid scavenging additives: zinc stearate (ZnSt), calcium stearate (CaSt), zinc oxide (ZnO), and the hydrotalcite-like compound (HT), were obtained commercially as free-flowing powders.

The polyolefin resins used for capillary rheometry and blown film analysis were obtained commercially, and are described in Tables 1 and 5.

Equipment and Sample Preparation

Thermal aging and differential scanning calorimetry (DSC) studies utilized neat samples of the fluorocarbon polymer and acid neutralizers, or 50/50 weight blends thereof. The blends were prepared by milling the components on a two roll mill at ambient temperature. For DSC analyses, the samples were sealed in aluminum pans and scanned at 20° C/min under air pressure (70 cc/s). The effects of time and temperature on additives and blends were observed by subjecting 2 gram samples in open aluminum pans to temperatures of 232° C or 275° C in a thermostated oven. Weight losses for individual components after 30 minutes were averaged to predict values for the binary blends. Samples were also judged visually for discoloration or other evidence of reaction.

Formulations for capillary rheometry were prepared using a torque rheometer and mixing bowl fitted with roller blades. The mixing sequence began with a two minute loading period at 15 rpms and 230° C. During the third minute, the rotors were ramped to 50 rpms and the temperature was decreased to 180° C. This set of conditions was maintained for an additional five minutes. Final resin temperatures were in the range of 200-210 °C. Masterbatches of the metal stearates were prepared with the above sequence at a level of 6%. The HT and ZnO additives were compounded at 2%. LLDPE-1 was used as the masterbatch carrier resin. A PPA-1 masterbatch was prepared at a 2% level using the same carrier resin.

Appropriate quantities of the required masterbatches were melt mixed with the base resin of interest to produce samples with the desired additive levels for testing in the capillary rheometer. Samples were chopped and ground at ambient temperature to facilitate loading of the rheometer.

Capillary rheometry experiments utilized a flat entry die with a 0.508 mm diameter and a 40/1 L/D. Samples were extruded at 190° C and 210° C following a 10 minute dwell time. Viscosities are reported uncorrected. Photomicrographs of the air-cooled extrudates were used for melt fracture analyses.

Masterbatches of the acid neutralizers (CaSt and HT) for blown film analysis were prepared at 5% levels in LLDPE-1. Prior to compounding, resin and additive were dry-blended in a pail tumbler. Melt compounding was accomplished in a counter-rotating, intermeshing, conical twin screw extruder. The extrudate was water quenched and strand pelletized. Masterbatches of PPA-1 and PPA-2 were obtained from commercial vendors at 3% levels. To obtain desired additive levels, masterbatches of the required materials were preblended with the pelletized host polymer (LLDPE-2) in a 5 gallon pail tumbler.

The blown film line employed a 40 mm extruder with a 24/1 length to diameter (LID) ratio screw. The die was 40 mm in diameter, with a 0.61 mm die gap. Film from LLDPE-2 was produced at a 3.3 blow-up ratio with a gauge of 25-35 microns. The extrusion rate was 0.65 kg/hr/cm, corresponding to a shear rate of 400 s-1. Melt temperature at the die was 200° C.

In order to compare the effectiveness of a PPA in the presence of another additive, it was necessary to ensure that the blown film line was free of residual process additive from previous evaluations. This was accomplished by extruding, for 60 minutes, a 3/1 blend of base resin and a commercial masterbatch containing 25% diatomaceous earth. The die pin was then removed and soaked in acetone while the outer die lip was washed with acetone to remove any residual fluorocarbon polymer. After the die was reassembled, the base resin was extruded until previous pressure measurements were observed and the resultant film was fully melt fractured.

To determine the minimum level of a PPA required to eliminate melt fracture in the presence of the various additives, PPA levels were increased in 100 ppm increments from an initial concentration of 500 ppm, with the above purge procedure repeated prior to each ensuing level. Each formulation was extruded into film for a one hour period to determine the amount of melt fracture removed by the given PPA.

RESULTS AND DISCUSSION

Chemical Reactivity - Differential Scanning Calorimetry

A DSC scan of the neat fluorocarbon polymer over the range of -40° C to 300° C gave a flat base line, except for a glass transition occurring around -20° C. A second scan replicated the first, evidencing the stability of these materials in this temperature range. The HT material showed an initial loss of water in the first scan at 240-280° C, while a second heat trace produced essentially a flat base line. The initial scan of the HT and fluorocarbon in milled combination showed the same water loss at a slightly higher temperature. A subsequent scan showed no heat gains or losses, giving no evidence for reactivity between the two additives.

The milled blend of the ZnO and fluorocarbon polymer showed no evidence of reactivity. Both the first and second scans were flat with the exception of the Tg of the fluorocarbon polymer. The neat ZnSt and its 50/50 blend with the fluorocarbon polymer also remained unchanged during first and second scans, providing no evidence that any type of chemical reaction had occurred.

In the case of the neat CaSt, a distinct shift in peak positions was observed between the first and second scans. When tested in combination with the fluorocarbon polymer, this same shift transpired between scans, but the original endotherm was broader, and contained multiple peaks. These observations along with previous work in this laboratory suggests the possibility for a reaction between the CaSt and the fluorocarbon polymer (3). Species such as CaO, which may be present in some commercial CaSt samples, may also be a source of reaction.

Chemical Reactivity—Thermal Aging

As shown in Table 2, the weight losses for the neutralizer/fluorocarbon polymer blends at both 232° C and 275° C were, in most cases, just slightly less than those predicted from the individual components. In no instance was the weight loss of a blend greater than that predicted, a situation which could have indicated a chemical reaction. The slight decreases in weight loss that were observed were most likely due to physical restraints of the far less volatile fluorocarbon polymer on the volatility of the neutralizer.

While visual inspection of the ZnO/PPA-1 and HT/PPA-1 combinations showed little change in appearance, both the CaSt and ZnSt combinations turned dark brown to black after 30 minutes of aging at 275° C. Whereas the ZnSt/PPA-1 combination retained its elasticity after the thermal aging, the CaSt/PPA-1 combination displayed surface cracking and brittleness, consistent with the reactivity suggested by the DSC analyses.

Capillary Rheometry—Comparisons of Neutralizer Effects

Previous work has shown that certain inorganic additives, though not chemically reactive with PPAs, can still reduce PPA effectiveness in certain resin formulations. Examples include diatomaceous earth and titanium dioxide(4,5). Such interference is thought to be due to either an abrasive removal of PPA coated onto metal parts, and/or an adsorption of the PPA to the metal oxide additive that could interfere with coating of the die. Capillary rheometry experiments were thus designed to detect evidence of functional interaction among acid neutralizers and PPA-1.

Results in Figure 1 show that the presence of 500 ppm of HT could significantly limit the apparent viscosity reducing ability of an equivalent level of PPA-1 in the range of 100 s-1 to 600 s-1. However, as shown in Table 3, the HT did not prevent PPA-1 from eliminating sharkskin melt fracture in this range and, in fact, permitted extension of defect-free processing from 800 to 1000 s-1. The impact of interaction from an additive like HT will, of course, be greatest near the threshold of minimum PPA concentration, and does not necessarily predict the effect of equivalent levels of PPA and HT at higher concentrations.

Figure 1 also shows that 500 ppm of zinc oxide had virtually no impact on PPA-1 performance even though the ZnO, in contrast to the HT, was in a combined masterbatch with the PPA. (This method of incorporation allows for additional contact of additives, and can exacerbate the interactions of the PPA with inorganics (5).)

Further consideration of Figure 1 shows that at a 1 :1 ratio of PPA-1 with CaSt or ZnSt (500 ppm each), the ability of PPA-1 to reduce the apparent viscosity was only slightly affected. At 100 s-1, 500 ppm of PPA-1 in the presence of either CaSt or ZnSt could lower the apparent viscosity by 25%, versus 30% for the PPA-1 by itself. (Percent reductions in apparent viscosity are in comparison to the neat LLDPE-1 without neutralizer or PPA.) At higher extrusion rates the impact of the metal stearate appeared to diminish. At 600 5-1, a formulation with PPA-1 and ZnSt had an apparent viscosity 34% lower than that of base resin. A formulation of PPA-1 without ZnSt gave a 37% reduction.

Capillary Rheometry—Effect of Concentration

Metallic stearates, in addition to neutralizing acidic species, are also used as lubricants and are thus believed to exude to the surface of polymers during extrusion. Commercial use levels of these additives, when used for both neutralizing and lubrication, can be several times higher than those of the PPA, so the effect of concentration on performance was explored.

While a 1/1 ratio of PPA-1 to CaSt showed only a slight impact

on PPA performance, a 4/1 ratio (2000 ppm CaSt to 500 ppm PPA-1), as shown in Figure 2, significantly reduced the ability of PPA-1 to lower the apparent viscosity at 100 s-1 in LLDPE-1. Again, as the shear rate was increased, the effect of the CaSt diminished, so that at 600 s-1 the same formulation allowed for PPA-1 to provide a 29% viscosity drop. Although PPA-1 provided a smaller viscosity reduction at low shear rates, it was again able to fully suppress sharkskin melt fracture.

As shown in Figure 3 the same level of ZnSt appeared to be less of a hindrance to PPA-1 than was the 2000 ppm of CaSt. At 100 s-1, 2000 ppm ZnSt permitted PPA-1 to decrease the apparent viscosity by 17%, whereas a 10% drop was provided by PP A-1 in the presence of 2000 ppm CaSt. Similarly, when shear rates were increased, the ZnSt caused less interference to PPA-1 as did the CaSt. As shown in Figures 2 and 3, the interference created by 2000 ppm of either metal stearate with 500 ppm of PPA-1 is inversely related to the shear rate of extrusion. This suggests for extrusion operations involving low output rates or wide die gaps, that the level of metal stearate must be kept at a minimum if optimum performance of this particular PPA is to be achieved. Otherwise, PPA-1 may function only to eliminate melt fracture, and not to reduce operating pressures.

As listed in Table 3, melt fracture was eventually encountered for the stearate IPPA-1 formulations at slightly lower shear rates than the 1800 s-1 observed without the neutralizer. The formulation with 2000 ppm ZnSt and 500 ppm PPA-1 exhibited a slip phenomenon at 1400 s-1. The same 411 ratio with CaSt entered cyclic melt fracture at 1400 s-1.

Considering that commercial extrusion lines can operate for days to weeks and that substantial accumulation of additives can occur, higher ratio 811 blends of metal stearates with 500 ppm PPA-1 were also evaluated.

Results generated with 4000 ppm stearate continued the trend evident from the 500 and 2000 ppm comparisons (Figures 2 and 3). PPA performance was affected most at low shear rates. As shown in Figure 2, 500 ppm PP A-1 in the presence of 4000 ppm CaSt provided only a 6% reduction in viscosity at 100 s-1. Furthermore, in the presence of 4000 ppm of either the CaSt or ZnSt, instability was observed in the coating of the die. Thus, the PPA was often partially removed from the die when output (shear) rates were increased, requiring additional conditioning time at each shear rate. Still, within the time .frame of the capillary experiment, sharkskin did not reappear in the presence of 4000 ppm metal stearate and cyclic melt fracture remained substantially delayed. (Table 3). However, under continuous blown film conditions, reoccurrence of melt fracture would most likely be a concern.

Capillary Rheometry—Effect of Temperature

The effect of extruding a sample of LLDPE-1 containing 500 ppm PPA-1 in the capillary rheometer at 190° C and 210° C is shown in Figure 4. In this example, the PPA-1 appeared to have equal efficiency in lowering the apparent viscosity at either temperature. The same figure shows that 2000 ppm of CaSt is less detrimental to 500 ppm PPA-1 at 210° C than at 190° C. However, temperature appeared to have little influence on the effect of 2000 ppm ZnSt on 500 ppm PPA-1. As shown in Figure 5, the ZnSt at 100 s-1, 400 s-1 and 600 s-1 had about the same effect on 500 ppm PPA-1 at 190° C or 210° C. It should be noted that CaSt was more detrimental than ZnSt at 190° C, whereas at 210° C, these two additives have nearly the same effect. Although the reasons for these differences in temperature dependence are not immediately obvious, the results with calcium stearate imply that chemical reaction with the PPA may not be the major factor affecting performance changes. Increasing temperature would be expected to decrease PPA performance in such instances. This type of behavior has been observed and reported in several cases where strong chemical reactions have been identified (4).

Comparison of data in Figure 6 show that 500 ppm of HT also created less of an interference with PPA-1 at 210° C than it did at 190° C. At 190° C, the HT did not allow PPA-1 to decrease the apparent viscosity significantly. At 210° C and 400 s-1, PPA-1 was able to provide a 16% decrease. At both temperatures, and below 1000 s-1, PPA-1 was able to eliminate melt fracture.

Capillary Rheometry—Effect of Additive Incorporation Method

As shown previously in this laboratory, combined masterbatches of a PPA with other additives can sometimes further decrease the PPAs performance relative to separate masterbatches (5). Since the HT created interference using the separate addition technique, a combined masterbatch was not explored. (Addition of ZnO and PPA-1 by this method was shown in a previous section to have essentially no added impact.)

To observe the effect of combined compounding on metal stearate/PPA-1 interactions, masterbatches containing 6% CaSt or 6% ZnSt and 1.5% PPA-1 were prepared. These masterbatches were then let-down 30/1 in LLDPE-1 to a level of 2000 ppm metal stearate and 500 ppm PPA-1, and were subsequently tested in the capillary rheometer. Results were then compared to those of the same formulations prepared using separate masterbatches of the ZnSt, CaSt, and PPA-1.

The data in Figure 7 and Table 3 show the effects of combined masterbatch preparation for samples containing PPA and metal stearate versus those from separate

masterbatches. The added interference from this type of addition is most noticeable in the lower shear rate ranges. At 200 s-1, the 2000 ppm CaSt, when added separately, allowed PPA-1 to reduce the apparent viscosity by 24%, but, when compounded together, the PPA-1 gave only a 9% drop. In contrast, PPA-1 by itself lowered the viscosity by 42% at 200 s-1. The ZnSt/PPA-1 composite had a similar effect of reducing PPA-1 performance (Figure 7). As was shown earlier, the metal stearates (even when masterbatched with PPA-1) have a decreasing influence at higher extrusion rates.

One explanation for the effect of combined masterbatches of metal stearates and PPAs results from a comparison of photomicrographs of the PPA with and without the metal stearate. The separate PPA-1 masterbatch shows particles of the fluorocarbon polymer averaging 1 micron in diameter. When the fluorocarbon polymer was dispersed in the presence of either metal stearate, particles on the order of 50-100 microns were formed. Such a dispersion could be detrimental to the overall performance of the PPA.

Blown Film Extrusion Trials in LLDPE-2

In order to confirm the findings of capillary rheometer experiments and to provide additional information under more commercial type conditions, the HT and CaSt additives were tested with PPA-1 and PPA-2 in a blown film extrusion line using LLDPE-2. In these experiments complete elimination of melt fracture was a prerequisite; therefore, the levels of CaSt and HT were fixed, and the minimum level of PPA-1 or PPA-2 to eliminate melt fracture in their presence was determined.

As shown in Table 4, 500 ppm of PPA-1 without neutralizers was sufficient in suppressing melt fracture in less than one hour, while the same level of PPA-2 eliminated sharkskin melt fracture in 30 minutes. In the presence of 1000 ppm CaSt, 500 ppm of either PPA was still sufficient to eliminate all of the melt fracture. However, PPA-1 provided only a 6% pressure drop versus 11% in the control without CaSt. The only hindrance to PPA-2 by the CaSt was that more time was required to eliminate all of the melt fracture. Pressure reductions given by PPA-2 with or without the CaSt were identical.

Figure 8 shows the comparative effect of acid neutralizer type on the performance of PPA-1 in LLDPE. In the presence of 500 ppm HT, 600 ppm of PPA-1 was required to achieve the same reduction in gate pressure as 500 ppm PPA-1 in the presence of 1000 ppm CaSt. Similarly shown on Figure 9, an additional 100 ppm of PPA-2 was required for a formulation with 500 ppm HT to achieve the same pressure reduction as a blend containing 500 ppm PPA-2 and 1000 ppm CaSt. Furthermore, it is shown in Table 4 that 800 ppm of PPA-1 was required to eliminate the melt fracture in the formulation containing 500 ppm HT. These studies confirm the PPA-1 sensitivity to HT in LLDPE as seen in the capillary rheometer, but also show that PPA-2 can be used to reduce this sensitivity.

Blown Film Extrusion Trials in HMW-HDPE Resins

Table 5 contains the results of several HMW-HDPE blown film trials with different levels and types of neutralizers. As shown, the PPAs were better able to eliminate melt fracture and reduce the die pressure when acid neutralizer levels were the lowest. In HMW-HDPE, metal stearate interactions seem to be a greater factor than in LLDPE. In fact, as shown in Table 5 and Figure 10, 1500 ppm of CaSt appeared to eliminate PPA-1 processing benefits, while 500 ppm of HT proved to be a satisfactory option for minimizing acid neutralizer impact on the PPA. Other observations in our laboratory have shown some variations, especially in metal stearate effect, that may depend on HDPE resin characteristics.

CONCLUSIONS

The studies described in this paper have shown that acid neutralizers can have a definite influence on the performance of fluorocarbon polymer-based processing additives. Though there is some evidence for a chemical reaction with calcium stearate, the primary source of acid neutralizer interferences with PPAs is not believed to be due to chemical interactions.

Rather, other factors that can affect the ability of a processing additive to coat extrusion dies come into consideration. Concentration, temperature, processing and compounding can all have a role, as can the choice of resin, neutralizer, or even the processing additive. With attention to these factors, ratios or levels can be determined so that a selected PPA can perform optimally in the presence of a given neutralizing agent. In the case of zinc oxide, there is little evidence of interference or the need for specific precautions. Use of hydrotalcite-like compounds, particularly in LLDPE, suggest a strong preference for a specific type of PPA (in this case PPA-2). Metal stearate interactions are minimized at higher extrusion rates and under separate masterbatch conditions. These interferences may also be diminished by increasing temperatures. Of the two metal stearates analyzed, zinc stearate appears to be less interactive than calcium stearate.

Direct translation of the results obtained in these studies to specific commercial operations is not advised due to likely differences in die design, resin characteristics, processing conditions, etc. (Subsequent work is underway to further explore these variables.) However, consideration of the parameters discussed above to design additive formulation experiments should lead to the most efficient use of processing additive/neutralizer combinations.

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Table 1

Resin ivieit in	dex Density	/ Copolymer
LLDPE-1 0.9 MI	0.918	1-Hexene

Table 2

Effect of Thermal Aging on Milled Fluorocarbon Polymer/Neutralizer Blends

Percent Weight Loss After 30 Minutes for 50/50 Acid Neutralizer/PPA Blends

	232	2° C	275° C		
Neutralizer	Predicted*	Observed	Predicted*	Observed	
CaSt	4 9	4.3	14.6	9.5	
ZnSt	3.3	2.8	9.0	3.8	
HT	7.5	2.8	10.1	7.7	
ZnO	0.3	0.3	0.7	0.8	

* Predicted weight loss is the average of the losses for the individual components under the same conditions.

Note that the fluorocarbon polymer has a weight loss of less than 1% at either temperature.

Table 3

Capillary Rheometry Data LLDPE-1, 190° C

Neutralizer ppm	Туре	PPA-1 ppm	Percent Sharkskin	Shear Rate (s-1) for Melt Fracture Onset / Comments
0 500 500 2000 2000	HT ZnO CaSt ZnSt	0 0 0 0 0	100 100 100 100 100	800 CMF 800 CMF 800 CMF 800 CMF 800 CMF
0 500 500 500 500	HT ZnO CaSt ZnSt	500 500 500* 500 500	0 0 0 0	>1800 Smooth filament 1000 CMF >1800 Smooth filament 1400 Slip 1400 Slip
2000	CaSt	500	0	1400 CMF
2000	ZnSt	500	0	1400 Slip
4000	CaSt	500	0	1200 Slip
4000	ZnSt	500	0	1200 CMF
2000	CaSt	500*	0	1000 Slip
2000	ZnSt	500*	0	1000 Slip

CMF: Cyclic melt fracture

Slip: Extrusion instability where polymer loses die wall contact

* : Indicates that the PPA-1 was added via a combined masterbatch with the neutralizer in question.

Table 4Blown Film Analysis LLDPE-2

Effect of CaSt and HT on Performance of PPA-1 and PPA-2

	PPA-1	Pressure	Time	PPA-2	Pressure	Time
Formulation	ppm*	Drop. %	Min**	ppm*	Drop. %	Min**
LLDPE-2	0	0	N/ A	0	0	N/A
LLDPE-2	500	11	<60	500	12	30
+ 1000 ppm CaSt	500	6	<60	500	12	<60
+ 500 ppm HT	800	4	<60	600	14	45

* Denotes the minimum level required to eliminate sharkskin melt fracture, 500 ppm was the lowest level tested.

* * Time required to fully eliminate melt fracture.

Table 5							
Blown	Film	Trials	HMW-HDPE				

Examples of Acid Neutralizers in Combination With PPAs

			PPA **	Remove	Improve
HLMI	Neutralizer	ppm*	500 ppm	Melt Fracture	Output
	7.0	500		2/50	N/50
4	ZnSt	500	PPA-1	YES	YES
5	HT	500	PPA-1	YES	YES
	CaSt	1500	PPA-1	NO	NO
11	CaSt	1000	PPA-2	YES	YES

* Rounded to nearest 500 ppm increment.

* * PPAs added via a 3% masterbatch at the film line.

Figure 1

Capillary Rheometry, LLDPE-1, 190° C Effect of Acid Neutralizers on the Performance of 500 ppm PPA-1



Figure 2



Figure 3

Capillary Rheometry, LLDPE-1 , 190 C Effect of ZnSt Level on 500 ppm PPA-1





Figure 5 Capillary Rheometry, LLDPE-1, 190° C and 210° C Effect of Temperature on 500 ppm PPA-1 in the Presence of 2000 ppm ZnSt







Figure 8



Figure 9 Blown Film Extrusion, LLDPE-2 Acid Neutralizer Effect on PPA-2



Figure 10



Blown Film Extrusion, HMW-HDPE, 5 HLMI Effect of Acid Neutralizer on 500 ppm PPA-1



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