

# **Chemiluminescence Studies of Comparative Antioxidant Effectiveness on Multiextruded Polyethylenes.**

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## **Abstract**

Several polyethylene resins; high density polyethylene (Ph-HDPE, Phillips metal oxide catalyst) and linear low density polyethylenes (LLDPE, formed using Ziegler-Natta catalyst and metallocene catalyst technology, m-LLDPE) were used in order to acquire insight in to the effect of different polymerization catalyst systems on the melt stabilization performance of single AO. Chemiluminescence (CL) and melt flow rate (MFR) were used to analyse the degradation as a function of the number of passes through a twin-screw extruder. A good correlation was obtained, and the additives resulting with the best melt flow stability in the polymer were the same as those that promote best CL results.

*Keywords:* Chemiluminescence, degradation, polyethylene, melt flow index.

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## 1. Introduction

Most of the polymeric materials are not environmentally stable enough to withstand the conditions of normal use. In contact with atmospheric oxygen, they undergo oxidation reactions which lead to a deterioration of their properties and characteristics. Anti-oxidants are important additives used in most thermoplastics to protect polymers during initial melt processing, end use and recycling, since those additives inhibit or retard the progress of these oxidation reactions. Therefore, the evaluation of the stabilizer effectiveness is of prime importance in industrial polymer research. Screening of stabilized materials under real conditions would take a long time, so studies are carried out by means of accelerated tests, as using multiple pass extrusion [1,2,3,4], where the influence of zinc stearate during melt processing [5], type of polymerization catalyst system [6], or content of comonomers [7] on the degradation of polyolefines in the melt state may be studied. The stabilized polymer is subjected to four or more consecutive extruder passes, and the melt flow index (MFI) and yellowness index (YI) are the primary evaluated parameters. The stabilizers that maximize retention of performance properties with successive passes are considered most effective. Alternative methods to MFI determinations for ranking the relative stabilization effectiveness in polymers are desirable, in order to reduce time and material consuming comparing to MFI analysis [8].

The technique of chemiluminescence (CL) has proved to be a sensitive tool for the study of polymer degradation [9,10,11,12], and its use continues to attract much interest. It is well known [13,14], that the degradation of polymer is accompanied by a weak emission of light produced as direct results of a chemical reaction. Chemiluminescence from polymers is due to the recombination of secondary alkyl peroxy radicals, which promotes ketone products to its lowest triplet state and the radiative deactivation gives the light emission in the visible region [15,16,17,18]. The chemiluminescence emission can be related to the hydroperoxide (POOH) content, since generation of peroxy radicals depends on the peroxide concentration formed during processing or in-service life of the material under

ambient conditions [19]. As peroxide species are the primary oxidation intermediates of the polyolefin degradation, CL can be used to evaluate the degree of degradation [10], to study the reaction mechanisms [20] and oxidation kinetics, [21,22] or to assess the stabilization efficiency of additives [23,24].

From an applied point of view, the measurement of CL intensity gives about the rate of degradation and the efficiency of antioxidants (AO) since the stabilizer reduces the concentration of excited ketone. Thus, the main goal of this work was to study the CL emission of different stabilized polyethylene in order to investigate the difference in the thermo-oxidative behaviour of these polymers under conditions of extrusion processing. For that purpose, Primary antioxidants: hindered and low hindered phenols, and Secondary antioxidants: phosphites and thioesters were selected and included in Ph-HDPE (Cr catalyst), ZN-LLDPE (Ziegler-Natta catalyst) and metallocene m-LLDPE (Zr). The CL emission was analysed after multi-pass extrusion and the results compared to those obtained by Melt Flow Rate.

## 2. Experimental

### 2.1. Materials.

The polyethylene types investigated were commercially produced via three different catalyst technologies, (a) Phillips-type catalysts, called Ph-HDPE, supplied by Borealis, (b) Ziegler–Natta catalysts, called ZN-LLDPE, and (c) single site metallocene catalysts, called m-LLDPE, both supplied by Exxon.

The stabilizers selected were commercially available grades, and supplied by Chemtura. Their corresponding structures are shown in Figure 1, together with their trade code, melting point of the products, molar activity and molecular weight (Table 1). For comparative use, all the products were tested individually at a load level of 250 ppm. All the formulations also contained 500 ppm zinc stearate (ZnSt) as an acid scavenger.

**Table 1**

**Figure 1**

### 2.2. Multi-pass extrusion and film preparation.

Polyethylenes were subjected to six extrusion passes (0-5) and samples of each pass were collected for further analysis. The extruder used was a Brabender single screw extruder (D=19 mm, L/D=0.44 and compression ratio of 4) attachment for a Brabender PL2000 dynamometer drive unit. Processing began with 1.2 kg of polymer for pass 0, under nitrogen atmosphere, (Set Zones Temperature: Hopper 175/ 175/ 180/ 190 °C Die). After passes 0, 1, 3 and 5, under air, (Set Zones Temperature: Hopper 200/ 210/ 220/ 230°C Die), 19 g of extrudate was collected.

Polymer films were made by compression moulding of a fixed amount of blended powder (1g) in a Collin-200 press under the same temperature (190°C) and pressure cycle (1 min. 0bar, and 1min. at

150 bar). Also, the cooling rate, from 190°C until room temperature, was controlled and maintained constant to assure the same crystalline index in all the samples. Under such conditions, circular polymer films (100  $\mu\text{m} \pm 10 \mu\text{m}$  thick) were obtained.

### *2.3. Characterization.*

The Melt Flow Rate (MFR) of material collected after extrusion passes: 0, 1, 3, 5 were determined at 190°C, 10 kg masses using a semiautomatic Ceast16412 and 16861 MFR instrument [25].

FTIR spectra were obtained using a Perkin Elmer BX-FTIR spectrometer coupled with an Attenuated Total Reflectance (ATR) accessory, MIRacle-ATR from PIKE Technologies. Carbonyl index (C.I.), defined as the ratio of carbonyl and methylene absorbances, was calculated according to the baseline method, as the ratio of the absorbance of the carbonyl peak at 1714  $\text{cm}^{-1}$  and that of the methylene absorption band at 1435  $\text{cm}^{-1}$  (CH<sub>2</sub> scissoring peak) taken as an internal thickness band [26].

Chemiluminescence (CL) emission of film samples were obtained as described earlier [21] using a CL400 ChemiLUME apparatus developed by Atlas Electric Devices Co. Samples for chemiluminescence measurements were prepared by cutting circular specimens of 2 cm in diameter from the polymer films; hence the emission area was maintained constant in all the experiments. The polyethylene films were held in aluminium pans and isothermal tests were performed by heating the samples to a constant temperature of 180 °C, and CL emission was recorded as a function of time under constant flow (50 ml/ min) of dry nitrogen gas. The collected data were processed using the specific software supplied with the instrument.

## **3. Results and discussion**

### *3.1. CL analysis of the antioxidants*

The different commercial antioxidants studied in this work were previously tested to determine the possible presence of hydroperoxides in the powder products supplied. Several antioxidants exhibited CL emission when they were heated at 180 °C under nitrogen, confirming that a certain quantity of hydroperoxide was present in the products, which has been generated during their manufacturing process. The antioxidant chemiluminescence emissions observed are shown in Figure 2. L-CPL in particular shows significant CL emission, in comparison with the other ones, and this may be explained by its relatively complex polymeric structure. DSTDP also showed slightly higher CL emission than the other AOs, the CL active species are likely to exist within the long alkyl chains of their structures, with hydrogen atoms each able to form peroxide radicals in a thermal process. The remaining stabilizers, including the phenolic AOs, showed limited CL emission and this can be due to the aliphatic carbons present in their structures that can also give hydroperoxides but to a lesser extent.

### **Figure 2**

Whilst these observations are interesting it has to be appreciated that the CL emission associated with the stabilizers after dilution by the PE matrix is likely to be negligible. All the formulations discussed in this study contain 250 ppm of AO, it can be safely assumed that the contribution of the hydroperoxide associated with the AO is insignificant relative to the hydroperoxide generated during the processing of the polymer, as it will see in the next section.

### *3.2. AO effectiveness in Ph-HDPE determined by CL under nitrogen*

Through the measurement of the chemiluminescence intensity it is possible to obtain information about the rate of degradation and the efficiency of additives since the presence of antioxidant stabilizers reduces the rate formation of excited ketones responsible for the emission of light. Under nitrogen, the oxidation is inhibited and the CL emission is a measure of the peroxides present in the material formed

during its processing at high temperatures. As illustrative example of the curves obtained under nitrogen at 180 °C, for Ph-HDPE containing the antioxidants, all at 250 ppm, and after the fifth extruder pass, are shown in Figure 3.

### Figure 3

In general, the intensity of chemiluminescence and the area of the emission curve decreases for those films containing the stabilisers when compared with the additive free polyethylene after pass 0, thus demonstrating their protective effect, Figure 4. In order to aid elucidation of relationships between  $A_{CL}$  and the concentration of stabilization active groups in the PE,  $A_{CL}$  (after passes 0, 3 and 5) is plotted against number of moles of stabilizing group per kg of PE in Figure 4 (a), (b) and (c) respectively. In order to visualize the performance of the different classes of AO in Ph-HDPE, they were divided into different groups: Primary antioxidants: hindered and low hindered phenols ( $\diamond$ ), and Secondary antioxidants: phosphites and thioesters ( $\blacklozenge$ ) in Figures 4 and 5.

### Figure 4

It is evident after pass 0 that there is a general inverse correlation between  $A_{CL}$  and the concentration of stabilizing group in the PE. The low  $A_{CL}$  values recorded for the phenolic AOs are related to the well-established CB-D mechanism which involves hydrogen atom transfer from the phenolic group to the peroxy radical. The latter occurs faster than the abstraction of a hydrogen atom from the polymer by the radical. This reaction results in the chemical transformation of the original phenolic structure via a phenoxyl radical to give quinonemethides, which are the principal ultimate transformation products, and the regeneration of the phenolic group in subsequent steps is possible. These quinones can act similarly to macroalkyl radical scavengers via a chain breaking acceptor mechanism, and frequently they are superior to the original phenolic antioxidant in terms of trapping carbon-centered radicals in the polymer melt. Both mechanisms for these antioxidant additives will give rise to stable



products, contributing to a reduction in the concentration of  $R\bullet$  and  $ROO\bullet$  species and, subsequently, the value of  $I_{CL}$ .

In presence of the primary AOs ( $\diamond$ ), except for N-431, there is some clustering of data, which exhibited the lowest values of  $A_{CL}$ , with L-22IB46, Vit E and L-1790 being close to zero value. N-431 showed the poorest antioxidant efficiency under processing conditions, and it would be related to the higher level of steric hindrance of the phenolic OH group. On the other hand, the lower stabilising performance of the aryl phosphites is observed, whose function is as peroxide decomposer and are usually used in combination with chain-breaking antioxidants such as hindered phenols. The secondary AOs ( $\blacklozenge$ ) with the exception of A-TNPP) form a cluster higher up the  $A_{CL}$  for primary antioxidants but remaining below the  $A_{CL}$  of the unstabilized PE.

After pass 3 and pass 5, for the unstabilised PE a drastically decrease of CL emission intensity was observed, which may be related according to the well-established oxidation mechanism of polyolefins, among the various reactions that can take place, the formation of hydroperoxides and their decomposition to give ketone products are involved. It was confirmed by using FTIR spectroscopy, the carbonyl index (CI) calculated on Ph-HDPE sample was seen to gradually increase from the pass 0 up to pass 5 (CI = 0.6 and 1.0 respectively). Otherwise, the chemiluminescence intensity continued increasing after extrusion passes, and the above trend was remained largely true through the data points for samples containing stabilizers.

The MFR test is a simple and convenient method for monitoring polymer degradation related to chain scission or crosslinking during multi-pass extrusion as MFR is inversely related to the molar mass of the polymer and indicative of the flow characteristics of the polymer melt. Therefore, a decrease of the MFR is indicative of crosslinking and is usually observed during melt processing of PH-HDPE. On the other hand, an increase in MFR relates to chain scission, i.e. reduction in molar mass. Therefore MFR can provide insight in to the overall balance of these reactions.  $A_{CL}$  is plotted against MFR after

passes 0, 3 and 5 in Figure 5 (a), (b) and (c) respectively. It should be noted that after pass 0 there was no marked difference of MFR data between samples, Ph-HDPE exhibited slightly lower value respect to stabilised samples, indicating the melt stabilising efficiency of antioxidants. Figure 5 shows the MFR values resulting from the different AOs (at 250 ppm) after multi-pass extrusion. Clearly, it can be seen that MFR decreases after multi-pass extrusion in all the samples, thereby reflecting a dominance of degradation via crosslinking. The melt stabilization capability of the additives is best assessed after the fifth extruder pass, on this basis the best performance was attained by the phenolics afforded the best melt stabilization performance, and the phosphites predictably afforded relatively poor melt stabilization as did the thioesters.

### Figure 5

Hindered phenolic AOs such as: L-CPL, L-44B25, L-22IB46, L-1790, N-431, A-PP18 and Vitamin E are effective in terms of enabling the polymer to avoid crosslinking as they are effective chain breaking donor antioxidants. These AOs compete effectively with the polymer substrate for the alkyl peroxy radicals; the latter is a propagation reaction resulting in the formation of further macro-alkyl radicals. Hindered phenolic stabilizers would therefore, be expected to lead to lower concentration of macroalkyl radicals and have a rate of reduced addition of macro-alkyl radicals to vinyl group relative to unstabilized PE. This must be responsible for the observed lowering of the extent of crosslinking indicated by lower MFR changes for the stabilized polymers.

Phenolic AOs act as H-donors in order to prevent the degradation of polymers during processing. The activity of the Ph-OH group in terms of being an H donor depends mainly on two parameters: (a) Number of moles of OH groups per unit mass of AO, expressed as molar activity (mol OH/ kg of AO). It is expected that the higher the molar activity, the better the stabilization efficiency of the antioxidant. This figure affects the number of moles of Ph-OH per unit mass of PE. (b) Steric hindrance of the Ph-OH groups (principally by substituents in the 2 and 6 positions of the phenyl ring). This aspect

influences the speed of reaction of the AO with radicals. It is generally expected that the lower the hindrance the better the stabilization efficiency of the antioxidant.

Considering the relationship between  $A_{CL}$  and the melt flow rate, Figure 5, it is evident that after pass 0 the different classes of stabilizer formed clusters of data points with all the primary phenolic antioxidants ( $\diamond$ ) (with the above mentioned exception of N-431) showing the lowest  $A_{CL}$ , significantly below that of the unfilled matrix, and slightly higher values of MFR. The secondary antioxidants (phosphites and thioethers ( $\blacklozenge$ )) formed a cluster above and slightly to the left of the primary AOs. In general, subsequent to multipass extrusion, a decrease in MFR was observed for all samples, accompanied by increase of CL emission, as it has been above mentioned (Figure 5 (b and c)). After pass 3, a tentative negative correlation between  $A_{CL}$  and melt stabilization activity (as measured by MFR) is just beginning to become apparent, and clearly established after pass 5 (Figure 5c). Therefore crosslinking is dominant relative to chain scission. Comparing the response of the additives, it may be seen that primary antioxidants promote better melt flow stability than the secondary antioxidants.

### *3.3. AO effectiveness in ZN-LLDPE and m-LLDPE determined by CL under nitrogen*

The efficiency of a selection of representative primary and secondary stabilizers was evaluated in polyethylenes of different manufacturing histories, ZN-LLDPE and m-LLDPE. The effect of the number of extruder passes on  $A_{CL}$  for these samples is shown in Figure 6 and Figure 7 respectively.

Initially, unstabilised ZN-LLDPE and m-LLDPE samples showed lower chemiluminescence emission compared to Ph-HDPE. That result corroborates with the literature [27] that highlighted a relationship between melt flow and oxidative degradation during processing, and showed the potential importance of polyethylene melt flow rate on its susceptibility to oxidative degradation in melt state. Initiation of oxidative degradation in polymer melt mixing equipment has been attributed to the formation of free

radicals by mechanical breakdown of the polymer chains by shear, rather than by free radicals formed from hydroperoxide decomposition [28], and lower melt flow rate grades of polyethylenes showed higher initial rates of melt oxidation.

On the other hand, it is significant that the m-LLDPE exhibited the lowest initial chemiluminescence emission, which may be attributed to their minimal unsaturation content and low metal ion catalyst residue [29]. Catalyst residues such as transition metals (e.g. chromium) and acidic impurities are believed to catalyse peroxide decomposition and therefore accelerate autooxidation. The observed trend would be in good agreement to the literature, which states that Phillips type PE contain a large amount of vinyl unsaturation [30]. In a previous paper [31], the thermal and photooxidative stability of high, linear low and metallocene grade polyethylene was studied, and the thermal degradation of polyethylenes was found to be influenced by the concentration and nature of different vinyl types. The metallocene polymer exhibited the lowest initial concentration of oxidised products associated with a low oxidation level during the manufacturing process, and showed the lowest CL intensity for initial sample. For HDPE, higher initial concentration of vinyl groups compared to LLDPE and m-PE was found, and that polyethylene resulted to be more susceptible to oxidation, than LLDPE and m-PE.

As it was described for HDPE in previous section, it is evident that after pass 0 all the stabilizers significantly reduce the intensity of the CL emission in comparison of unstabilised ZN-LLDPE and m-LLDPE. The phenolic AOs promoted the most significant reduction as they are likely to be most effective in terms of interruption of the oxidation cycle. After extruder passes 3 and 5, the CL emission from the unstabilized ZN-LLDPE, decreased due to decomposition of the hydroperoxides to give ketone products. However, CL emission from the stabilized samples increased after passes 3 and 5; and consequently all samples containing the stabilizers exhibited higher CL emission than the unstabilized polymer. It may be argued that the increase in CL emission (in some cases to similar levels as the unstabilized polymer after pass 0) observed with the stabilized samples may be due to

progressive depletion of the stabilizer during passes 3 and 5, such depletion will enable the processes observed in the unstabilized sample after pass 0 to continue unabated.

### **Figure 6**

### **Figure 7**

The effect of degree of melt processing on CL emission for the metallocene polymer is shown in Figure 7. Here, the unstabilized m-LLDPE showed a low CL emission after pass 0, and increased after pass 3 then decreased slightly after pass 5. All the stabilizers give a progressive increase in  $A_{CL}$  with increasing extruder passes, and after pass 5 all the stabilizers apart from L-CPL resulted in higher  $A_{CL}$  than the unfilled matrix.

The  $A_{CL}$  versus MFR correlation for ZN-LLDPE and m-LLDPE samples after the fifth extruder pass are plotted in Figure 8 and Figure 9 respectively. In general, subsequent to multipass extrusion, a decrease in MFR was observed for all samples, accompanied by increase of CL emission, as it has been observed for Ph-HDPE. Therefore crosslinking is dominant relative to chain scission. Comparing the response of the additives, it may be seen that primary antioxidants promote better melt flow stability than the secondary antioxidants, showing that L-CPL and APP18 gave the best melt stability which went hand in hand with low  $A_{CL}$ .

### **Figure 8**

### **Figure 9**

#### 4. Conclusions

The thermal stabilizing efficiency of a range of different AOs was determined in different polyethylenes after multipass extrusion by using Chemiluminescence analysis. For Ph-HDPE, the CL intensity decreased for those films containing the stabilisers when compared with the additive free polyethylene after pass 0, and a general inverse correlation between  $A_{CL}$  and the concentration of stabilizing group in the PE was found. After multipass extrusion, for the unstabilised PE a drastically decrease of CL emission intensity was observed, which may be related to the formation of hydroperoxides and their decomposition to give ketone products are involved. Otherwise, the CL emission continued increasing after extrusion passes for samples containing stabilizers, and a good correlation was obtained with the MFR data relative to melt stabilization. The additives resulting in the lowest hydroperoxide content in the polymer were the same as those that promote high melt stability, confirming the role of hydroperoxide functionality and its stability in the oxidative process.

A comparative study was established with polyethylenes of different manufacturing histories, ZN-LLDPE and m-LLDPE. The results showed the importance of polyethylene melt flow rate on its susceptibility to oxidative degradation in melt state, related to the formation of free radicals by mechanical breakdown of the polymer chains by shear. Otherwise, the thermal degradation of polyethylenes may be influenced by the concentration and nature of different vinyl types and metal ion catalyst residue.

For stabilised polymers, almost the same ranking of the effectiveness was observed for antioxidants included on ZN-LLDPE and m-LLDPE samples respect to Ph-HDPE. It can be concluded that CL is a useful method as alternative for significantly increasing the speed of evaluating processing stabilizer effectiveness.

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Tables

**Table 1.** Antioxidants used in this work.

Type of AO	Trade name	Melting Range (°C)	Molar Activity (mol active group/ kg AO)	Molecular Weight
<b>Hindered phenols</b>	Anox PP18 (A-PP18)	49-53	1.9	531
	Naugard 431 (N-431)	liquid	3.17	315
<b>Low hindered phenols</b>	Lowinox CPL (L-CPL)	>105	4.3	700-800
	Lowinox 1790 (L-1790)	159-162	4.3	700
	Lowinox 22IB46 (L-22IB46)	127-129	6.7	298
	Lowinox 44B25 (L-44B25)	208-210	5.2	383
	Vitamine E (Vit E)	Liquid	2.3	431
<b>High performance phosphites</b>	Ultranox 626 (U-626)	170-180	3.31	604
	Ultranox 641 (U-641)	84-103	2.2	450
<b>Phosphites</b>	Alkanox TNPP (A-TNPP)	Liquid	4.36	688
	DVS 005 (DVS005)	-	5	-
<b>Thioester</b>	Naugard DLTD (DLTD)	39-41	1.94	514
	Naugard DSTDP (DSTDP)	67	1.46	683

Figure 1. Structures of the antioxidants used in this work

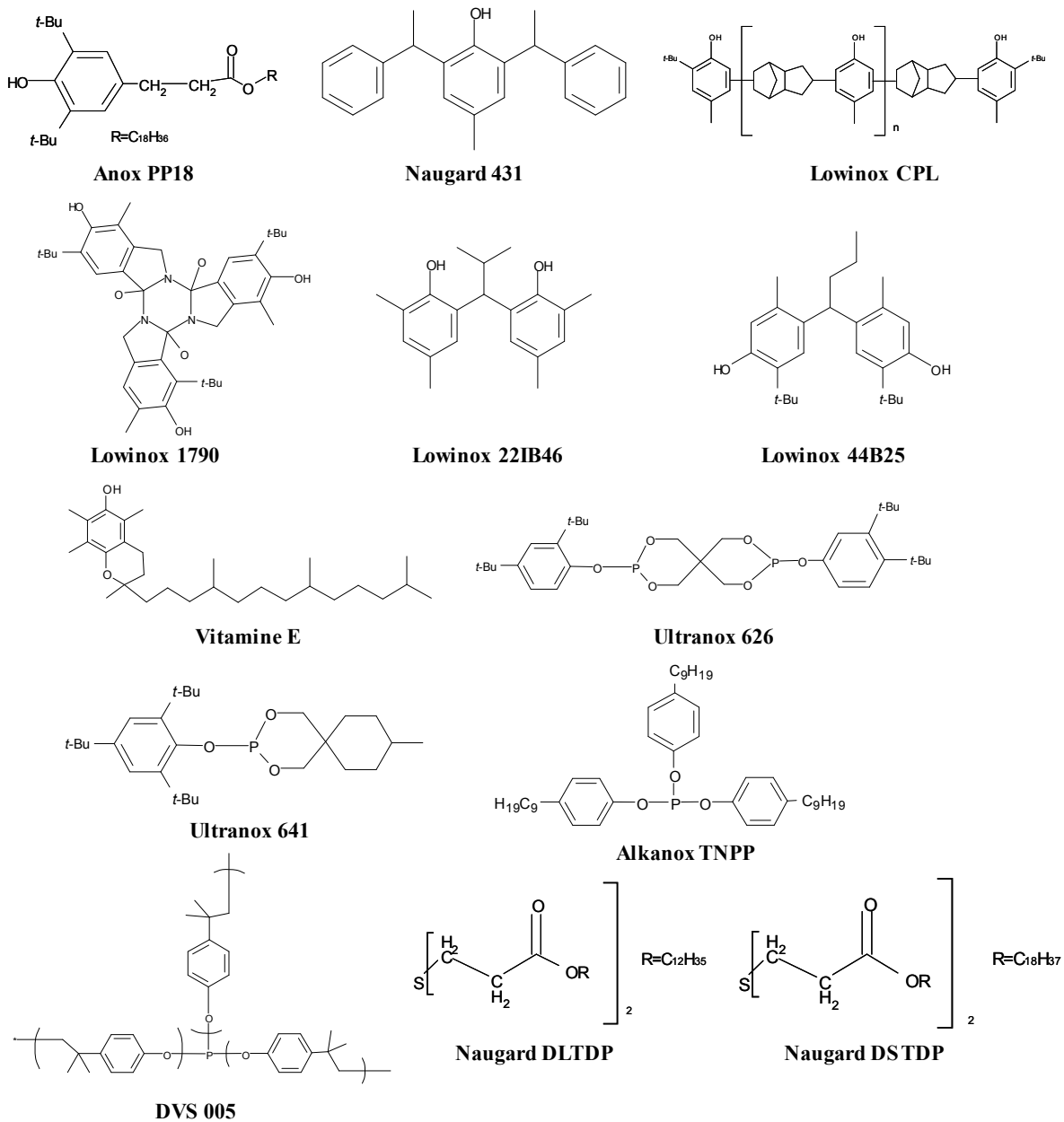


Figure 2. CL curves for the antioxidants in powder bulk from obtained at 180 °C under nitrogen after pass 5. ■ DLTDP, □ L-CPL, ▼ A-PP18, ▲ L-1790, ☆ DSTDP, ● L-22IB46, ◆ U-626, ◇ U-641, + L-44B25.

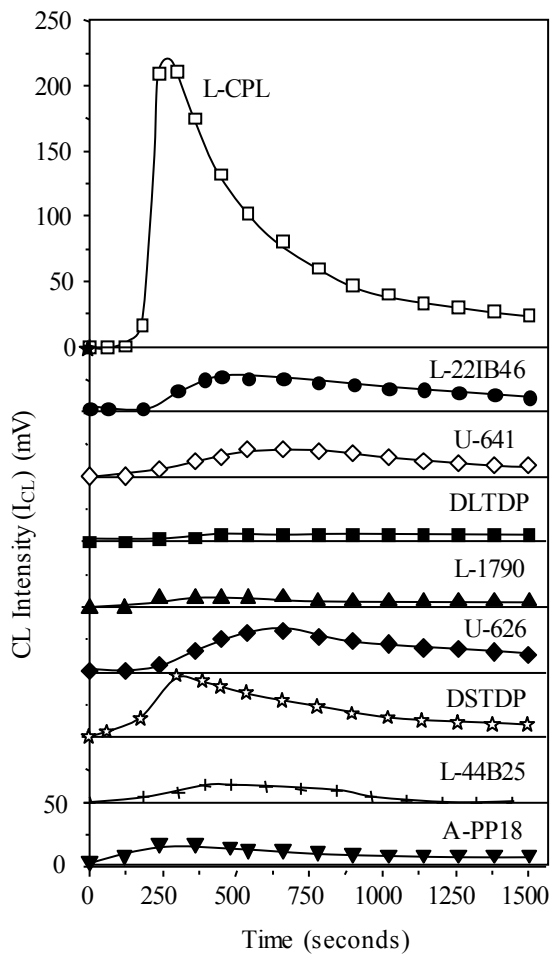


Figure 3. CL curves versus time at 180 °C under nitrogen for free and stabilized (250 ppm) Ph-HDPE films after pass 5 (a) primary AOs (b) secondary AOs.

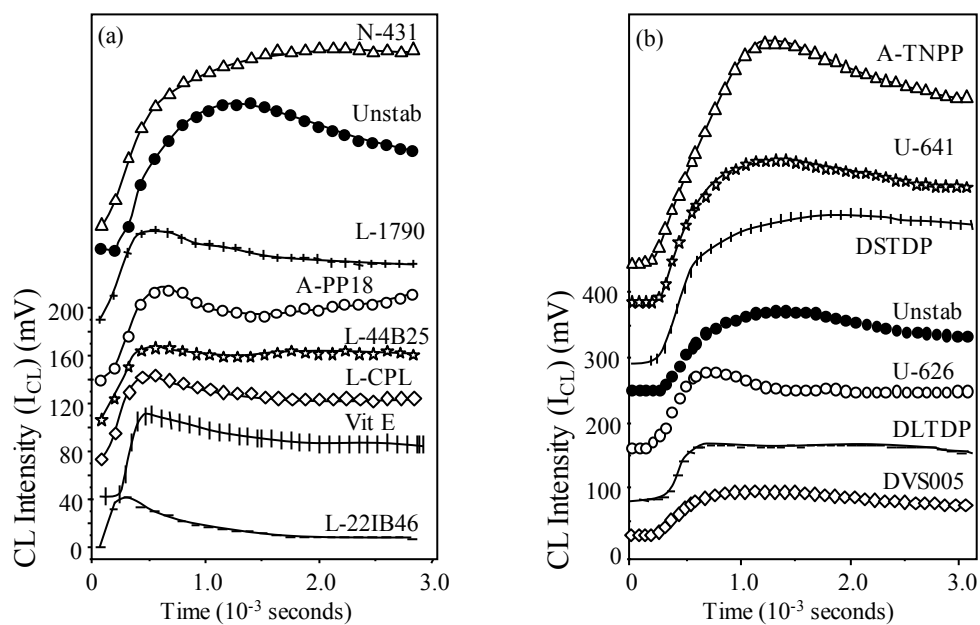


Figure 4. ACL (after passes 0,3 and 5) plotted against number of moles of stabilizing group per kg for Ph-HDPE films.

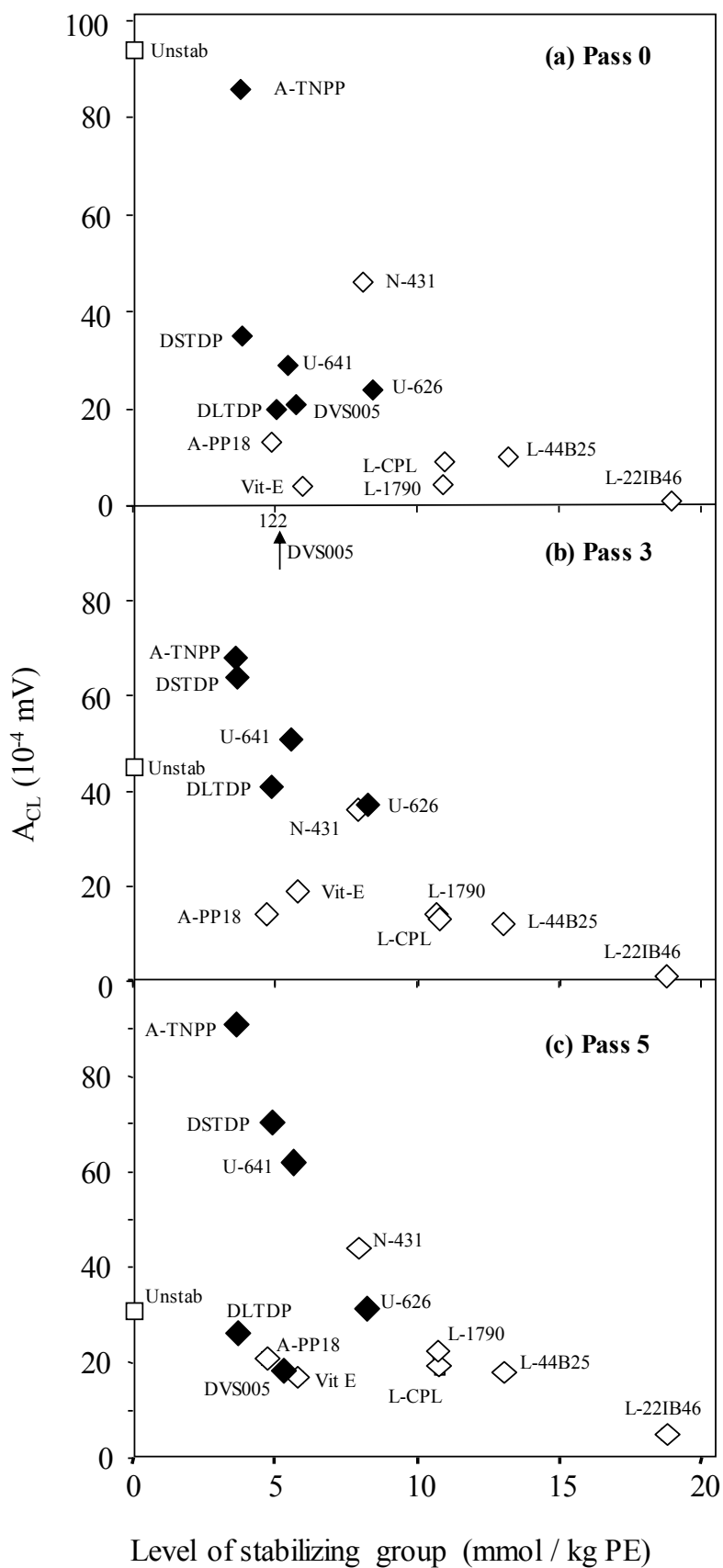
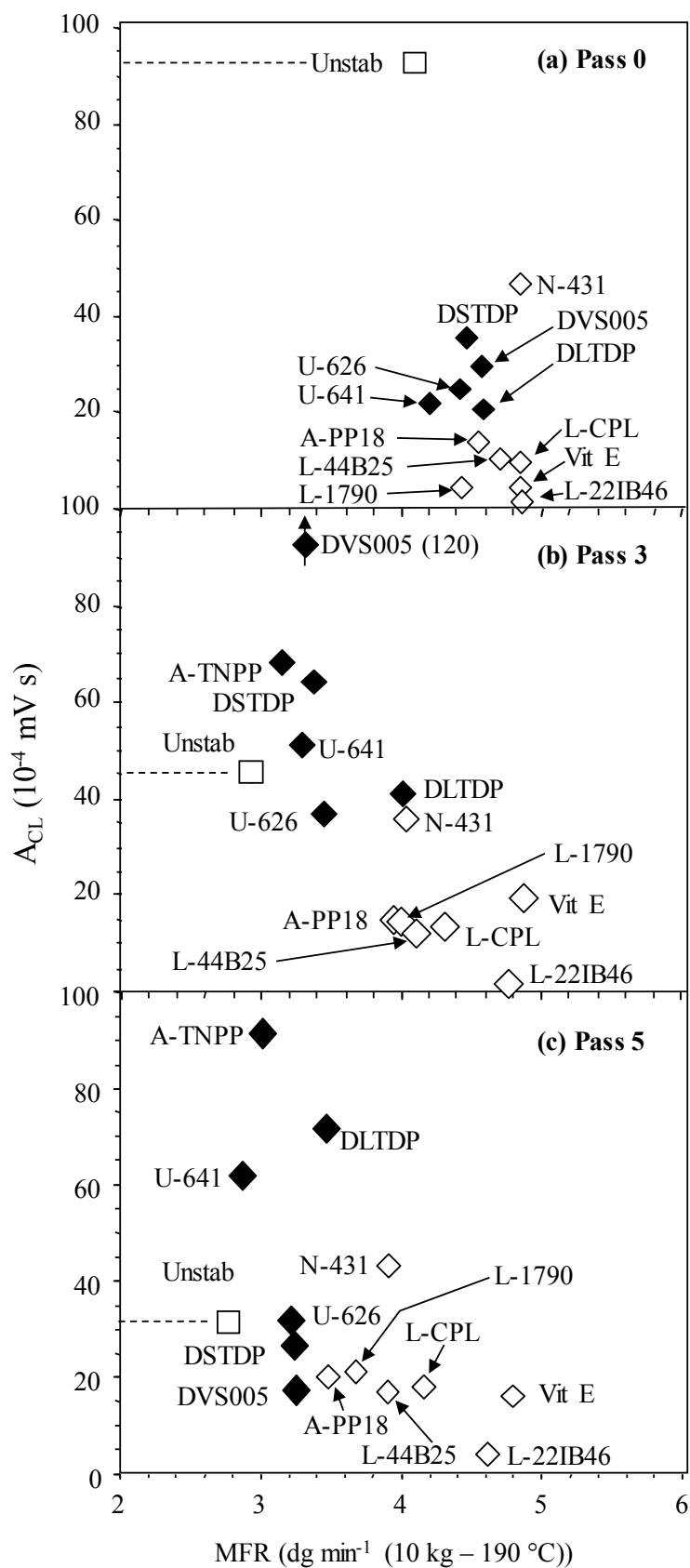


Figure 5. ACL (after passes 0,3 and 5) plotted against MFR for Ph-HDPE films



**Figure 6.**  $A_{CL}$  (after passes 0,3 and 5) at 180 °C under nitrogen for free and stabilized, ZN-LLDPE films.

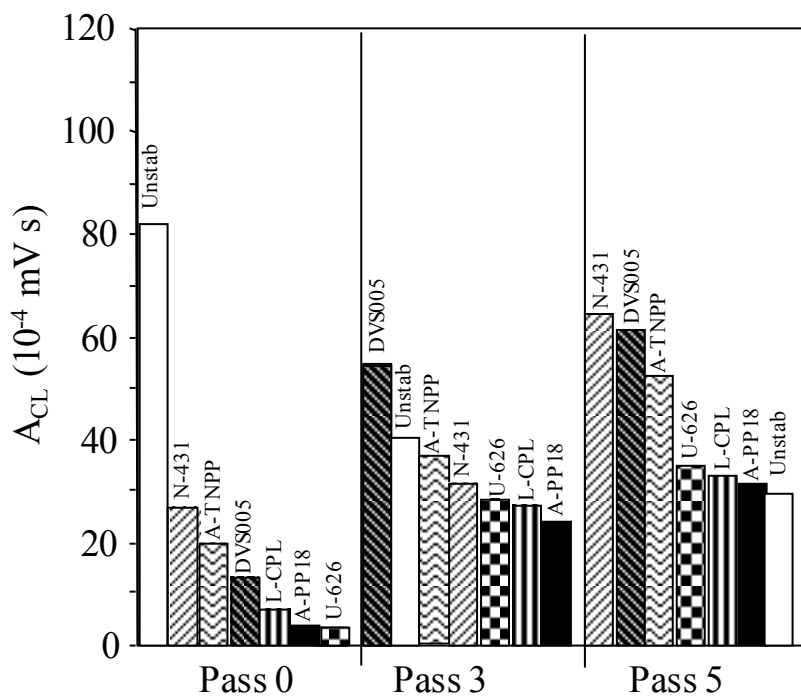




Figure 7. ACL (after passes 0,3 and 5) at 180 °C under nitrogen for free and stabilized, m-LLDPE films.

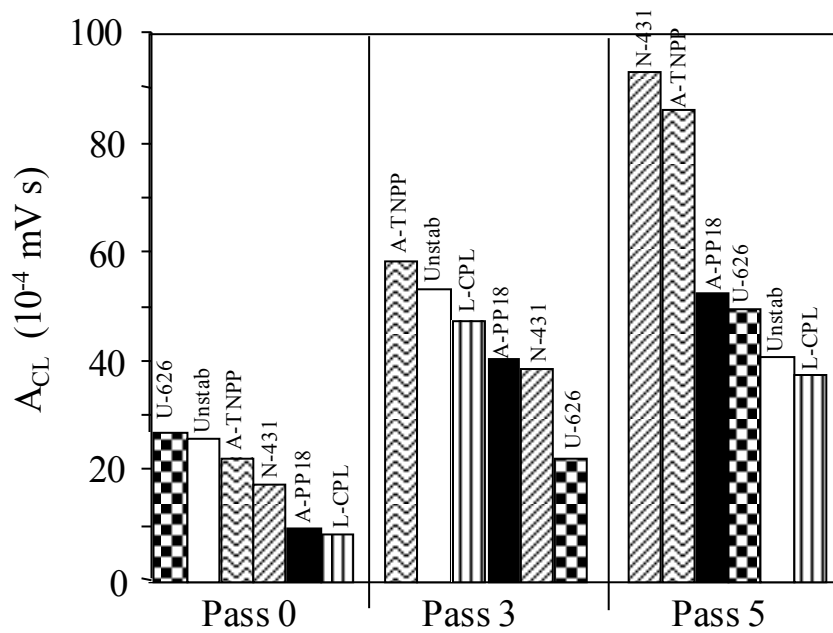
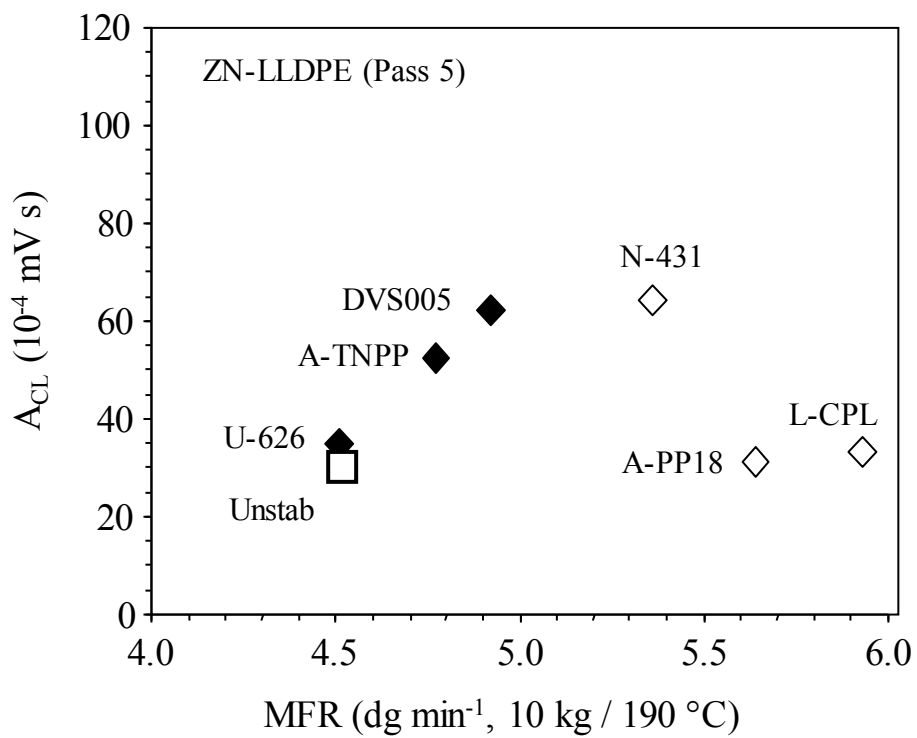


Figure 8. ACL versus MFR correlation plot for samples after the fifth, for ZN-LLDPE films.



**Figure 9.**  $A_{CL}$  versus MFR correlation plot for samples after the fifth extruder, for m-LLDPE films.

