Inhibition of Phosphite Antioxidant Hydrolysis via Synergistic Blends for the Thermal Processing of Polyolefins

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To my parents, Maite and Eric

Declaration

This is to certify that the material contained in this thesis has not been accepted in substance for any other degree and is not currently submitted in candidature for any other academic award.

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ABSTRACT

Secondary phosphite antioxidants are widely used as polymer additives. They are good processing stabilisers and form good synergistic blends with primary phenolic antioxidants. However, some phosphites suffer from poor hydrolytic stability that leads to storage and handling problems. The hydrolytic stability of eight commercial phosphites under controlled temperature and relative humidity conditions were examined. The excellent processing stability afforded by Alkanox P-24 is well known in the literature. However, it was found that Alkanox P-24, (Great Lakes Chemical Corporation) is hydrolytically unstable. Enhancement of its hydrolytic stability is therefore a key objective and some binary and ternary blends were developed using other additives that are often used polymer stabilisation, including the primary antioxidant Tetrakis [methylene 3-(3',5'-di-*tert*-butyl-4-hydroxyhyphenyl)propionate] methane (Anox 20, Great Lakes Chemical Corporation), acid scavengers calcium stearate (DW, Faci SpA) and the hydrotalcite-like compound (DHT-4A, Kyowa Chemical Industry). An improvement in the hydrolytic stability of Alkanox P-24 was found when it was blended with these additives. A comparison with different physical forms of blends (traditional powders versus recently introduced No Dust Blends) was undertaken. Better performance was observed with NDB relative to powders. Spectroscopic studies (FTIR, and Mass Spectrometry) were also undertaken to elucidate the hydrolysis mechanism of the phosphite antioxidant Alkanox P-24. Mechanistic schemes were devised and interpreted. Hydrolysis products of Alkanox P-24 are believed to be involved in the mechanism of stabilisation. In this programme of work, the role of the hydrolysis products was investigated by controlled thermomechanical degradation in an extruder and stabilisation activity evaluated by following the yellowness index and the melt flow rate. The influence of partially hydrolysed Alkanox P-24 on polymer processing was studied. It was found that some active hydrolysis products showed significant antioxidant activity and retarded polymer degradation during processing. Finally, the statistical experimental design proved to be a very powerful tool for studying the impact of each additive in the stabilisation of HDPE. Also the possible interactions between additives present in the additive system were investigated.

CONTENTS

Aims and Objectives of the PhD

Over the last ten years or so, significant advances have been made in polyolefin stabilisation technologies. Process stabilisation is of primary importance, with long-term heat stability being of secondary consideration. Traditional systems for process stabilisation would entail the use of a single phenolic antioxidant, combined with a single phosphite at a specific ratio. One major problem facing the industry, however, is the fact that more effective processing phosphites are hydrolytically unstable. The development of low cost, effective and hydrolytically stable phosphites has been the goal of many manufacturers, but from a structural point of view, this is not feasible. Consequently, this has resulted in the development of alternative technologies. Stabiliser manufacturers have developed binary and multiple blend systems of phosphite antioxidants with other additives that are used in a particular formulation. Great Lakes Chemical Corporation has developed the No Dust Blends (NDBs), which are highly effective in many ways and offer the polymer industry significant advantages over current, free powder technologies. These include, ease of handling, dosing, environmental issues, health and safety, easy cleaning, good dispersability and homogeneity in processing.

Phenolic antioxidants, such as Anox 20 (Tetrakis [methylene 3-(3',5'-di-*tert*-butyl-4-hydroxyhyphenyl)propionate] methane) are the most widely used stabilisers for polymers. They are used in combination with hydroperoxide decomposers or phosphites Alkanox P-24 (bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite). Therefore it is interesting to study the effect of this particular antioxidant on the hydrolytic stability of Alkanox P-24. In addition to antioxidants and processing stabilisers, acid scavengers are the third kind of stabilisers to be found in the basic stabilisation package for polyolefins. Their importance is due to catalyst residues remaining in polymers whose synthesis was catalysed by chloride-containing substances. The more common acid scavengers such as metal stearates and hydrotalcite have been chosen for this study. On the other hand, the impact on the hydrolytic stability of Alkanox P-24 of different polymer co-additives and the influence of different physical forms (powder and NDB) will be investigated for some specific formulations.

Detailed hydrolytic stability investigations on mixed formulations of Alkanox P-24 with other co-additives (phenolic antioxidants, acid scavengers) will be undertaken via High

Performance Liquid Chromatography (HPLC) analysis. Fourier Transform Infrared Spectroscopy (FTIR) and mass spectrometry will be pursued, in depth, with a view to determining, in more detail, the exact nature of the hydrolysis products.

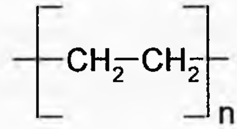
Finally, interactions between additives present in an additive package will be examined in High Density Poly(ethylene) (HDPE). The additive system includes the primary phenolic antioxidant, a secondary phosphite processing stabiliser, an acid scavenger (Calcium stearate), a nucleating agent and an antistatic agent. A two level factorial design of experiment will be used for such purpose. Responses of interest are the melting processing stability, any discoloration and the long-term thermo-oxidative stability of the products.

Chapter 1. INTRODUCTION

1.1. Degradation of polyolefins

1.1.1. Poly(ethylene)

The basic repeat unit of a poly(ethylene) is



Poly(ethylene) was first prepared accidentally from diazomethane by Von Pechmann in 1838[1,18]. Currently poly(ethylene)s are available as the following grades:

High-density poly(ethylene)

High-density poly(ethylene) (HDPE), being the closest in structure to pure poly(ethylene), consists of unbranched molecules. It can have fewer than 7 branch points per 1000 carbon atoms[2].

HDPE is a highly crystalline polymer due to the lack of branches and high linearity, which does not hinder the crystallization process. HDPE has a crystallinity approximately between 65-95 % and densities in the range of approximately 0.94-0.97 g/cm^3 [1,2,3,4,18].

HDPE is used for the manufacture a wide range of products. It has high crystallinity, the highest modulus and the lowest permeability of all the poly(ethylene)s make this polymer suitable for liquid's storage drums and chemical storage tanks.

It can also be used for, food packaging, water pipes, sewer pipes, and natural gas pipes, crates, general merchandising bags, cosmetic containers, toys, etc[1,2,4].

Low-density poly(ethylene)

Low-density poly(ethylene) (LDPE) contains a high concentration of branches that affect the crystallisation process. LDPE can have 60 branch points per 1000 carbon atoms per chain[2]. Due to the high level of branching, the ability to crystallise is much reduced, resulting in a lower density relative to that of high-density poly(ethylene). The density of LDPE is typically in the range of 0.90-0.94 g/cm^3 [4,1,2,18].

The branches from intramolecular chain transfer are usually ethyl and butyl groups together with some longer branches that are product from intermolecular chain transfer and these long branches can also have short chain branches[4,18]:

The branched high pressure polymers have the lowest density, greatest transparency (due to the absence of large crystalline structures), lower melting point, yield point, surface hardness and Young's modulus in tension, because all these properties are dependent on the degree of crystallinity[1]. They have apart from lower crystallinity and greater branching, greater permeability to gases and vapours[1,2]. LDPE has good film forming properties, being suitable for film-blowing processes. Therefore the main application is as film for packaging and cable coatings[2,18].

Linear low-density poly(ethylene)

The linear low-density poly(ethylene) (LLDPE) consists of a poly(ethylene) backbone to which short alkyl groups are attached. The material is produced by the copolymerisation of ethylene with 1-alkenes.

The branches are usually ethyl, butyl and hexyl groups but can be a variety of linear or branched, alkyl groups. LLDPE can also contain some long chain branches but there is not the same degree of complexity as in low-density poly(ethylene)[4]. The density of LLDPE is in the range of 0.90-0.94 g/cm^3.

LLDPE films are used for grocery sacks, fresh produce packages, etc. Due to this similar density to low-density poly(ethylene) they common the markets[18].

1.1.1.1. Production processes of poly(ethylene)

The production processes for poly(ethylene) can be divided in three groups:

1. High-pressure polymerisation

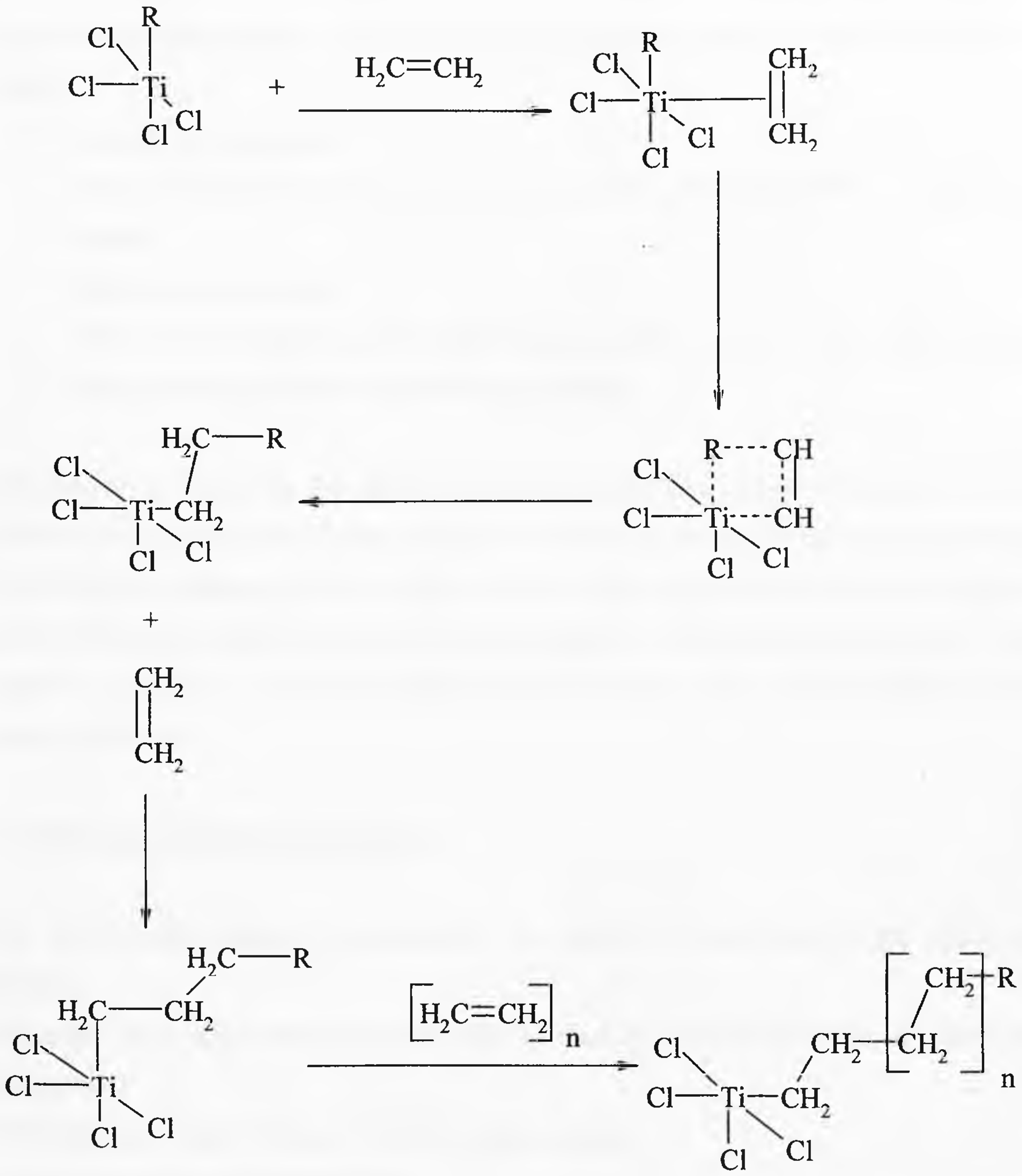
This method is used to produce low-density poly(ethylene) (LDPE). The polymers are produced by high-pressure free radical polymerisation. An initiator is used as the source of free radicals. These initiate the polymerisation process when the monomers are forced into close proximity by high pressure. The radical species abstract a hydrogen atom from an ethylene monomer and the growth of the poly(ethylene) chain continues when the free radical on the end of a growing chain reacts with an ethylene molecule. Termination is achieved when two radicals (a growing chain end, an initiator fragment or an ethylene radical) meet and quench each other[4].

2. Low pressure polymerisation

There are two commercially used methods to produce high-density poly(ethylene) (HDPE). These are based on the use of Ziegler-Natta type catalysts and metal oxide catalysts. These two methods were developed in 1954. These processes allowed the preparation of polymer at lower temperatures and pressures than the polymers obtained with the high-pressure polymerisation. That is the reason why, with the low-pressure polymerisation, higher density and harder polymers were prepared (HDPE) with higher softening points [1,18].

- Ziegler-Natta catalysis:

A Ziegler-Natta catalyst is a complex formed from a base metal alkyl or halide with a transition metal (titanium, vanadium, chromium, molybdenum or zirconium) salt[1,2,4,18]. A well-known catalyst for the polymerisation of ethylene to HDPE is the complex of triethyl aluminum with titanium tetrachloride ($AlEt_3$ + $TiCl_4$). This catalyst was developed in 1953 for the manufacture of HDPE[1,2,5]. The reaction scheme for a Ziegler-Natta catalysed polymerisation of ethylene is shown in Scheme 1.1.



Scheme 1.1. Monometallic Ziegler-Natta catalysed polymerisation of ethylene[4,6].

The active centre is formed from a titanium atom coordinated with four chlorine atoms and an alkyl group in an octahedral configuration with an empty site. The ethylene molecule will coordinate with the titanium atom at this empty site, thereafter inserting between the alkyl and the titanium atom. Repetitive addition of ethylene molecules will lead to the poly(ethylene) chain[4].

Depending on the production process, there are two possible variations of the Ziegler-Natta catalysts:

- Homogeneous catalysis:
  Here, the polymerisation is carried out in solution. The Ziegler-Natta catalysts are soluble.
- Heterogeneous catalysis:
  Here the polymerisation takes place in gas-phase reactors. The Ziegler-Natta catalysts are supported on materials such as silica.

According to the literature, the activity of the non-supported catalysts decreases when the polymerisation is carried out. This can be due to the encapsulation of the catalyst particles by the forming polymer as the reaction proceeds. The supported catalysts have higher activities than the unsupported ones; the activity depends on the kind of silica as well[7]. The supported catalyst on SiO_2 gives better catalytic control of the size and shape of the polymer particles[7].

3. Metal oxide catalysed polymerisation

The Metal oxide catalysed polymerisation is carried out according to the following methods.

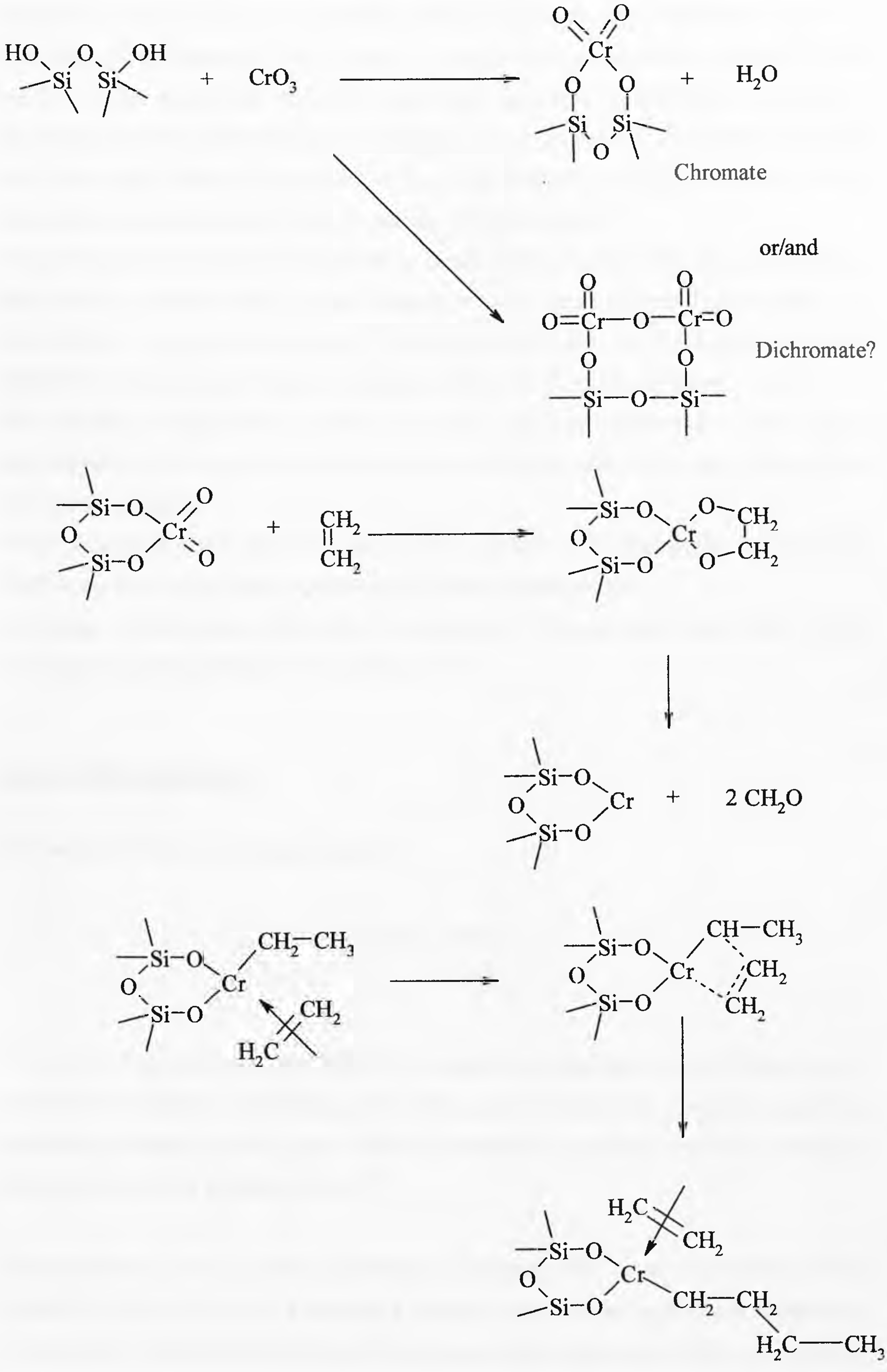
The major silica supported catalysts complexes used in HDPE production are based on chromium[8]:

-Chromocene and silyl chromate (Union carbide process).

-Chromium trioxide (Phillips process).

The Phillips process is the most widely used method for the production of HDPE. The Phillips-type catalysts are based on a highly porous silica or aluminosilicate of low alumina content support that is impregnated with an aqueous solution of chromic acid or chromium trioxide. After drying, the activation of the catalyst is carried out by heating to 500 °C-700 °C in an oxidative environment, which creates surface silyl chromate species. These species are precursors to the activated site[4].

The following reaction scheme (Scheme 1.2) shows the possible proposed mechanism for the chromium oxide catalysis.



Scheme 1.2. Chromium oxide catalysed polymerisation of ethylene[4, 9].

Scheme 1.2 is one is just one of many possible mechanisms that have been proposed[4]. According to the literature, it is not clear if a chromate or a dichromate is formed in the reaction of the silica with the CrO_3. Mc Daniel measured the difference in hydroxyl populations between activated silicas containing varying amounts of chromium and it did not always yield $\Delta OH/Cr$ replacement of two. The findings did not rule out a secondary formation of some dichromate from the initially formed chromate[9].

The production process that is catalysed by metal oxides is carried out using temperature and pressure conditions that are intermediate between those used in Ziegler-Natta and those used in high pressure processes[4]. It is possible to carry out the Ziegler-Natta and chromium oxide catalysed reactions in the gas phase, in a slurry or in solution.

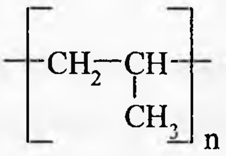
The solution polymerisation process is normally used to produce low molar mass poly(ethylene). The reaction is carried out in a small reactor and allows easy control of the polymer properties.

Slurry (suspension) method is the only method capable of producing the full range of HDPEs from low molar mass materials to high molar mass materials.

Gas-phase polymerisation, the newest technology, is increasingly used due to low investment required and the lower operating costs[15].

1.1.2. Poly(propylene)

The basic repeat unit of poly(propylene) is:



$$\left[-CH_2-\underset{\displaystyle CH_3}{CH}-\right]_n$$

In 1954, G. Natta following the work of K. Ziegler discovered that certain “Ziegler-Type” catalysts were capable of producing high molar mass polymers from propylene and from many other olefins. Over the years, different generations of catalysts have been developed for the production of poly(propylene)[1,10].

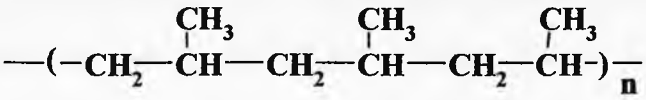
Poly(propylene) (PP) is a linear hydrocarbon containing little or no unsaturation. PP is similar to poly(ethylene) but it contains a methyl group attached to alternate asymmetric carbon atoms on the chain backbone. The presence of the asymmetric carbon atom results in the possibility of tactic variations. Tacticity is the orderliness of the succession of configurational repeating units in the main chain of a regular macromolecule. Crystal structure and crystallization behaviour are, therefore, not only dependent upon molar mass distribution, but also upon the tacticity[11]. The following types of PP can be produced[1,12]:

- Isotactic
- Syndiotactic
- Atactic

The thermal and mechanical properties of PP are dependent on the isotacticity, the molecular weight and on other structure features such as crystallinity[1].

Isotactic poly(propylene)

Isotactic poly(propylene) (iPP) is the most regular because all the asymmetric carbon atoms in the polymer chain are in a constant stereochemical configuration. Therefore, if the chains were formed in a zig-zag configuration (sterically imposible), all the methyl groups would face in the same direction.

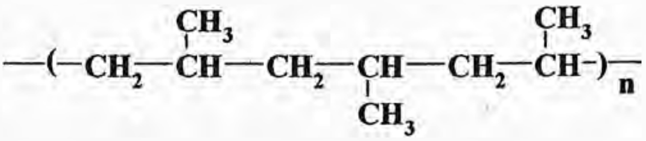


$$-(-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-)_n-$$

Figure 1.1. Example of isotactic poly(propylene)[11,13].

iPP, is able to crystallize as it forms a regularly shaped helix, in which all methyl groups are on the same side of the zigzag plane. Isotactic poly(propylene), therefore cannot dissolve in any solvent at room temperature. This is due to the high crystallinity of iPP. Usually an iPP includes at least 95% of isotactic configuration. The remaining 5% corresponds to other configurations.

Syndiotactic poly(propylene)



$$-\!\left(-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2-\overset{CH_3}{\overset{|}{C}H}-\right)_n\!-$$

Figure 1.2. Example of syndiotactic poly(propylene)[11,13].

Syndiotactic poly(propylene) (sPP) is defined by the methyl groups being arranged alternatively on either side of the zigzag chain. sPP is also able to crystallise as it forms a regular zigzag helix. The stereochemistry of the PP depends upon the catalyst system and the solvent system used in the polymerisation. It can be appreciated that a random mixture of isotactic and syndiotactic placements will result in a random helix that will be unable to pack into a crystal lattice. Atactic PP used to be a bi-product of earlier Ziegler-Natta polymerisations, and has some commercial applications as sealants, mastics and bitumens.

1.1.3. Degradation of poly(ethylene) and of poly(propylene)

The degradation of polyolefins takes place when some chemical and/or physical processes lead to a deterioration of the quality of the polymer and the loosening of its final functionality.

There is a variety of factors that can promote the degradation of polyolefins including oxygen, heat, catalyst residues, water, light, ultrasound, etc. Polyolefin degradation gives rise to the production of a range of products that may be volatile and of low molar mass. The structure of the polymer can also be modified[5]. Degradation includes embrittlement, colour development, loss of clarity, changes in viscosity[4], etc. There are different types of degradation such as, thermal, mechanical, ultrasonic, hydrolytic, chemical, biological, oxidative and radiation[14].

1.1.3.1. Thermo-oxidative degradation

The following reactions take place during the thermo-oxidative degradation of polyolefins, e.g. poly(ethylene).

1. *Initiation*

$$\begin{matrix} R-H \\ R-R \end{matrix} \xrightarrow{h\nu, T, \text{shear}} R\cdot \tag{1}$$

As it can be observed in Reaction 1, the first step in the degradation of polyolefins is the generation of alkyl radicals. During the initiation step, primary alkyl radicals, R· are formed. The generation of radicals can be due to either abstraction of a hydrogen atom that is attached to the backbone or, more rarely, via cleavage of the backbone chain to yield terminal radicals. The latter process is rarely encountered, as severe mechanical deformation is required[4]. The rupture of C-H bonds is more frequent during chemical or radiation attack[4].

The formation of radicals can also be due to the presence of catalytic residues (such as transition metals and radical fragments), impurities in the monomer and oxygen. Oxygen can react with alkyl radicals giving peroxy radicals that can abstract hydrogen from the polymer and regenerate another alkyl radical (Reaction 3). Furthermore, during extrusion, additional peroxy radicals are formed under conditions of high temperature and mechanical shear[15].

Initiation by chain scission, followed by the generation of radicals occurs more readily at weak points in the chain such as allylic groupings[5].

2. *Propagation*

$$R\cdot + O_2 \longrightarrow ROO\cdot \tag{2}$$

$$ROO\cdot + RH \longrightarrow ROOH + \overset{\substack{\text{generation of alkyl radicals} \\ \uparrow}}{\boxed{R\cdot}} \tag{3}$$

$$RH + O_2 \longrightarrow R\cdot + HOO\cdot \tag{4}$$

The last reaction (Reaction 4) is complicated because of kinetic and thermodynamic issues[4].

During propagation, alkyl radicals react with molecular oxygen to generate peroxy radicals (Reaction 2). In a second reaction, the peroxy radicals will abstract a hydrogen from the polymer chain to regenerate other alkyl radicals, R·. The whole process is autocatalytic[4,15].

In poly(ethylene), the propagation step is limited to the non-crystalline regions into which the absorbed oxygen is free to migrate. In the case of high crystallinity samples, where the concentration of absorbed oxygen and its rate of diffusion are low, the rate of the first propagation reaction will be retarded relative to that of samples of lower crystalline content[4]. The rate of Reaction 2 is dependent on the concentration of oxygen in the mixer or extruder. Under low oxygen conditions, the hydroperoxides, formed in Reaction 3, will undergo thermolysis to give hydroxyl radicals and alkoxyl radicals (Reaction 5)[16]. In the absence of oxygen, the radicals migrate until they meet other radicals; this termination reaction causes cross-linking to dominate[4,17].

The oxidative degradation reaction is quite slow during the early stages of degradation (giving rise to the induction period) and is the rate determining step for all the other processes. There is an acceleration of the reaction when the concentration of the resulting hydroperoxides increases[15].

The rate of the Reaction 6, in which a hydrogen atom is abstracted from the polymer, is dependent on the chemical structure of the polymer chain. The abstraction of a hydrogen atom from a tertiary carbon atom requires less energy than is needed for the extraction of a H-atom from secondary and primary carbons atoms[4].

3. Branching

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{HO\cdot} \qquad (5)$$

$$\mathrm{RO\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R\cdot} \qquad (6)$$

$$\mathrm{HO\cdot} + \mathrm{RH} \longrightarrow \mathrm{H_2O} + \mathrm{R\cdot} \qquad (7)$$

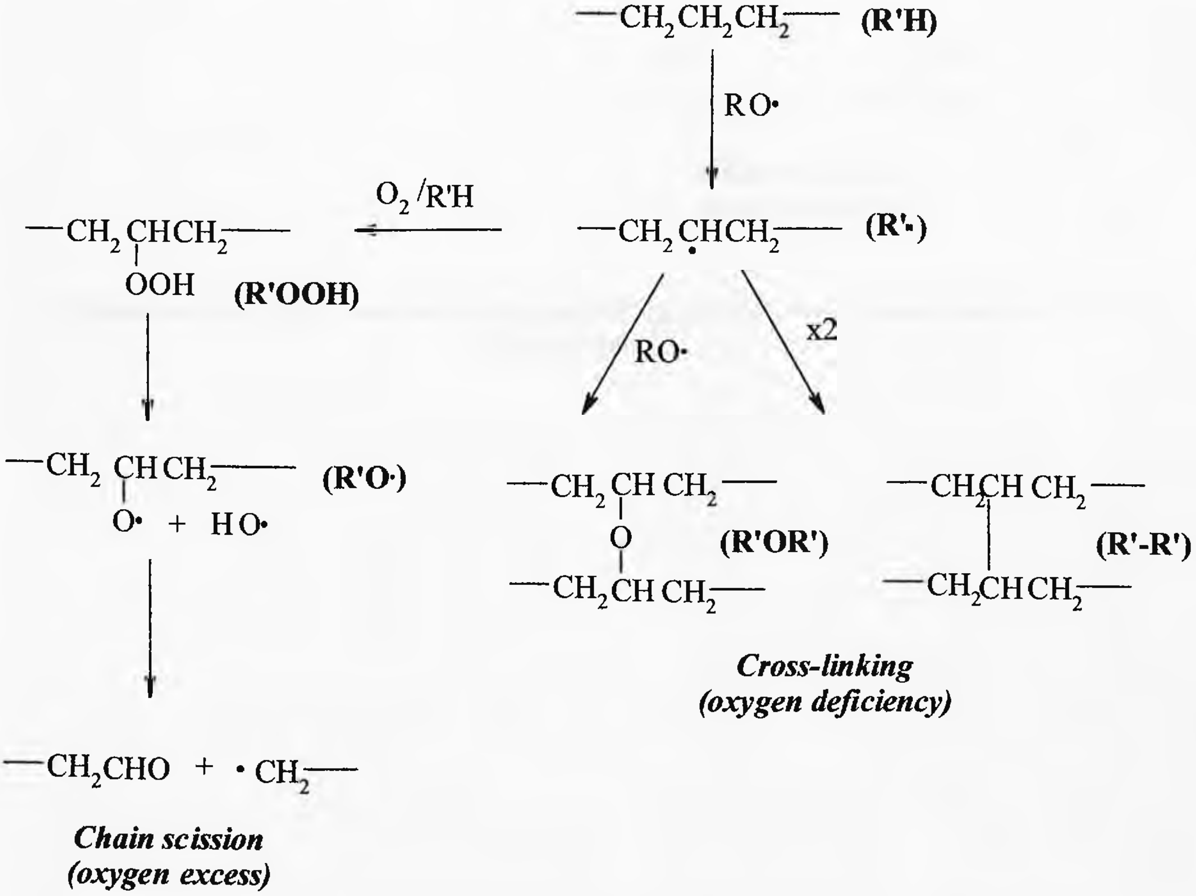
The hydroperoxides decompose to yield alkoxy radicals and hydroxyl radicals (Reaction 5). The rate of this reaction increases with rising temperature, exposure to light and by the presence of metal ions[15].

The alkoxy radicals and the hydroxyl radicals may abstract a hydrogen atom from the polymer chain to generate an alcohol, water and more alkyl radicals (Reaction 6 and 7)[4].

4. *Chain scission*

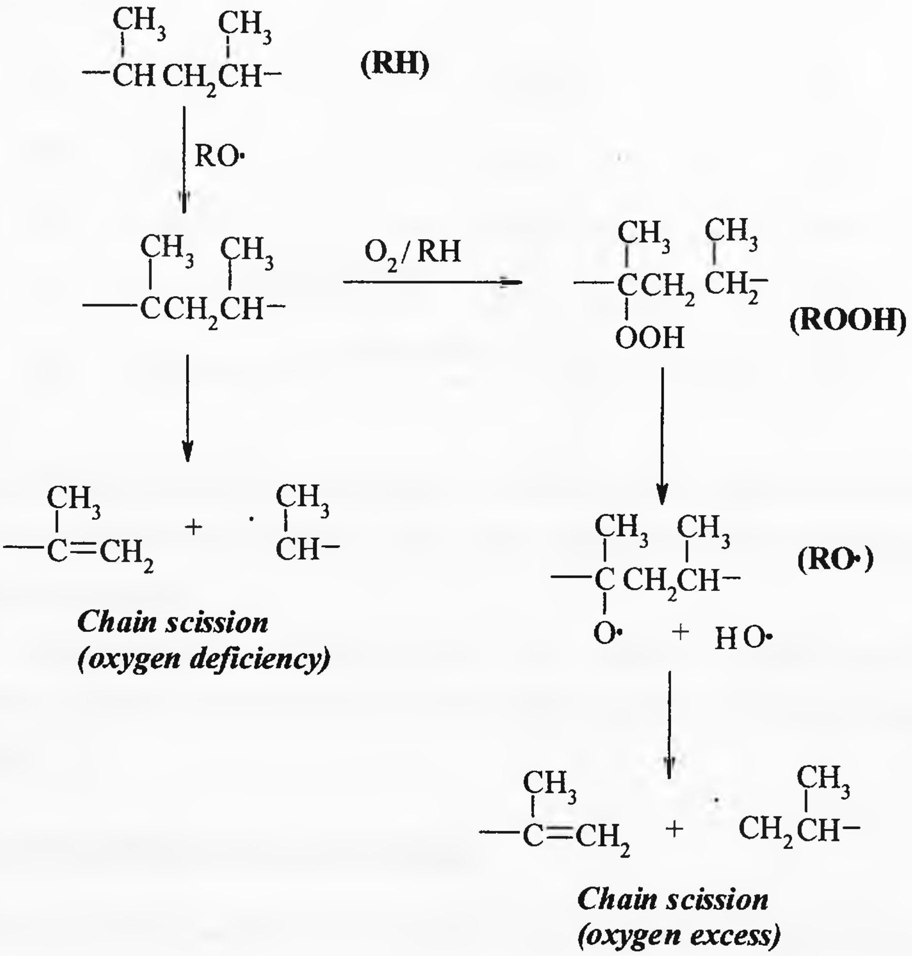
Polymers of different structures show different levels of degradation during processing. Poly(propylene) undergoes an increase in melt flow rate (MFR) during normal melt processing, in a non-closed system such as an extruder. However, under the same conditions, poly(ethylene) shows a decrease in MFR due to cross-linking reactions. Increasing the concentration of oxygen by deliberately allowing access of air leads to predominant chain scission in all polymers. At low oxygen concentrations poly(propylene) undergoes depolymerisation[16]. When chain scission reactions occur more rapidly than cross-linking reaction, an overall decrease in the average molar mass will be observed[4]. The processing degradation reactions of poly(ethylene) and poly(propylene) are summarised in Schemes 1.3 and 1.4 respectively.

Poly(ethylene)



Scheme 1.3. Alternative reactions of alkyl radicals during high-temperature processing of poly(ethylene)[16].

Poly(propylene)



Scheme 1.4. Alternative reactions of alkyl radicals during high-temperature processing of poly(propylene)[16].

5. *Termination*

$$R\cdot + ROO\cdot \longrightarrow ROOR \qquad (8)$$

$$R\cdot + R\cdot \longrightarrow R{-}R \qquad (9)$$

$$R\cdot + RO\cdot \longrightarrow R{-}O{-}R \qquad (10)$$

$$R\cdot + R\cdot \xrightarrow{\text{Disproportionation}} RH + \text{olefin} \qquad (11)$$

$$R\cdot + H_2C{=}CH{-}R' \xrightarrow{\text{Polymerisation}} R{-}CH_2{-}HC\cdot{-}R' \qquad (12)$$

The termination step involves the quenching of alkoxy and alkyl radicals by reaction with one another or with atomic hydrogen. When alkyl radicals from adjacent chains quench, cross-linking is produced[4].

With the disproportionation reaction there is no change in molar mass of the macromolecule, whilst combination of two macroalkyl radicals leads to an increase in the molar mass[15].

1.1.3.2. Cross-linking versus chain scission

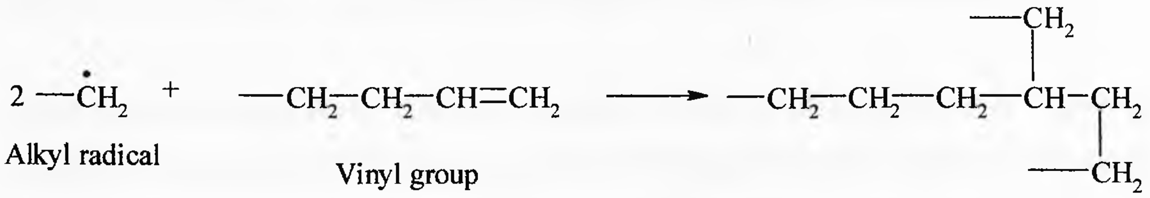
Cross-linking and chain scission are competing reactions during the processing of high-density poly(ethylene) (HDPE).

Among the factors that influence the course of degradation, (i.e., cross-linking or chain scission/oxidation takes place) are the abundance of alkyl radicals and the level of absorbed oxygen. When the initiation step takes place rapidly or there is low concentration of oxygen, cross-linking predominates. When there is abundant oxygen, the propagation step will be followed after the initiation step, leading to autoxidation (Scheme 1.3)[4]. In HDPE, another factor that affects the course of degradation is the presence of olefinic unsaturation in the virgin polymer[4]. Typical double-bond structures are vinyl ($CH_2{=}CH{-}$, 990-910 cm^{-1} in the IR spectrum), vinylidene ($CH_2{=}C{<}$, 890 cm^{-1}) and trans-vinylene ($-CH{=}CH-$, 970 cm^{-1}).

The presence of one or other group depends on the nature of the catalyst (supported or non supported) used for the polymerisation process[18].

Cross-linking has always been attributed to radical coupling, but this is much less significant than the addition reaction of alkyl radicals to vinyl unsaturation[19,20,21,22].

Although different theories have been observed to explain the cross-linking phenomena that arise when the polymer is processed, the addition of alkyl radicals to vinyl groups (Scheme 1.5) and long-chain branching formation are considered to be the major routes to crosslink formation during the melt processing of poly(ethylene)[19,20].



$$2\ -\dot{C}H_2 + -CH_2-CH_2-CH=CH_2 \longrightarrow -CH_2-CH_2-CH_2-\overset{\overset{-CH_2}{|}}{CH}-\underset{\underset{-CH_2}{|}}{CH_2}$$

Scheme 1.5. Addition reaction of alkyl radical to vinyl group.

The addition of alkyl radicals to vinyl groups is accompanied by a decrease in the concentration of vinyl groups present in the original polymer[19,22].

Apart from the decrease in concentration of vinyl groups, an increase in concentration of trans-vinylene groups has been observed. Although the vinylidene and the trans-vinylene groups do not participate in addition reactions (due to steric hindrance), the formation of such unsaturation has been attributed to disproportion reactions of secondary alkyl radicals at low oxygen concentrations[19].

The temperature and synthesis route also influence the relative rates of crosslinking and chain scission reactions. Johnston studied the behaviour of different poly(ethylene)s using a torque rheometer. It was found that lower melt processing temperatures caused cross-linking to predominate whereas chain-scission predominated at higher melt temperatures[20,5,23].

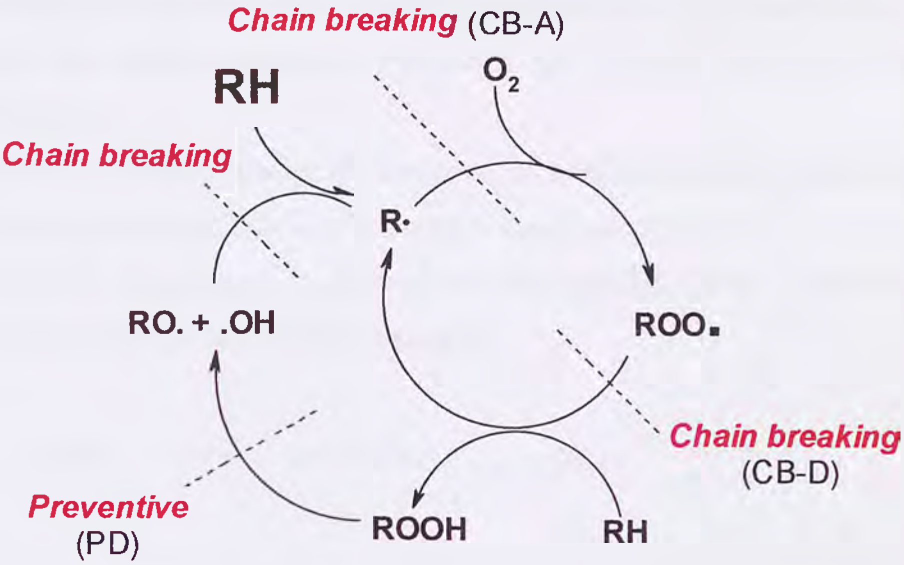
Finally, another factor influencing the predominance of chain scission or crosslinking are the shear forces experienced by the polymer during processing conditions. It has been observed that mechanical shear (thermo-mechanical degradation) favours formation of long chain branches compared to thermal degradation (without shear) at a given temperature[23].

Johnston concluded that if the oxidation rate of different poly(ethylene)s, processed under the same processing conditions, is similar, the main factor influencing the route of degradation during processing is the unsaturation content[20]. Therefore, in a Ziegler-Natta HDPE, where the vinyl concentration is low, there is no cross-linking under extrusion conditions. An increase in MFR (decrease in molar mass) has been observed during extrusion, in a range of different studies. This, therefore confirms the predominance of chain scission[19,21,23]. On the other hand, for poly(ethylene) that has been produced using the Phillips process, the opposite has been observed, the MFR decreased (molar mass increased) during the multiple extrusions studied. The predominance of crosslinking reactions was attributed to the higher concentration of vinyl groups in the polymer[19,21,23].

In summary, the degradation behaviour associated with polyolefins depends on processing conditions (the severity of the shear and the melt temperature) and presence of oxygen. Vinyl unsaturation in the polymer also leads to a predominance of crosslinking.

1.2. Mechanism of action and classification of antioxidants

The terms "antioxidants" covers different classes of compounds that can interfere with the oxidative cycle to inhibit or to retard the oxidative degradation of polymers. Scheme 1.6 shows an outline mechanism of action for the two major antioxidant types. These are categorized according to the manner in which they interrupt the overall oxidation process: the chain breaking antioxidants and the preventive antioxidants.



Scheme 1.6. Oxidative degradation processes and antioxidant mechanism.

Chain breaking (CB) antioxidants interrupt the primary oxidation cycle by removing the propagating radicals, ROO· and R·. Therefore these antioxidants are often referred to as primary antioxidants.

Chain breaking donor antioxidants (CB-D) are electron donors or hydrogen atom donors. They are capable of reducing ROO· to ROOH, as shown in Reaction 13.

Hindered phenols and aromatic amines are important examples of commercial CB-D antioxidants.

Chain breaking acceptor antioxidants (CB-A) act by oxidising alkyl radicals in a stoichiometric reaction. Quinones (Q) and stable free radicals, which can act as alkyl radical trapping agents, are good examples of CB-A antioxidants (Reaction 14).

$$\mathrm{AH} + \mathrm{ROO}\bullet \longrightarrow \mathrm{ROOH} + \mathrm{A}\bullet \qquad (13)$$

$$\mathrm{Q} + \mathrm{R}\bullet \longrightarrow \text{Non radical products} \qquad (14)$$

On the other hand, preventive antioxidants (secondary antioxidants) interrupt the second oxidative cycle by preventing or inhibiting the generation of free radicals. The most important preventive mechanism is the non-radical decomposition of hydroperoxides.

Phosphite esters and sulphur-containing compounds are the most important classes of peroxide decomposers.

The simple molecule trialkyl phosphite decomposes hydroperoxides stoichiometrically (PD-S) to yield phosphates and alcohols, as shown in Reaction 15.

Sulphur compounds decompose hydroperoxides catalytically (PD-C) whereby one antioxidant molecule destroys several hydroperoxides.

$$\mathrm{P(OR')_3} + \mathrm{ROOH} \longrightarrow \mathrm{O{=}P(OR')_3} + \mathrm{ROH} \qquad (15)$$

1.2.1. Phosphite antioxidants

Phosphites and phosphonites are widely used on a large scale as non-discolouring antioxidants for the stabilisation of organic materials against degradation during fabrication, processing and long-term applications[24].

All phosphites and phosphonites are hydroperoxide-decomposing secondary antioxidants, as previously mentioned.

Phosphorus antioxidants are used in synergistic combination with hindered phenols and other stabilisers[15]. However, the sterically hindered aryl phosphites and phosphonites can be effective enough on their own without the need for primary phenolic antioxidants. This is especially the case during processing stabilisation of polyolefins[24].

Phosphites decompose hydroperoxides into non-radical products, suppressing the chain-breaking step (hydroperoxide decomposition into hydroxyl radicals and alkoxy radicals), while hindered phenols act as primary antioxidants by trapping alkyl peroxy radicals and alkoxy radicals[25].

1.2.1.1. Hydroperoxide-decomposing antioxidant action of phosphites and phosphonites

1.2.1.1.1. The stoichiometric reaction of phosphites and phosphonites with hydroperoxides

Organic phosphites reduce hydroperoxides, to give alcohols and the corresponding phosphate esters, which are non-reactive, non-radical, and thermally stable products. The reaction proceeds with a 1:1 stoichiometry by a non-radical mechanism[15,24,26].

$$\mathrm{ROOH} + \mathrm{P(OR')_3} \longrightarrow \mathrm{RO^-} + \mathrm{HO{-}\overset{+}{P}(OR')_3} \longrightarrow \mathrm{ROH} + \mathrm{O{=}P(OR')_3} \qquad (16)$$

The reactivity of the phosphites towards hydroperoxides depends mainly on the polar groups and the steric groups that are bound to the phosphorus atom. The reactivity decreases with increasing electron-acceptor ability and size of the substituent groups that are bonded to the phosphorus atom[24,27], Thus,

Phosphonites>alkyl phosphites>aryl phosphites>hindered aryl phosphites

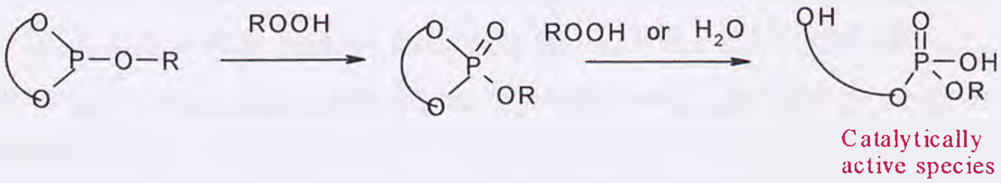
Phosphonites react with hydroperoxides in an analogous way to phosphites, giving the corresponding phosphonates[24].

During the processing of polymers, Reaction 16 may be unlikely because the thermal stability of hydroperoxides at the processing temperatures is very poor. Also hydroperoxides undergo very fast thermal scission to RO· and ·OH. Although the non-radical decomposition of hydroperoxides is well established as the main mechanism responsible for the processing stabilisation performance of phosphites, the importance of this mechanism is not clear[25].

1.2.1.1.2. Catalytic decomposition of hydroperoxides by phosphites and phosphonites

In addition to and following the stoichiometric reaction, five-membered cyclic phosphites are capable of reacting with alkyl hydroperoxides catalytically, so that more than a stoichiometric amount of hydroperoxide is decomposed by these phosphites[24,27,28].

This reaction (Scheme 1.7) takes place by the acidic transformation products of these phosphites, formed during the reaction with hydroperoxides[27,28].



Scheme 1.7. Formation of acidic phosphoric acid diesters from five-membered cyclic phosphites[27].

1.2.1.2. Chain breaking antioxidant action of phosphites and phosphonites.

It is generally accepted that certain phosphites, particularly the sterically hindered aryl phosphite, are also able to act as chain-terminating antioxidants in addition to their hydroperoxide-decomposing action[24,25,29,30].

In order to act as a chain-breaking antioxidant, a stabiliser must have two fundamental requirements: it must be able to compete effectively with the substrate (RH) for the chain-propagating peroxy ($RO_2\cdot$) radicals and it must form an efficient chain-terminating agent in its reaction with RO_2 radicals[24,30].

Hindered aryl phosphites always meet the second requirement. They react with alkylperoxyl radicals to give hindered aryloxyl radicals that are able to terminate the auto-oxidation chain reaction, as shown in Reactions 17, 18 and 19[24,27,30,31].

$$ROO\bullet + P(OAr)_3 \longrightarrow ROOP(OAr)_3 \longrightarrow RO\bullet + O{=}P(OAr)_3 \qquad (17)$$

$$RO\bullet + P(OAr)_3 \longrightarrow ROP(OAr)_3 \longrightarrow ROP(OAr)_2 + ArO\bullet \qquad (18)$$

$$ROO\bullet + ArO\bullet \longrightarrow \text{Inactive products} \qquad (19)$$

On the other hand, alkyl phosphites react with $RO_2\cdot$ radicals to form the corresponding phosphates in a rapid chain oxidation involving $R\cdot$ and $RO\cdot$ radicals, which are unable to terminate the auto-oxidation chain, as shown in Reactions 20 and 21[27,30]. The reaction always leads to the formation of new, active radicals propagating the oxidation chain reaction.

$$ROO\bullet + P(OR')_3 \longrightarrow ROOP(OR')_3 \longrightarrow RO\bullet + O{=}P(OAr)_3 \qquad (20)$$

$$RO\bullet + P(OR')_3 \longrightarrow ROP(OR')_3 \longrightarrow R\bullet + O{=}P(OR')_3 \qquad (21)$$

To meet the first requirement for chain-breaking antioxidant action, phosphites must be able to react with peroxyl radicals faster than the substrate RH[30]. The efficiency of aryl phosphites as chain-breaking antioxidants is much lower than that of phenols at low temperature[27,31].

Schwetlick studied the kinetics and mechanism of the reactions of phosphites with $RO_2\cdot$ and $RO\cdot$ radicals that were generated by the thermal degradation of azo-bis-isobutyronitrile (AIBN) in the presence of oxygen and of di-tert-butyl peroxalate (DTBPO). It was found that aliphatic phosphites react completely with AIBN and oxygen via cyanoisopropylperoxyl radicals according to Reactions 20 and 21 to give the corresponding phosphates in a rapid chain reaction, whereas the reaction of sterically hindered aryl phosphites initially results in formation of an equimolar mixture of phosphate and phosphite, according to Reactions 17 and 18 in a slow non-chain process[30,31,32].

With *tert*-butoxyl radicals from DTBPO, aliphatic phosphites react to form the corresponding phosphates according to Reaction 21. The aryl phosphates preferently give the *tert*-butyl phosphite, which is easily oxidised to form the *tert*-butyl phosphate (Reaction 18)[30,31,32].

On the other hand, phenyl phosphite reacts with cyanisopropoxyl and tert-butoxyl radicals in a different way. With the former, corresponding phenyl phosphates are built up by β-scission of the intermediate phosphoranyl radicals, whereas with the latter, *tert*-butyl phosphites are formed by α-scission[30,31,32].

Therefore, the chain-breaking efficiency of phenyl phosphites depends on the chemical nature of the substrate to be stabilised. Furthermore, the chain-breaking efficiency can be due to reaction products (mainly phenols) formed by hydrolysis of aryl phosphites and phosphonites during the oxidation[27,31].

1.3. Hydrolytic stability of phosphites

It is well known that phosphites inhibit thermo-oxidative changes during processing and that they provide good protection to polyolefins in combination with phenolic antioxidants.

There are different kinds of phosphites used to protect the polyolefins against thermo-oxidative degradation. Structural variation of phosphites influences their hydrolytic stability, i.e.: hindered aryl phosphites show greater hydrolytic stability than the alkyl-aryl and alkyl phosphites[15,33].

An example of a phosphite with poor hydrolytic stability is bis (2,4-di-*tert*-butylphenyl)-pentaerythritol diphosphite (Alkanox P-24, Great Lakes Chemical corporation). A representation hydrolysis reaction is shown in Reaction 22.

Hydrolysis reaction of phosphites

$$P(OR')_3 + H_2O \longrightarrow HOP(OR')_2 + R'OH \qquad (22)$$

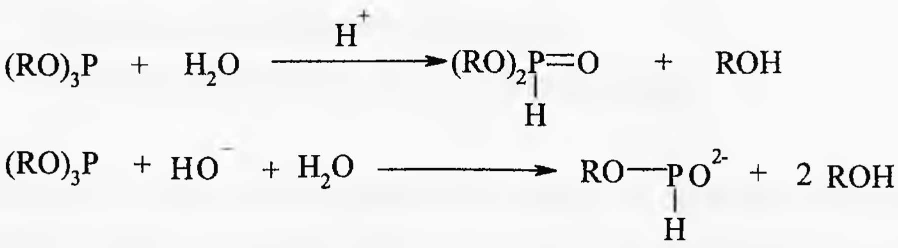
Due to such poor hydrolytic stability, phosphite antioxidants degrade during storage[34]. As a consequence, caking can occur.[35] Acidic products formed during hydrolysis can also cause corrosion of the processing equipment and further catalyse the hydrolysis[35]. Moreover, when solid phosphites start to hydrolyse, they can become sticky and cause caking problems in the packaging feeders[33]. On the other hand, it is well known that they are good processing antioxidants, as well as good antioxidants for avoiding colour development in the polymer, during processing. Also, when the phosphites are properly stored hydrolysis problems are reduced.

There are different approaches to enhancement of the hydrolytic stability of phosphites. According to studies carried out by Aksnes, the hydrolysis of tripropyl phosphite in water with acetonitrile was significantly retarded using a small amount of a tertiary base[35,36]. This effect can be commercially achieved by addition of triethanolamine to phosphites or by incorporation of amine functionality into the structure of the phosphites[37]. Triisopropanolamine (TiPA) has also been shown to enhance the hydrolytic stability of phosphites[33]. Reducing the electron density at the phosphorus atom and synthesising a phosphite that contains a piperidinyl group, which is typical of HALS (Hindered amine light stabilisers) could also improve hydrolytic stability[35,38]. Apart from improving the hydrolytic stability, a strong synergistic effect in thermal and photoxidation of poly(propylene) has been found for such molecules that feature both HALS and phosphite moieties[39,40,41,42].

However, reactions in the presence of acids and metal cations as Cu^{+2},Ag^{+}, and Fe^{+3} accelerate hydrolysis when they are present above a specific concentration[36]. An enhancement in the rate of hydrolysis was observed under acidic conditions catalysed hydrolysis by a protonation step of the phosphorus atom because the phosphorus atom in a trialkyl phosphite holds an unshared electron pair and will presumably react with protons to form a phosphonium salt.

The phosphonium salt will rapidly react with water forming a phosphorane that cleaves to give phosphonate and an alcohol. However the same reaction in basic conditions leads to the formation of the anions and the hydrogen phosphonate[43].

The reaction of phosphite with water in acidic and basic conditions is shown in Scheme 1.8.



$$(RO)_3P + H_2O \xrightarrow{H^+} (RO)_2\underset{H}{P}{=}O + ROH$$

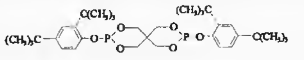
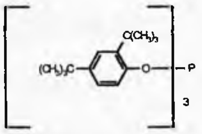
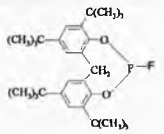
$$(RO)_3P + HO^- + H_2O \longrightarrow RO{-}\underset{H}{P}O^{2-} + 2\,ROH$$

Scheme 1.8. Reaction of phosphite with water in acidic and basic conditions.

Tryalkyl phosphites are hydrolysed very rapidly to dialkyl esters in the presence of acids but quite slowly in alkaline solution[53].

Tochacek and Sedlar carried out some experiments to assess the hydrolytic stability of different phosphites. Their structures and properties of the phosphites investigated are shown in Table 1.1[44].

Table 1.1. Structures and properties of used phosphites[44].

Abbreviation	Structure	Trade name	M.W g/mol	Phosphorus content (%)	m.p. (° C)
P-1		Alkanox P-24	604	10.3	170-180
P-2		Weston 619	732	8.5	40-70
P-3		Alkanox 240	647	4.8	180-186
P-4		Ethanox 398	487	6.4	200

The phosphites were exposed to water vapour at 25 °C. Under these conditions, the ranking of hydrolysability was follows[44]

P-2>P-1>>P-3≥P-4

The results confirm the theory that ease of hydrolysability decreases with[35,44]:

- Increasing steric hindrance of substituents,
- Decreasing the electron density of phosphorus atom.

Therefore, the linear alkyl substituted P-2 exhibits the minimum hydrolytic stability, P-4, possessing hindered phenols and a fluorine atom directly bonded to phosphorus, exhibits greater hydrolytic stability[44].

Klender *et al.* observed the same trend where the fluorophosphonite investigated exhibited outstanding hydrolytic stability relative to that of the non-fluorinated studied phosphite[45,46,47]. Fluorophosphonites exhibit more pronounced hydrolytic stability due to phosphorus-fluorine bond due to the reduced electron density of phosphorus atom.

Another factor affecting the hydrolysis of phosphites is the state of the products. Some phosphites are hydrolytically more stable in the solid state than others although the contrary occurs in the liquid state[45,46,47].

The aim of stabiliser industry is to improve the hydrolytic stability of phosphites, so that hydrolysis during storage is minimised together with the handling and feeding problems caused by caking. Bis (2,4-di-*tert*-butylphenyl) pentaerythritol-diphosphite (P-1) is one of the more effective phosphites for the protecting of polymers during their processing and during their service lifetime.

In addition, P-1 reduces the discoloration of polymer products that have been exposed to nitrogen oxides (NOx) and enhances the UV resistance. However, the poor hydrolytic stability of P-1 (mentioned previously) is a disadvantage[48].

Another phosphite has been proposed as a substitute for bis (2,4-di-*tert*-butylphenyl) pentaerythritol-diphosphite. This is bis (2,4-di-cumyl) pentaerythritol-diphosphite, shown below (Figure 1.3).

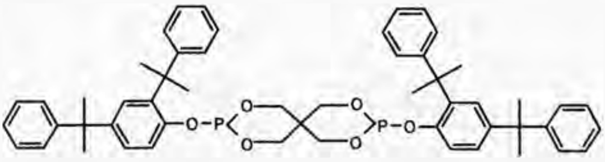


Figure 1.3. Structure of bis (2,4-di-cumylphenyl) pentaerythritol-diphosphite.

The phosphite shown above (Figure 1.3), chemically close to bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite is very resistant to hydrolysis.

Experiments were carried out by Constanzi *et al.* to verify the effectiveness of this diphosphite[48]. It has been found to be effective in the following uses:

- Retaining the viscosity of polymer articles exposed to nitrogen oxides and to gamma rays.
- Improving the resistance of polymer articles when they are exposed to UV light.
- Protection of the polymer melt under normal and severe processing conditions.

This phosphite can be considered to be better than bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite in terms of its hydrolytic stability, its lower volatility and its improved melt protection during processing[48].

Other products that exhibit an improved hydrolytic stability are the fluorophosphonites. Studies carried out by Klender *et al.* showed that the performance (in terms of melt flow rate and colour stability) in PP of the fluorophosphonite 2,2'-ethylidene bis (4,6-di-*tert*-butylphenyl) fluorophosphonite is comparable to the perfomance of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite[45,46].

In HDPE, the fluorophosphonite exhibits better performance in terms of melt flow rate retention whereas the phosphite bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite is better at resisting colour development[45,46].

1.3.1. Long-term hydrolytic stability of bis (2,4-di-*tert*-butylphenyl)-pentaerythritol diphosphite (Alkanox P-24)

In order to assess the long-term hydrolytic stability of Alkanox P-24, some authors have studied the hydrolysis of the phosphite during storage. Different samples were kept under regular storage conditions from 0 to 5 years periods of time. The concentrations of intact phosphite and the 2,4-di-*tert*-butylphenol (hydrolysis product) were determined in order to study the hydrolysis reaction[34].

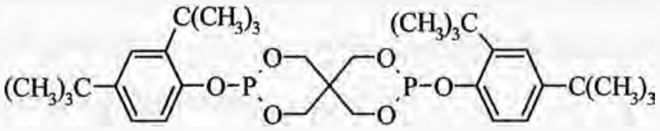


Figure 1.4. Structure of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite.

In its solid, crystalline structure the compound has three different conformers in the unit cell. The structure of each is very similar to that of the others, differing mainly in the rotational conformations of the aryl *tert*-butyl groups[49]. Two six-membered rings form the remainder of the structure, each in a chair conformation with a common spiro atom[49].

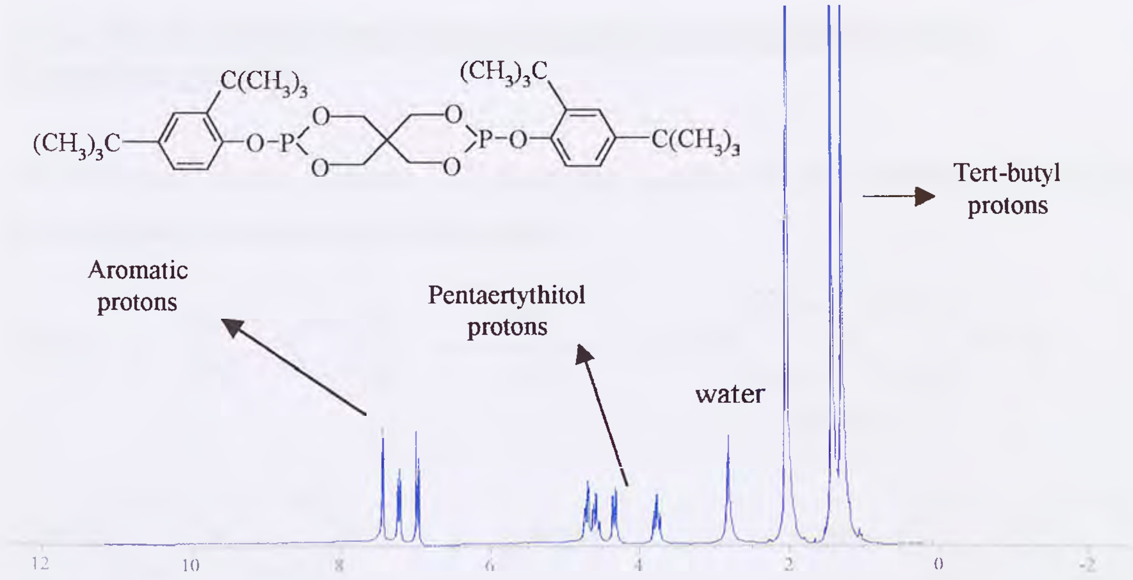


Figure 1.5. N.M.R spectra of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite (Alkanox P-24)

The molecule bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite has two phosphorus atoms. It is a symmetric molecule with six points where the hydrolytic attack could occur. Due to the symmetry of the molecule, there are four equivalent $P\text{-}O_{pentaerythritol}$ and two equivalent $P\text{-}O_{phenol}$ bonds.

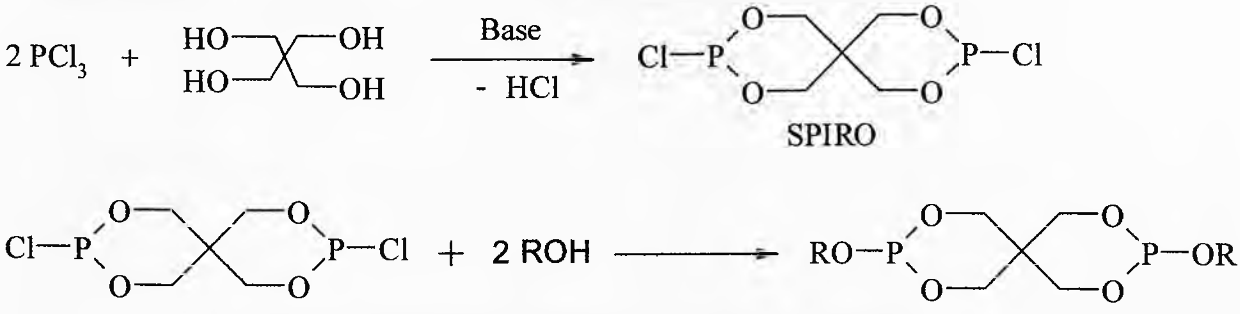
After the first hydrolysis reaction, the molecule loses its symmetry and with subsequent attacks different intermediate products may be formed. It is believed that the total hydrolysis of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite leads to 2,4-di-*tert*-butylphenol, phosphorus acid and pentaerythritol[34]. The samples investigated were hydrolysed at room temperature, in air, with normal humidity in order to study the behaviour of the phosphite under storage conditions.

The samples were stored in a variety of different packaging materials in order to analyse the influence of the packaging material on rate and degree of hydrolysis.

Significant differences in the hydrolytic stability of the phosphite were found depending on the type of package used. It could be concluded that the kind of package used to store the phosphite plays an important role moderating the bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite's hydrolysis rate[34].

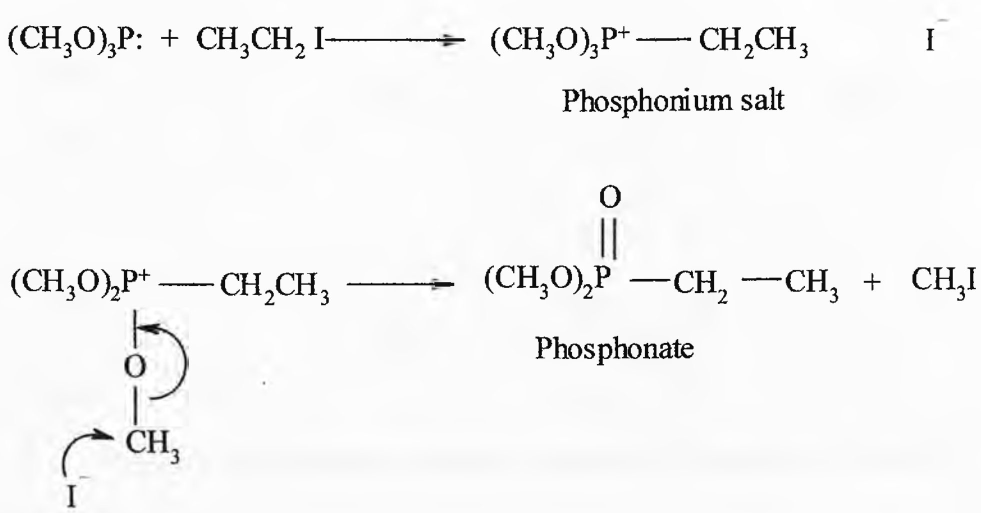
1.3.2. Bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite: Formation reaction

The following scheme (Scheme 1.9) shows the reactions for the formation of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite:



Scheme 1.9. Formation reactions of a phosphite[50,51,52,53,57].

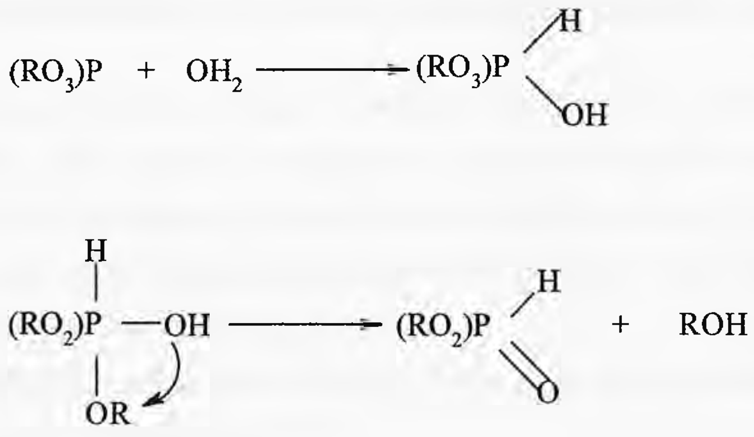
The reaction of phosphorus trichloride with pentaerythritol in the presence of a base (e.g., triethylamine) will lead to dichloropentaerythritol diphosphonite. The spiro compound will react with an aromatic or aliphatic alcohol to produce the alkyl or aryl pentaerythritol diphosphite. In the case of bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite, the alcohol 2,4-di-*tert*-butylphenol would be used[50,51,52,53,57]. According to Arbuzov, the mechanism of the reaction between a trialkylphosphite and water is similar to an ordinary Michaelis-Arbuzov reaction involving a trialkyl phosphite and an alkyl halogenide[54,55]. Alkyl halides undergo initial substitution reaction with trialkyl phosphites, $(RO)_3P$ to give the phosphite equivalent of a phosphonium salt. However, the salt is unstable in the presence of nucleophiles and is rapidly attacked by the iodide ion at one of the methoxy carbon atoms to give a phosphonate[54].



Scheme 1.10. Example of Michaelis-Arbuzov reaction[54].

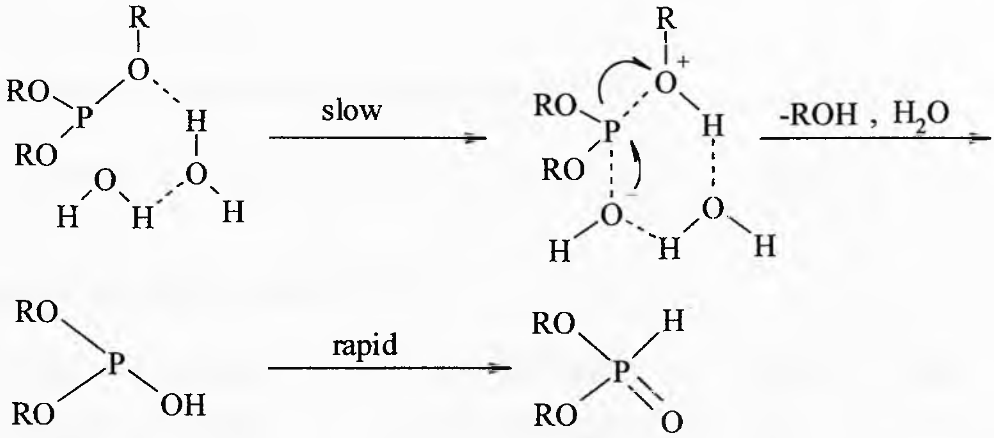
The mechanism of Michaelis-Arbuzov (Scheme 1.10) reaction has been widely studied and the generation of the alkoxyphosphonium ion intermediate has been confirmed. The reaction has been used to synthesise many phosphonites[55].

A Michaelis-Arbuzov reaction could undergo a type of intramolecular reaction as follows:



Scheme 1.11. Intramolecular Michaelis-Arbuzov reaction.

However, some authors[36] propose the following hydrolysis mechanism (Scheme 1.12)



Scheme 1.12. Hydrolysis mechanism proposed by G.Aksnes and D.Aksnes[36].

According to the mechanism of Arbuzov the oxygen atom of the alcohol formed should come from the water, whereas according to the proposed mechanism in Scheme 1.12 the water oxygen will be found in the phosphoryl group of the dialkyl phosphite produced. In the latter case, when ^{18}O-enriched water is used, an infrared phosphoryl band containing ^{18}O appeared[36]. Therefore, they confirmed oxygen from the phosphonate formed it was from the water and not the phosphite. The reaction of Alkanox P-24 with water may probably follow the same mechanism.

1.3.3. Effect of phosphite hydrolysis on the melt processing of polyolefins

During processing, polyolefins undergo degradation due to thermo-mechanical stress and thermo-oxidation. This is usually accompanied by the loss of mechanical properties and, sometimes, by colour development. Small amounts of stabilisers, phenolic antioxidants and phosphites, can hinder the degradation processes via reaction of the stabilisers with the radical species that are formed during processing.

Whilst the stabilisation mechanisms of phenolic antioxidants are quite well defined, those of phosphites are not completely clear[48,56].

During the stabilisation of poly(propylene), there are several possible reactions of the phosphite with radicals during processing[56].

A. *Non-radical decomposition of hydroperoxides*[37,44,48,56].

$$\mathrm{P(OR')_3} + \mathrm{ROOH} \longrightarrow \mathrm{O{=}P(OR')_3} + \mathrm{ROH} \tag{23}$$

B. *Reaction with alkoxy radicals*[30,31,32,56].

$$\mathrm{RO\cdot} + \mathrm{P(OR')_3} \longrightarrow \mathrm{ROP(OR')_2} + \mathrm{R'O\cdot} \tag{24}$$

$$\mathrm{RO\cdot} + \mathrm{P(OR')_3} \longrightarrow \mathrm{O{=}P(OR')_3} + \mathrm{R\cdot} \tag{25}$$

C. *Reaction with alkylperoxylradicals*[30,31,32,56].

$$\mathrm{ROO\cdot} + \mathrm{P(OAr)_3} \longrightarrow \mathrm{O{=}P(OAr)_3} + \mathrm{RO\cdot} \tag{26}$$

D. *Inhibition of the prodegradant effect of catalytic residues of transition metals through complexation*[56].

E. *Stabilisation by the phenols that are formed by the partial hydrolysis of aromatic phosphites*[56].

Reaction A appears improbable because the hydroperoxides are not stable at the processing temperature. They undergo very fast thermal scission to RO· and ·OH[56].

The non-radical decomposition of hydroperoxides has been postulated as the main mechanism behind the melt stabilisation that is afforded by phosphites. However, it is important to appreciate that this may not be the only mechanism. Certain studies supporting the non radical route have been carried out under idealised model conditions and at too low temperatures to properly simulate melt processing[57]. Alkyl hydroperoxides undergo thermal decomposition at temperatures as low as 100 °C. Therefore, the importance of this reaction is questionable because the usual polyolefin processing temperatures range between 200 °C and 300 °C[37,44].

In reaction B, the reaction of the phosphite with the alkoxy radicals depends on the R' substitution of the phosphite.

Reaction C more closely represents a propagation step, unless reaction B occurs[44,56]. It is known that phosphites can react with alkoxy radicals, as a consequence of which the phosphite may therefore be acting as a radical scavenger as well as a hydroperoxide decomposer, during processing. This dual mode of action associated with phosphites may account for the more effective behaviour. The effectiveness of reactions with oxygenated alkyl radicals is determined by the nature of the R' substituent of the phosphite[44]. The reactions are not considered important at temperatures below 100 °C because the rate constants of reactions with peroxy radicals and stoichiometric factors are much lower than those of phenols[44]. During the oxidation of polymers at high temperatures (150 °C-200 °C), however, sterically hindered aryl phosphites and phosphonites exhibit a rather high antioxidative activity. Under such conditions, reactions with alkoxy radicals and with alkylperoxy radicals could take place[44].

Hypothesis D: Phosphites show a pronounced metal deactivation activity as complexes can be formed between the phosphite and metal ions. In some cases such complexes afford a stabilisation effect[58].

Hypothesis E is possible only for phosphites having phenolic moieties and poor hydrolytic stability[56].

It has been suggested, but not generally accepted, that phenols that are formed by hydrolysis of the parent phosphites are the species responsible for the antioxidant activity of phosphites at higher oxidation temperatures[37]. A completely degraded sample of Alkanox 240 in PP was less effective at melt stabilisation than was an undegraded (unhydrolysed)[47]. However, the totally hydrolysed sample contributed to the processing stability of the polymer relative to a total absence of phosphite, this confirms that the hydrolysis products show a degree of stabilisation activity. The performance of different phosphites in combination with the phenolic antioxidant, tetrakismethylene (3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) methane has been evaluated by Tochacek and Sedlar in terms of melt stabilisation performance using multiple extrusion experiments[44].

The two major reasons why hindered phenol antioxidants and secondary antioxidants are used in conjunction are the enhanced colour stability and additional melt processing stability, that enables maintenance of the original MFR of the polymer to be achieved[59].

Phosphites featuring hindered steric hindrance and poor hydrolytic stability, such as bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite, are able to function via all the possible reaction mechanisms mentioned previously. On the other hand, the overall stabilisation activity of phosphites without phenolic moieties and extremely low hydrolytic stability, such as disteryl pentaerythritol diphosphite (Weston 619, General Electric) is dependent on mechanism A, the non-radical decomposition of hydroperoxides[44]. Due to the lack of phenolic moieties this molecule cannot function as a chain-terminating antioxidant.

On the other hand, one can compare Alkanox P-24 with Alkanox 240. Alkanox 240 exhibits higher steric hindrance and, as a consequence, a better hydrolytic stability, showing reduced activity in terms of processing stabilization[44,59].

In terms of processing stability, the phosphite Alkanox P-24 is able to perform as an efficient antioxidant even at different stages of hydrolysis. Even in cases where the phosphite was totally hydrolysed, some stabilisation effect was observed[34]. The performance was dependent on the degree of hydrolysis. A higher degree of hydrolysis resulted in improved melt stabilisation[34].

However, some authors have expressed doubt regarding the direct correlation of the effectiveness of phosphites with their hydrolytic instability. Indeed, no evidence of hydrolysed products was found after ten extruder passes even in the case of an aliphatic phosphite, which shows very poor hydrolytic stability[56].

1.4. Co-additives used in polyolefins

It is now common industrial practice to use combinations of stabilisers in polyolefins in order to achieve effective polymer stabilisation in the melt during processing and under the designed service condition of the product flow when it is exposed to environmental and other external factors.

Combinations of various stabilisers in differing ratios are used in order to get an overall synergistic effect. However, additive and antagonistic effects can occur as a consequence of using mixture of stabilisers. Sometimes, co-additives are added to a formulation to reduce the additive package cost. Different types of co-additives are used in polyolefin stabilisation, such as acid scavengers, nucleating agents, antistatic agents, lubricants, etc.

In the this chapter, the properties of the co-additives used in this work in conjunction with the phosphite Alkanox P-24 (bis (2,4-di-*tert*-butylphenol) pentaerythritol diphosphite) will be analysed in more detail.

1.4.1. Acid scavengers

Acid scavengers are the third most frequently used additives in stabilisation packages. They are also known as antacids or co-stabilisers. Their main function is to neutralise the halogen containing catalyst residues (e.g., Ziegler-Natta HDPE and PP)[60]. During the polymerisation, different chloride-containing catalysts are used and, as a consequence, the catalyst residues will cause corrosion of the metallic equipment[60,61].

The basic criteria that should be met for an additive to perform as an acid scavengers[60,61]:

- High purity, to avoid undesirable side reactions.
- Thermal stability and low volatility.
- Proper price-performance ratio.
- Compatibility with polymer matrix.

  Metallic stearates and other fatty acid derivatives are compatible under processing conditions when molten together with or before the addition of the polymer.
- Optimun dispersability.

1.4.1.1. Metal stearates

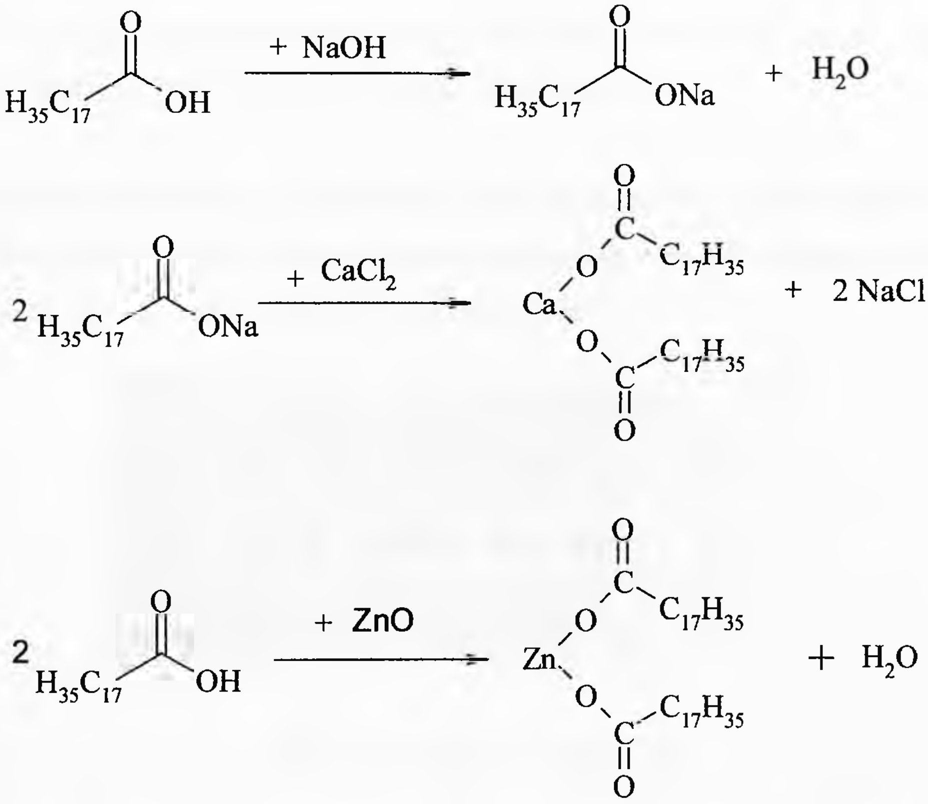
In poly(ethylene), the most common metallic stearates used are calcium stearate (CaSt) and zinc stearate (ZnSt). In poly(propylene), CaSt is the most widely used stabilizer.

A group II metal based metallic stearate has an inorganic centre with a strong separation of charge, two linear hydrocarbon chains. As a neutraliser, the metallic constituent contributes to reactivity with acids and acidic catalyst residues[60].

Stearates give some lubricity to the resin, providing it with slip properties, which is important in production in order to reduce shear forces during the extrusion step. When melt lubrication is required together with neutralisation, the stearate dosage can be several times greater than that required for neutralisation alone[60,61]. Acid scavengers can also be used as dispersion aids for pigments, fillers and reinforments. In reinforced polymers, stearate addition can result in an improved surface finish[60]. Some sodium salts and the calcium salts of higher fatty acids, exhibit certain nucleating effects[61].

The metallic stearates are produced with two general processes (Scheme 1.13)[60,61]:

- Precipitation process (An example is shown with calcium stearate)
- Direct or fused process (An example is shown with zinc stearate)



Scheme 1.13. Formation of calcium stearate and zinc stearate[60].

Depending on the process used to produce the stearate, a wide range of qualities is available in various commercial forms[61].

The precipitation process involves the use of large quantities of water as a vehicle for the reaction. The ratio of stearic acid to water affects the particle size, and therefore, the surface area of the stearate. It is not possible to obtain a plate-like shape and high surface area with the fused process. The production of powdered, fused metallic stearates yields more regular, less plate like particles due to a grinding step[60].

1.4.1.2. Hydrotalcite

Hydrotalcite is a naturally occurring layered aluminum magnesium hydroxycarbonate, an anionic clay mineral.

The general formula for synthetic hydrotalcite can be described as:

$$[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}\,[A^{n-}{}_{x/n}\cdot mH_2O]^{x-}$$

where, M^{2+} and M^{3+} are metal cations, such as $M^{2+}=Mg^{2+}$, Zn^{2+} or Ni^{2+} and $M^{3+}=Al^{3+}$ or Fe^{3+}; A^{n-} is an anion, NO_3^-, Cl^-, CO_3^{2-} or SO_4^{2-}; and X=0.2-0.33.

As it can be observed in Figure 1.6, the cations are distributed among the octahedral layers to formed positively charged layers, whereas the negatively charged interlayers lie between the sheets contain interlayer anions and water molecules[60].

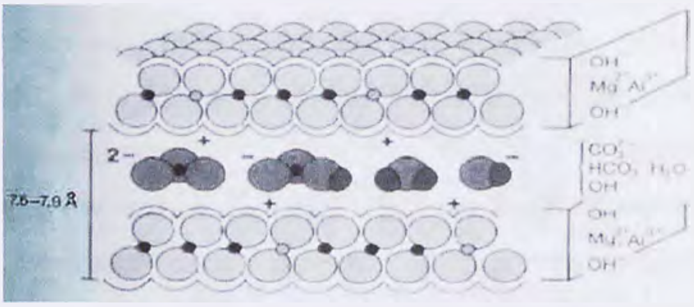


Figure 1.6. Hydrotalcite's structure.

The empirical formulae for some natural hydrotalcites and synthetic hydrotalcites are[60]:

- Natural mineral hydrotalcite

  $Mg_6Al_2(OH)_{16}CO_3\ 4H_2O$

- L-55RII (Reheis Inc.,USA)

  $Mg_{4.35}Al_2(OH)_{11.36}(CO_3)_{1.67}\ xH_2O$

- DHT-4A (Kyowa Chemical Inc., Japan)

  $Mg_{4.5}Al_2(OH)_{13}CO_3\ 3.5H_2O$

- Baeropol MC 6280 (Baerlocher GmbH, Germany)

  $Mg_4Al_2(OH)_{12}CO_3\ 2.85H_2O$

The hydrotalcites used in polymer applications are finely divided, free-flowing, odourless, amorphous powders. In order to improve the dispersion and compatibility in the polymer matrix, different sodium stearate, calcium stearate and zinc stearate coatings are used. If the hydrotalcite has a pH value higher than 9.5, it can easily lead to an over-basing of the entire additive system, resulting in discolorations by side reactions. The phenolic antioxidant and the product can develop a pinkish colouration[60,61].

1.4.1.3. Influence of acid scavengers on stabilisation packages for polyolefins

It is not possible to generalise about the performance of acid scavengers in the polyolefins. Depending on the type of polyolefin used, such as, spheripol process poly(propylene), Ziegler-Natta catalysed poly(ethylene), etc. The performance of the acid scavenger in terms of MFR and colour stability will vary[60].

In poly(propylene) homopolymer reduction in colour development, with Irganox 1010 (phenolic antioxidant) and Irgafos 168 (phosphite antioxidant) was observed with calcium stearate (CaSt). However, hydrotalcite did not afford the same performance, the combination of CaSt/hydrotalcite gave the best colour protection[60]. Therefore, indicating a degree of synergism between the two additives. CaSt had a positive effect on colour development after a few extrusion passes, when the levels of the acid scavenger were higher than those required to prevent corrosion of the processing equipment[60,62]. In terms of melt stabilisation neither CaSt nor hydrotalcite had any significant effect on the poly(propylene) homopolymer. An increase in CaSt level showed an increase on the poly(propylene) MFR after the fifth extrusion, but it has to be taken into consideration that this could be due to the lubricity of CaSt[60].

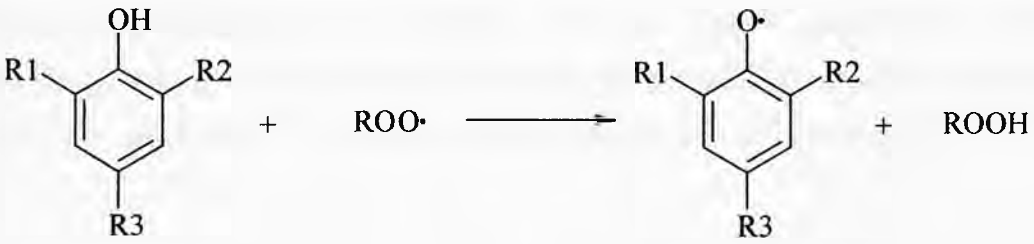
On the other hand, different behaviour was observed in terms of colour protection for a third generation poly(propylene), where the CaSt was able to improve the colour stability of the polymer but the same level of hydrotalcite significantly decreased the colour stability. This is thought to be due to interaction of the hydrotalcite with the phenolic antioxidant, independently of the type of hydrotalcite. However, the extent of yellowing is highly dependent on the type of hydrotalcite[60,63]. Ziegler-Natta catalysed HDPE and Cr-catalysed HPDE's do not show the same behaviour in terms of colour stability. This difference arises because the Cr-catalysed HDPEs do not have acidic residues due to the nature of the catalyst. However, the addition of small amounts of ZnSt results in improved colour stability relative to the control sample containing only base stabilisation or additional CaSt. CaSt seems to have no effect on colour stability as the number of extrusion passes increases[60]. The addition of acid scavengers to Ziegler-Natta catalysed HDPE with base stabilisation, results in a much improved colour stability after multiple extrusion processes. ZnSt improves the colour stability more significantly than CaSt. However, the formulation-containing CaSt afforded improved resistance to crosslinking than the formulations containing ZnSt[60].

1.4.2. Primary antioxidants, hindered phenols

Primary antioxidants are the most widely used antioxidants to stabilise polyolefins during processing and long-term heat ageing.

1.4.2.1. Phenolic antioxidants during processing

Phenolic antioxidants act as radical scavengers. During polymer processing different types of radicals are formed due to mechanical shear, thermal break down and oxidation. Consequently, the radicals are able to abstract hydrogen atoms from the polymer backbone and degrade the polymer. However, to avoid polymer degradation, phenolic antioxidants (H-donors) are added to the polymer. These antioxidants react with the radicals formed[15,64]. The key reaction in the stabilisation of the polymer by phenolic antioxidants is the formation of hydroperoxides by transferring an electron and a proton from the phenolic moiety to a peroxy radical (Scheme 1.14)[15,65].



Scheme 1.14. Reaction of phenolic antioxidant with peroxy radicals[15].

The following reactions could compete with each other, where the rate constants of the reaction are represented by k1, k2 and k3 (Scheme 1.15).

$$\mathrm{ROO\cdot} + \mathrm{RH} \xrightarrow{k1} \mathrm{ROOH} + \mathrm{R\cdot}$$

$$\mathrm{ROO\cdot} + \mathrm{InH(H\text{-}Donor)} \xrightarrow{k2} \mathrm{ROOH} + \mathrm{In\cdot}$$

$$\mathrm{In\cdot} + \mathrm{RH} \xrightarrow{k3} \mathrm{InH} + \mathrm{R\cdot}$$

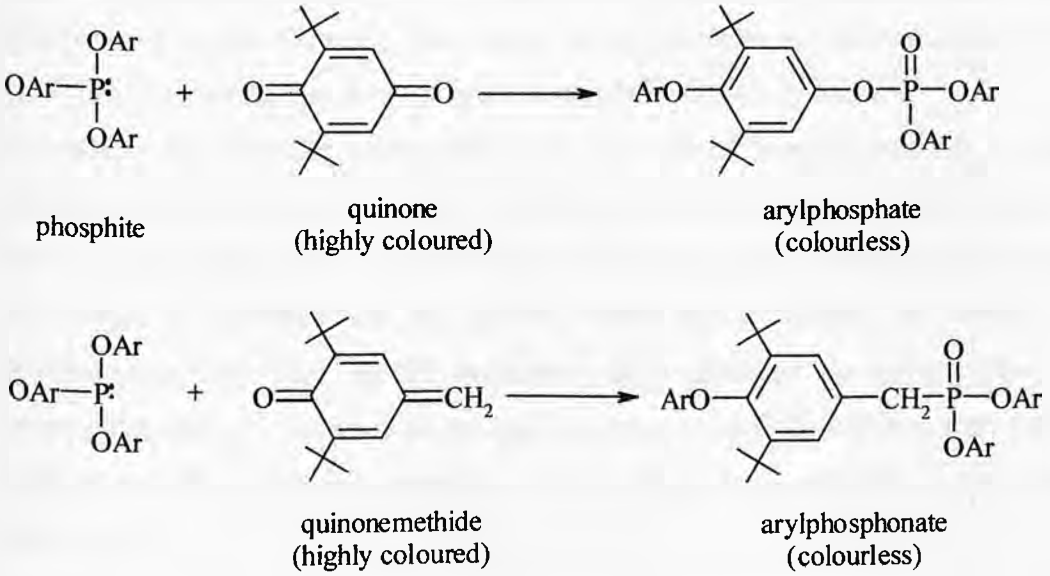
Scheme 1.15. Inhibition reactions involving H-Donors (the phenolic antioxidant is represented by InH, where the peroxy radicals abstract a hydrogen and the phenoxy radicals are formed, In·[15].

The reaction of the peroxy radicals with the H-Donor (Scheme 1.15) is faster than the abstraction of the hydrogen atom from the polymer backbone ($k_2 >> k_1$). Therefore, the antioxidant will avoid the degradation until the external H-Donor is consumed. Suitable H-Donors are characterised by the fact that they do not react further by abstraction from the polymer backbone ($k_3 << k_2$)[15].

The effectiveness of the phenolic antioxidant depends on[15].

- The number of phenolic groups that serve as H-Donors.
- The steric hindrance in the 2- and 6- positions.

The stabilisation activity depends on the retention of the phenol in the polymer at elevated temperature. Therefore the molar mass is of prime importance. Low molar mass phenols are not effective due to their high volatility during processing conditions[25,65]. The main drawback of the phenolic antioxidants is the formation of oxidation products such as highly chromophoric quinone methides that are responsible for discoloration in the polymer[15,66]. Such discoloration in polyolefins can be avoided by using a suitable phosphite or phosphonites in combination with the phenolic antioxidant. Aromatic phosphites prevent the discoloration produced by the phenolic antioxidants reacting with the quinoidal compounds[15,58]. This is also shown schematically in Scheme 1.16.



Scheme 1.16. Reaction of phosphite and quinone[58].

It is well known that the combination of phenolic antioxidants and phosphite antioxidants exhibit synergistic effects in polyolefin stabilisation[19,21,25,65,66,67].

The best synergism is usually observed with phenol/phosphite ratios between 1:1 and 1:4, depending on the substrate and the processing conditions. Several studies have observed that the best performance during processing stabilisation of poly(propylene) is achieved within the ratio mentioned previously[21,65,66,68].

It has been observed that the change in MFR after multiple extrusions is dependent on the activity of the phosphite and not on the activity of the phenolic antioxidants. The role of the phosphite antioxidant seems to be more important than that of the phenolics[66]. However, it is important to mention that the synergism is only possible under conditions where the hydroperoxide decomposing action of the phosphite affects the rate of oxidation, at temperatures where the hydroperoxides homolytically decompose. At low temperatures, in the oxidation of hydrocarbons and polymers below about 80 °C, phosphites have no effect on the antioxidative efficiency of phenols[69]. Habicher and co-workers studied a combination of tri-n-butylphosphite with the phenolic antioxidant BHT at 65°C for its stabilising ability of AIBN initiated auto-oxidation. Since hydroperoxides are stable at this temperature, phosphites have no influence on the oxidation process. In this case, the phenol alone is responsible for the inhibition[69]. On the other hand, these studies showed that in poly(propylene) at 140°C hydroperoxide decomposition by phosphites contributed to the overall stabilisation of the polymer. This results in a heterosynergistic action with hindered phenols. In mixtures with phenols at higher temperatures, the hydroperoxide capability of phosphites is crucial. However, the hindered aryl phosphites are better synergists than alkyl phosphites, indicating that their chain breaking ability plays a role here[69].

Recently, a new phenolic antioxidant that is capable of trapping both alkyl radicals and peroxy radicals has been developed. A phenol radical scavenger can trap peroxy radicals but not alkyl radicals, due to its fast reaction with the oxygen. During polymer degradation, the oxygen is abundant near the surface, where peroxy radicals are formed, whereas degradation where alkyl radicals participate takes place on the inside, where there is oxygen deficiency[70]. It has been found that some o-alkylphenols can trap both peroxy radicals and alkyl radicals, depending on the oxygen concentration in the surrounding atmosphere[70].

1.4.3.Nucleating agents

1.4.3.1.Crystallization of semi-crystalline polymers

Poly(ethylene) and poly(propylene) are classified as semi-crystalline polymers. Semi-crystalline polymers consist of two or more solid phases. In one of these phases chains are ordered forming the crystalline regions whereas in the other phases the chains are disordered giving the non-crystalline regions[4].

Degree of crystallinity varies from one polymer to another. Other examples of semi-crystalline polymers are: poly (ethylene terephthalate), poly (butylene terephthalate), and polyamide[71].

To crystallise, a polymer must fulfill the following requirements[71]:

- The molecular structure of the polymer must be regular enough to allow crystalline ordering.

  A regular structure is potentially capable of crystallinity whereas an irregular structure will tend to give amorphous polymers.

  There are different factors that affect the crystallinity of polymers: Branching will also reduce the ability to crystallize. The presence of side groups will interfere in the crystallization process[1,71]. Copolymerisation would be an effective way of introducing irregularities and reducing the ability to crystallize. Poly(ethylene) is a semicrystalline material but, with random ethylene-propylene copolymers, crystallization becomes a difficult process[1,72]. The same effect would be achieved with the introduction of groups in an irregular manner, e.g: partially chlorinated poly(ethylene). Apart from the factors mentioned before, the lack of stereoregularity would be affected as well the crystallization process. Poly(propylene) is a clear example, where the regular syndiotatic and isotactic structures are capable of crystallization. On the other hand the atactic poly(propylene) cannot normally crystallize[1].
- The crystallization temperature must be below the melting temperature, but not close to the glass transition temperature of the polymer.
- Nucleation must occur prior to crystallization.
- The crystallization rate should be sufficiently high.

The onset of crystallinity is termed nucleation. Nucleation may occur randomly through the matrix as polymer molecules begin to align, which is called *homogeneous nucleation.* However, the nucleation may occur due to a foreign impurity, such as a nucleating agent, *heterogeneous nucleation*[4,71].

Due to their chain connectivity, polymers crystallize in such a way that only limited crystallinity is obtained[71].

Table 1.2. Representative degrees of crystallinity of several polymers[72].

	Representative degrees of crystallinity (%)
Low-density poly(ethylene)	45-74
High density poly(ethylene)	65-95
Poly(propylene) fiber	55-60
Poly (ethylene terepthalate) fiber	20-60

The values of crystallinity shown in the table (Table 1.2) are representative because the degree of crystallinity and the mechanical properties of a particular crystallisable sample depend on the polymer structure and also on the conditions under which crystallization has occurred[72]. When the polymer crystallizes from the melt, the polymer crystals (lamellae) organize from a primary nucleus and form spherical macro structures called spherulites. The spherulites continue to grow from the melt until their growth fronts find the growth fronts of neighbouring spherulites[71].

1.4.3.2. Nucleating agents in melt processing

The role of nucleating agents is to increase the rate of crystal nucleation by acting as heterogeneous nuclei. The nucleating agents cannot affect crystallisation rate of all polymers significantly. For a polymer to be sensitive towards nucleation of the crystallisation process, the rate of crystal growth should not be too high or too low[71].

Some general features of a good nucleating agent are[71]:

- Content of both organic and polar group.
- Good dispersion in the polymer.
- Insolubility or becoming insoluble in the polymer.

- Epitaxial match with the polymer crystal.
- Chemical reactions with the polymer and nucleation of the polymer from the reaction product.

A nucleation agent can be an impurity (catalyst residue), organic compound (benzoic acid), inorganic compound (talc or pigment), foreign polymer crystal, etc. Nucleating agents that enhance the transparency of semi-crystalline polymers are referred to as clarifying agents[73]. In poly(propylene), the nucleating agents can be classified as being melt sensitive and melt insensitive. The melt sensitive nucleators (sorbitol based the compounds that they are referred as clarifiers) have a melting point, which is below or near the normal processing temperature of poly(propylene)-based polymers.

Melt insensitive nucleators (such as sodium benzoate or organic phosphates) do not melt at normal temperatures. Sodium benzoate is used to enhance the physical properties of poly(propylene), although it is less efficient than clarifiers at improving transparency[74].

In the case of HDPE, which has an extremely fast growth rate, nucleating agents are not very effective because as soon as a nucleus is formed, the resulting crystal grows extremely fast[71]. It is not common to deliberately add heterogeneous nucleating agents to poly(ethylene)[4]. However, some moderately effective nucleating agents have been identified. Potassium stearate, benzoic acid, sodium benzoate, talc and sodium carbonate affect the nucleation density of HDPE[71].

The addition of nucleating agents can affect the mechanical properties and the optical properties of semi-crystalline polymers due to a decrease of the spherulite size[71,74,75].

1.5. No Dust Blends (NDB's)

A NDB is a composition of a number of individual components (additives), typically three or four although any number from one to seven is now possible. These are based on the concept that the lowest melting component acts as a binder, or carrier, for the other components. Depending on the additive, they can be non-melting, low melting, hygroscopic, of low thermal stability, dusty, irritant and occasionally toxic. All these characteristics cause their own problems that can mean physical loss of the additives, sticking in the hopper, dusty working environment, increased changeover times, feeding problems, clumping, segregation of pre-blends or loss of activity, etc. The NDB not only significantly overcomes these difficulties, but also offers a number of other benefits[76]. The physical form of NDB pellets is shown in Figure 1.7.

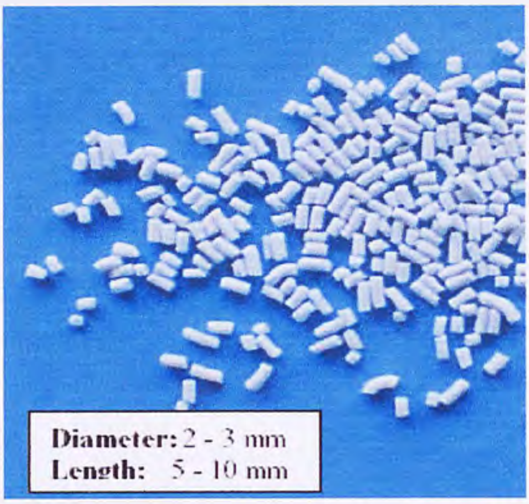


Figure 1.7. The physical form of NDB pellets[76].

1.5.1. Benefits of no dust blends

- Low Dust Physical Form

  NDBs have very low levels of dust associated with them. This leads to a number of benefits, particularly during the additive handling stages. There is no risk of explosion resulting from powder or dust dispersion in the air. In addition, the use of NDB virtually eliminates the irritation and toxicity problems, that face workers assigned to handling operations[77]. Reduction of dust in a plant has other benefits, the risk of cross contamination of one type of additive with another is reduced and the risk of the final polymer having quality problems is lower[77].

- High Abrasion Resistance

  NDB present a better hardness than the granulated version of the same product and comes very close to that of flakes. The high abrasion resistance results in quite a robust pellet which is advantageous during NDB handling and transportation and also means that there is a minimal risk of compaction of the NDB during transport and storage, especially under non-ideal conditions[77].

- Good Flow Properties

  It has been shown that NDBs have very good flow properties compared to the respective powder physical form. In addition, NDBs also reduce the potential for problems that might arise during feeding into the extruder that can lead to segregation of the additive mix subsequently to concentration variations in the polymer[76,77].

- High Melting Rate

  This property allows an easy incorporation and a good level of dispersion into the polymer[77].

- Alloy Effect of Additive Blends

  The behaviour of some NDBs is sometimes similar to that of an alloy with respect to its melting point leading to an easy incorporation into the polymer, wider range of applications for some additives, an enhancement in the performance and an improved dispersion in the polymer[77].

- Wide Range of Possible Formulations

  The use of NDB affords the opportunity to optimise the additive blend ratio and obtain either the same performance at a reduced cost or an improved performance at the same cost[77].

- Constant "Pre-Blended" NDB composition

  It is possible to get a homogeneous composition in a NDB. The advantages of the consistent, accurate and homogeneous composition of NDBs are numerous and contribute to polymer quality, productivity improvements and cost savings. Due to the consistency of the ratio of additives fed and dispersed into the polymer, no loss in performance that could be due to differences in relative additive concentration will occur[77].

- Single Pellet Formulation

  There are other benefits from an industrial point of view. Less storage is required than is need for either powder or masterbatch products. Logistical benefits arise, due to the need to buy one single product rather than several smaller volume ones.

Reduced administration and purchasing efforts and having a single contact supplier are also a benefit[77].

Chapter 2. EXPERIMENTAL

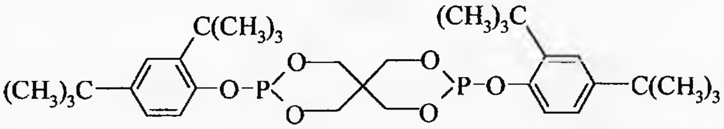
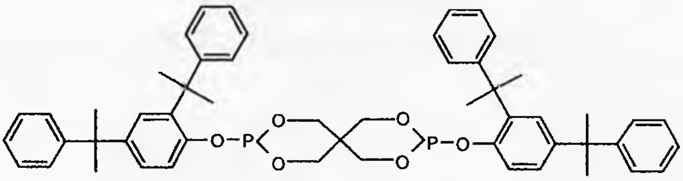
2.1. MATERIALS

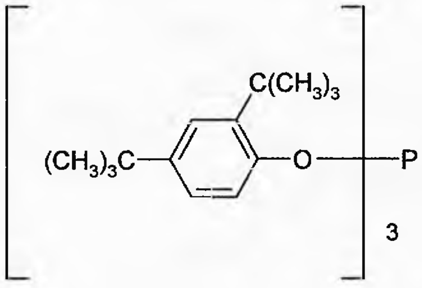
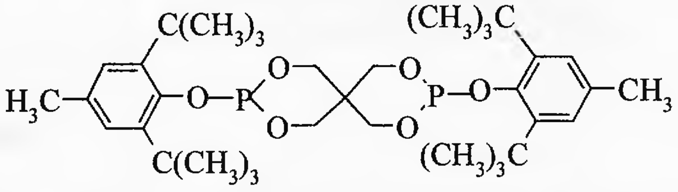
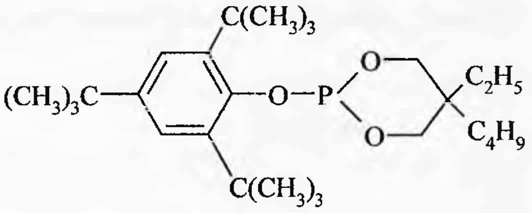
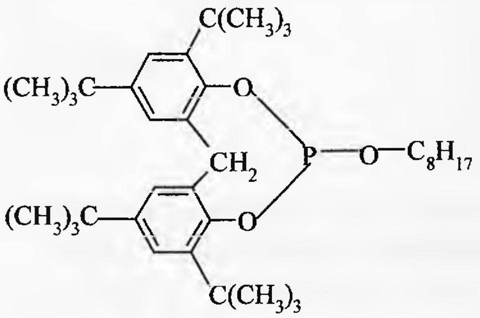
2.1.1. Additives

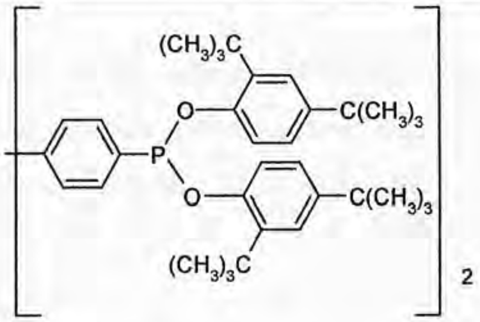
2.1.1.1. Phosphites antioxidants

The phosphites investigated were Alkanox P-24 (Great Lakes Chemical Corporation), Alkanox 28 (Great Lakes Chemical Corporation), Alkanox 240 (Great Lakes Chemical Corporation), Alkanox 24-44 (Great Lakes Chemical Corporation), Ultranox 641 (General Electric), ADK STAB HP-10 (Asahi Denka Kogyo) and ADK STAB PEP-36 (Asahi Denka Kogyo). Structures and further details are given in Table 2.1.

Table 2.1. Properties of the phosphite antioxidants.

Trade name (Supplier)	Structure
Alkanox P-24 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	 Bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite (M.W.: 604 g/mol, m.p.: 178°C)
Alkanox 28 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	 Bis (2,4-dicumylphenyl) pentaerythritol diphosphite (M.W.: 852 g/mol, m.p.: 225°C)

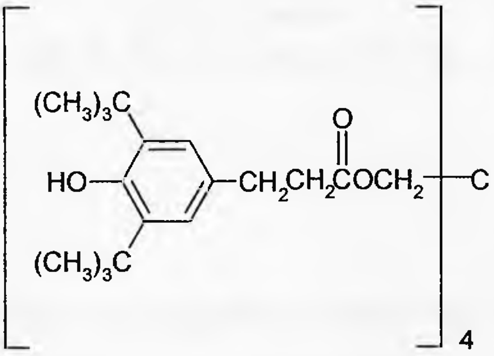
Trade name (Supplier)	Structure
Alkanox 240 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	 Tris (2,4-di-tert-butylphenyl) phosphite (M.W.: 647 g/mol, m.p.: 180°C)
ADK-PEP 36 (Asahi Denka Kogyo 7-2-35 Higashiogu, Arakawa-ku Tokyo,116-8553 Japan)	 Bis (2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite (M.W.: 633 g/mol, m.p.: 237°C)
Ultranox 641 (GE Specialty Chemicals, 1000 Morgantown Industrial Park North Morgantown, WV 2650, USA)	 2,4,6-tri-tert-butylphenyl-2-butyl-2-ethyl-1,3-propanediol phosphite (M.W.: 420 g/mol, m.p.:>90°C)
ADK-HP-10 (Asahi Denka Kogyo 7-2-35 Higashiogu, Arakawa-ku Tokyo,116-8553 Japan)	 2,2'-methylene bis (4,6-di-tert-butylphenyl) octylphosphite (M.W.: 583 g/mol, m.p.: 148°C)

Trade name (Supplier)	Structure
Alkanox 24-44 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	 Tetrakis (2,4-di-tert-butylphenyl) 4,4'-biphenylene-diphosphonite (M.W.: 1035 g/mol, m.p.: 75-95°C)

2.1.1.2. Phenolic antioxidants

The main hindered phenolic antioxidant used in this study was Anox 20 (Great Lakes Chemical Corporation). Structures and further details are given in Table 2.2.

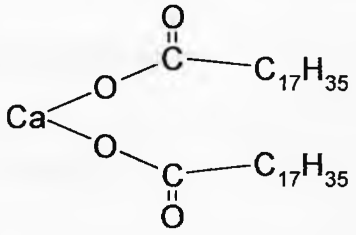
Table 2.2. Properties of the main phenolic antioxidant studied, Anox 20.

Trade name (Supplier)	Structure
Anox 20 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	 Tetrakis [methylene 3-(3', 5'-di-tert-butyl-4'-hydroxyphenyl) propionate] (M.W.: 1178 g/mol, m.p.: 118°C)

2.1.1.3. Acid scavengers

In order to study the effect of acidic species on the hydrolytic stability of the phosphite Alkanox P-24, DHT-4A (a hydrotalcite like compound from Kyowa Chemical Industry) and calcium stearate DW (Faci SpA) were used. Structures and further details are compiled in Table 2.3.

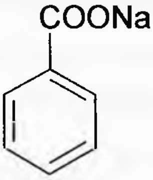
Table 2.3. Properties of acid scavengers studied.

Trade name (Supplier)	Structure
DHT-4A (hydrotalcite like compound) (Kyowa Chemical Industry Co.,Ltd. 4285 Hayashida-cho, Sakaide, Kagawa, 762, Japan)	$Mg_{4.5}Al_2(OH)_{13}CO_3\ 3.5H_2O$ (M.W: 517.4 g/mol)
Calcium stearate (DW) (3% water content) (Faci SpA Via Privata Deveto, 36 Carasco 16042 Genova, Italy)	 Calcium Stearate (M.W: 586 g/mol ,m.p.: 118 ° C)

2.1.1.4. Nucleating agents

The nucleating agent used for the hydrolysis and degradation studies was Palmarole MI.NA.08 (Palmarole Ltd). The structure and further details are given in Table 2.4.

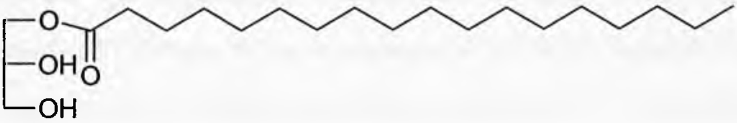
Table 2.4. Properties of the nucleating agent investigated.

Trade name (Supplier)	Structure
Palmarole MI.NA.08 (Palmarole UK Ltd 20 Jordangate Macclesfield, Cheshire, UK, SK10 1EW)	 Micronised sodium benzoate (M.W.: 144 g/mol, m.p.: 410-430°C)

2.1.1.5. Antistatic agents

The antistatic agent used for the hydrolysis study was Atmer 129 (Uniquema). The structures and further details are shown in Table 2.5.

Table 2.5. Properties of antistatic agent.

Trade name (Supplier)	Structure
Atmer 129 (ICI Surfactants PO Box 90 Wilton Centre Middlesbrough Cleveland TS 90 8JE UK)	 Glycerol monostearate (High monoester content, 90% minimum)

2.1.1.6. No Dust Blend and powder blend formulations

The following formulations were prepared to study the influence of different co-additives on the hydrolytic stability of Alkanox P-24 and the influence of partially hydrolysed phosphite Alkanox P-24 on the performance of standard poly(propylene). All the formulations were prepared in different physical forms, the No Dust Blend (NDB) and powder. Composition and proportion of different formulations are shown in Table 2.6.

Table 2.6. Composition and proportion (by weight) of different formulations

Formulation	Anox 20	Alkanox P-24	DHT-4A	CaSt
	40	40	20	-
	20	40	40	-
	20	40	-	40
	50	50	-	-

2.1.2. Polymers

2.1.1.1. High-density poly(ethylene)

The poly(ethylene) used for the degradation studies was Alcudia® 6006-L high-density poly(ethylene) from Repsol-YPF (Paseo de la Castellana, 280, 28046, Madrid, Spain). This poly(ethylene) is a homopolymer of medium molecular weight and it is specially designed for the manufacture by blow moulding of sterilized milk bottles[78]. Properties of the polymer are shown in Table 2.7.

Table 2.7. Properties of the high-density poly(ethylene) studied.

Alcudia® 6006-L		
Main application	MFI (2,16kg/190°C)	Density
Blow moulding for sterilized milk and mineral water bottles.	0.6 g/10min	956 kg/m^3

2.1.1.2. Poly(propylene)

The poly(propylene) used to study the effect on performance of the partially hydrolysed Alkanox P-24 is a standard poly(propylene) grade with a nominal MFI of 12.

2.2. Hydrolysis studies

2.2.1. Degree of hydrolysis studies

2.2.1.1. Sample preparation

The hydrolytic stability of different selected phosphites was investigated first of all. In order to determine the degree of hydrolysis of the phosphites, 0.01g of each was placed in one of several glass bottles, which were then placed in a desiccator. This was then placed in an oven (Binder) at 60° C and 75±1 % relative humidity (R.H.). Samples were periodically removed from the oven and analysed by High Performance Liquid Chromatography (HPLC).

Furthermore, the influence of some co-additives (acid scavengers and phenolic antioxidants) on the hydrolytic stability of Alkanox P-24 was investigated. A binary blend approach was undertaken for this study. Binary blends (additives without polymer) were prepared by **melt blending** the additives on a hot plate (Jenway 1203).

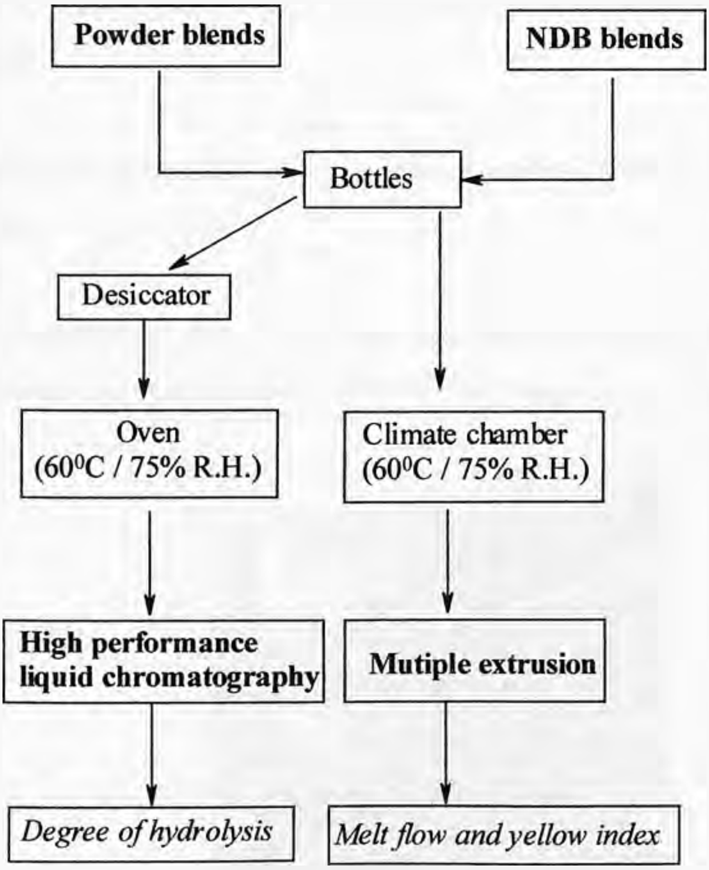
The additive with lowest melting point was melted first and subsequently mixed with the second additive. The above hot and humid conditions were used to analyse the influence of the co-additives on the hydrolytic stability of Alkanox P-24.

The following binary blends were prepared in different ratios:

Alkanox P-24/Anox 20	(80:20, 70:30, 50:50)
Alkanox P-24/CaSt	(80:20, 70:30, 50:50)
Alkanox P-24/DHT-4A	(80:20, 70:30, 50:50)

The influence of the physical form on the hydrolytic stability was investigated by comparison of the traditional powder blend with the no dust blends. Different physical forms were prepared in a pilot extruder and stored in one of several aluminium bags that were received from Great Lakes Chemical Corporation in order to carry out the hydrolysis studies. In this case, 0.4 g/bottle ($Ø_{inside}$=20mm) of sample were weighed and they were introduced in the oven at the same conditions and in the same way as described before. The composition and the proportion of the different powder and NDB blends were given in the materials section (Table 2.6).

On the other hand, in order to study the impact of the partially hydrolysed Alkanox P-24 on the performance of poly(propylene), 0.94 g (glass –inside $Ø_{inside}$= 47mm) of NDB and powder blend formulations were exposed in a climate chamber at 60°C and 75% relative humidity. In this case, the samples were removed periodically and mixed with the poly(propylene) (939.06 g) to be processed. The ratio of additives to polymer was 0.1 % of additive blend in the polymer. The whole experiment is summarized in Scheme 2.1.



Scheme 2.1. Experimental study

2.2.1.2. Ageing techniques

2.2.1.2.1. Oven hydrolysis ageing

Firstly, the powder and NDBs were introduced in small bottles of 5.8x2.2 cm. In order to achieve the relative humidity required, they were placed in a desiccator and the device was introduced in a Binder oven at 60° C. An excess of a water soluble salt in contact with its saturated solution and contained within an enclosed space produces a constant relative humidity (R.H.) and vapour pressure according to

$$RH = A \exp (B/T)$$

Where RH is the percent relative humidity (generally accurate to ±2 %), T is the temperature in Kelvin, and the constants A and B and the range of valid temperatures are given in a table.

In this experiment NaCl was used. The constants for NaCl were *A=69.20 and B=25.*
So theorically,
RH=74.6 %
A relative humidity of 75 ± 1 % was determined experimentally, measured with an electronic thermo hygrometer Model ETHG913R (Oregon scientific).

Figure 2.1. Hydrolysis test set-up

2.2.1.2.2. Climate Chamber

In order to study the effect of partially hydrolysed phosphite Alkanox P-24 on the processing stability of poly(propylene), before doing the multi-pass extrusion, the samples were exposed in a climate chamber (Espec Temperature & Humidity Chamber, model PR-2KP) at 60 °C and 75 % relative humidity. Periodically, the samples were removed from the climate chamber and immediately ground with a mortar to be mixed with the polymer (the ratio of additives to polymer was 0.1 % of additive blend in the polymer) and multiple extrusion passes were carried out.

2.2.1.2.3. Multi-pass extrusion

The samples that were removed from the climate chamber were mixed with the polymer (poly(propylene)) by bag-mixing during 2 minutes. The resulting mix was extruded on a Brabender single-screw extruder (screw diameter = 19 mm, L:D = 25:1) at a melt temperature of 275 °C and a screw rotation speed of 60 rpm. Five extrusions were carried out and the melt flow rate and yellowness index were measured after the 1st, 3rd and 5th extrusion passes. The tubular extrudate was cooled in a water bath and pelletised with a pelletiser. All extrusions were undertaken in air.Temperature profile shown in Table 2.8.

Table 2.8. Temperature profile for the compounding extrusion

Extruder temperature (°C)	Melt temperature (°C)
Barrel zones	Die zone
200/225/250	275

2.2.1.3. Analysis techniques

2.2.1.3.1. High performance liquid chromatography

High performance liquid chromatography (HPLC) is the most common technique used for the analysis of polymer additives. In HPLC, a solvent system is pumped through a column packed with a stationary phase. Different additives are separated due to differences in the partition coefficients of solutes between the stationary phase and the mobile phase[79].

The relative distribution of a solute between two phases is determined by the interactions of the solute species with each phase. The relative strengths of these interactions are determined by the variety and the strengths of the intermolecular forces that are present, by the polarity of the sample and that of the mobile and stationary phases[80].

In *normal phase chromatography* the stationary phase is relatively polar and the mobile phase is relatively non-polar[79,81].

In reverse phase chromatography the column is packed with a non-polar phase and a polar solvent is used as the mobile phase[79,81].

The stationary phases used nowadays are microparticulate column packings and are commonly uniform, porous silica particles, with spherical or irregular shape, and nominal diameters of 10, 5 or 3 μm. The separation can be realized by the bonding of different chemical groups to the surface of the silica particle, to produce what are called the bonded phase, in which C-18 alkyl groups are attached to the surface of the silica particles. There types are called ODS (octadecylsilane) bonded phases[80]. The mobile phase in HPLC may be water, organic solvents or buffers either on their own or mixed with one another[80].

The general instrumentation for HPLC incorporates the components, shown in Figure 2.2.

There is one or more glass or stainless steel solvent reservoir for the mobile phase. Two solvent reservoirs were used, one for acetonitrile and the other one for the propan-2-ol. If the composition of the mobile phase is constant the method is called *isocratic* elution. However, when the composition of the mobile phase is made to change in a predetermined way during the separation, the technique is called *gradient* elution. Pockets of air can collect in the pump or in other places, causing strange behaviour from the detector and irregular pumping action[80,82,83]. The mobile phase is delivered to the column by a pump. To obtain separations either based on short analysis time or under optimum pressure, a wide range of pressure and flows is desirable[82]. Sampling valves or loops are used to inject the sample into the flowing mobile phase just at the head of the separation column. A variety of loop volumes is available, commonly 10-50 μl[80]. 20 μL volume loop was used.

The separation column contains the packing needed to accomplish the desired HPLC separation[82]. Different kinds of packing can be found depending on the application. When packed into a column, the small size of these particles leads to a considerable resistance to solvent flow, so that the mobile phase has to be pumped through the column under high pressure[80].

A detector with some type of data handling device completes the basic instrumentation[82]. These are the most popular detectors in HPLC. The principle is that the mobile phase from the column is passed through a small flow cell held in the radiation beam of a UV/Visible photometer or spectrophotometer. These detectors are selective in the sense that they will detect only those solutes that absorb UV (or visible) radiation[80]. The analytes need chromophoric groups in their structure, which many polymer additives do not possess[89]. Once the signal is detected, the data are summarised in the chromatogram.

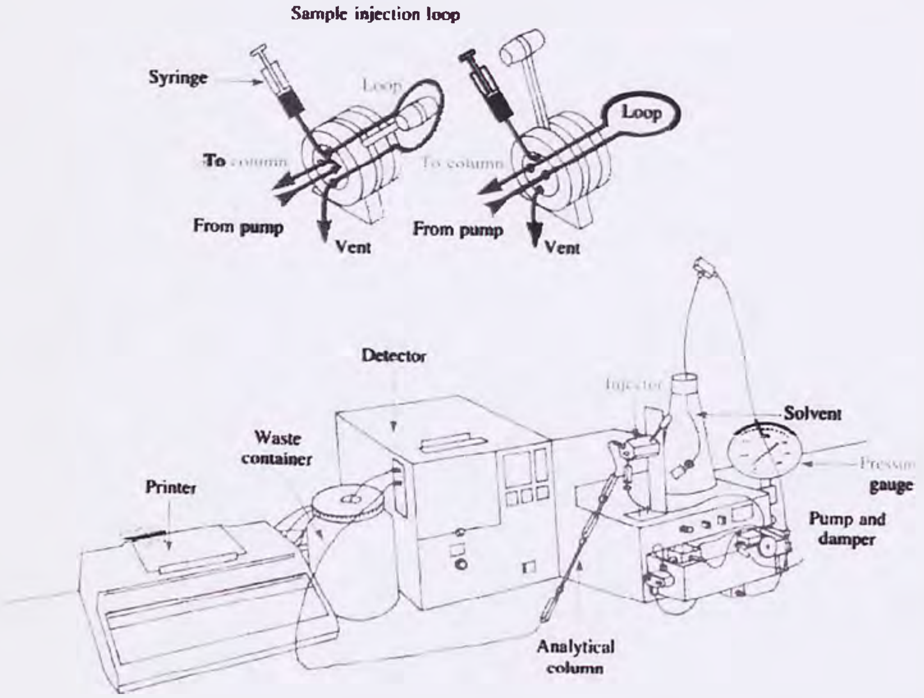


Figure 2.2. General instrumentation for HPLC[82].

Hydrolytic stability of different phosphites

In order to compare the hydrolytic stability of different phosphites, the following experimental conditions were used.

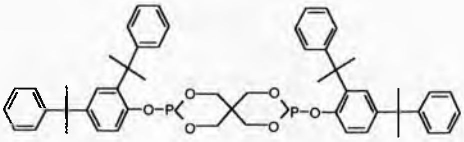
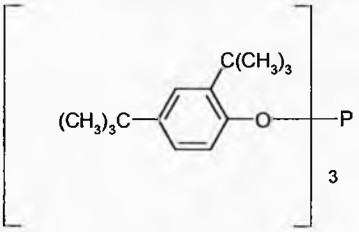
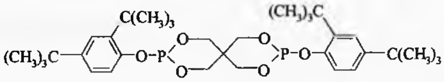
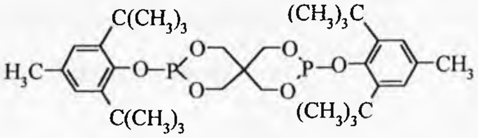
Apparatus: Hewlett-Packard Series 1000.
Column: HyPURITY Elite C18 (reverse phase) HYPERSYL column.
Flow rate: 1.5 cm^3/min (1.2 cm^3/min in PEP-36 and Alkanox 24-44).
Detector: UV, 230 nm
Sample volume: 20 µL.

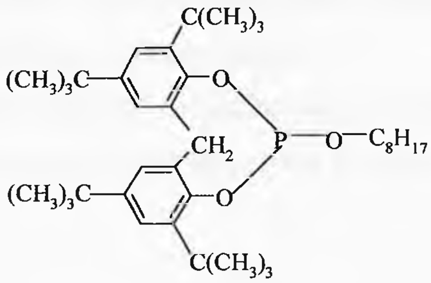
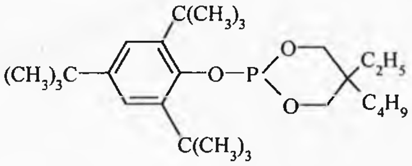
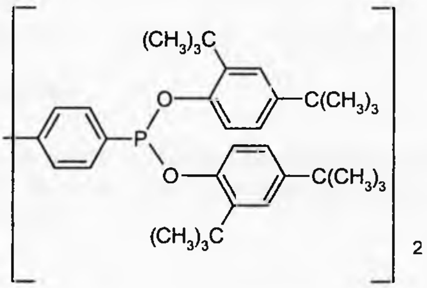
Firstly, a calibration curve of each phosphite was plotted. For each known concentration the height of the peak was obtained. Concentrations of phosphite during the hydrolysis were then determined from the calibration curve, as was their degree of hydrolysis, following the depletion of the phosphite peak.

In order to achieve the best separation between the solvent and the phosphite, a specific mobile phase was used for each phosphite as shown in Table 2.9.

All of the phosphites were dissolved in dichloromethane because they were not all soluble in the mobile phases.

Table 2.9. Mobile phase ratios for different phosphites

Phosphite	Propan-2-ol (%)	Acetonitrile (%)	Structure
Alkanox 28 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	20	80	
Alkanox 240 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	30	70	
Alkanox P-24 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	-	100	
PEP-36 (Asahi Denka Kogyo 7-2-35 Higashiogu, Arakawa-ku Tokyo,116-8553 Japan)	30	70	

HP-10 (Asahi Denka Kogyo 7-2-35 Higashiogu, Arakawa-ku Tokyo,116-8553 Japan	30	70	
Ultranox 641 (GE Specialty Chemicals, 1000 Morgantown Industrial Park North Morgantown, WV 2650, USA)	30	70	
Alkanox 24-44 (Great Lakes Chemical Corporation Kruisveg 2 Haven 650 2040 Antwerp, Belgium)	40	60	

Hydrolytic stability of phosphite blends

In order to study the influence of different co-additives (phenolic antioxidant, acid scavengers) on the hydrolytic stability of Alkanox P-24, the samples removed from the oven were analysed by HPLC using the following conditions.

Apparatus: Hewlett-Packard Series 1000.
Column: HyPURITY Elite C18 (reverse phase) HYPERSYL column.
Flow rate: 1.5 cm^3/min (1.2 cm^3/min in PEP-36 and Alkanox 24-44).
Detector: UV, 230 nm
Sample volume: 20 µL.
Mobile phase: 100 % acetonitrile

After being removed from the oven, the samples were dissolved in acetonitrile. In some cases, the solid particles were separated due to their non-solubility in acetonitrile and to avoid blockage of the column. A calibration curve was established with different concentrations to define the corresponding peak height for each concentration.

The peak of Alkanox P-24 was followed (depletion) and, with the calibration curve, the degree of hydrolysis was calculated. The calibration curve of Alkanox P-24 is shown in Figure 2.3.

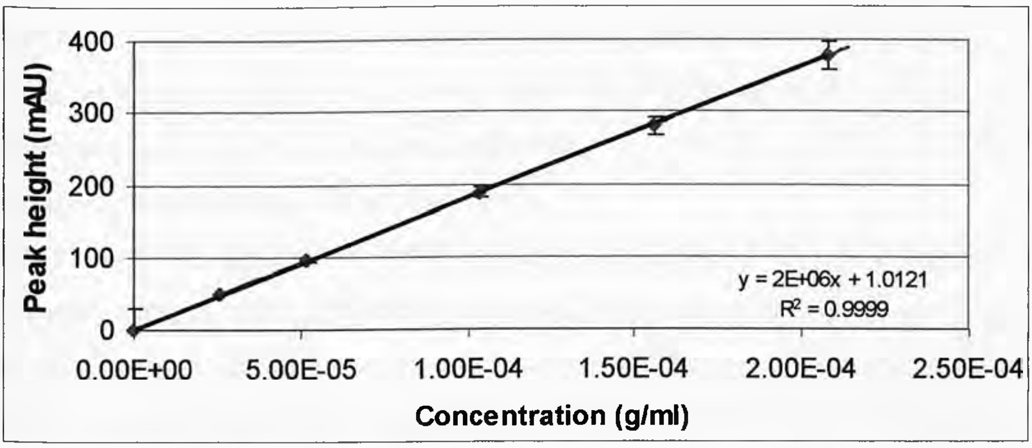


Figure 2.3. Calibration curve of Alkanox P-24. Concentration (g/ml) versus the height of the peak (measured with a U.V. detector in the HPLC) is represented. The error bars represent the standard deviation of the measurement.

On the other hand, the conditions used to study the influence of the physical form in different commercial formulations are the following:

Apparatus: Hewlett-Packard Series 1000.
Column: HyPURITY Elite C18 (reverse phase) HYPERSYL column.
Flow rate: 1.2 cm^3/min
Detector: UV, 230 nm
Sample volume: 20 μL.
Mobile phase: 80 % acetonitrile.
20 % propan-2-ol.

2.2.1.3.2. Melt flow rate

The melt flow rate (MFR) test is a simple and convenient method for characterizing both the type of degradation (chain scission, cross-linking) and the extent of degradation of a polymer. The MFR is inversely related to the molar mass of the polymer and is indicative of the flow characteristics of the molten polymer. This parameter is measured using a capillary melt viscometer by applying a standard weight and a melt temperature, in accordance with ASTM D1238[89].

The MFR can serve to assess the extent and mechanistic pathway of polymer degradation. A decrease in the MFR of the polymer is indicative of cross-linking and is usually observed as a result of gamma irradiation or during melt processing operations such as extrusion. An increase in the MFR is related to chain scission, which, leads to a reduction in molar mass. This is usually the dominant mode of breakdown of poly(propylene) in the melt. It is well known also that, in some cases cross-linking and chain scission can occur simultaneously and the MFR measurements may prove to be misleading if both cross-linking and chain-scission reactions take place[89].

In order to study the influence of partially hydrolysed Alkanox P-24 on the performance of the polymer, samples were periodically removed from the climate chamber. These were mixed with the polymer and a multi-pass extrusion experiment (as explained in section 2.2.1.2.3) was carried out. MFR was determined after the 1st, 3rd and 5th extruder passes. This parameter was measured using a Ceast Automatic MFR machine by applying a 2.16 kg standard weight at a melt temperature of 230 °C, in accordance with ASTM D1238.

2.2.1.3.3. Yellowness index

Polymers containing acidic moieties tend to discolour and deteriorate with time. The tendency towards discoloration is enhanced by the presence of phenolic antioxidants or certain flame-retardants in the polymers. Yellowing is associated with a degradation process, but this is not always the case. It can be due to interaction of additives in the formulation. The extent of yellowing of polymers is usually expressed as the yellowness index (YI). YI is a numerical representation of how yellow a material is in comparison with a white standard. The intensity of discoloration can be measured by colorimetric evaluation of compression-moulded films or of pellets themselves. This method is intended for determining the degree of yellowness under daylight illumination of nonfluorescent, nearly colourless transparent or nearly white translucent or opaque plastics.

The influence of additives on the discoloration of the polymer, after multiple extrusion passes was studied by measuring the colour development in the pellets after the first, third and fifth extruder passes. A Gretag Macbeth Color-Eye 3000 Colorimeter was used to measure colour development according to ASTM E-313 on the granules. A pulsed xenon light source was used and a spectral range from 360 to 750 nm.

2.2.2. Alkanox P-24 hydrolysis mechanistic studies

2.2.2.1. Analysis techniques

2.2.2.1.1. Fourier transform infrared spectroscopy (FTIR)

Infrared spectroscopy (IR) is one of the more powerful tools available to chemists for identifying pure organic and inorganic compounds because all molecular species absorb infrared radiation (with exception of a few homonuclear molecules)[83].

Molecular vibrations (periodic motions involving stretching or bending of bonds) can be measured in an infrared spectrum. Functional groups have vibration frequencies, characteristic of that functional group. The fact that many functional groups can be identified by their characteristic vibration frequencies makes the infrared spectrum the simplest, most rapid and often most reliable means for assigning a compound to its class[84,85].

A large molecule has a large number of vibrational modes that involve the whole molecule. Some of these molecular vibrations are associated with the vibrations of individual bonds or functional groups while others are considered as vibrations of the whole molecule. These individual bonds vibrations are stretching, bending, rocking, twisting or wagging[84].

The power of IR spectroscopy is greatly enhanced by the Fourier transform (FT) processing of data. The IR beam, composed of all the frequencies in the IR range, is passed through the sample and generates interference patterns, which are then transformed electronically, using Fourier transformations, into a normal IR spectrum. The advantages of FTIR are: rapid scanning speed, simplicity of operation, much enhanced sensitivity and reduced noise, the integral computer system enables the use of libraries of spectra and simplifies spectrum manipulation, such as the subtraction of contaminant or solvent spectra[86].

IR spectra are very useful for identifying compounds by direct comparison with spectra from standard samples, but IR spectra are limited in deducing structures from spectroscopic data. The hydrolysis of the phosphite, Alkanox P-24, under the conditions previously mentioned (60 °C/75 % R.H.) was followed using FTIR spectroscopy. Small samples were periodically removed from the oven and the IR spectrum recorded in the transmission mode using the KBr disc method. Spectra were developed from 10 scans with the resolution set at 4 cm^{-1}.

A Nicolet NEXUS™ FT-IR spectrometer was used for this investigation.

2.3. Stabilisation studies (High density poly(ethylene))

2.3.1. Sample preparation

2.3.1.1. Extrusion blending

Compounding is the general term used for the operation of converting the polymer produced in a polymerisation reactor into a palletised form. It is also used to incorporate and homogenise additives into the polymer. Extrusion is the most important technique used for polymer processing. There are different types of extruders; single–screw extruder, twin-screw extruder...

A practical method for mixing additives with polymers is the twin-screw extrusion, which is a continuous mixing operation component of the mix being fed on a continuous basis into the machine. This processing method was used to mix the additives to the polymer.

In the extrusion process, polymer is propelled continuously along a screw through regions of high temperature and pressure where it is melted and compacted, and finally forced through a die shaped to give the final object.

The components of an extruder are illustrated in Figure 2.4.

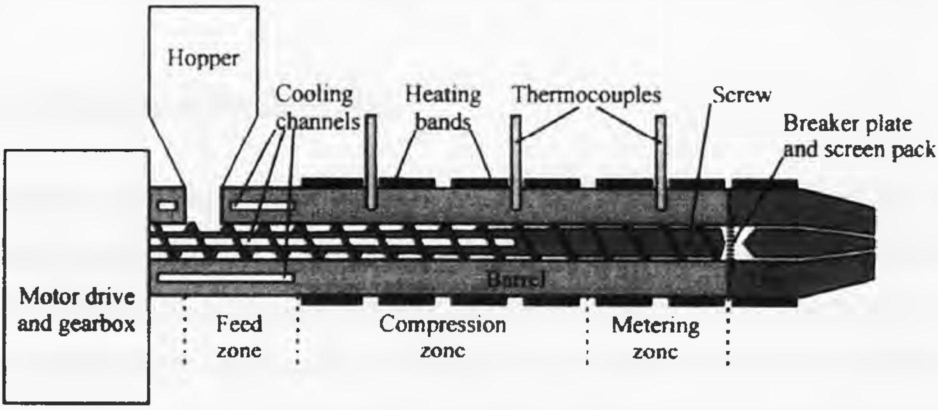


Figure 2.4. Basic components of an extruder[87].

The screw of an extruder is divided into several sections, each with a specific purpose. The feed zone picks up the polymer from a hopper and propels it into the main part of the extruder. In the compression zone, the loosely packed feed is compacted, melted, and formed into a continuous stream of molten plastic. The metering zone contributes to uniform flow rate, required to produce uniform dimensions in the finished products, and builds up sufficient pressure in the polymer melt to force the plastic through the rest of the extruder and out of the die[88]. The main operating variables are the speed of screw rotation and the barrel temperature profile but the main design variables are the screw diameter and length, usually expressed as length-to-diameter ratio L/D. The two more important factors determining the success of an extrusion operation are the screw design and the heating profile along the extruder.

The polymer was initially dry blended with the additives. Each dry blend was then extruded on a Betol® BTS 30 laboratory corotating twin-screw compounding extruder (screw length = 690 mm, screw diameter = 30 mm, L:D = 23:1) at a melt temperature of 230 °C and a screw rotation speed of 60 rpm. The tubular extrudate was cooled in a Betol® model 119 water bath and pelletised with a Acrapak pelletiser. All extrusions were done in air. The temperature profile was as described in Table 2.10. All the polymer additive ratios are shown in section 3.5.2 of the results and discussion part.

Table 2.10. Temperature profile for the compounding extrusion.

Extruder temperature (°C)	Melt temperature (°C)
Barrel zones	Die zone
220 / 220 / 220 / 225 / 227	230

2.3.1.2. Compression moulded film

In compression moulding, the polymer is heated in a mould, compressed to shape and cooled. The process is slow since heating and cooling of the mould must be carried out in each cycle. This approach is employed only for the manufacture of large blocks and sheets, for relatively strain-free objects such as test pieces and where alternative processes cannot be used because of lack of equipment[1]. Pressing the polymer sample between heated platens in a hydraulic press usually produces films. In the case of semi-crystalline polymers, the platens should be at a temperature at least 50 °C above melting point, T_m or 50 °C above the glass transition temperature T_g of the amorphous polymers.

A two-stage moulding cycle is generally used to press the samples. First, the polymer is held in contact with the heated plate at a low pressure for about 2 minutes to allow uniform heating and melting. Then, the applied pressure is increased and the sample is maintained at this temperature for a period of 1 minute.

Poly(ethylene) pellets were compressed moulded into films using a steam press (J.R. DARE Limited, Manchester, UK) between two aluminium plates at 160 °C with constant minimum pressure and then cooled immediately in a cold press (Francis Shaw and Co., Manchester, UK) with circulating water. Different trials were carried out until a good film was obtained. A final thickness of 100 μm was obtained. The sample thickness was regulated by careful selection of sample quantity and pressure. The sample thickness was recorded at various locations across its surface using a digital micrometer (Mitutoyo Corporation, Japan).

The cycle time is described in Table 2.11.

Table 2.11. Time steps, pressure and temperature for poly(ethylene) film preparation

Step	Time (min)	Pressure (MN/m^2)	Temperature (°C)
Pre-warming	1	0	160°C
Pressing	2	13	160°C
Cooling	3	15	0

2.3.2. Ageing techniques

2.3.2.1. Oven ageing

Oven ageing is the most established accelerated method for assessing the oxidative stability of polymers. Oven ageing is carried out in a thermostatted air-circulating oven that involves subjecting a suitable fabricated polymer sample (generally either a film or a moulded strip) to temperatures below the melting point of the polymer. The criterion for establishing when failure has occurred during oven ageing varies considerably, from the onset of discoloration, any visible cracking, cracking upon twisting or bending and changes in weight[89].

Compression moulded films of HDPE were cut into 20 x 40 mm strips and were aged in a thermostatted air-circulating oven (Binder) at 110 °C.

2.3.2.2. Multiple pass extrusion

Multiple pass extrusion experiments can be regarded as a form of accelerated ageing in the melt state. This is useful for simulating processing conditions. The method involves repeatedly passing the polymer through an extruder and then collecting samples after each pass. The melt flow rate (MFR) and yellowness index (YI) were measured for the samples collected[89].

Multiple extrusions were carried out with the same twin-screw extruder as that used for compounding at the same temperature profile and screw speed. The compounding step was counted as the first extruder pass, two more extruder passes were made, a sample being taken after each pass. The samples from the first and third extruder passes were subjected to MFR and colour development measurements in order to acquire insight into the melt stability of the polymer.

2.3.3. Analysis techniques

2.3.3.1. Carbonyl index measurement

The poly(ethylene) samples that were prepared by compression moulding were oven aged at 110 °C in order to study the long-term thermal stability of the polymer. The method chosen to assess the oxidative stability was the well-established carbonyl index measurement[14].

Infrared (IR) spectroscopy has been the method of choice for detecting changes and the chemical nature of the products formed in oxidizing polymers[90]. The hydroxyl groups and the carbonyl groups usually account for most of the oxidation products arising from the thermooxidative degradation of poly(ethylene). In this respect, carbonyl group concentrations are often used to monitor oxidative degradation of polyolefins[91].

The more significant absorptions that arise in polymers as a result of oxidation arise from the carbonyl groups. The formation of carbonyl species, such as ketones, aldehydes, carboxylic acids, etc. in the polymer, generally gives a broad carbonyl band in the 1705-1735 cm^{-1} region. In degraded poly(ethylene) the carbonyl species are mainly ketones and carboxylic acids[89]. In order to detect the formation of carbonyl groups, a Nicolet NEXUS™ FT-IR spectrometer was used. Spectra were made from 10 scans with resolution set at $4cm^{-1}$. Carbonyl growth was studied in the region 1650-1850 cm^{-1}, (at 1715-1720 cm^{-1}) which corresponds mainly to the carbonyl stretching of ketone species.

Carbonyl band growth in this region of the spectrum was determined by the relative carbonyl index method, defined as described in Equation 2.1.

Equation 2.1. Carbonyl Index

$$\text{Carbonyl index} = (A/d) \times 100 \qquad \text{(Equation 1)}$$

A is the absorbance at 1715-1720 cm^{-1} and d is the film thickness (μm)

2.3.3.2. Melt flow rate measurement

In order to study the influence of different additives during the multiple pass extrusion of high-density poly(ethylene), the melt flow rate (MFR) was measured after each pass.
This parameter was measured using a Ray-Ran® Melt Flow Indexer capillary melt viscometer by applying a 10 kg weight at a melt temperature of 190 °C, in accordance with ASTM D1238. Different weight and temperature conditions from the conditions explained in the section 2.2.1.3.2 were used because the performance of different polymers (poly(propylene) and poly(ethylene)) after multiple pass extrusion were studied. Poly(propylene) and poly(ethylene) are different polymers (different melting temperature, different behaviour when melted). Therefore, according to the ASTM to measure the MFR different conditions are used for different polymers.

2.3.3.3. Yellowness index measurement

The influence of additives on discoloration of the polymer granules after first and third extrusions was measured using a Gretag Macbeth Color-Eye 3000 Colorimeter, according to ASTM E-313.

Chapter 3. RESULTS AND DISCUSSION

3.1. Hydrolytic stability of different phosphites

The objective of this chapter is to discuss the results of the comparative study carried out to investigate the hydrolytic stability of different commercial phosphites. Phosphites were introduced in the oven at 60 °C and 75 % relative humidity and the degree of hydrolysis was measured by HPLC, following the depletion of each phosphite peak (section 2.2.1.3.1) The degree of hydrolysis of the different phosphites investigated is given in Figure 3.1. It is striking that the phosphites investigated can be divided into two groups: the hydrolytically unstable phosphites (Alkanox P-24, Ultranox 641, ADK STAB PEP-36, ADK STAB HP-10) and those that show good hydrolytic stability (Alkanox 240, Alkanox 28).

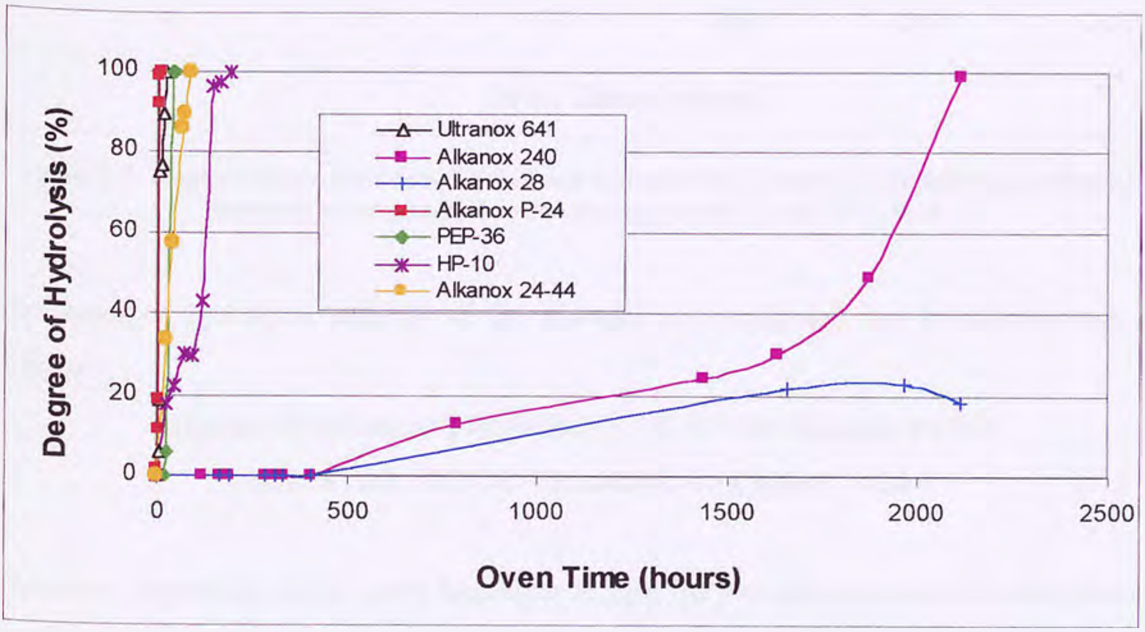


Figure 3.1. Degree of hydrolysis data for all the phosphites quantified as depletion of the phosphite after exposure to 60 °C and 75 % R.H.

Of the hydrolytically unstable phosphites, Alkanox P-24 (Great Lakes Chemical Corporation) was the most unstable, followed closely by Ultranox 641 and ADK STAB PEP-36, and then by ADK STAB HP-10 (Figure 3.2).

Whereas Alkanox P-24 was totally hydrolysed in less than 10 hours, Ultranox 641 reached total hydrolysis in 20 hours, ADK STAB PEP-36 in 40 hours and ADK STAB HP-10 in 144 hours.

On the other hand, Alkanox 240 was totally hydrolysed after about 2000 hours, whereas the degree of hydrolysis of Alkanox 28 reached only 20 % after this oven time.

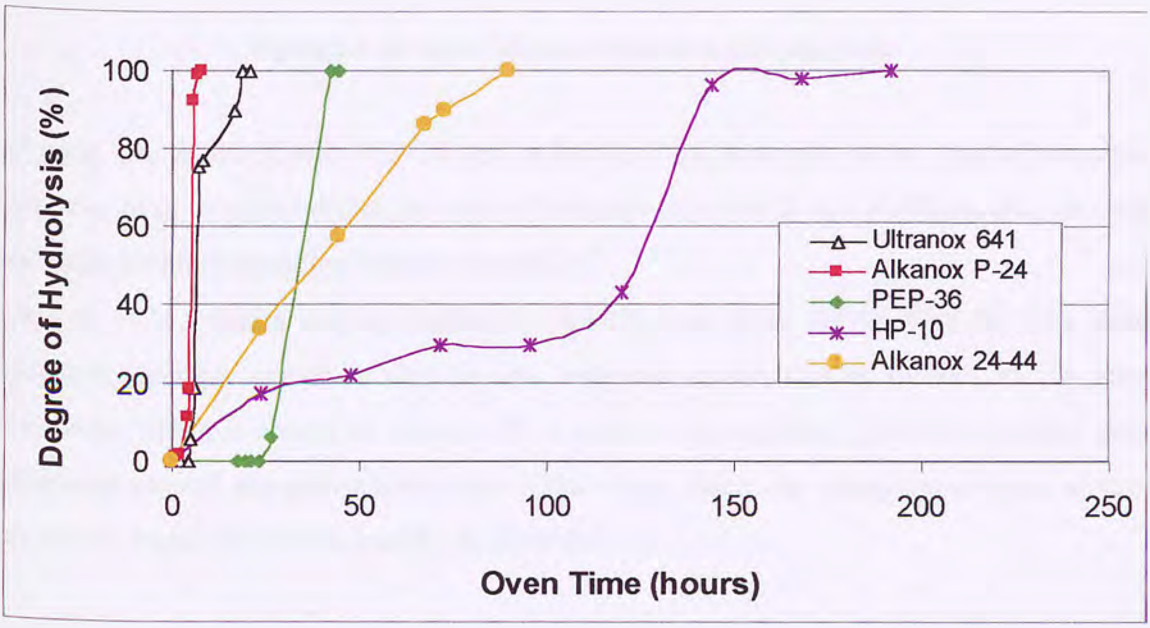


Figure 3.2. Degree of hydrolysis data for the most hydrolytically unstable phosphites quantified as depletion of the phosphite after exposure to 60 °C and 75 % R.H.

The order of hydrolytic stability of the phosphites investigated can be summarised as follows:

Alkanox 28>Alkanox 240>ADK STAB HP-10>Alkanox 24-44>
ADK STAB PEP-36>Ultranox 641>Alkanox P-24

Therefore, depending on the steric hindrance around the phosphorus atom and reduction of electron density, the rate of hydrolysis differs. Goghova *et al.*[51] studied the influence of substituents R1, R2 and R3 on degree of hydrolysis of phosphites of the following general form (Figure 3.3):

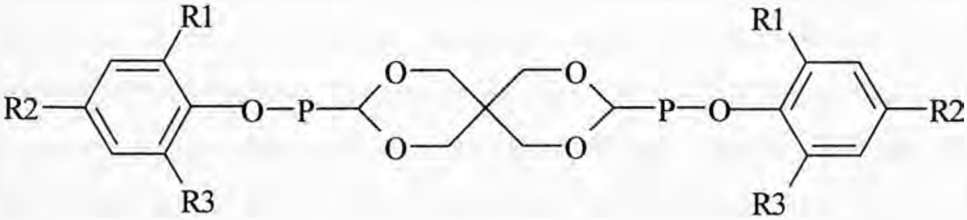


Figure 3.3. Structure of pentaerythritol based phosphites.

Alkanox 28, ADK STAB PEP-36 and Alkanox P-24 have the same type of structure. Goghova *et al.* concluded that the type of substitution in the 2 or 4 positions affords cyclic phosphites with outstanding hydrolytic stability[51].

Alkanox P-24 exhibits a lower hydrolytic stability than ADK STAB PEP-36. The lower hydrolytic stability could be due to the *tert*-butyl group that is present in the latter phosphite, which is absent in Alkanox P-24 and, as consequence, generates greater steric hindrance around the phosphorus atom. Therefore, since the phosphorus atom is more protected, higher hydrolytic stability is observed.

On the other hand, Alkanox 28 is very hydrolytically stable because of the greater steric hindrance in the molecule, where a possible attack by water on the phosphorus atom appears to be more difficult. In previous studies Tochacek and Sedlar[34] demonstrated the difference in hydrolysabilities at 25 °C between Alkanox P-24 and Alkanox 240 exposed to water vapour. The same ranking was observed between these two phosphites but at a lower temperature. Klender[92] proposes three methods for increasing the hydrolytic stability of phosphites for application as a polymer stabiliser.

- Internal or external addition of a basic component to the phosphite.
- Increase of the steric hindrance around the phosphorus atom.
- Reduction of electron density on the phosphorus atom.

The results confirm Klender's theory[52], where the hydrolysability decreases with increasing steric hindrance of substituents and/or their ability to decrease the electron density on the phosphorus atom.

Stevenson and Farber[93] carried out a hydrolytic stability test at 40 °C and 90 °C obtaining similar results to the ones obtained in this study. Alkanox 28 and Alkanox 240 were the most hydrolytically stable and Alkanox P-24, ADK STAB PEP-36, Ultranox 641 were shown to be less stable. Some authors relate high hydrolytic stability of phosphites to high crystalline melting points of the phosphites. This implies high lattice energy[94]. The high melting point along with the large hydrophobic substituents makes it difficult for the water molecule to penetrate the tightly bound crystal and thus hydrolyse the phosphite.

It is observed that ADK STAB HP-10 contains an aliphatic chain in its molecule. Thus, it could be concluded that the hydrolytic stability of this phosphite should be theoretically worse than ADK STAB PEP-36 or Alkanox 24-44. This is not shown in the results. ADK STAB PEP-36 and Alkanox 24-44 exhibit higher steric hindrance than ADK STAB HP-10 around the phosphorus atom. Various authors[46,47,95] have studied the hydrolytic stability of several commercial phosphites and reached the same conclusions as reported here. Alkanox P-24 is one of the most hydrolytically unstable phosphites and Alkanox 28 and the fluorophosphonites are among the most hydrolytically stable.

3.2. Influence of different co-additives on the hydrolytic stability of Alkanox P-24: Binary blends.

Alkanox P-24 [bis (2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite], is one of the more hydrolytically unstable phosphites (as confirmed in the previous chapter). However, it is well known from the literature that this phosphite is a very good processing antioxidant for polyolefins. As a consequence of its excellent processing performance, one of the major objectives of this work was to study the influence of other co-additives on the hydrolytic stability of this particular phosphite.

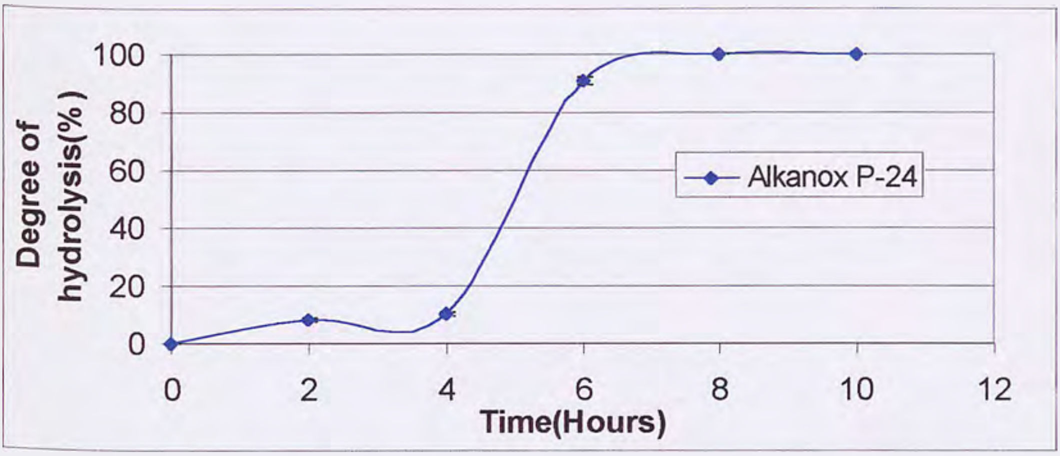


Figure 3.4. Hydrolytic stability of Alkanox P-24 at 60 °C and 75 % R.H. Results reported as mean value ± standard deviation.

The hydrolytic stability of Alkanox P-24 is shown in Figure 3.4. It has been observed that after a certain time, after 4 hours at 60 °C and 75 % R.H., there is a dramatic decrease in hydrolytic stability. Acids or bases are known to have an influence on the rate of the hydrolysis reaction of phosphites. Acids and metal cations accelerate the reaction of tryalkyl phosphites and water[36]. It has been observed in the literature that the trimethyl phosphite is sensitive to acid-catalysed hydrolysis[43]. An autoacceleration effect is observed for the reaction of Alkanox P-24 with water. During this reaction, acidic species, such as phosphorus acid are formed leading to the autocatalysis and, hence, a sharp increase in rate of hydrolysis.

To investigate the effect of the phenolic antioxidant Anox 20, and acid scavengers (CaSt and the hydrotalcite-like compound DHT-4A), a variety of binary blends was prepared by melt blending. The binary blends were exposed to 60 °C and 75±1 % relative humidity, the same experimental conditions used with Alkanox P-24.

3.2.1. Alkanox P-24/Anox 20

In this section the results for the first binary blend (Alkanox P-24/Anox 20 at different ratios by weight) are discussed. The sample was exposed to 60 °C and 75 % R.H. The degree of hydrolysis was measured as the depletion of the phosphite Alkanox P-24 peak in HPLC analysis.

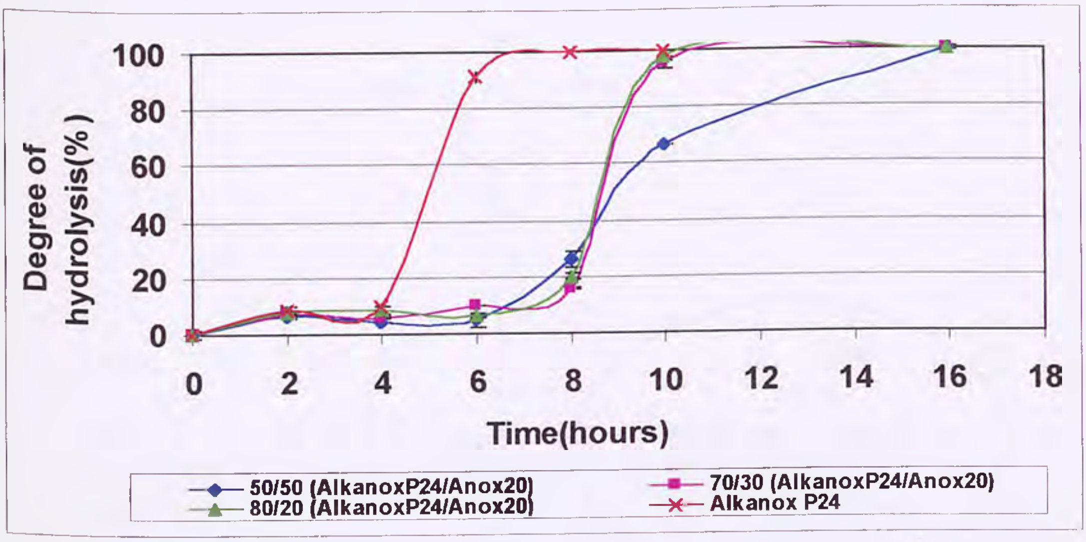


Figure 3.5. Hydrolytic stability of Alkanox P-24 in combination with Anox 20 at 60 °C and 75 % R.H. Results reported as mean value ± standard deviation.

It is highly apparent that the phenolic antioxidant Anox 20 increases the hydrolytic stability of Alkanox P-24 (Figure 3.5). Dilution of Anox 20 extended the induction time to the onset of hydrolysis, relative to that of the phosphite alone. The phenolic antioxidant Anox 20 improves the hydrolytic stability of Alkanox P-24.

It is believed that the improvement of the hydrolytic stability of Alkanox P-24 in combination with Anox 20 is due to a dilution effect. On the other hand, an increase in the ratio Alkanox P-24/Anox 20 gives an improvement to the hydrolytic stability of the phosphite although it is not significant in the early stages of the hydrolysis or for the ratios 80:20 and 70:30 Alkanox P-24/Anox 20.

It is also important to take the possible hydrolysis reaction of the phenolic antioxidant Anox 20 into consideration. Recent studies have shown that Hostanox 010 (Anox 20) hydrolyses under certain conditions. Structure of Hostanox 010 is shown in Figure 3.6. According to the literature the hydrolysis reaction of Hostanox 010 will lead to pentaerythritol and the corresponding acid[96].

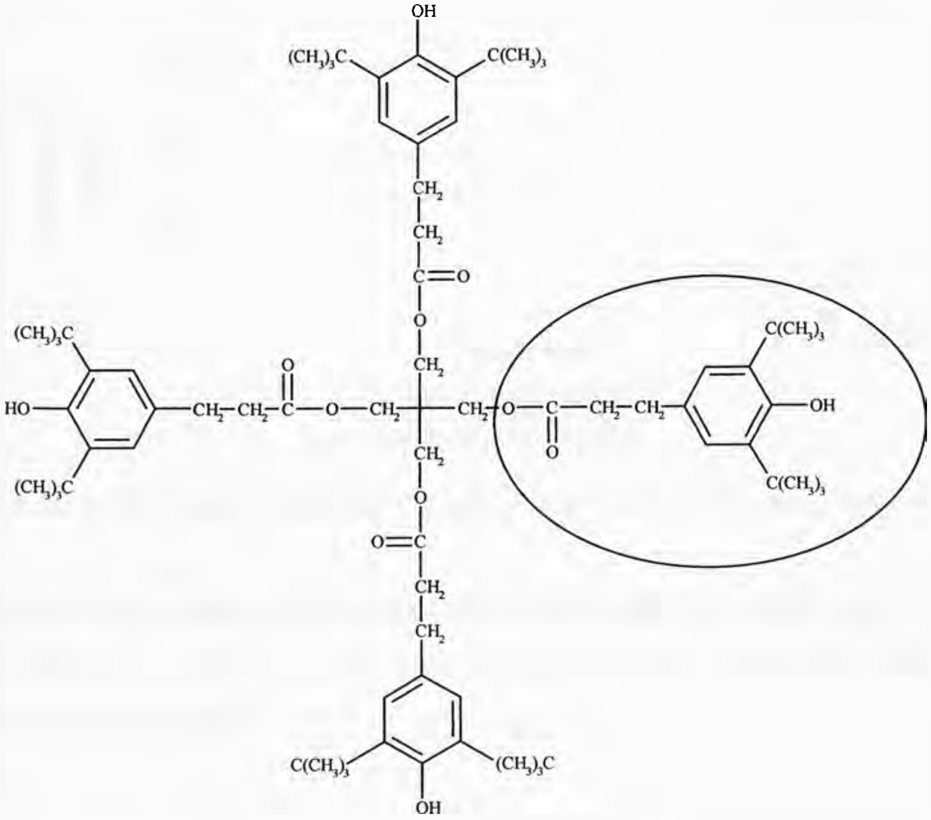


Figure 3.6. Fragment split off Hostanox 010 (Anox 20) during model hydrolysis[96].

The possible hydrolysis of the Anox 20 during the study of Alkanox P-24 has been considered. However, during the period at which the hydrolysis of the phosphite occurs the concentration of Anox 20 in the blend remains constant for 80:20 Alkanox P-24/Anox 20 and 70:30 Alkanox P24/Anox 20 blends (as observed in the HPLC chromatogram). However, a decrease on the Anox 20 peak is observed after 16 hours of exposure time to 6 0 °C and 75 % R.H. This suggests that the phenolic antioxidant also hydrolyses after certain time of exposure. The height of the Anox 20 peak versus the oven time is shown in Figure 3.7.

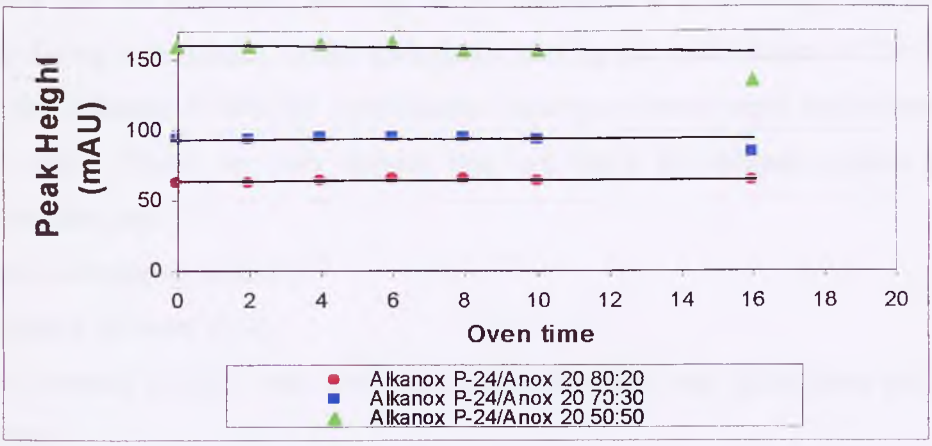


Figure 3.7. UV detector signal (Peak height of Anox 20 in HPLC chromatogram) versus oven time.

After the hydrolysis reaction of Alkanox P-24 the phenolic antioxidant Anox 20 starts to hydrolyse. However, under normal processing industrial conditions, the phenolic antioxidant Anox 20 is stable.

3.2.2. Alkanox P-24/Calcium stearate

The hydrolytic stability of Alkanox P-24 in combination with calcium stearate (CaSt) is shown in Figure 3.8.

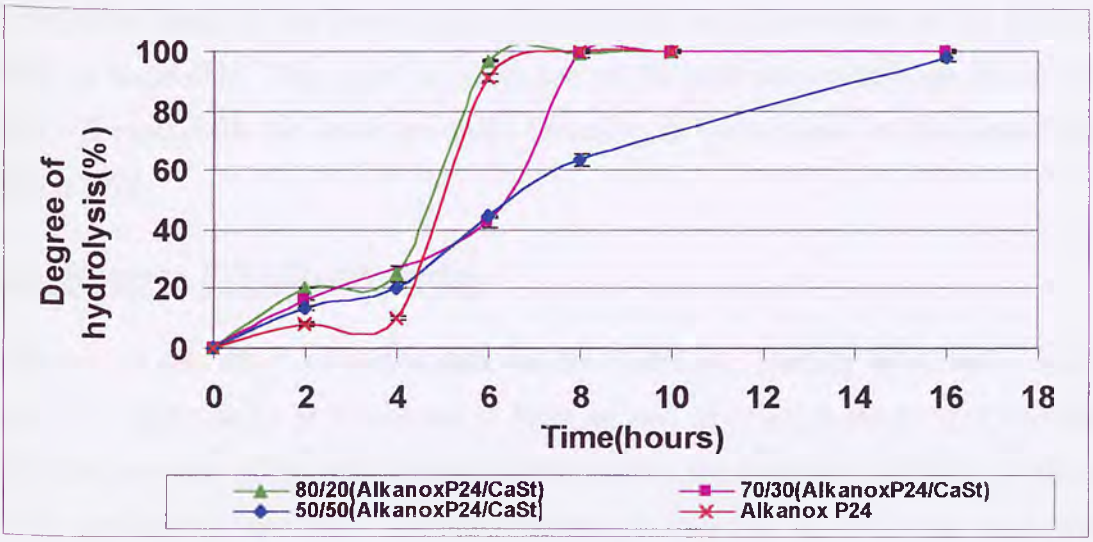


Figure 3.8. Hydrolytic stability of Alkanox P-24 in combination with CaSt at 60 °C and 75 % R.H. Degree of hydrolysis versus the exposure time to 60 °C and 75 % R.H. Results reported as mean value ± standard deviation.

It is evident that the hydrolytic stability of the phosphite is improved by the presence of CaSt, but during later stages of the hydrolysis. During the early stages of the hydrolysis reaction, the Alkanox P-24/CaSt combination undergoes more rapid hydrolysis than the phosphite alone. There are two factors that are likely to mitigate against phosphite stabilisation, they are:

- Acid scavenging capacity
- Content of water (3%).

The water content in CaSt was not determined; the data was taken from the company technical data.

It is believed that the improvement of the hydrolytic stability of Alkanox P-24 in combination with acid scavenger CaSt is due to a dilution effect. However, the effect was lower than that seen with the Alkanox P-24/Anox 20. This fact could be associated with the size of different molecules. Anox 20 has a higher molecular mass and could create a greater barrier effect for the water to attack than the CaSt.

However, a chemical effect is also observed. The two factors mentioned before, the acid scavenging capacity of CaSt and water content may play an important role. Due to the water content of the CaSt, the hydrolysis reaction is accelerated. This effect can be observed in Figure 3.8 at early stages of hydrolysis and with the sample containing 80:20 Alkanox P-24/Anox 20 where the hydrolysis reaction is faster than the reaction for Alkanonx P-24 alone.

On the other hand, at the latter stages of hydrolysis an improvement in the hydrolytic stability is noticeable. This could be attributed to the acid scavenging capacity of CaSt, which will react with the acidic products generated as consequence of the hydrolysis of Alkanox P-24.

3.2.3. Alkanox P-24/Hydrotalcite

In Figure 3.9 the effect of hydrotalcite on the hydrolytic stability of Alkanox P-24 is shown. The hydrotalcite is considered to have an acid scavenging effect. It is interesting that in the presence of the acid scavenger hydrotalcite, the hydrolytic stability of Alkanox P-24 is significantly improved. The same tendency is followed as well in this case, where an enhancement in hydrolytic stability is observed by increasing the quantity of the acid scavenger.

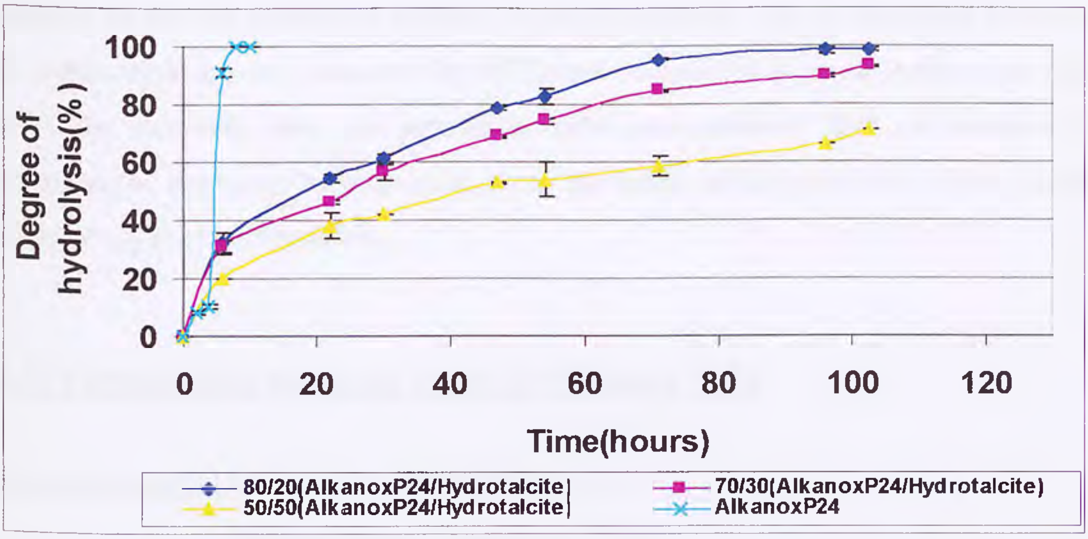


Figure 3.9. Hydrolytic stability of Alkanox P-24 in combination with Hydrotalcite at 60 °C and 75 % R.H. Degree of hydrolysis versus exposure time to 60 °C and 75 % . Results reported as mean value ± standard deviation.

Increasing amounts of hydrotalcite increases the hydrotalcite stability of Alkanox P-24 within the composition range investigated. The improvement of the hydrolytic stability of Alkanox P-24 in the presence of the acid scavenger hydrotalcite is due to a dilution effect.

It is clear that the impact of hydrotalcite is higher than that of the Anox 20 or CaSt. Indeed, the structure of hydrotalcite must be carefully considered. Since the hydrotalcite has a layered structure, the phosphite may be able to intercalate between the layers.

On the other hand, a chemical effect should be taken into consideration. Indeed, due to the acid scavenging nature of the hydrotalcite, the acidic species formed during hydrolysis reaction of Alkanox P-24 would react with the acid scavenger and the hydrolysis reaction would not be auto-catalysed. According to the literature, the hydrolysis of tripropyl phosphite in water with acetonitrile was significantly retarded using a small amount of tertiary base.[36]

3.3. Influence of different co-additives and different physical forms on the hydrolytic stability of Alkanox P-24: Multiblends

In this section, the influence of different co–additives and different physical forms on the hydrolytic stability of the phosphite Alkanox P-24 will be discussed. Also, the processing performance of hydrolysed Alkanox P-24 (the phosphite was exposed to the same conditions as for the hydrolysis studies) in poly(propylene) will be discussed in terms of melt stabilisation activity (measured by MFR) and colour development (yellowness index). Finally, the analytical data and processing data are combined (melt performance as a function of the degree of hydrolysis) to study the effect of the hydrolysis of the phosphite on poly(propylene) performance.

3.3.1. Formulation based on Anox 20/Alkanox P-24

Hydrolysis studies: [Anox 20 + Alkanox P-24] (50:50)
Physical forms: Powder and NDB
The hydrolysis studies were carried out with the additives only (without polymer).
Compounding: 500 ppm Anox 20
500 ppm Alkanox P-24

The additives were mixed with the polymer at 0.1% of additives (50:50 by weight of Anox 20 and Alkanox P-24 that were already premixed) in the poly(propylene). This stabiliser system will be considered as reference. All the other systems studied will be compared to this reference system.

3.3.1.1. Hydrolytic stability studies

The samples, powder and no dust blend (NDB) binary blend were exposed to 60 °C and 75 % R.H. The degree of hydrolysis (depletion of Alkanox P-24) was measured to study the influence of the phenolic antioxidant Anox 20 on the hydrolytic stability of Alkanox P-24 and the impact of the different physical forms. Degree of hydrolysis versus the exposure time at 60 °C and 75 % R.H for the binary blend based on Anox 20/Alkanox P-24 is shown in Figure 3.10.

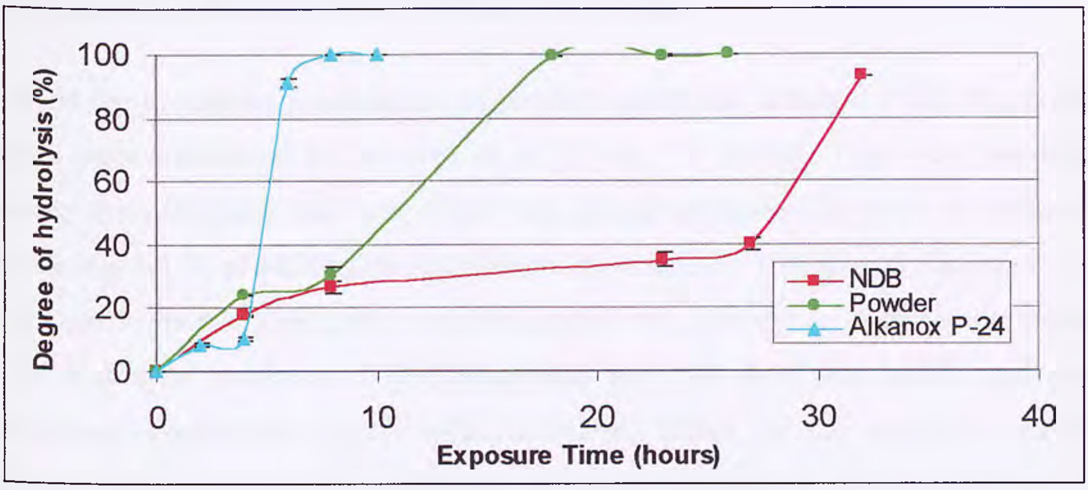


Figure 3.10. Effect of exposure time and physical forms of degree of hydrolysis of Alkanox P-24 at 60 °C and 75 % R.H. Results reported as mean value ± standard deviation.

In Figure 3.10 the effect of the phenolic antioxidant as a co-additive is clearly shown. The hydrolysis reaction of the phosphite Alkanox P-24 is retarded in the presence of Anox 20. This is believed to be due to a dilution effect. The complete disappearance of Alkanox P-24 takes place between 10 to 17 hours of exposure time, whereas it takes about 6 to 8 hours for the pure material.

Furthermore, the impact of the physical form on the hydrolytic stability of the phosphite Alkanox P-24 is obvious. The hydrolysis of Alkanox P-24 is substantially retarded when the phosphite is part of the binary no dust blend relative to the hydrolysis of the phosphite in the powder blend. This could be due to a physical effect, where the reaction rate of the phosphite with the water could be partially controlled by the diffusion rate of water into the pellet. Due to the higher and compact size of the NDB pellet (lower surface area) relative to the powder particles, the diffusion of water and its attack on the phosphite could be more difficult and consequently delay the hydrolysis rate.

Furthermore, in the case of pure Alkanox P-24, an auto-acceleration is observed as mentioned before. For the NDB blend, a steady increase is observed before the auto-acceleration occurs. This could be due to the diffusion control part of the reaction. Finally, the auto-acceleration is observed where enough water has been absorbed (samples were exposed to 60 °C and 75 % R.H.) and the autocatalytic effect dominates over the diffusion effect. On the other hand, for the powder blend, there were not enough data to draw any general conclusions.

3.3.1.2. Melt flow rate after multiple pass extrusion

To study the processing performance of partially hydrolysed Alkanox P-24, the phosphite samples were introduced in the oven at 60 °C and 75 % R.H. They were periodically removed from the oven and melt mixed with poly(propylene). The ratio of additives to polymer was 0.1 % of additive blend (500 ppm of Anox 20 + 500 ppm of Alkanox P-24) in the polymer. Multiple extrusions were then carried out. In order to study the performance of the hydrolysis products on poly(propylene) the melt flow rate (MFR) and colour development (yellowness index) were measured. Effect of the partially hydrolysed Alkanox P-24 on the melt performance of poly(propylene) is shown in Figure 3.11 (powder blend) and Figure 3.12 (NDB blend). Melt flow rate (after 1st, 3rd and 5th extrusion pass) versus exposure time is shown.

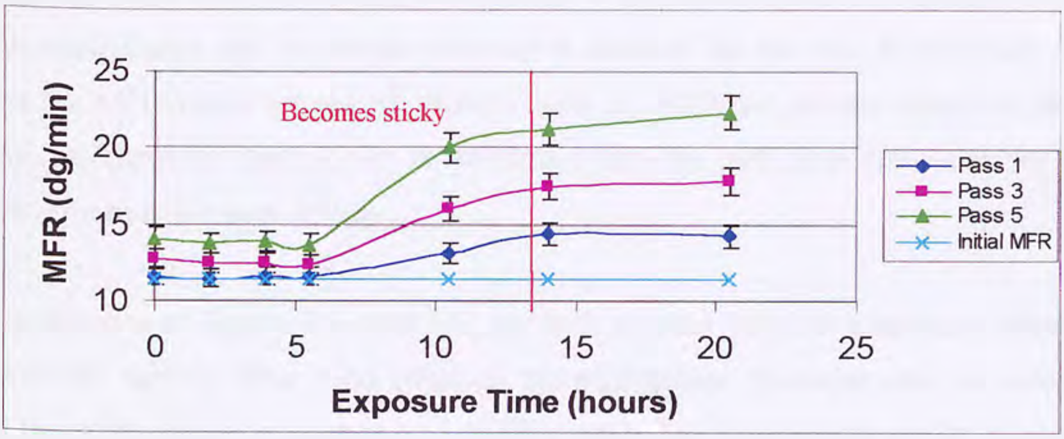


Figure 3.11. Effect of exposure time on melt performance for the Anox 20/Alkanox P-24 POWDER form in poly(propylene). Results reported as mean value ±5 % error range.

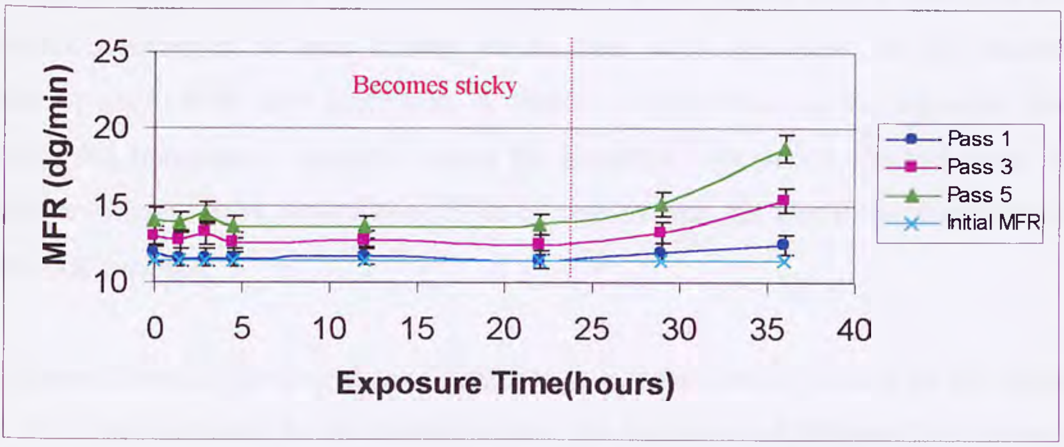


Figure 3.12. Effect of exposure time on melt performance for Anox 20/Alkanox P-24 NDB form. Results reported as a mean value ±5% error range.

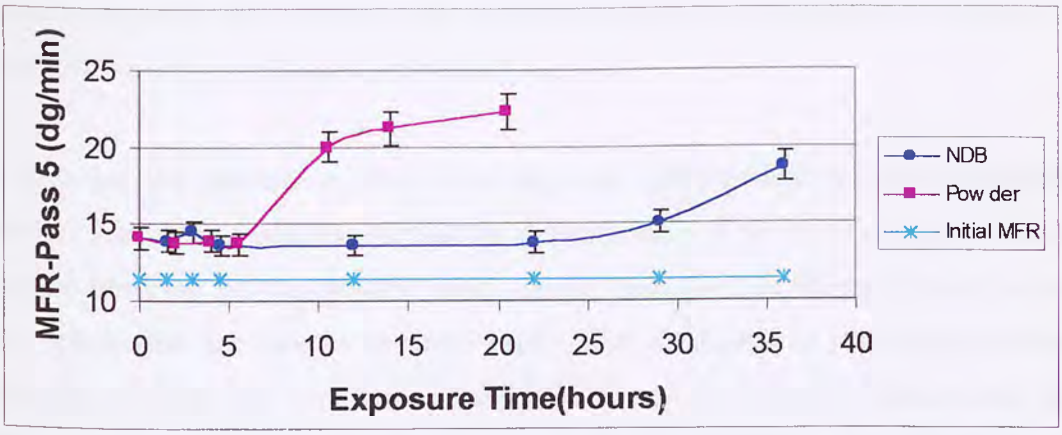


Figure 3.13. Effect of exposure time on melt performance for Anox 20/Alkanox P-24 for NDB and POWDER in poly(propylene). Results reported as a mean value ±5% error range

The first observation to be made is that NDB and the powder physical forms should have initially the same melt processing performance if the initial quality of Alkanox P-24 is within specification and the dosing accuracy is identical for the two. From Figure 3.13, where the MFR values for the 5th extruder pass for NDB and powder blend are plotted versus the exposure time, it can be confirmed that the melt flow rate value for both physical forms is the same initially.

On examination of Figures 3.11 and 3.12, for both physical forms the same main behaviour is observed. Initially there is no effect on the performance. However after an induction time the MFR begins to increase to a limiting value that is dependent on the number of passes through the extruder. It is evident that even at zero exposure time, some processing induced degradation occursl. However, at exposure times greater than 5 hours, the rate of degradation increased to near-limiting values that were dependent on the number of extruder passes. Melt flow protection is, therefore, dependent on the exposure time to moisture and temperature. Initially, during the induction time period, the hydrolysis of the phosphite Alkanox P-24 cannot directly be correlated with the loss of performance of the antioxidant package.

The physical form of the stabilisers (NDB versus powder) has an impact on the induction time. As it has been seen for the hydrolysis test, the hydrolysis of Alkanox P-24 (when part of the NDB form) is retarded. The induction times, quantified as the intersection between the two asymptotes on the different parts of the curves, are around 5.5 hours for the powder blend and 26.5 hours for the NDB. As can be seen in Figure 3.10, a good correlation is obtained comparing these results to the induction times for the hydrolysis of Alkanox P-24 in combination with the phenolic antioxidant Anox 20.

The fact that the material is sticky is a sign that the stabiliser is losing performance. However, this is not a criterion that allows determination of the onset of performance loss as can be observed for the powder blend. In this case, the loss of performance seems to occur before than the sample becomes sticky. The difference in stickiness/performance relationship between the two forms is probably due to the diffusion phenomenon in the NDB, which creates a composition gradient across the pellet. In the NDB form, the stickiness appears later (double time) than in the powder form. It both cases, it corresponds to a degree of hydrolysis of 70 to 80 %.

Another fact is that a significant difference is observed; from pass 1 to pass 5 in the powder blend in terms of melt flow protection, from 5 to 10 hours of exposure. However, in the NDB form, the significant difference between the first and fifth extruder pass takes place after 30 hours of exposure. This is another indication that reflects the differing hydrolytic stability of the two physical forms. Since the hydrolysis reaction is faster in the powder form during exposure conditions, the performance of the powder form during processing is, therefore, affected and becomes worse.

3.3.1.3. Colour development after multiple pass extrusion

During processing, polymers tend to develop colour under conditions of high shear and temperature. Discoloration is due to the oxidative products generated as a consequence of the degradation. For instance, colour development during processing of polyolefins, is generally due to the presence of phenolic antioxidants in the stabiliser package. In this section, colour development (yellowing) of samples that have been processed with partially hydrolysed phosphite Alkanox P-24 are analysed. The ratio of additives to polymer was 0.1 % of additive blend (500 ppm of Anox 20 + 500 ppm of Alkanox P-24) in the polymer.

Table 3.1. Yellowness index data for Anox 20/Alkanox P-24 blend.

Exposure Time (hours)	Pass 1	Pass 3	Pass 5
Powder			
0	-1.3	1.4	3.4
2	-1.4	0.3	2.3
4	-1.5	0.4	2.3
5.5	-1.7	-0.1	1.9
10.5	-1.1	0.8	2.2
14	0.1	2.1	3.8
20.5	-0.1	1.6	3.9
NDB			
0	-0.9	2.4	4.4
1.5	-1.2	1.4	2.9
3	-1.3	1.1	3.2
4.5	-1.6	0.1	1.8
12	-1.8	0.1	1.1
22	-1.3	0.5	2.2
29	-2.0	0.2	1.8
36	-0.9	0.9	1.7

As developed for the MFR data, the yellowness index versus exposure time is plotted for the NDB and powder blends for all the extruder passes (Figure 3.14 and Figure 3.15). This provides information concerning the influence of partially hydrolysed phosphite Alkanox P-24 on the colour development of the poly(propylene) used. Yellowness index data from the fifth extruder passes (Figure 3.16) for both physical forms will be also plotted to study the influence of physical form, powder and NDB.

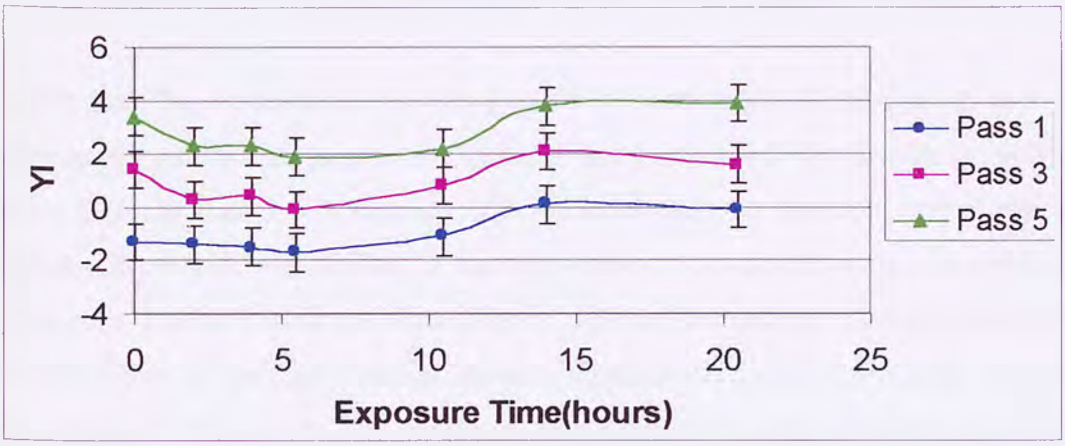


Figure 3.14. Effect of exposure time on colour for the Anox 20/Alkanox P-24 POWDER form in poly(propylene). Results reported as a mean value ±0.7 units error range.

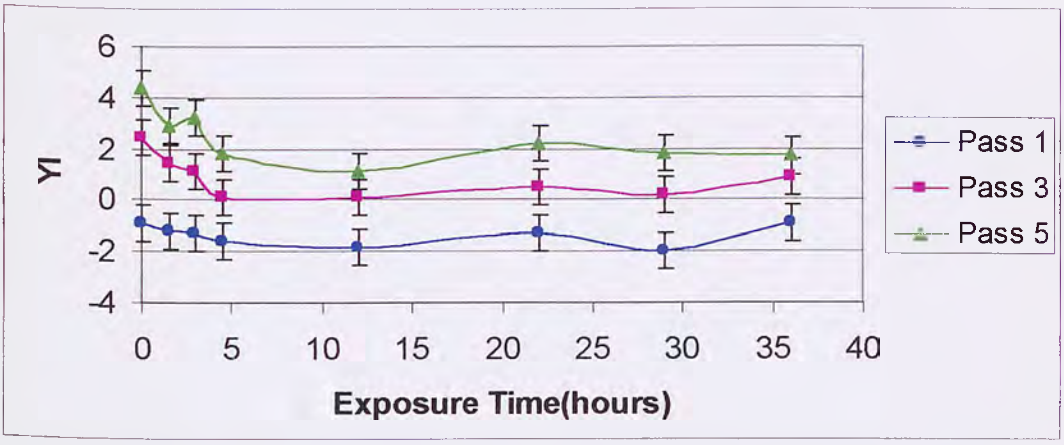


Figure 3.15. Effect of exposure time on colour for the Anox 20/Alkanox P-24 POWDER form in poly(propylene). Results reported as a mean value ±0.7 units error range.

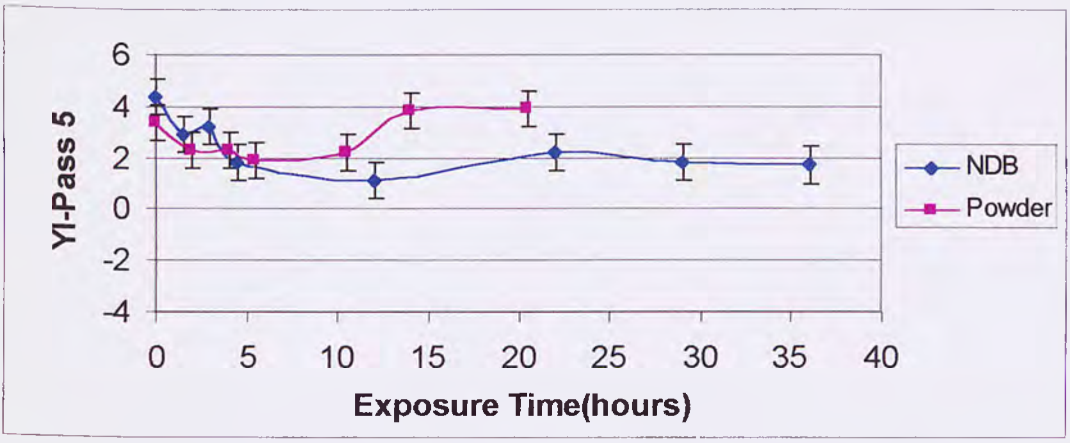


Figure 3.16. Effect of exposure time on colour for the Anox 20/Alkanox P-24 for NDB and POWDER in poly(propylene). Results reported as a mean value ±0.7 units error range.

It is seen that the development of colour in the polymer depends on the exposure time. Phosphites are widely used to prevent oxidative degradation and discoloration of polymers. They are typically used in combination with hindered phenols. However, one of the major drawbacks of phenolic antioxidants is that they strongly contribute to the discoloration of the polymers. This is due to the formation of quinone and quinone methide derivatives[27]. The combination of both antioxidants shows a significant overall improvement in terms of colour stability[59]. Alkanox P-24 is known to perform well in terms of colour protection to the polymer[97].

During the early stages of the hydrolysis, both blends become more efficient in protecting the polymer against colour development. This fact would suggest that some intermediate or final products of the hydrolysis of Alkanox P-24 are more efficient in protecting the polymer from discoloration, than is the phosphite itself.

As was observed for the melt flow protection, the fact that the material becomes sticky after a certain exposure time is a sign that the stabiliser is losing its performance. However, this is not a criterion that allows the determination of the onset of colour development as was observed for the powder blend. In this case, there is an increase in yellowness index before the sample has become sticky (around 14 hours of exposure time). On the other hand, for the NDB form, once the period at which a decrease in yellowness index occurs has past; there is no significant change in terms of yellowness index. For the powder blend, a more pronounced increase in colour development is observed. The difference in stickiness/colour increase relationship between the two forms is probably due to the diffusion phenomenon in the NDB, which creates a composition gradient across the pellet. In the NDB form, the stickiness appears later (double time) than in the powder form. It both cases, it corresponds to a degree of hydrolysis of 70 to 80%.

As has been seen for the MFR, a difference in performance is observed between the powder blend and the NDB form, corresponding to the difference in hydrolysis resistance.

Finally, from Figure 3.16 it can be concluded that when the stabilisers are part of an NDB a more pronounced colour protection in the polymer is achieved than when they are part of the powder blend. Although at the early stages of the exposure there is no significant difference between both of them a higher colour is observed with the NDB physical form. It is important to take into consideration that the physical form may play a role in the hydrolysis mechanism of Alkanox P-24 that will be discussed in the following chapter.

3.3.1.4. Melt performance as function of degree of hydrolysis

In the previous chapters the processing and analytical data were discussed independently from each other as a function of exposure time to moisture and temperature. In this chapter the relationship between the degree of hydrolysis and the loss of performance will be analysed. Binary blends based on Anox 20 and Alkanox P-24 were exposed to 60 ° C and 75 % R.H. Degree of hydrolysis and the MFR of the binary blends was measured. The samples were periodically removed from the climate chamber and they were processed with poly(propylene), the ratio of additives to polymer was 0.1 % of additive blend (500 ppm of Anox 20 + 500 ppm of Alkanox P-24) in the polymer.

In the following graphs (Figure 3.17, Figure 3.18 and Figure 3.19), MFR values versus the degree of hydrolysis were plotted combining the data.

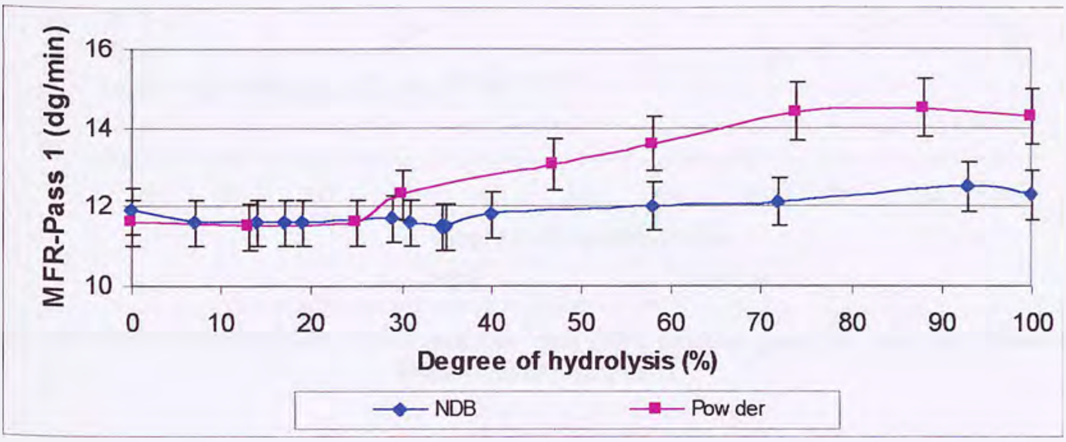


Figure 3.17. Melt flow rate (first extruder pass) versus degree of hydrolysis for the Anox 20/Alkanox P-24 blend in poly(propylene).

It must be taken into consideration that the same formulations (different in physical form) should give the same performance in terms of melt flow protection for the same degree of hydrolysis.

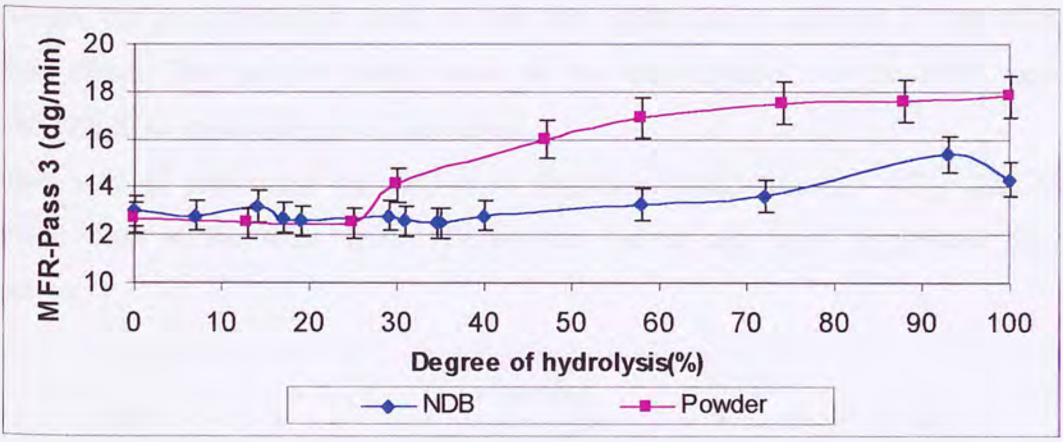


Figure 3.18. Degree of hydrolysis versus melt flow rate (third extruder pass) for the Anox 20/Alkanox P-24 blend in poly(propylene).

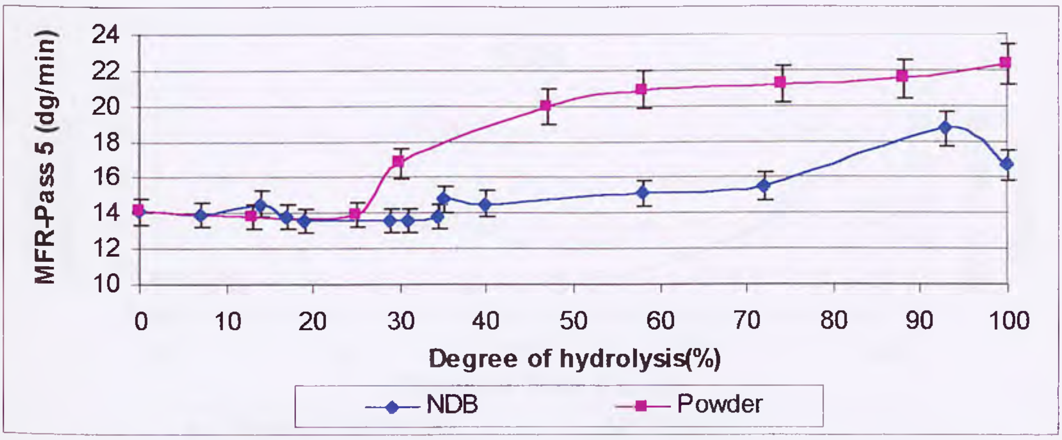


Figure 3.19. Degree of hydrolysis versus melt flow rate (fifth extruder pass) for Anox 20/Alkanox P-24 blend in poly(propylene).

From the above graphs (Figures 3.17, 3.18 and 3.19) it is observed that an increase in the degree of hydrolysis of Alkanox P-24 gives an increase in the MFR. In the early stages, where the degree of hydrolysis is less than 30%, there is no significant change observed between the NDB and the powder physical forms in terms of MFR. The same formulations for a given degree of hydrolysis should have the same performance independently of the physical form. Surprisingly, this does not occur. After a certain level of degree of hydrolysis, the performance in terms of melt flow protection is different for the NDB and powder blend. The powder blend seems to be less effective, as the MFR increases significantly from lower degrees of hydrolysis.

Another way of presenting the data is to degree of hydrolysis and MFR data versus exposure time in the same graph. Polynomial curves can them be plotted for both properties.

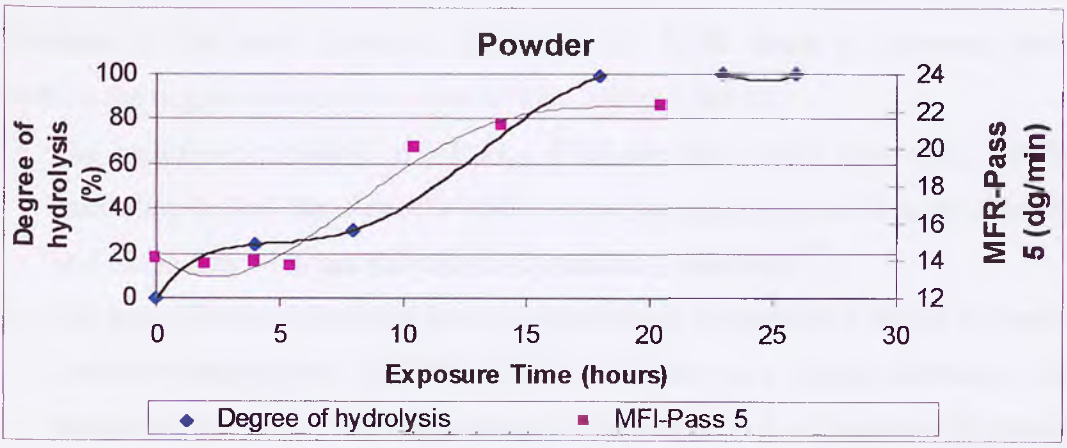


Figure 3.20. Effect of the degree of hydrolysis on melt performance after 5th extruder pass. Interpolation graph.

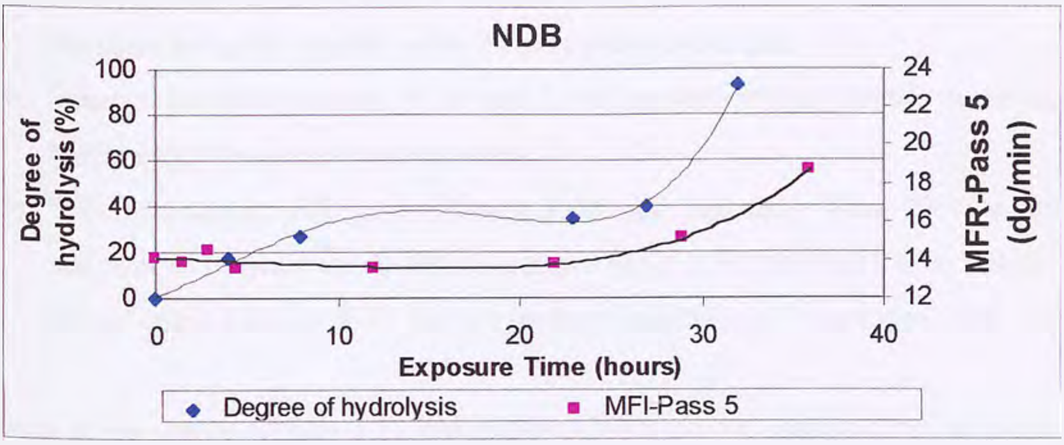


Figure 3.21. Effect of the degree of hydrolysis on melt performance after 5th extruder pass. Interpolation graph.

As mentioned previously, for both physical forms of additives the same main behaviour is observed in terms of MFR retention. Initially, there is no effect on the performance, a linear behaviour is observed, with an induction time. At a certain point in time, once the induction period has finished, there is a steep increase in MFR. The induction period is longer for the NDB physical form than for the powder blend.

Phosphites are widely used as processing stabilisers for poly(propylene). The most efficient stabiliser system developed for the stabilisation of poly(propylene) during processing is the combination of sterically hindered phenols and phosphites[46,66,98]. The phosphite stabiliser plays a more important role than the phenolic antioxidant in the process stability of poly(propylene) when they are used in combination[98].

Initially, the loss of the phosphite Alkanox P-24 cannot be correlated with the loss of performance. In the early stages of hydrolysis, the MFR seems to decrease when an increase on the degree of hydrolysis occurs. This could be due to:

- The hydrolysis products of Alkanox P-24 are also active processing stabilisers. According to the literature, the hydrolysis of phosphonites will lead to phosphorus acid monoesters that are still effective processing stabilisers[97].
- The loss of active phosphite due to hydrolysis is compensated by the formation of 2,4-di-*tert*-butylphenol (DTBP), which could act as a radical scavenger during processing and hinder the degradation of the polymer. It is important to appreciate that the 2,4-di-*tert*-butylphenol is a low molecular mass compound. It has a low

melting point (57 °C) and a boiling point of 263 °C. This compound would therefore be highly volatile under the processing conditions.

- Synergy between Alkanox P-24 and 2,4-di-*tert*-butylphenol initially resulting in a MFR, which keeps more or less stable.
- The formulation, 500 ppm Alkanox P-24 and 500 ppm Anox 20 (the ratio of additives to polymer was 0.1 % of additive blend in the polymer), is so rich that the loss of active Alkanox P-24 has not yet have an effect on the melt flow rate.

Looking at the graphs (Figure 3.21 and Figure 3.20) it can be observed that an increase in the degree of hydrolysis is accompanied by an increase in MFR. When the hydrolysis reaction of Alkanox P-24 takes place, different intermediate and final products are formed. This could be one of the reasons why, at the onset of the hydrolysis the average molar mass of the polymer increases leading to a reduction in MFR. However, at a certain point in time the MFR increases in accordance with the degree of hydrolysis. In this case, there is not enough Alkanox P-24 to protect the polymer from degradation.

Comparing the powder blend to the NDB, it is observed that for the same degree of hydrolysis of the same formulation (Alkanox P-24 + Anox 20) the powder blend is less effective than the NDB. This could suggest that the hydrolysis mechanism of Alkanox P-24 when it is part of the NDB is different in terms of kinetics (section 3.4.1) from its hydrolysis mechanism when the phosphite is part of a powder blend.

Another observation to be made is that once the induction period is over (where the MFR for both physical forms does not show any significant change) the poly(propylene) processed with the additives in the powder physical forms suffers more pronounced increase in the MFR than occurs in the presence of the NDB.

3.3.1.5. Colour development as function of degree of hydrolysis

In the previous chapters, the processing and analytical data were discussed independently from each other as a function of exposure time to moisture and temperature. In the current chapter, the relationship between the degree of hydrolysis and the loss of performance in terms of colour development will be analysed. Binary blends based on Anox 20 and Alkanox P-24 were exposed to 60 ° C and 75 % R.H. Degree of hydrolysis and the MFR of the binary blends was measured. The samples were periodically removed from the climate chamber and they were processed with poly(propylene), the ratio of additives to polymer was 0.1 % of additive blend (500 ppm of Anox 20 + 500 ppm of Alkanox P-24) in the polymer. In the following graphs (Figure 3.22, Figure 3.23 and Figure 3.24), combining the data, yellowness index values versus degree of hydrolysis have been plotted after 1st, 3rd and 5th extrusion passes.

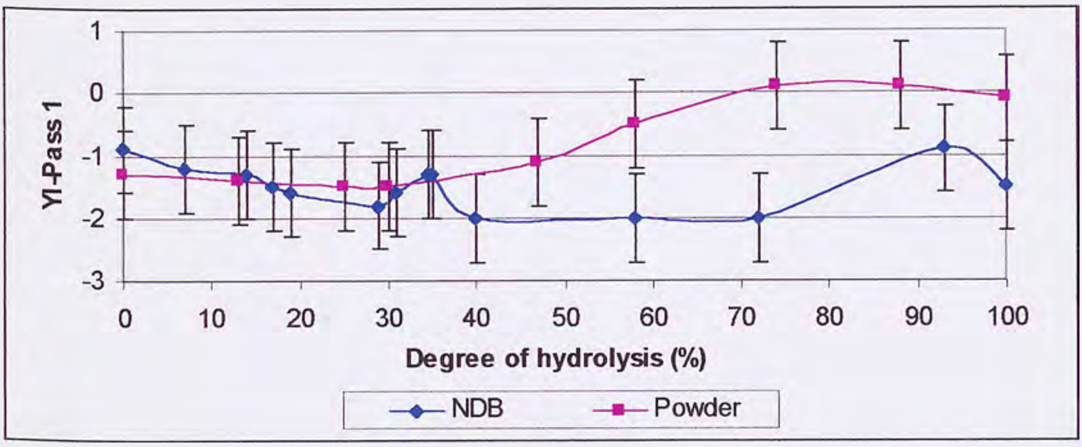


Figure 3.22. Degree of hydrolysis versus yellowness index (first extruder pass) for the Anox 20/Alkanox P-24 blend in poly(propylene).

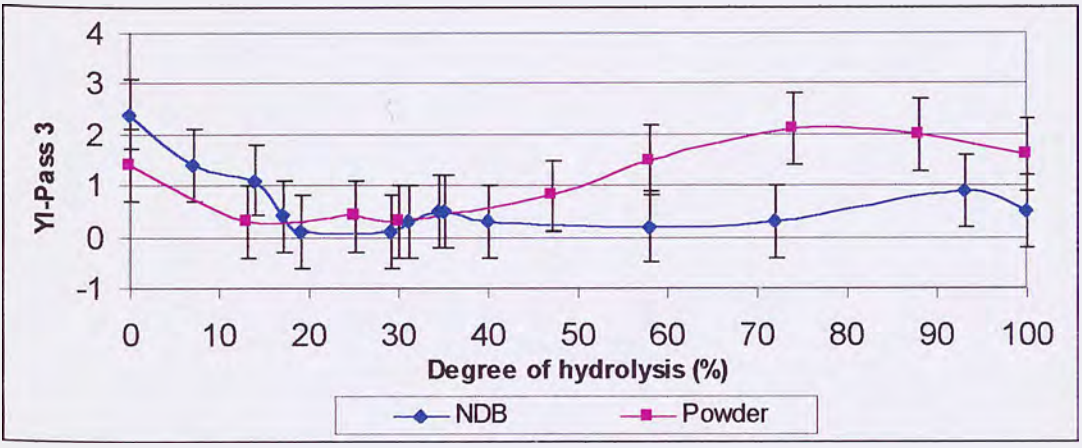


Figure 3.23. Degree of hydrolysis versus yellowness index (third extruder pass) for the Anox 20/Alkanox P-24 blend in poly(propylene).

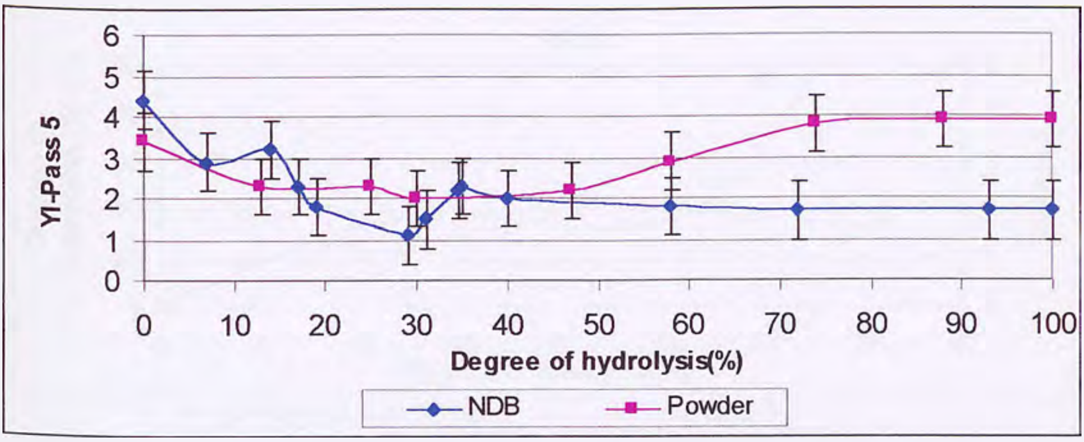


Figure 3.24. Degree of hydrolysis versus yellowness index (fifth extruder pass) for the Anox 20/Alkanox P-24 blend in poly(propylene).

As mentioned previously for the MFR data, one must take into consideration the fact that the same formulations (with different physical form but the same degree of hydrolysis) should give the same performance in terms of colour development. From the above graphs (figure 3.22, Figure 3.23 and Figure 3.24) it can be observed that when the hydrolysis reaction of Alkanox P-24 takes place, and as consequence, the degree of hydrolysis increases, an increase in the polymer colour (yellowness index) occurs.

The same formulation (Alkanox P-24 + Anox 20) for a given degree of hydrolysis does not give the same yellowness index independently of the physical form. At a certain level of degree of hydrolysis, the performance in terms of colour protection is significantly different for both physical forms. The powder blend seems to be less effective than the NDB form. At early stages of hydrolysis (less than 50%) there is no significant difference between both physical forms.

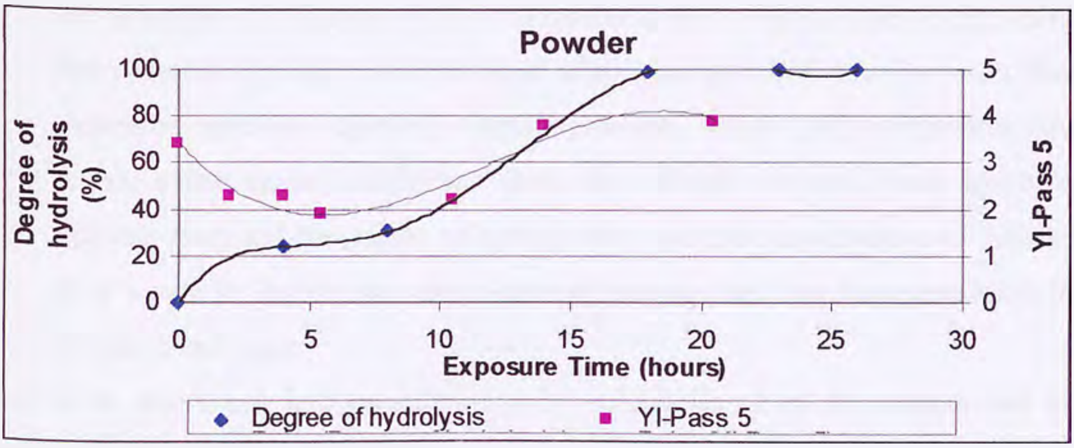


Figure 3.25. Effect of degree of hydrolysis on colour development after fifth extruder pass. Interpolation graph.

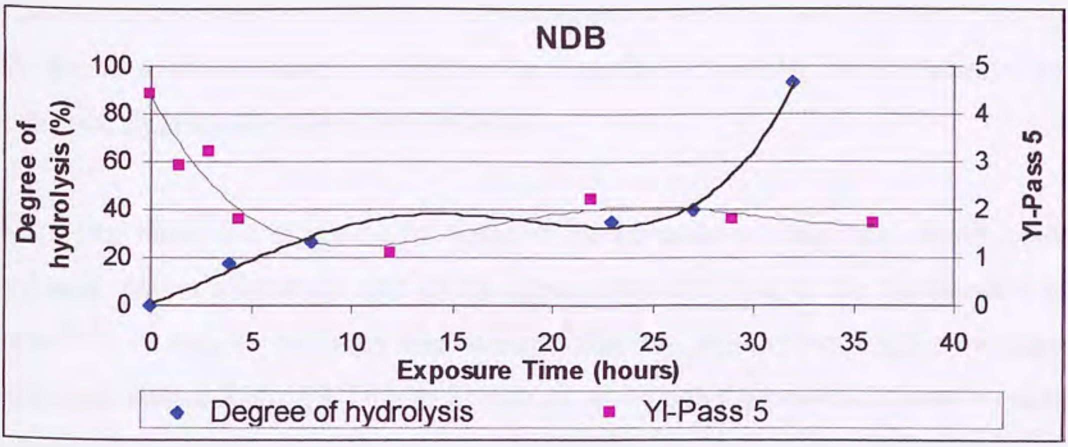


Figure 3.26. Effect of degree of hydrolysis on colour development after fifth extruder pass. Interpolation graph.

Examination of Figures 3.25 and 3.26 where the yellowness index values after the 5th extrusion pass is plotted in conjunction with the degree of hydrolysis, a decrease in yellowness index is observed during the early stages of the Alkanox P-24 hydrolysis. This behaviour is observed until about 50% degree of hydrolysis point. Beyond this point, the powder blend exhibits different behaviour to that of the NDB blend. While there is an increase in colour for the powder blend it stays flat for the NDB.

The different behaviour in terms of colour protection between both physical forms could be due to:

- Different chemical routes could be followed depending on the physical forms.
- It has been taken into consideration that the degree of hydrolysis of Alkanox P-24 is quantified as the depletion of the phosphite. Therefore, this does not mean that the hydrolysis of Alkanox P-24 is complete. It has to be considered that there are two phosphite groups on the molecule where the hydrolysis reaction takes place. A sequential reaction scheme is highly probable, where the intermediate species remain active against oxidation. Since the different physical forms hydrolyse at different rates and the degree of hydrolysis is quantified as depletion of Alkanox P-24 it would be logical that these intermediate moieties also disappear faster in the powder blend form.

It has to be also taken into consideration the solubilities of all the components in the polymer and the migration possibilities.

The behaviour observed for the colour development it is in line with the one observed for MFR. Above a critical value of degree of hydrolysis, the powder blend seems to lose its performance significantly faster than the NDB.

On the other hand, the oxidation products of the phenolic antioxidants, mainly quinoidal compounds, play a significant role in the appearance of colour in the stabilisation of the polymer[99,100]. It has to be taken into account that the studied formulation contains the phenolic antioxidant Anox 20. Due to its role of protecting the polymer against oxidation it will generate quinoidal products and be responsible for the colour development in the polymer. Therefore, apart from the increase in the degree of hydrolysis of Alkanox P-24 and its consumption, the role of the Anox 20 is important in forming coloured products giving an increase in the yellowness index values.

Phosphites are commonly used in conjunction with hindered phenols to minimize discolouration of polyolefins during processing[46,59,101].

Polyolefins stabilized with phosphites and phenolic antioxidants show less yellowing than the formulations containing phenolic antioxidants only. The reason why this behaviour is observed could be due to the lower consumption of phenolic antioxidants, possible reactions of phosphites with conjugated quinoidal compounds and with the complexation of polymerisation-catalyst residues, which are a cause of colour development[101].

According to the literature, pentaerythritol shows good colour suppression effects especially on initial colour, compared to phenolic antioxidants alone. However, because of its high melting point it produced problems in some poly(propylenes)[100].

The hydrolysis of Alkanox P-24 leads to 2,4-di-*tert*-butylphenol, phosphorus acid and pentaerythritol. This could suggest that the pentaerythritol plays a role as well in the studied additive system because of its generation as a consequence of the hydrolysis. However, according to the literature, it would not be necessary to propose hydrolysis to polyhydric alcohols, a source of colour suppression[100].

3.3.2. Formulation based on Anox 20/Alkanox P-24/calcium stearate

In this section the influence of different co-additives, the phenolic antioxidant Anox 20 and the acid scavenger calcium stearate (CaSt) and the influence of NDB and powder physical forms on the hydrolytic stability of Alkanox P-24 will be studied. On the other hand, the effect of partially hydrolysed Alkanox P-24 on processing of (poly(propylene)) is studied in terms of MFR and colour development. Finally, the performance of the studied formulation (Alkanox P-24/Anox 20/CaSt) is compared to the reference formulation (Alkanox P-24/Anox 20) that has been described in the previous section.

Hydrolysis studies:	[Alkanox P-24 + Anox 20 + CaSt] (40:20:40)
	Physical forms: Powder and NDB
Compounding:	400 ppm Alkanox P-24
	200 ppm Anox 20
	400 ppm Faci DW (CaSt)

The additive content in the polymer was kept constant, 1000 ppm (the ratio of additives to polymer was 0.1 % of additive blend in the polymer that were already premixed). However, the content (by weight) of the individual additives in the blend has changed. In this case, the blend also contains calcium stearate (CaSt).

3.3.2.1. Hydrolytic stability studies

Samples were exposed to 60 °C and 75 % R.H. The degree of hydrolysis, measured as the depletion of Alkanox P-24, was calculated to study the influence of the phenolic antioxidant Anox 20 and of the acid scavenger CaSt on the hydrolytic stability of the phosphite Alkanox P-24. Different physical forms were prepared to determine their influence on the hydrolytic stability of Alkanox P-24. On the other hand, the performance of the current formulation in terms of hydrolytic stability and processing was compared with that of the formulation studied as described in the previous section that was considered as a reference.

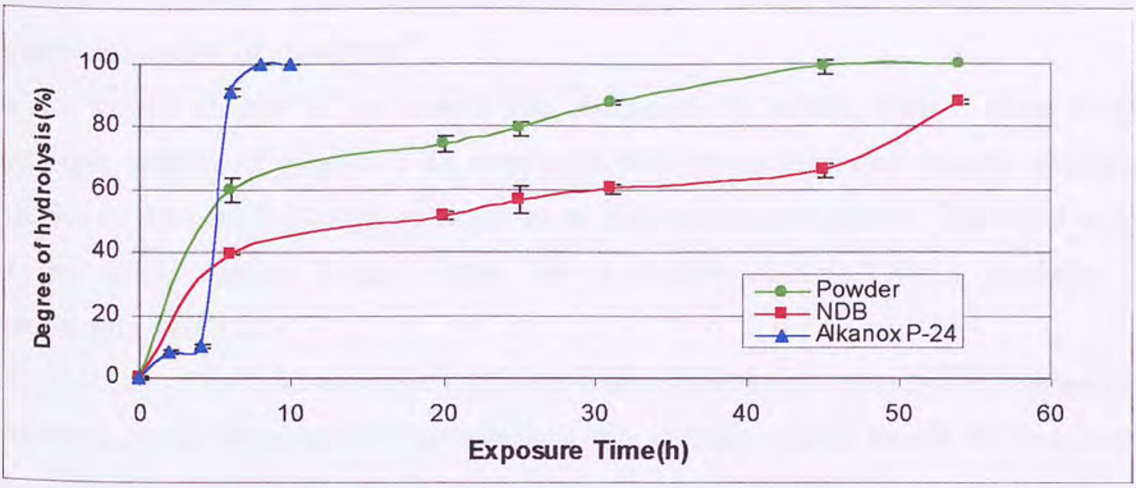


Figure 3.27. Effect of exposure time and physical form on the hydrolysis of Alkanox P-24 at 60 °C and 75 % R.H. Alkanox P-24/Anox 20/CaSt blend. Results reported as mean value ± standard deviation.

In Figure 3.27 the effect of the phenolic antioxidant Anox 20 and of the acid scavenger CaSt is shown. It can be seen that the hydrolysis reaction of the phosphite Alkanox P-24 is retarded in the presence of Anox 20 and the CaSt. In order to analyse the effect of the CaSt, it needs to be compared to the formulation containing only Anox 20.

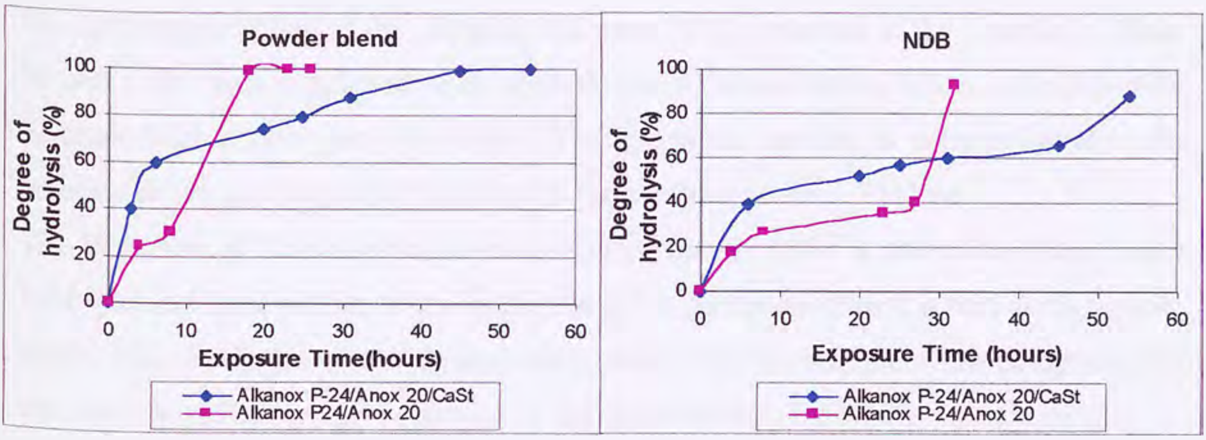


Figure 3.28. Effect of the presence of CaSt on the hydrolysis of Alkanox P-24 at 60 °C and 75 % R.H.

Acid scavengers are widely used as part of the additive package for the stabilisation of polyolefins. There are used to react with the catalyst residues remaining in polymers catalysed by chloride-containing substances[60].

The hydrolysis of the phosphite Alkanox P-24 leads to acidic products, such as phosphorus acid. As it is known from the literature, acids and metal cations catalyse the hydrolysis of phosphites. However, it has been shown that using a tertiary base strongly retards the hydrolysis reaction of phosphites[36].

In the second chapter of the results and discussion the arising from a study of the hydrolytic stability of Alkanox P-24 were preserved. It was concluded that the hydrolysis reaction of Alkanox P-24 with water shows an auto-acceleration pattern. This effect is due to the acidic species formed during the hydrolysis reaction, which produces an autocatalytic reaction.

The presence of the acid scavenger CaSt may lead to retardation of the hydrolysis reaction. However, in this experiment the hypothesis is only partially uphold. During the first hours, the hydrolysis reaction of Alkanox P-24, in the presence of CaSt, proceeds faster than in the absence of CaSt. The reaction occurs apparently even faster than that of Alkanox P-24 pure. Although this can not be entirely confirmed due to missing points during first hours of hydrolysis.

A possible explanation could be the presence of 3 % water in the CaSt. Due to the water content in the CaSt sample there is an extra supply of water that would accelerate the hydrolysis reaction. At a more extended exposure time the rate of hydrolysis falls possibly due to the acid scavenging character of the CaSt becoming predominant.

The hydrolysis reaction of the phosphite Alkanox P-24 is retarded in the presence of Anox 20 and CaSt. This is believed to be again due to a dilution effect, because the phosphite Alkanox P-24 is now part of a blend. The hydrolysis reaction is more retarded in the presence of the acid scavenger CaSt than in the presence of Anox 20 alone.

The hydrolysis of the phosphite is retarded when the phosphite is part of the blend in the NDB physical form relative to the hydrolysis of the phosphite when it is part of the powder blend. This could be due to a physical effect, where the reaction rate of the phosphite with the water would be partially controlled by the diffusion rate of the water into the pellet.

Due to the denser packing and lower surface area of the NDB form, the diffusion of the water and the attack on the phosphite will occur at a slower rate and consequently delay the rate of hydrolysis.

Due to the water content in the CaSt, the hydrolysis reaction is accelerated at the early stages relative to the sample that does not contain the acid scavenger. However, at higher exposures times the hydrolysis rate is slowed down relative to that with the Alkanox P-24/Anox 20 package. In this case, due to the acid scavenging capability and the water content on the sample a chemical effect is involved in the slowing down of the hydrolysis reaction.

3.3.2.2. Melt flow rate after multiple pass extrusion

Poly(propylene) containing the Alkanox P24/Anox 20/CaSt (40:20:40) package were exposed at 60 °C and 75 % R.H. They were removed periodically and processed with poly(propylene). The ratio of additives to polymer was 0.1 % of additive blend (200 ppm of Anox 20 + 400 ppm of Alkanox P-24 + 400 ppm CaSt) in the polymer. Multiple extrusions were then carried out. In order to study the performance of the hydrolysis products on poly(propylene) the melt flow rate (MFR) and colour development (yellowness index) were measured. Effect of the partially hydrolysed Alkanox P-24 on the melt performance of poly(propylene) is shown in Figure 3.29 (powder blend) and Figure 3.30 (NDB blend). MFR (after 1st, 3rd and 5th extrusion pass) versus exposure time is shown. The effect of adding partially hydrolysed Alkanox P-24 on processing stability was studied.

Table 3.2. Melt flow rate data after multi-pass extrusion for Alkanox P-24/Anox 20/CaSt (40:20:40) in poly(propylene).

Exposure Time (hours)	Pass 1 (dg/min)	Pass 3 (dg/min)	Pass 5 (dg/min)
Powder			
0	12.6	13.3	15.4
2	12.7	14.1	15.8
4	13.5	13.9	15.9
6	13.2	14.1	16.1
14	12.7	14.4	16.6
18.5	13.3	15.3	19.9
24	13.6	16.7	20.4

Exposure Time (hours)	Pass 1 (dg/min)	Pass 3 (dg/min)	Pass 5 (dg/min)
NDB			
0	12.3	13.7	15.3
2	12.6	13.9	15.3
4.5	12.7	13.9	15.5
6	12.5	14.0	15.5
15	12.5	14.2	15.5
26	13.0	14.7	16.2
30	12.9	14.6	16.4
34.5	12.9	14.9	17.0
40	13.5	15.1	17.9
50	13.4	15.8	20.0

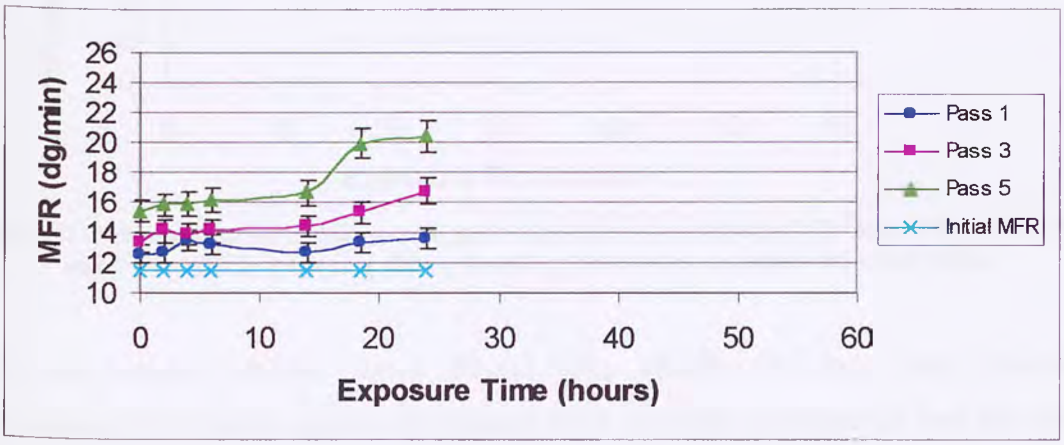


Figure 3.29. Effect of exposure time on melt flow performance for the Alkanox P-24/Anox 20/CaSt POWDER form in poly(propylene). Results reported as mean value ±5% error range.

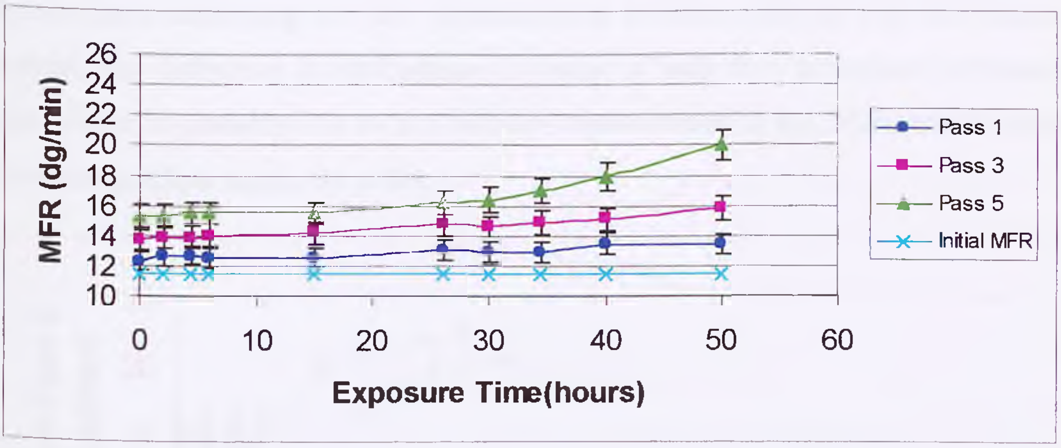


Figure 3.30. Effect of exposure time on melt performance for the Alkanox P-24/Anox 20/CaSt NDB form in poly(propylene). Results reported as mean value ±5% error range.

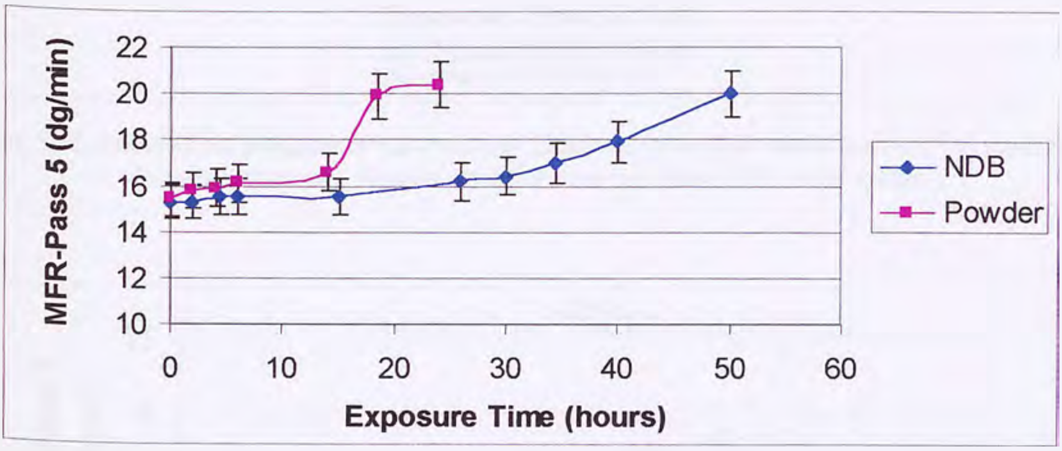


Figure 3.31. Effect of exposure time on melt performance for the Alkanox P-24/Anox 20/CaSt for NDB and POWDER in poly(propylene). Results reported as mean value ±5 error range.

NDB and powder physical forms should have initially the same melt processing performance if the initial quality of Alkanox P-24 is within specification and the dosing accuracy is identical for the two of them. This fact is confirmed; it can be observed that, initially, the MFR value for both physical forms is the same.

In terms of melt flow protection; both physical forms exhibit the same behaviour. Initially there is no significant difference in performance. A linear behaviour is observed. At a time, there is an increase in the MFR, which is more pronounced after the 5th extruder pass.

The linear behaviour observed initially is different for the NDB and the powder blend; the physical form of the stabilisers has an effect on the induction time. It can be seen that a MFR of 20 dg/min is reached at around 50 hours of exposure time for 5th pass of the NDB physical form. However, to reach the same MFR with the additives in powder physical form, 18-20 hours are required. Therefore, there is a difference in the performance of the poly(propylene) depending on the physical form of the additives and the degree of hydrolysis. The difference in performance in terms of melt flow protection between both physical forms is probably due to the diffusion phenomenon in the NDB, which creates a composition gradient across the pellet.

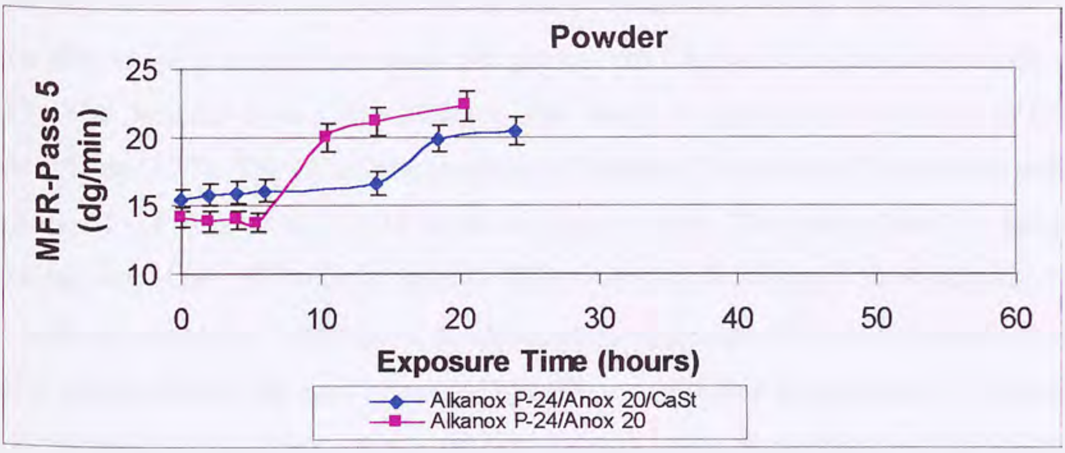


Figure 3.32. Effect of the presence of CaSt on melt flow rate. Melt flow rate after the 5th extruder pass in poly(propylene). Results reported as mean value ±5 % error range.

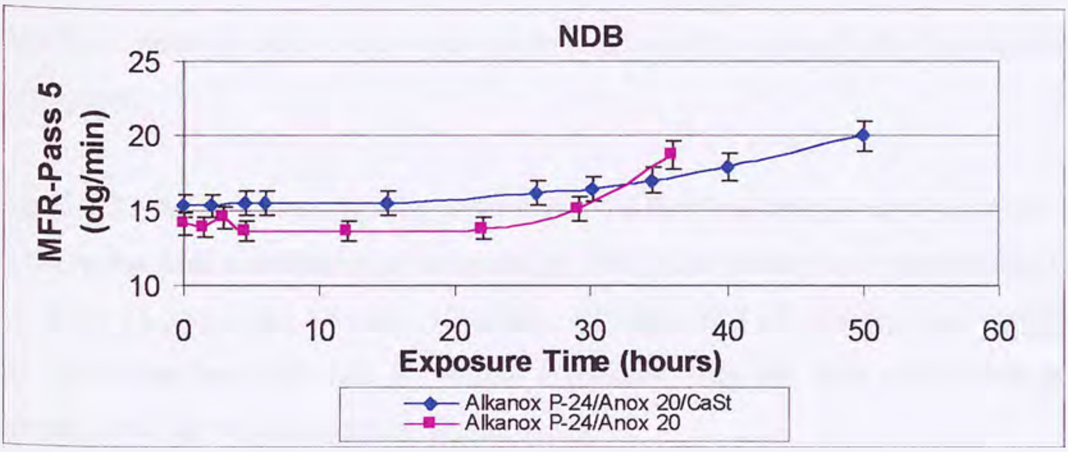


Figure 3.33. Effect of the presence of CaSt on melt flow rate. Melt flow rate after the 5th extruder pass in poly(propylene). Results reported as mean value ±5 % error range.

For both physical forms the same behaviour is observed when the Alkanox P-24/Anox 20/CaSt and Alkanox P-24/Anox 20 packages are compared. Initially the poly(propylene) stabilised by the blend without CaSt performs better than the poly(propylene) stabilised by the blend with CaSt.

The behaviour observed for the MFR is in concordance with the data from the hydrolysis studies. Firstly, considering the powder blend, during the early stages of the exposure (Figure 3.27); the Alkanox P-24 in the Anox 20/Alkanox P-24 blend is more hydrolytically stable than when the Alkanox P-24 is part of the blend containing CaSt. It is believed that the water content in CaSt acts to accelerate the hydrolysis reaction. In terms of the MFR, the blend without CaSt gives better protection than the one containing CaSt (Figure 3.32). After these early stages during which the CaSt accelerates the hydrolysis of Alkanox P-24, the increase in the degree of hydrolysis is less pronounced. During this period, the CaSt will be able to act as an acid scavenger and protect the Alkanox P-24 from hydrolysis. Melt stability also benefits from CaSt addition. The trends compare well with the hydrolysis trends (Figure 3.27). The hydrolytic stability of Alkanox P-24/Anox 20 becomes superior to Alkanox P-24 alone from 8 to 18 hours of exposure time. The change MFR for the blend containing only Anox 20 becomes inferior to the Alkanox P-24/Anox 20 blend after 5.5 to 10.5 hours of exposure. Although it is important to appreciate that no significant changes in MFR occurs during the early stages of hydrolysis with either formulation. This could be due to the antioxidant activity of the species generated as a consequence of the hydrolysis reaction.

The same performance is observed for the NDB blend. Initially, the hydrolytic stability of Alkanox P-24 is worst when it is part of the blend containing CaSt. The same conclusion is reached here, perharps due to the water in the CaSt sample causing hydrolysis reaction to be accelerated.

In Figure 3.33 demonstrates that the performance of the blend that does not contain CaSt gives the worst melt stabilisation as measured by MFR at exposure times greater than ca 33 hours. After 33 hours, the Alkanox P-24/Anox 20/CaSt blend affords superior retention of MFR. This cross over of data is entirely consistent with the data cross over in the hydrolysis curve for the same blends (Figure 3.28).

Another factor to take into consideration in this case should be the additive content. The synergism between phenolic and phosphite antioxidants in terms of melt stabilisation is well known in the literature. In the formulation containing Alkanox P-24/Anox 20/CaSt (40:20:40) the level of Alkanox P-24 and Anox 20 is reduced relative to the Alkanox P-24/Anox 20 (50:50) formulation. This could influence the melt stabilisation and could be one of the reasons why the performance is reduced for the formulation containing the lower level of antioxidant. Some authors have studied the influence of CaSt and water on Alkanox P-24 during processing. It has been found that if CaSt or water is present at sufficient concentrations during processing of poly(propylene), 2,4-di-*tert*-butylphenol is preferentially released rather than the oxidation products. This indicates that CaSt and water are able to induce the hydrolysis of such phosphites[102].

3.3.2.3 Colour development after multiple pass extrusion

Table 3.3. Colour development after multi-pass extrusion forAlkanox P-24/Anox 20/CaSt (40:20:40) in poly(propylene).

Exposure Time (hours)	Pass 1	Pass 3	Pass 5
Powder			
0	-1.7	0.6	2.7
2	-1.1	1.2	2.9
4	-1.0	0.8	2.6
6	-1.3	0.4	2.2
14	-1.1	0.7	2.5
18.5	-1.0	0.7	2.6
24	-0.2	2.0	3.3

Exposure Time (hours)	Pass 1	Pass 3	Pass 5
NDB			
0	-1.6	1.5	3.4
2	-1.6	0.9	3.1
4.5	-1.5	0.8	3.2
6	-1.9	0.5	2.7
15	-1.3	0.6	2.5
26	-1.5	-0.1	1.2
30	-1.2	1.1	2.8
34.5	-1.3	0.3	1.7
40	-1.7	0.6	1.5
50	-0.3	1.4	2.6

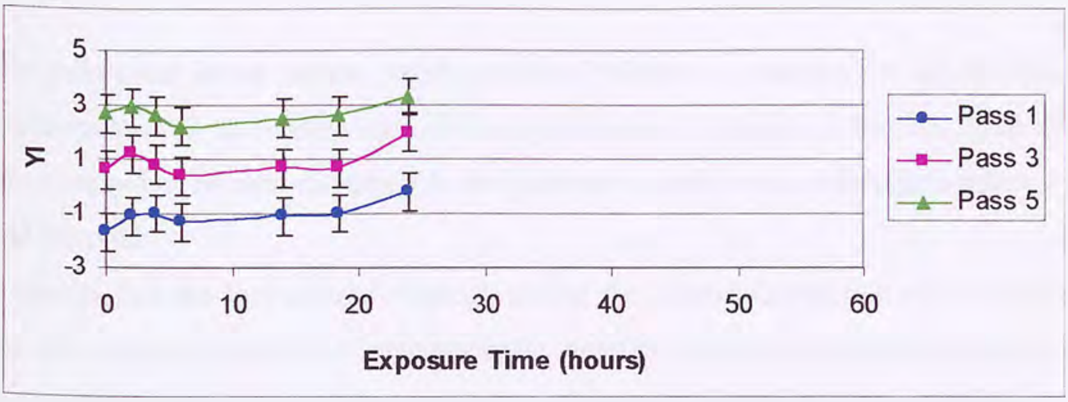


Figure 3.34. Effect of exposure time on colour development for the Alkanox P-24/Anox 20/CaSt POWDER form in poly(propylene). Results reported as mean value ±0.7 units.

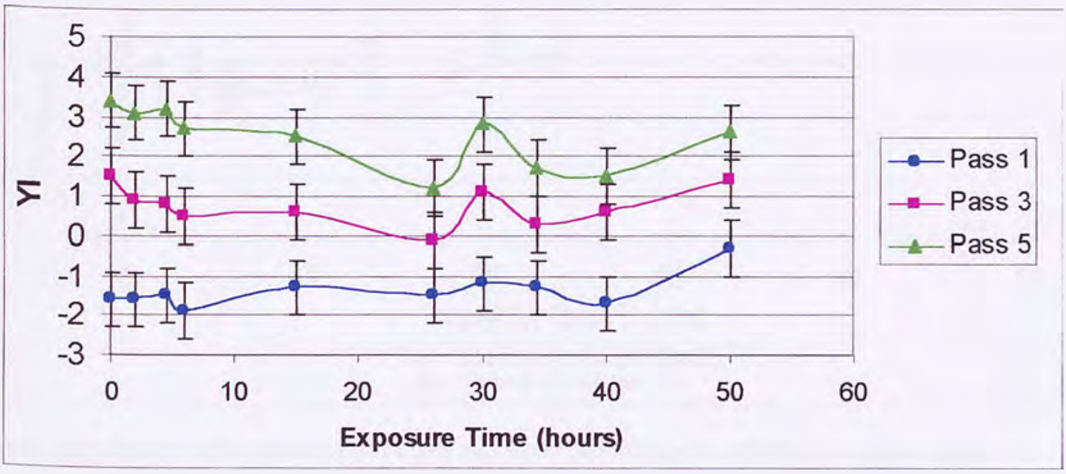


Figure 3.35. Effect of exposure time on colour development for the Alkanox P-24/Anox 20/CaSt NDB form in poly(propylene). Results reported as mean value ±0.7 units.

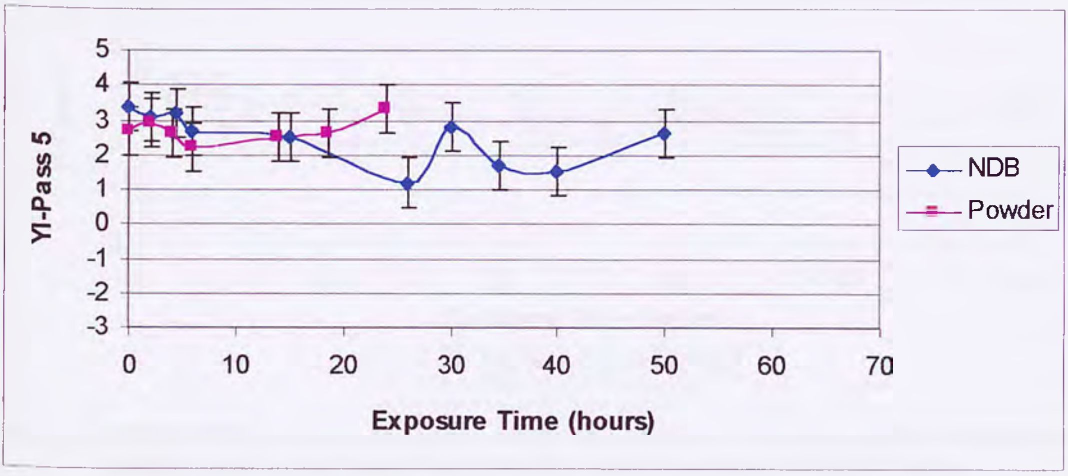


Figure 3.36. Effect of exposure time on colour development for the Alkanox P-24/Anox 20/CaSt for NDB and POWDER in poly(propylene). Results reported as mean value ±0.7 units.

The first observation to be made is that for both physical forms there is no significant difference in terms of colour development with an increase in the exposure time.

Examination of Figure 3.36 shows that there is no significant difference between the NDB and powder blends in terms of colour development. However, there are some fluctuations in the yellowness index values, which could be related to solubility of the intermediate products generated as consequence of the hydrolysis of Alkanox P-24. The intermediate products may not be well dispersed in the polymer; therefore the yellowness index values would fluctuate.

The species that are formed as a consequence of the hydrolysis reaction of Alkanox P-24 could also prevent formation of chromophoric moieties. Therefore yellowness index values are not affected even though differing degrees of phosphite hydrolysis have occurred.

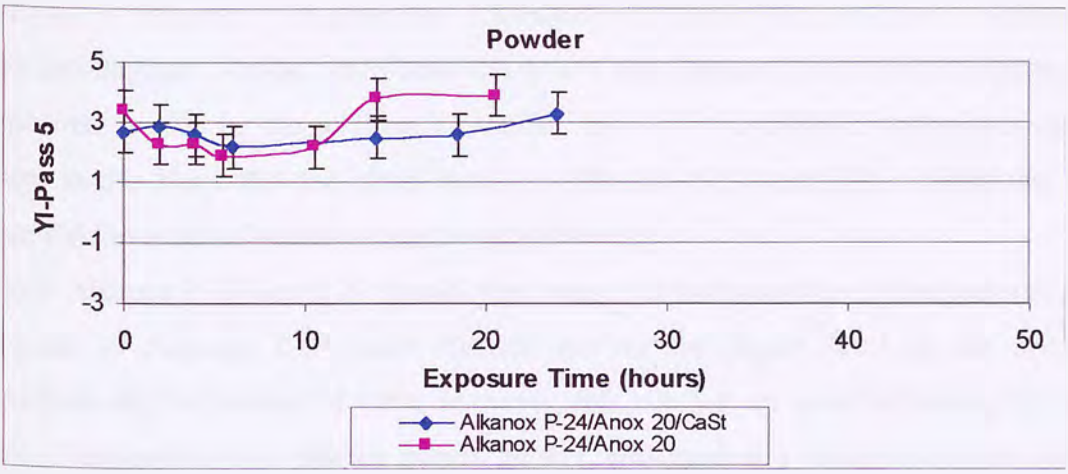


Figure 3.37. Effect of the presence of CaSt on colour development. Yellowness index values after 5th extruder pass in poly(propylene). Results reported as mean value ±0.7 units.

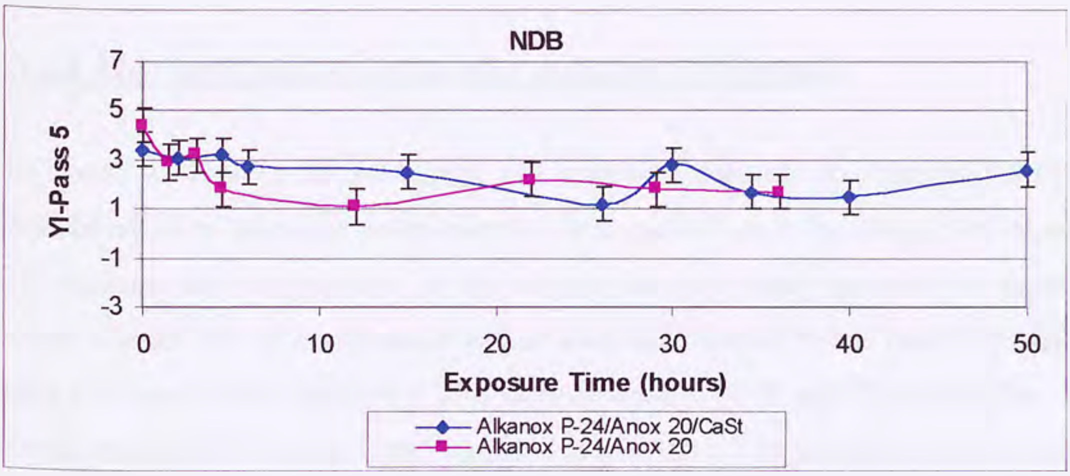


Figure 3.38. Effect of the presence of CaSt on colour development. Yellowness index values after 5th extruder pass in poly(propylene). Results reported as mean value ±0.7 units.

For the NDB blend there is no significant difference in terms of colour development between the poly(propylene)s stabilized with the two kinds of blends. For the powder blend, the presence of CaSt appears slightly to enhance colour stability (during melt processing) after ca. 11 hours of exposure, relative to the Alkanox P-24/Anox 20.

CaSt is commonly added to all poly(propylene)s with the primary purpose of neutralizing acid residues resulting from the catalyst. The acidity of the catalyst residues contributes to colour formation by producing hydrogen chloride, which reacts with the phenolic antioxidant. It has been observed in the literature that the addition of CaSt to a polymer stabilized only phenolic antioxidant reduces the colour development[100].

Several factors contribute to the generation of colour. It is well known that, during melt processing, phenolic antioxidants contribute to the discoloration of the polymer. The hydrolysis of Alkanox P-24 generates 2,4-di-*tert*-butylphenol that can also contribute to colour development. On the other hand, the factors that decrease the colour development in the polymer would be the addition of smaller levels of the phenolic antioxidant (lower content in this blend that the blend based on Alkanox P-24/Anox 20), CaSt would also reduce the formation of colour as mentioned previously.

A blend Alkanox P-24/Anox 20 should give worse colour protection to the polymer than the blend of Alkanox P-24/Anox 20/CaSt due to the higher level of the phenolic antioxidant and the absence of CaSt. However, this effect is not observed during the early stages of exposure of the powder blends. In fact, both packages perform in a very similar manner when added as a powder blend.

3.3.2.4. Melt performance as a function of degree of hydrolysis

In the previous chapters the processing and analytical data of the Alkanox P-24/Anox 20/CaSt blend were discussed independently from each other as a function of exposure time to moisture and temperature. In this chapter the relationship between the degree of hydrolysis and the loss of performance will be analysed. Ternary blends based on Anox 20 Alkanox P-24 and calcium stearate (CaSt) were exposed to 60 °C and 75 % R.H. Degree of hydrolysis and the MFR of the binary blends was measured. The samples were periodically removed from the climate chamber and they were processed with poly(propylene), the ratio of additives to polymer was 0.1 % of additive blend (200 ppm of Anox 20 + 400 ppm of Alkanox P-24 + 400 ppm of CaSt) in the polymer.

In the following graphs (Figure 3.39, Figure 3.40 and Figure 3.41), MFR values versus the degree of hydrolysis have been plotted combining the data.

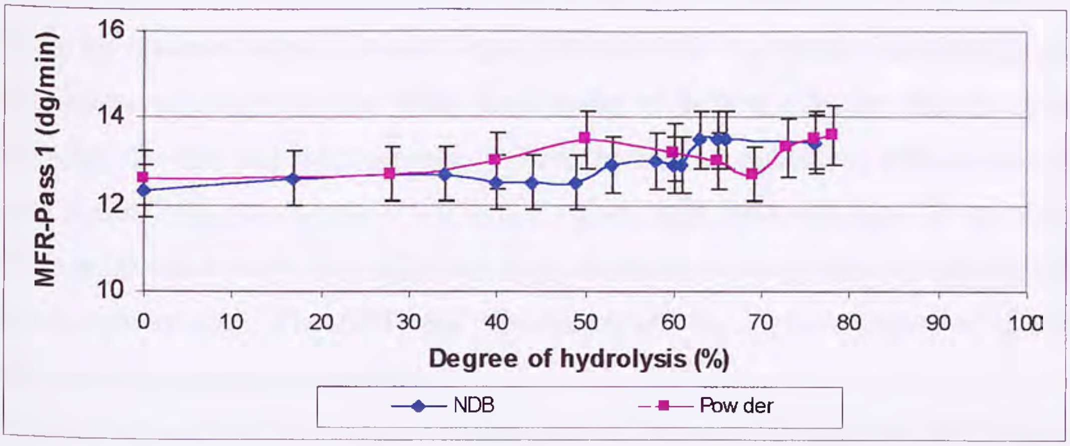


Figure 3.39. Melt flow rate (first extruder pass) degree of hydrolysis versus for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

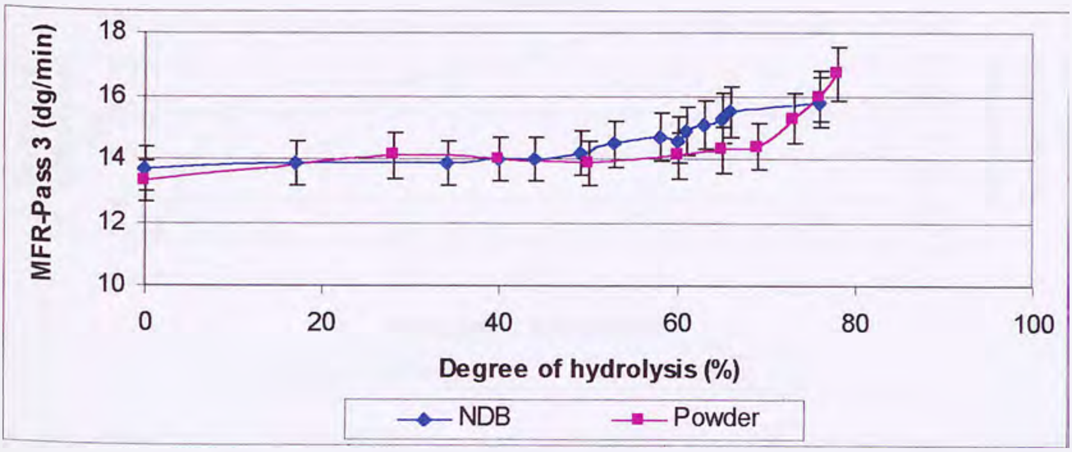


Figure 3.40. Melt flow rate (third extruder pass) degree of hydrolysis versus for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

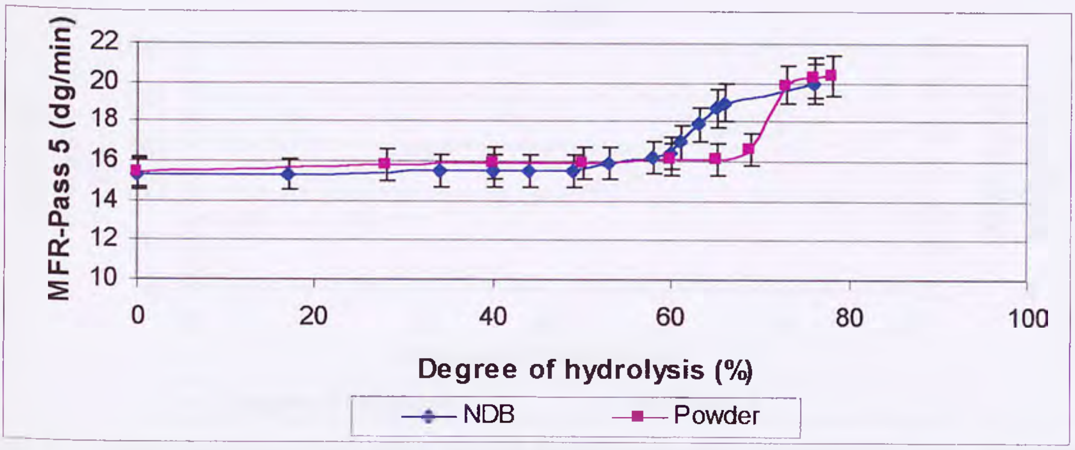


Figure 3.41. Melt flow rate (fifth extruder pass degree of hydrolysis versus) for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

From Figures 3.39, 3.40 and 3.41 it can be observed that after the first extruder pass there is no significant difference in the MFR versus degree of Alkanox P-24 hydrolysis trend for both NDB and powder forms. After the third and fifth extruder pass an increase in the MFR can be observed when a certain degree of hydrolysis is reached. Surprisingly, after a certain degree of hydrolysis the NDB blend seems to be less effective than the powder blend. After the first and third extruder passes, there is no significant difference between the two forms. This observation is not in accordance with what was seen for the Alkanox P-24/Anox 20 blend where the difference in performance between the two physical forms was more pronounced. The NDB and powder blends for a given degree of hydrolysis should exhibit the same performance.

In Figures 3.42 and 3.43 the degree of hydrolysis of Alkanox P-24 and the MFR values for the fifth extrusion are plotted together versus the exposure time.

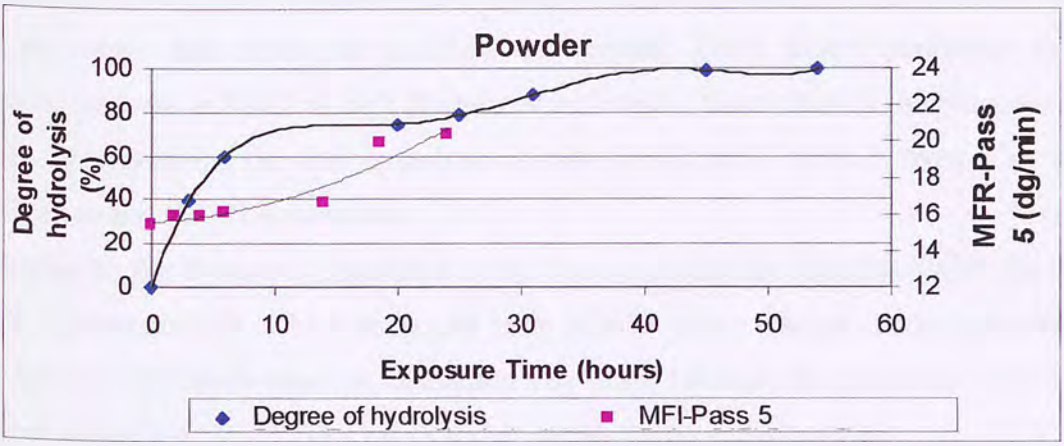


Figure 3.42. Effect of degree of hydrolysis on melt performance after fifth extruder pass. Interpolation graph.

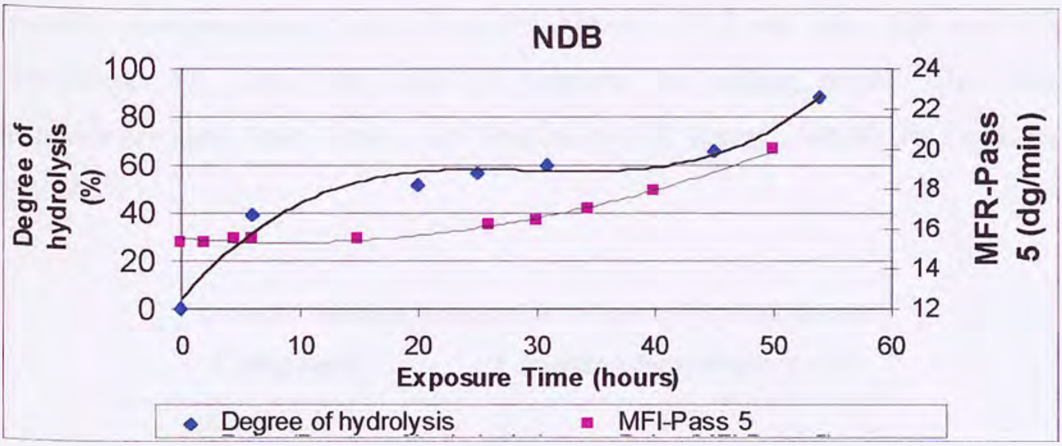


Figure 3.43. Effect of degree of hydrolysis on melt performance after fifth extruder pass. Interpolation graph.

First of all, the behaviour of the powder blend is considered. Initially the degree of hydrolysis increases rapidly. As mentioned before, this may be due to the water content present in the CaSt that accelerates the reaction during the early stages. On examination of MFR data an induction period is observed during the same period and no significant difference is seen. It is believed that the species generated as a consequence of the hydrolysis reaction will be active and be able to act as antioxidants and prevent degradation of the polymer. This is in accordance with the literature where it was found that a certain degree of hydrolysis has an influence on the efficiency of the phosphite[34].

At about 60% hydrolysis, the reaction rate decreased significantly as indicated by the change of slope of the curve (Figure 3.42). As mentioned before, the CaSt would perform as an acid scavenger at this stage. However, the MFR increases at hydrolysis levels greater than ca. 60-70 % (as measured by depletion of Alkanox P-24). At a more advanced extent of hydrolysis, very little phosphite will remain in the formulation. It is also highly likely that the active final hydrolysis products are formed. These factors contribute to the observed increase in MFR at high degrees of hydrolysis. Since there is no phosphite left, due to hydrolysis and the final hydrolysis reaction products are formed, there is no more stabilization and the MFR increases.

According to the literature, phosphites could form coordination complexes with the metal ions[58]. In formulations of high molecular mass HDPE, where calcium or zinc stearate and high levels of phosphite exist, an interaction may occur between the phosphite and the free calcium ions or zinc ions[58]. This effect should be taken into consideration.

Some DSC (Differential Scanning Calorimeter) experiments have been carried out to study the possible complexation of the phosphite Alkanox P-24 and the CaSt Faci DW. A Mettler-Toledo 320 DSC was used to measure the melting points. The following parameters were used: Rate K/min ; 10; Time iso min: 0; Range FS mW: 20; Offset %: 90; Limit mW: 0.

Table 3.4. Melting point data for Alkanox P-24/CaSt blends

Compound	**Melting temperature (°C)**
Alkanox P-24	177.8
CaSt	118
Alkanox P-24/CaSt blends	
Ratio 50:50	177.6/118.6
Ratio 70:30	177.8/116.3

The DSC traces are shown in Figures 3.44, 3.45, 3.46 and 3.47.

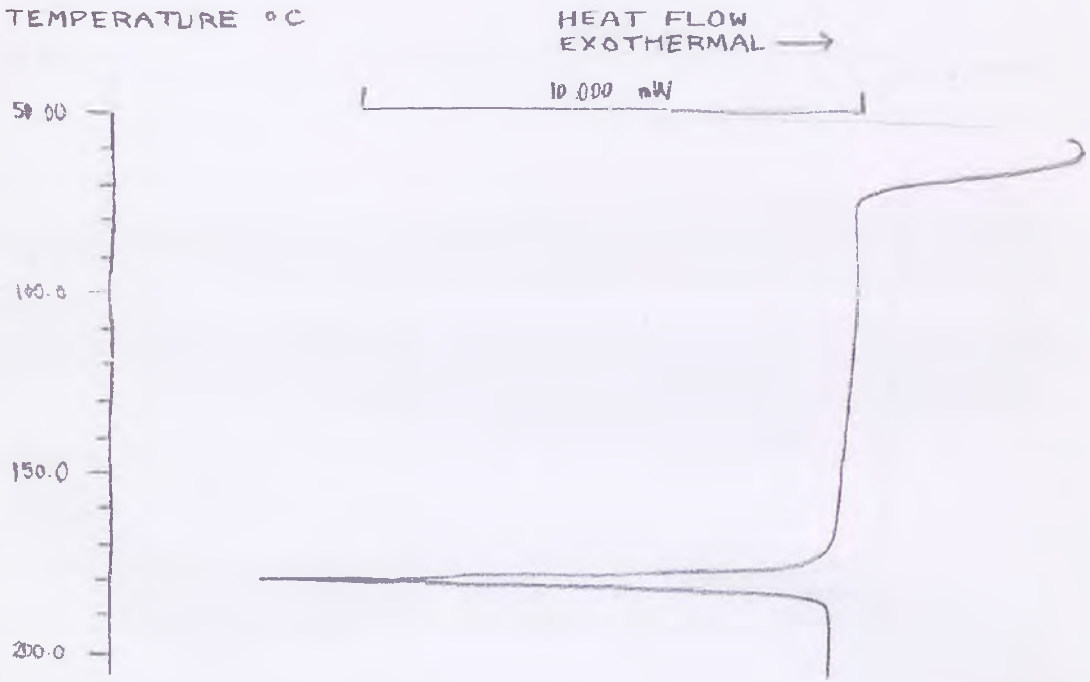


Figure 3.44. DSC trace for the phosphite Alkanox P-24. Melting temperature: 177.8 °C.

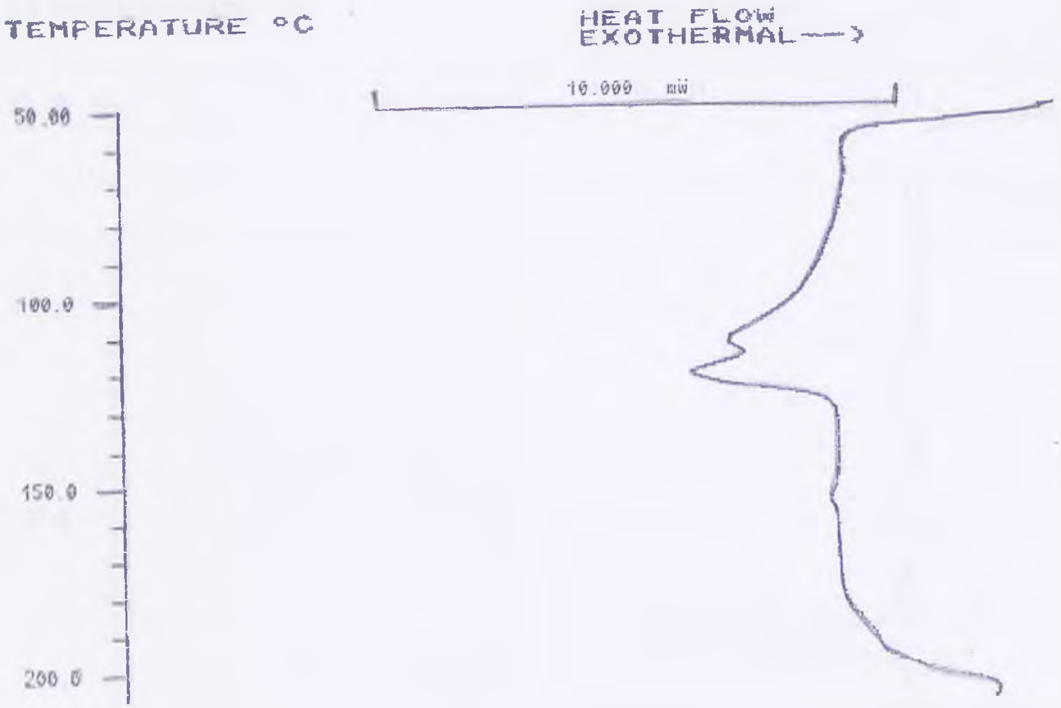


Figure 3.45. DSC trace for the calcium stearate. Melting temperature: 118 °C.

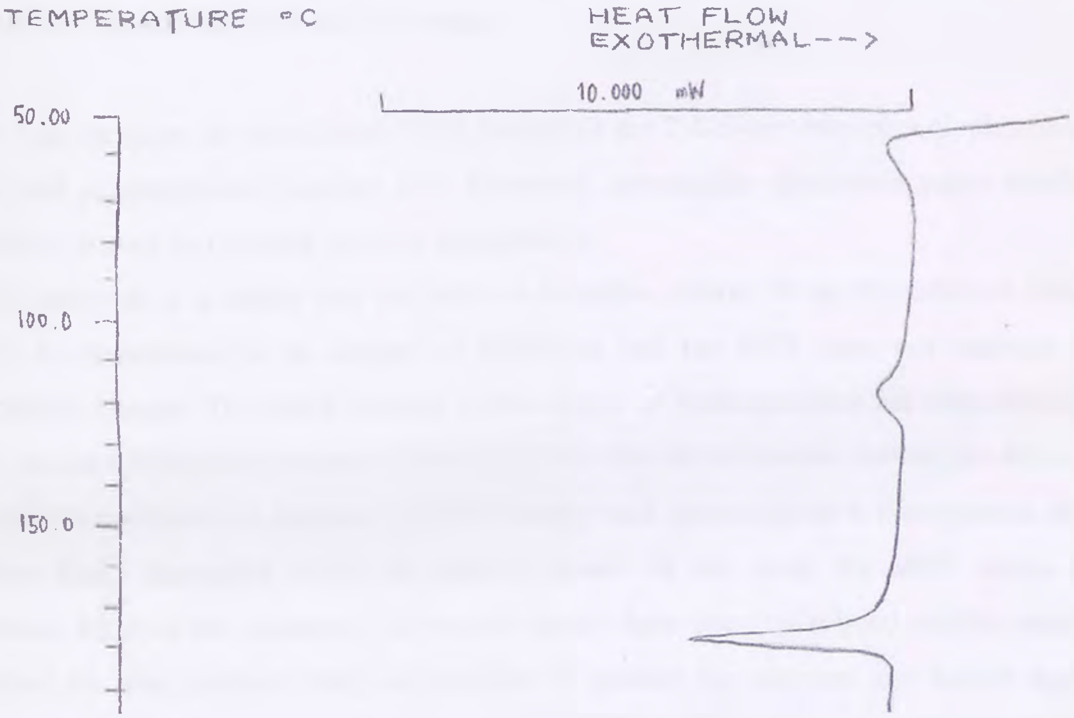


Figure 3.46. DSC trace for Alkanox P-24/CaSt in a 50:50 ratio (by weight). Melting temperatures at 177.6 °C and 118.6 °C.

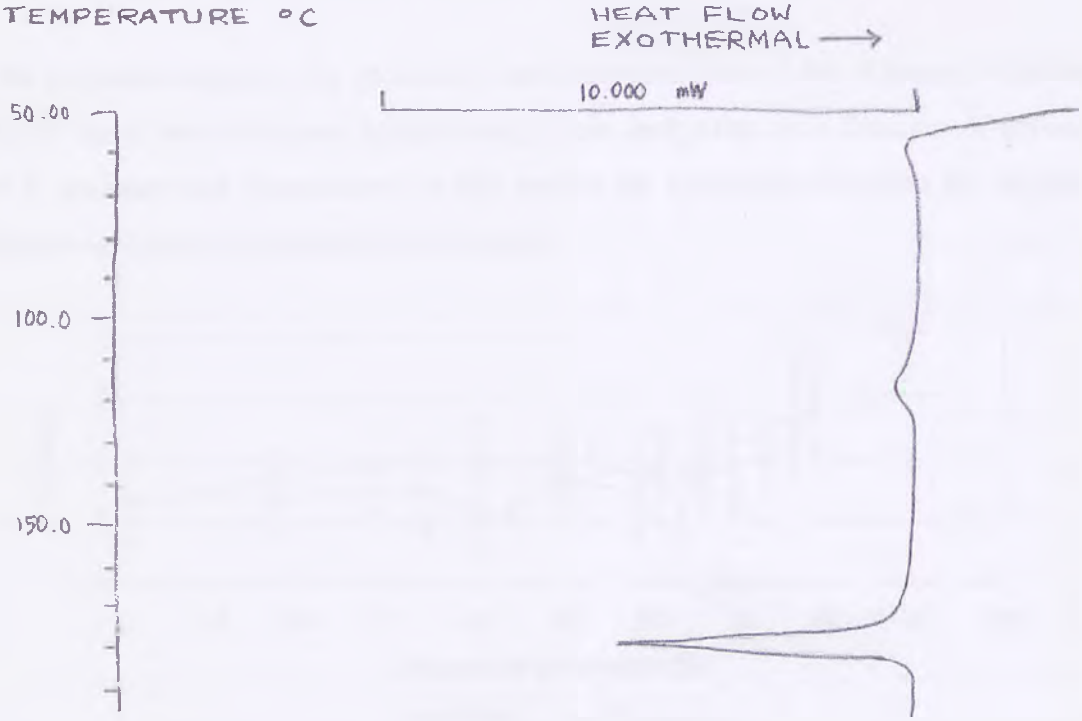


Figure 3.47. DSC trace for Alkanox P-24/CaSt in a ratio 70:30 (bu weight). Melting temperatures at 177.8 °C and 116.3 °C.

From these results, there does not seem to be any complexation between the phosphite Alkanox P-24 and the CaSt acid scavenger.

The final products of the Alkanox P-24 hydrolysis are 2,4-di-*tert*-butylphenol, phosphorus acid and pentaerythritol (section 3.4). However, intermediate hydrolysis active products could be formed and prevent polymer degradation.

NDB performs in a similar way but after an induction period. It can be seen that initially there is an increase in the degree of hydrolysis and the MFR does not undergo any significant change. The initial increase in the degree of hydrolysis that has been measured may be due to the water content of the CaSt. Once the initial increase occurs, the degree of hydrolysis continues to increase but less sharply and almost attain a near-plateau shape before finally increasing to 90 % after 40 hours. At this stage the MFR values also increase. Most of the Alkanox P-24 would already have been hydrolysed and the reaction reached its final products that are not able to protect the polymer any further against degradation.

3.3.2.5. Colour performance as function of degree of hydrolysis

In the previous chapters, the processing and analytical data of the Alkanox P-24/Anox 20/CaSt blend were discussed independently from each other as a function of exposure time to moisture and temperature. In this section the relationship between the degree of hydrolysis and colour development is discussed.

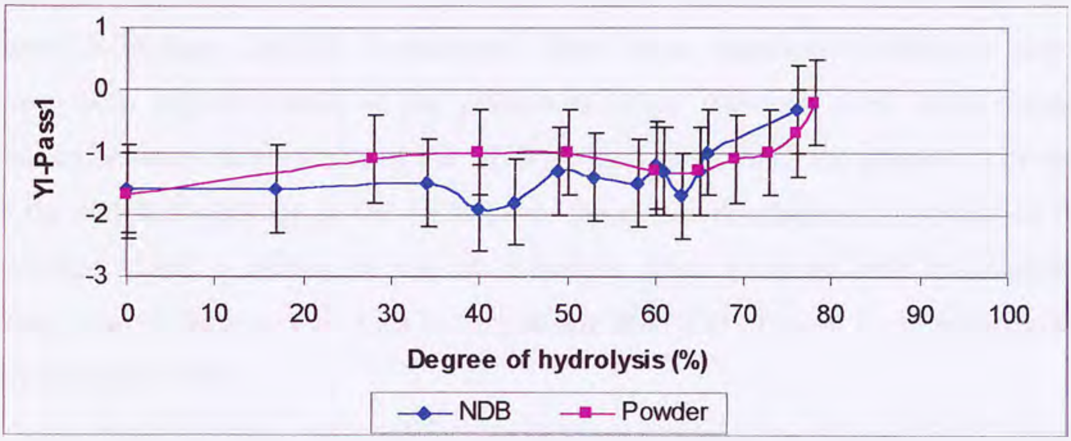


Figure 3.48. Degree of hydrolysis versus yellowness index (first extruder pass) for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

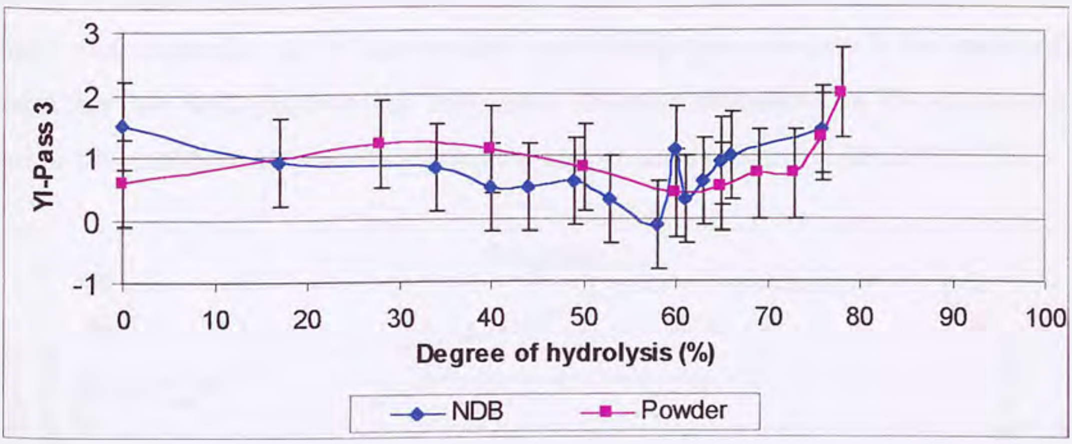


Figure 3.49. Degree of hydrolysis versus yellowness index (third extruder pass) for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

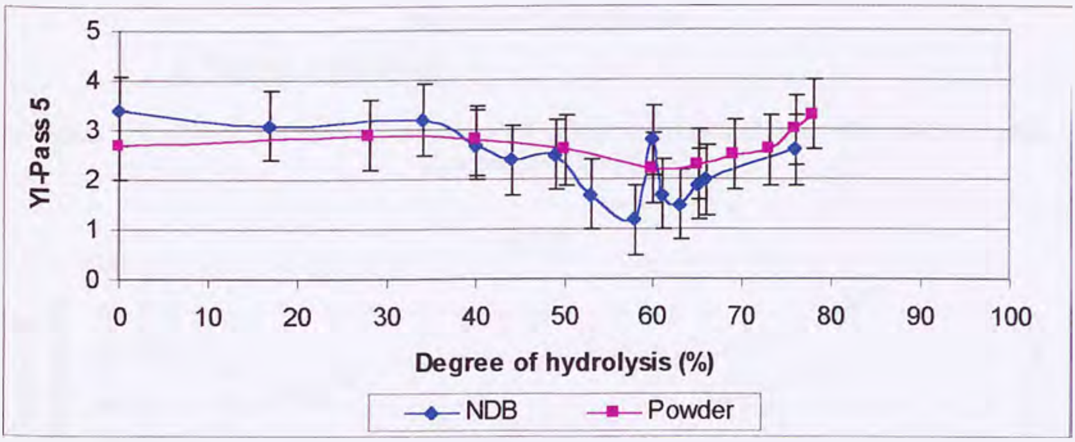


Figure 3.50. Degree of hydrolysis versus yellowness index (fifth extruder pass) for the Anox 20/Alkanox P-24/CaSt blend in poly(propylene).

The same formulations, with different physical form and the same degree of hydrolysis should give the same performance in terms of colour development. In this case, for the Alkanox P-24/Anox 20/CaSt formulation, there is no significant difference observed between both physical forms, in the yellowness index. Although there is no significant difference between the powder and the NDB physical form, when the polymer is protected with the stabiliser package in the NDB form, the colour development seems to be more pronounced. Until a certain degree of hydrolysis (that increases with the number of extruder passes) the powder seems to outperform the NDB physical form, giving a lower yellowness index value.

The same trend has been observed for the previous formulation, Alkanox P-24/Anox 20, even though there was no significant difference, until a certain level of degree of hydrolysis. The yellowness index values for the polymer that was stabilized with the NDB appear to be higher than for the powder form. It has to be also taken into consideration the solubility and dispersion of the intermediate products in the polymer. If the intermediate products are not well dispersed or they have different solubilities in the polymer it is normal to observe the scatter in the yellowness index values (Figures 3.48, 3.49, 3.50).

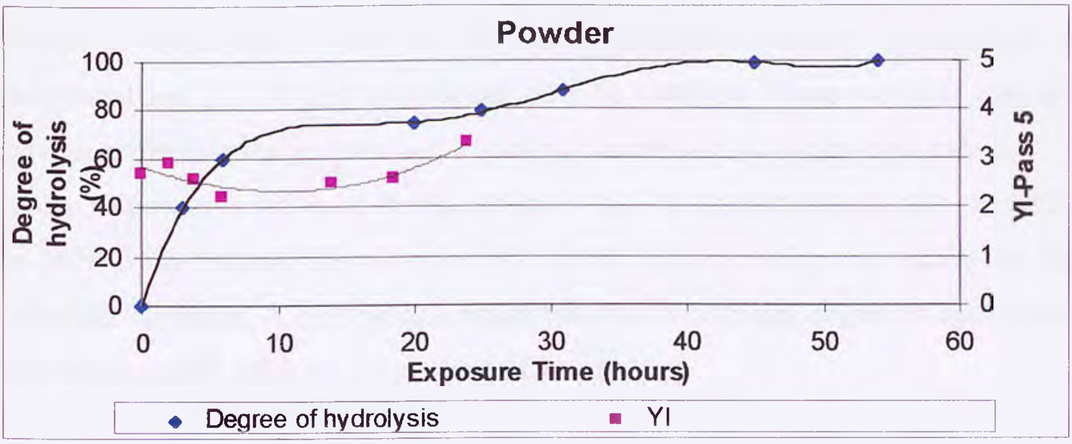


Figure 3.51. Effect of degree of hydrolysis on colour development after fifth extruder pass. Interpolation graphs.

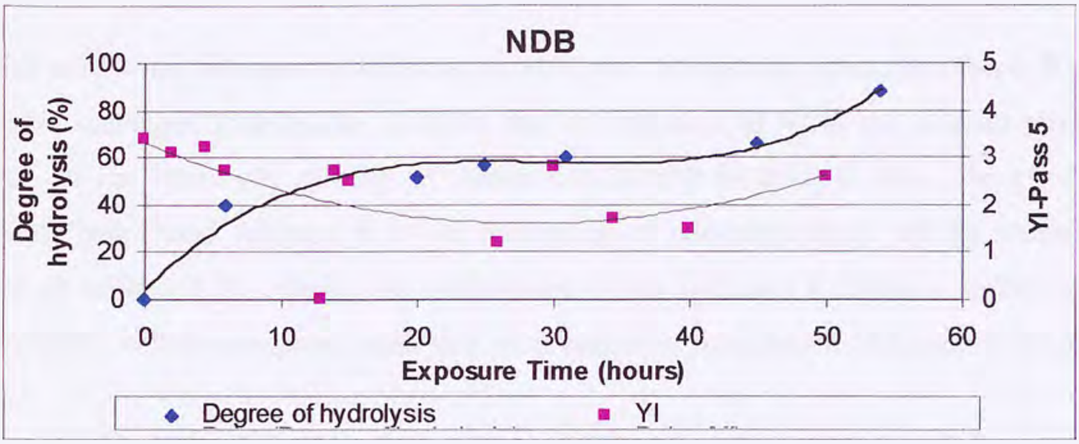


Figure 3.52. Effect of degree of hydrolysis on colour development after fifth extruder pass. Interpolation graphs.

Firstly, the behaviour of the powder will be considered. Initially the degree of hydrolysis increases quickly and as mentioned before it is thought to be to the water content present in the CaSt, which may accelerate the hydrolysis reaction in the early stages. The yellowness index does not exhibit any significant change during the same period; the trend seems to be a decrease in colour development. It is believed that the intermediate products that have generated as a consequence of the hydrolysis will be as active as the phosphite itself (the reason why an improvement in colour protection is observed) and hence just as able to resist the colour formation in the polymer as the initial phosphite. The same behaviour as with the MFR is observed; the yellowness index increases when the degree of hydrolysis also increases.

During the near-plateau shape of the curve, the CaSt would perform as an acid scavenger and be able to check the colour development of the polymer over a wide range of exposure times (from ca. 12-42 hours). However, when this period has elapsed and the degree of hydrolysis is quite high, (>60 %) the final hydrolysis products (phosphorus acid, pentaerythriol and 2, 4 di-tert-butylphenol) may be obtained. These products may not be effective at protecting the polymer and leads to an increase in the yellowness index.

The same behaviour is observed for the polymer that has been stabilized with the additives in the NDB form. Initially there is a decrease in the colour development where the degree of hydrolysis increases. A near-plateau shape follows for both the degree of hydrolysis and the yellowness index, followed by an eventual increase.

3.3.3. Formulation based on Anox 20/Alkanox P-24/DHT-4A

In this section the influence of different co-additives, the phenolic antioxidant Anox 20 and the acid scavenger hydrotalcite DHT-4A and the influence of NDB and powder physical forms on the hydrolytic stability of Alkanox P-24 will be studied. Also, the effect of partially hydrolysed Alkanox P-24 on processing of poly(propylene) will be studied in terms of MFR and YI. Finally, the performance of the (Alkanox P-24/Anox 20/DHT-4A) formulation will be compared with that of a reference formulation (Alkanox P-24/Anox 20).

Hydrolysis studies: [Alkanox P-24 + Anox 20 + DHT-4A] (40:20:40)
Physical forms: Powder and NDB
Compounding: 400 ppm Alkanox P-24
200 ppm Anox 20
400 ppm DHT-4A (hydrotalcite)

The additive content in the polymer was kept constant, 1000 ppm (the ratio of additives to polymer was 0.1 % of additive blend in the polymer). However, the content (by weight) of the individual additives in the blend has changed. In this case, the blend contains Alkanox P-24, Anox 20 and the acid scavenger DHT-4A.

3.3.3.1 Hydrolytic stability studies

Samples were exposed to 60 °C and 75 % R.H. The degree of Alkanox P-24 hydrolysis was calculated in order to study the influence of the phenolic antioxidant Anox 20 and the acid scavenger DHT-4A on the hydrolytic stability of the phosphite. In order to study the influence of different physical forms on the hydrolytic stability of Alkanox P-24 NDB and powder blends were prepared. The performance of the current formulation in terms of hydrolytic stability was compared to the first formulation containing Alkanox P-24 and Anox 20 as reference.

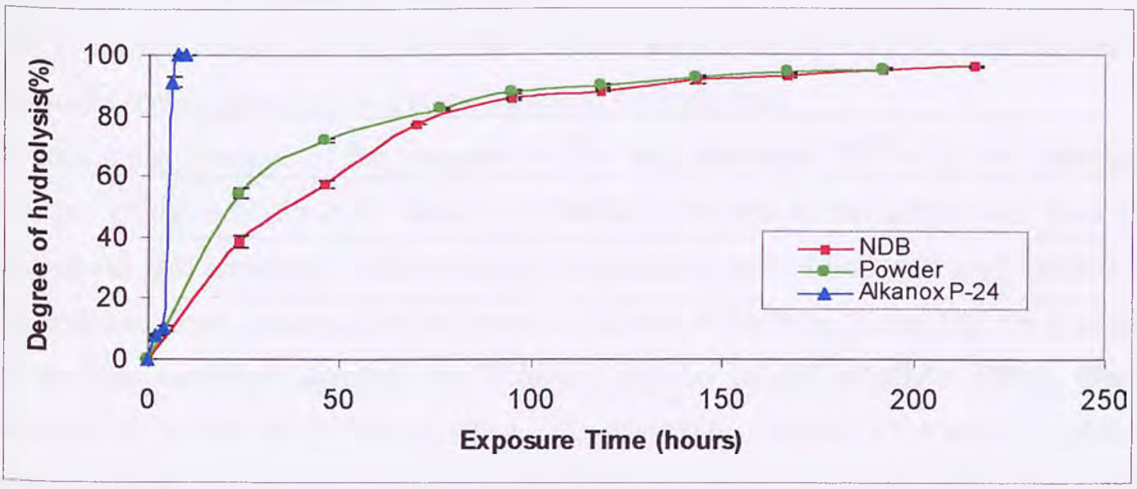


Figure 3.53. Effect of exposure time and physical form on the hydrolysis of Alkanox P-24 for the blend Alkanox P-24/Anox 20/DHT-4A. Results reported as mean value ± standard deviation.

In Figure 3.53 the effect of the phenolic antioxidant Anox 20 scavenger DHT-4A combination is shown. It is clear that the hydrolysis reaction of the phosphite Alkanox P-24 is retarded in the presence of Anox 20 and DHT-4A. In order to analyse the effect of the acid scavenger, the results need to be compared to those of the formulation containing Alkanox P-24 and Anox 20.

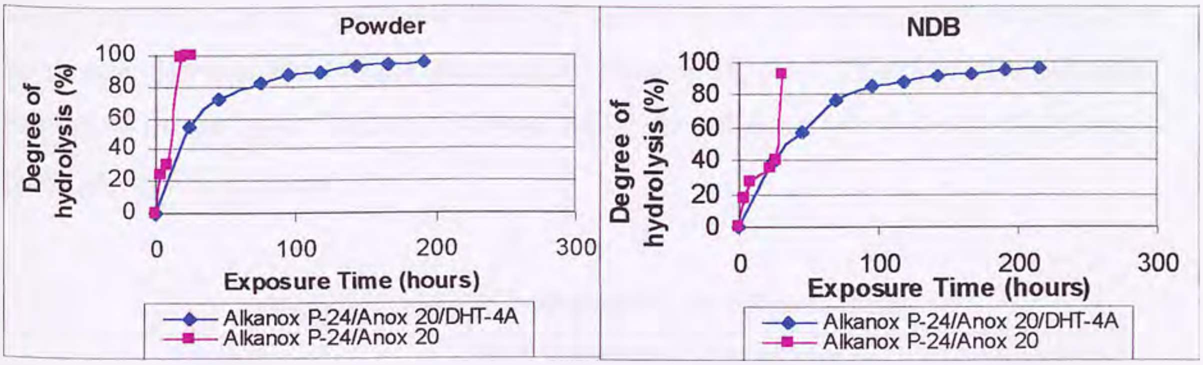


Figure 3.54. Effect of the presence of DHT-4A on the hydrolysis of Alkanox P-24 at 60 °C and 75 % R.H.

It is evident that hydrotalcite (DHT-4A) significantly retards the hydrolysis of Alkanox P-24. As mentioned previously, one of the final products of the hydrolysis reaction of Alkanox P-24 is the phosphorus acid, H_3PO_3.

The hydrolysis reaction of the phosphite Alkanox P-24 is an autocatalytic reaction due to the acidic species generated as a consequence of the hydrolysis.

Consequently, because of the presence of the acid scavenger DHT-4A, the hydrolysis reaction of the Alkanox P-24 should be retarded compared to the sample that does not contain the acid scavenger. In this case, it is seen that the hydrolysis reaction of Alkanox P-24 is slowed down compared to the blend of Alkanox P-24/Anox 20 and that the presence of the acid scavenger increases the hydrolytic stability of the phosphite. Firstly, this is believed to be due to a dilution effect. The phosphite Alkanox P-24 concentration is reduced in the formulation containing the DHT-4A. There is another effect that slows down the hydrolysis reaction of Alkanox P-24; a chemical effect. Due to the acid scavenging of the DHT-4A the hydrolysis reaction is retarded. The acidic species that are formed during the hydrolysis reaction would react with the acid scavenger. This effect would help the autoacceleration that is observed for the system that contains phosphite without acid scavenger.

Another observation to be made concerns the difference between the NDB and the powder physical form in terms of hydrolytic stability. The hydrolysis of the phosphite is slowed down when the Alkanox P-24 is part of a blend that is in NDB physical form compared to the hydrolysis of the phosphite when it is part of the powder blend. It is believed to be due to a physical effect, where the reaction rate of the phosphite with the water would be partially controlled by the diffusion rate of the water into the pellet. Due to the greater size of the NDB, and a lower surface area, the diffusion of the water into the pellet and the subsequent attack on the phosphite could be more difficult compared to its occurrence in the powder physical form where more surface area is exposed. Therefore, the hydrolysis reaction of the phosphite Alkanox P-24 would be slowed down when is part of a blend in the NDB physical form.

Table 3.5. Summary of hydrolysis data for different blends.

Time to:	60% depletion		80% depletion		100% depletion	
	powder	NDB	powder	NDB	powder	NDB
Alkanox P-24 pure	6h		6.5h		7h	
Alkanox P-24 /Anox 20 (1:1)	12h	29h	13h	31h	14h	34h
Alkanox P-24/Anox 20/CaSt (2:1:2)	6h	32h	25h	52h	45h	>55h
Alkanox P-24/Anox 20/DHT-4A (2:1:2)	28h	47h	70h	77h	>150h	>120h

Table 3.5 shows that the hydrolysis of Alkanox P-24 is more significantly retarded in the presence of the acid scavenger hydrotalcite (DHT-4A).

3.3.3.2. Melt flow rate after multiple extrusion

Samples containing the formulation Alkanox P-24/Anox 20/DHT-4A (40:20:40) were exposed to 60 °C and 75 % R.H. They were removed periodically from such environment and then processed with poly(propylene). The impact of partially hydrolysed Alkanox P-24 during processing of poly(propylene) was studied.

Table 3.6. Melt flow rate data after multiple extrusion for Alkanox P-24/Anox 20/DHT-4A (40:20:40) in poly(propylene).

Exposure Time (hours)	Pass 1 (dg/min)	Pass 3 (dg/min)	Pass 5 (dg/min)
Powder			
0	11.5	16.0	Not extruded
6	12.0	15.3	19.8
16	12.0	13.9	17.3
21	12.3	16.0	24.5
26	12.3	16.2	23.2
30	12.5	15.7	21.7
45	13.3	19.6	30.7
78	14.6	24.1	37.0

Exposure Time (hours)	Pass 1 (dg/min)	Pass 3 (dg/min)	Pass 5 (dg/min)
NDB			
0	11.6	14.0	18.3
20	11.5	14.1	17.8
48	12.0	14.4	18.9
64	12.3	14.6	18.4
71	12.9	16.4	23.2
78	13.5	17.3	25.2
90	13.5	17.1	24.7

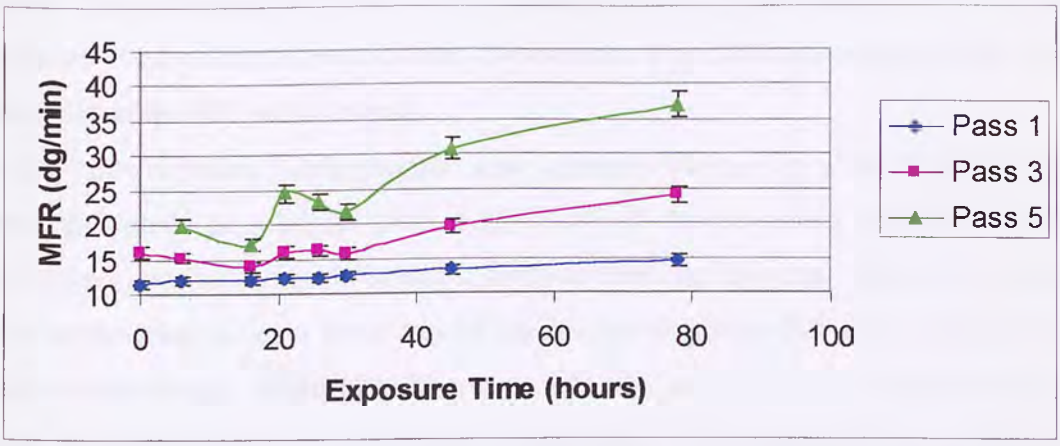


Figure 3.55. Effect of exposure time on melt flow performance for the Alkanox P-24/Anox 20/DHT-4A POWDER form in poly(propylene). Results reported as mean value ±5 % error range.

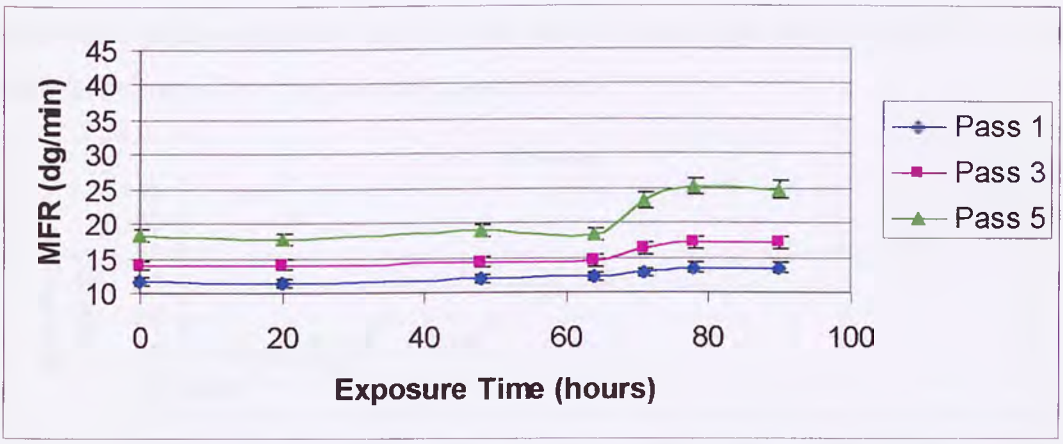


Figure 3.56. Effect of exposure time on melt flow performance for the Alkanox P-24/Anox 20/DHT-4A NDB form in poly(propylene). Results reported as mean value ±5 % error range.

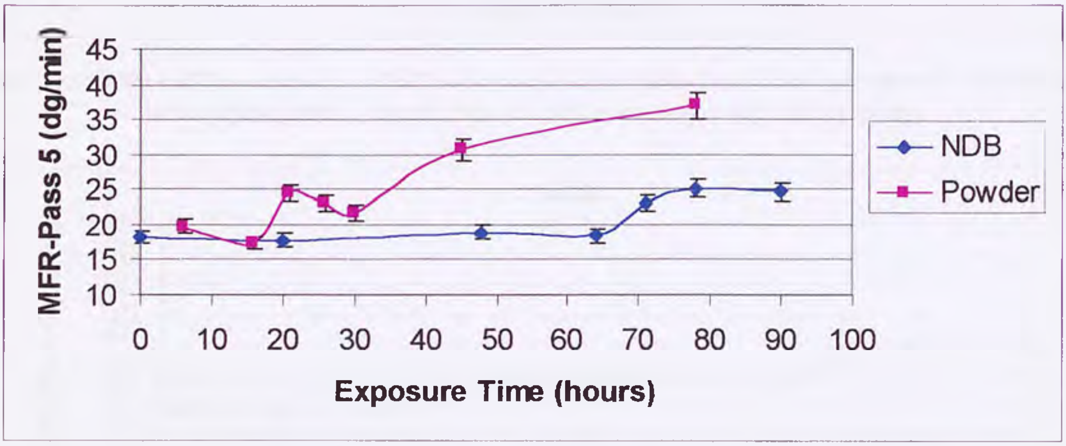


Figure 3.57. Effect of exposure time on melt performance for the Alkanoz P-24/Anox 20/DHT-4A for NDB and POWDER. Results reported as mean value ±5% error range.

From the Figures 3.55 and 3.56, it can be seen that for the NDB physical form, initially there is no significant change in terms of melt flow protection. At a certain stage of exposure time, at around 65 hours, which corresponds to approximately 75% of depletion of Alkanox P-24, a loss of performance is observed. The MFR increases and this is more pronounced in the fifth extruder pass.

For the powder blend, some scatter was apparent during the first 30 hours. These irregularities could be artefacts (they were observed) due to mixing problems associated with incorporation of the acid scavenger DHT-4A into the polymer. There is a significant loss of performance as seen the results of the third pass and the fifth pass. Initially, there is no significant change in the melt flow rate with the increase of the exposure time. At around 30 hours a loss of performance is observed. This corresponds to approximately 60% of depletion. Once again, some differences are observed between the two physical forms. There is a difference in performance of the poly(propylene) depending on the physical form of the additives used. It can also be seen also that the additives in NDB physical form outperform the powder physical form.

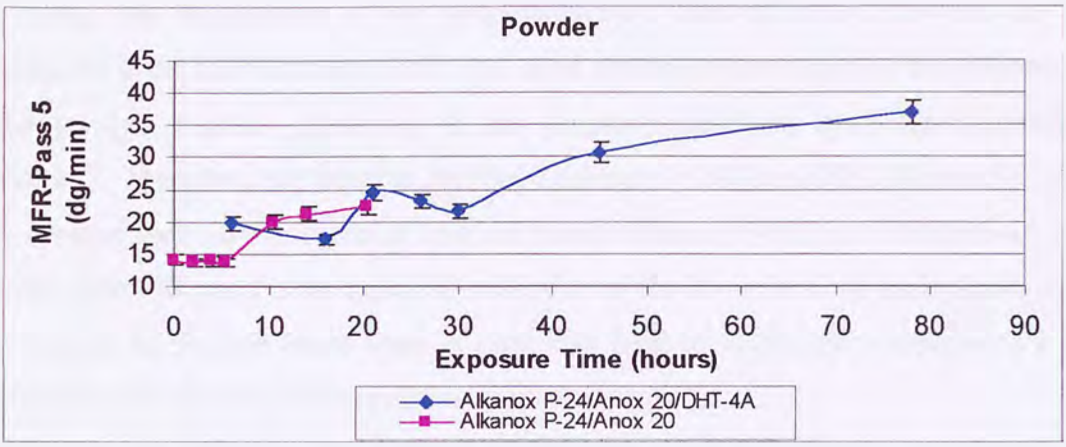


Figure 3.58. Effect of the presence of DHT-4A on melt flow index. Melt flow rate after 5th extruder pass in poly(propylene.) Results reported as mean value ±5% error range.

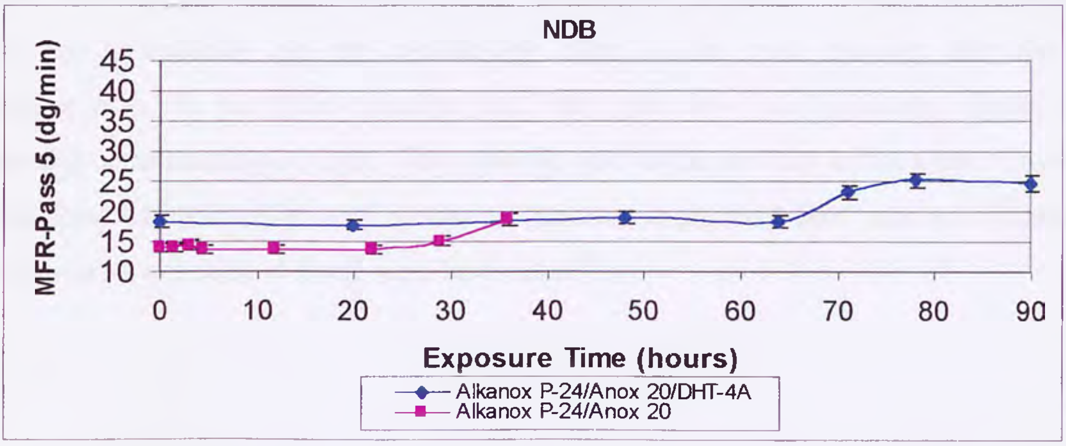


Figure 3.59. Effect of the presence of DHT-4A on the melt flow rate. Melt flow rate after 5th extruder pass in poly(propylene_. Results reported as mean value ±5 % error range.

Figures 3.58 and 3.59 show, that the performance in terms of MFR retention is better when the polymer is stabilized with phenolic antioxidant and phosphite antioxidant (Anox 20/Alkanox P-24) additive package.

Stabilisers can inhibit the thermo-oxidative degradation of polymers. Antioxidants are normally added prior to processing to inhibit any thermo-oxidative degradation. Phenolic and phosphite antioxidants are widely used to avoid degradation of the polymer during processing. The phenol/phosphite combinations commonly exhibit synergistic effects in polyolefin processing; the choice of the phenol and the phosphite, the total concentration, and the ratio of phenol to phosphite concentrations must be adjusted for specific polymer processing conditions, and equipment[15].

It is important to take into consideration that the standard stabiliser amount for a poly(propylene) homopolymer is 500 ppm phenolic antioxidant and 500 ppm phosphite antioxidant. Anox 20 and Alkanox P-24 are the antioxidants that are going to play a major role during the degradation of the poly(propylene). The difference between the two formulations is the acid scavenger DHT-4A. Acid scavengers are added to the polymer due to the catalyst residues remaining in the polymers catalysed by chloride-containing substances[60]. Therefore, the fact that the blend Alkanox P-24/Anox 20 (500 ppm:500 ppm) gives a better melt flow protection than the blend Alkanox P-24/Anox 20/DHT-4A (400 ppm:200 ppm:400 ppm) is an expected result due to the lower level of antioxidants in the latter system. In the first blend there is total load level of 1000 ppm compared to a 600 ppm total load level of antioxidants in the second system.

According to the literature, the addition of 500 ppm Anox 20 (phenolic antioxidant) and 500 ppm Alkanox 240 (phsophite antioxidant) as processing stabilisers limits the increase in melt flow rate significantly relative to the unstabilized polymer[60]. Neither the addition of CaSt, nor hydrotalcite has any considerable effect on the melt viscosity after the first extrusion pass. In the fifth extruder pass, the melt flow rate increases slightly with increasing concentration of CaSt. This could be due to the lubricity of the CaSt. However, the addition of hydrotalcite also causes an increase in the melt flow rate with increasing concentration, although at lower melt flow values[60].

3.3.3.3. Effect of the type of acid scavenger on the melt flow rate during the hydrolysis of Alkanox P-24

In the following chapter the effect of the type of acid scavenger on the melt flow rate will be analysed.

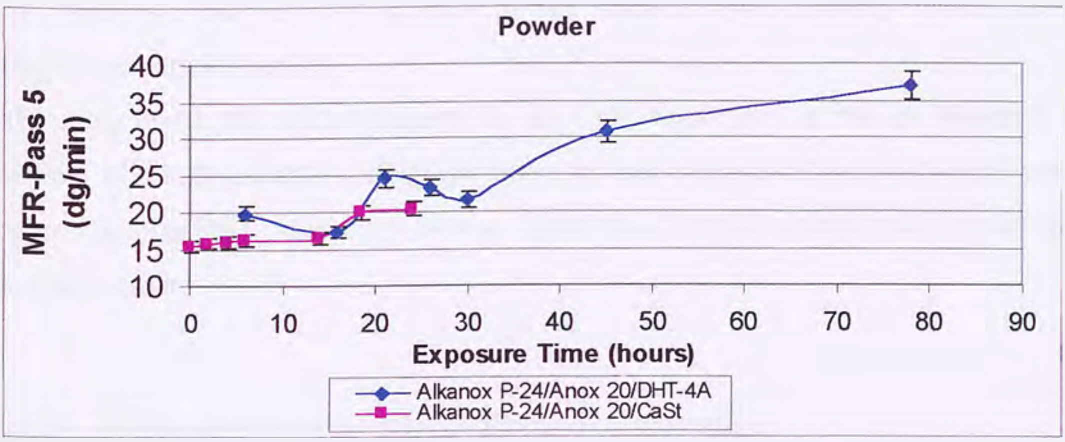


Figure 3.60. Effect of the type of acid scavenger on melt flow index after 5th extruder in poly(propylene) Results reported as mean value ±5 % error range.

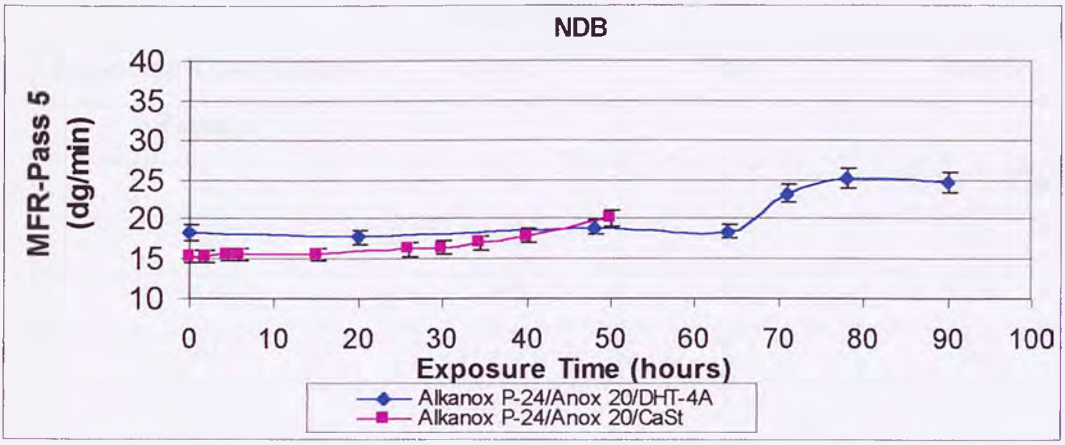


Figure 3.61. Effect of the type of acid scavenger on melt flow index after 5th extruder pass in poly(propylene). Results reported as mean value ±5 % error range.

Due to the mixing problems that were found in the powder blend with the DHT-4A, only the NDB physical form will be discussed. Surprisingly, despite the better performance in terms of hydrolytic stability, the blend Alkanox P-24/Anox 20/DHT-4A gives poorer melt flow retention during the low exposure times.

At the longer exposure times, the hydrolytic stability plays its role and the protection of the metl provided by Alkanox P-24/Anox 20/DHT-4A is the best.

In order to explain the behaviour during short exposure times, two hypotheses can be advanced; It could be possible that due to problems found during the incorporation of the mixtures based on DHT-4A, the acid scavenger does not disperse correctly in the polymer matrix. However, this kind of problem is not known in the industry where the acid scavenger is commonly used.

On the other hand, the water content in the CaSt could play a role in the melt flow protection. It is believed that initially the water present in the CaSt sample would partially hydrolyse the phosphite Alkanox P-24 that would lead to intermediate species with strong antioxidant activity.

3.3.3.4. Colour development after multiple pass extrusion

Table 3.7. Colour development after multi-pass extrusion for the Alkanox P-24/Anox 20/DHT-4A in poly(propylene).

Exposure Time (hours)	Pass 1	Pass 3	Pass 5
Powder			
0	-1.4	6.7	Not extruded
6	-1.2	1.5	2.4
16	-1.5	1.2	2.6
21	-1.5	1.2	2.2
26	-1.0	1.2	2.0
30	-1.0	1.3	2.2
45	-1.5	1.7	3.1
78	-1.7	0.5	2.1

Exposure Time (hours)	Pass 1	Pass 3	Pass 5
NDB			
0	-1.5	1.5	2.5
20	-1.5	2.5	4.4
48	-1.8	0.6	2.2
64	-1.6	0.3	1.6
71	-1.6	0.6	1.9
78	-1.1	1.2	3.1
90	-1.2	1.1	3.3

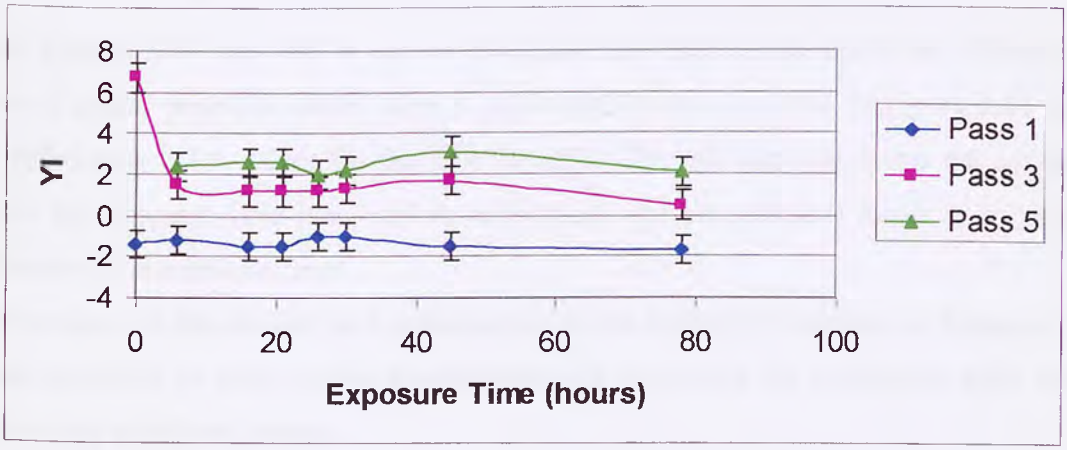


Figure 3.62. Effect of the exposure time on colour development for the Alkanox P-24/Anox 20/DHT-4A POWDER form in poly(propylene). Results reported as mean value ±0.7 units.

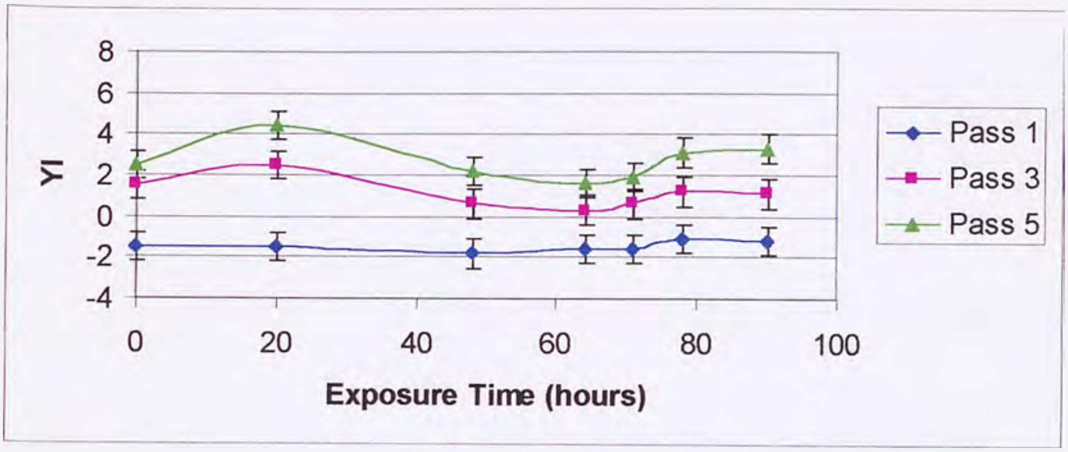


Figure 3.63. Effect of exposure time on colour development for Alkanox P-24/Anox 20/DHT-4A NDB form in poly(propylene). Results reported as mean value ±0.7 units.

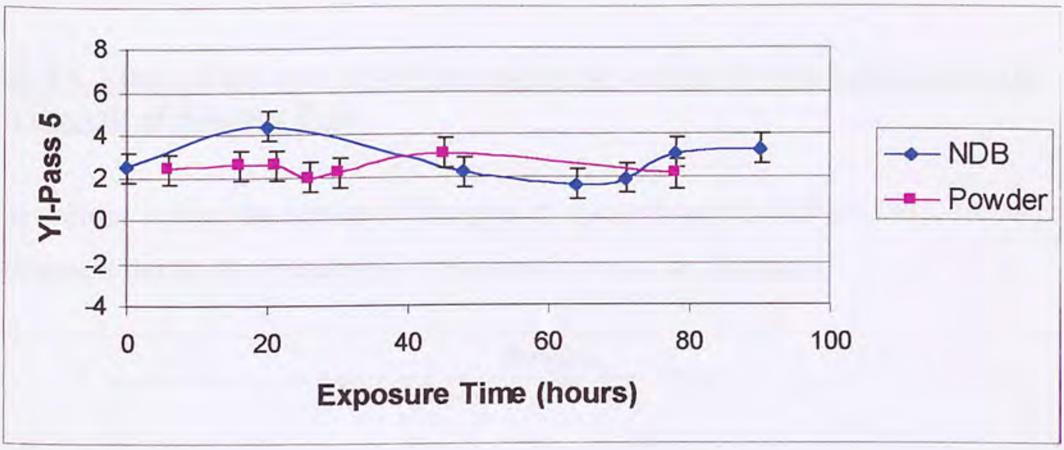


Figure 3.64. Effect of exposure time on colour development for Alkanox P-24/Anox 20/DHT-4A for NDB and POWDER. Results reported as mean value ±0.7 units.

From Figures 3.62 and 3.63 it can be concluded that there is no significant difference in terms of colour protection when there is an increase in exposure time. In Figure 3.64 where the yellowness index values for the fifth extrusion for both physical forms are compared versus the exposure time it is hard to differentiate the two physical forms or to see any influence of the exposure time.

The species that are formed as a consequence of the hydrolysis reaction of Alkanox P-24 could contribute to avoid colour development and to keeping the yellowness index values without any significant change.

3.3.3.5. Effect of the type of acid scavenger on colour development during the hydrolysis of Alkanox P-24

In the current section the impact of the type of acid scavenger, CaSt or DHT-4A on colour development during the hydrolysis of Alkanox P-24 will be discussed.

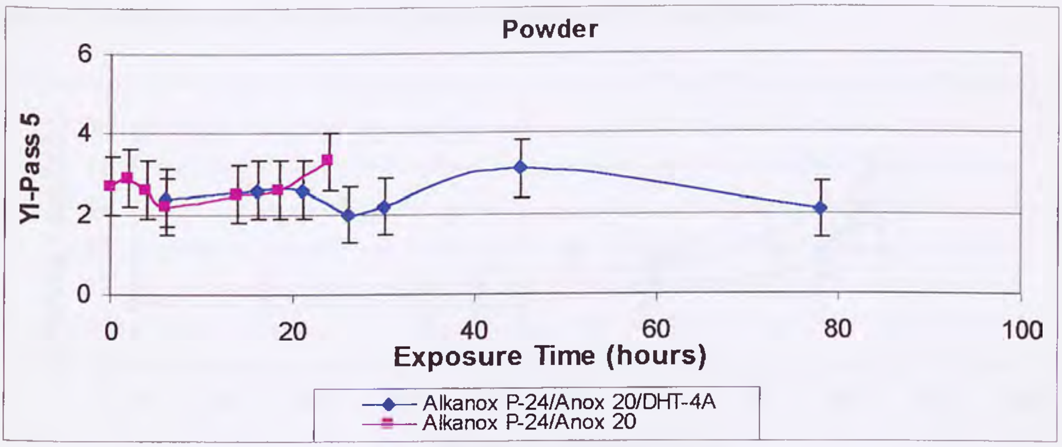


Figure 3.65. Effect of the type of acid scavenger (CaSt versus DHT-4A) on colour for the powder blend. Yellowness index after 5th extruder pass in poly(propylene). Results reported as mean value ±0.7.

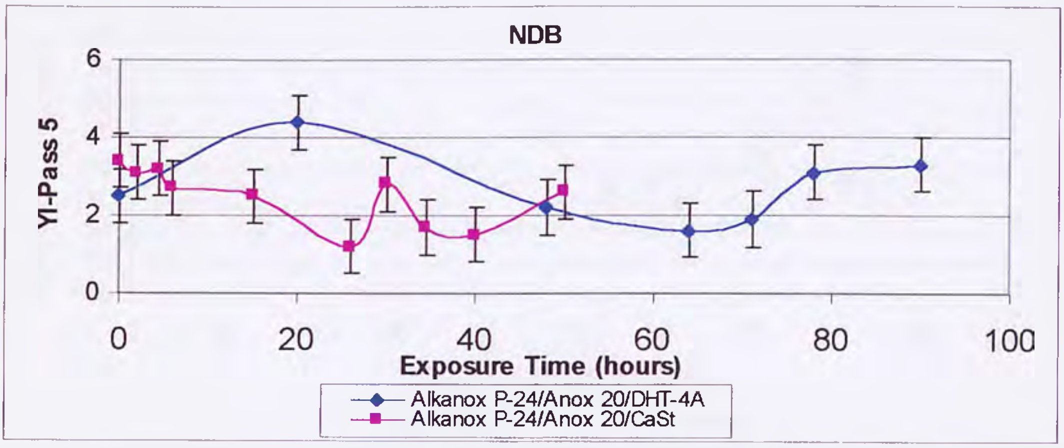


Figure 3.66. Effect of the type of acid scavenger (CaSt versus DHT-4A) on colour for the NDB blend. Yellowness index after 5th extruder pass in poly(propylene). Results reported as mean value ±0.7.

The differences between the two formulations in terms of colour development are hardly significant for both NDB and powder blends.

3.3.3.6. Melt performance as function of degree of hydrolysis

In the previous chapters the processing and analytical data of the blend Alkanox P-24/Anox 20/DHT-4A were discussed independently from each other as a function of exposure time to moisture and temperature. In this chapter the relationship between the degree of hydrolysis and the loss of performance will be analysed.

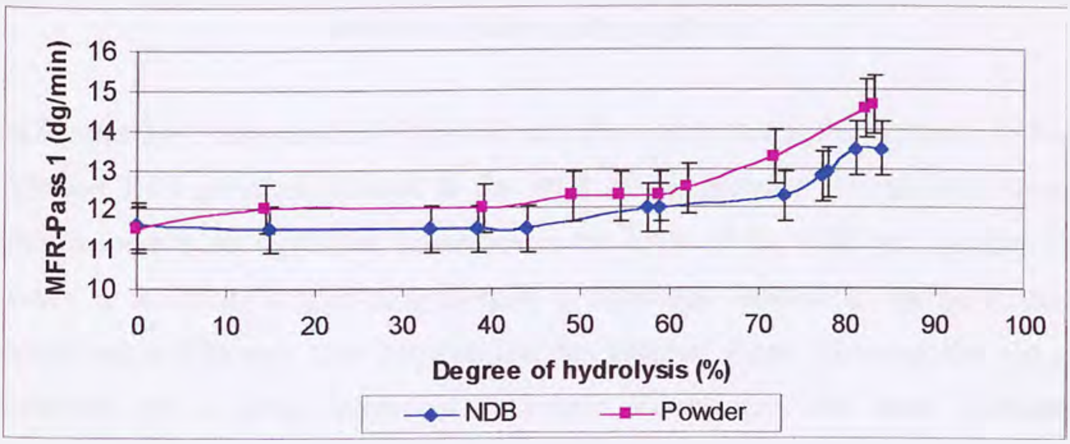


Figure 3.67. Degree of hydrolysis versus melt flow rate (first extruder pass) for Alkanox P-24/Anox 20/DHT-4A blend in poly(propylene).

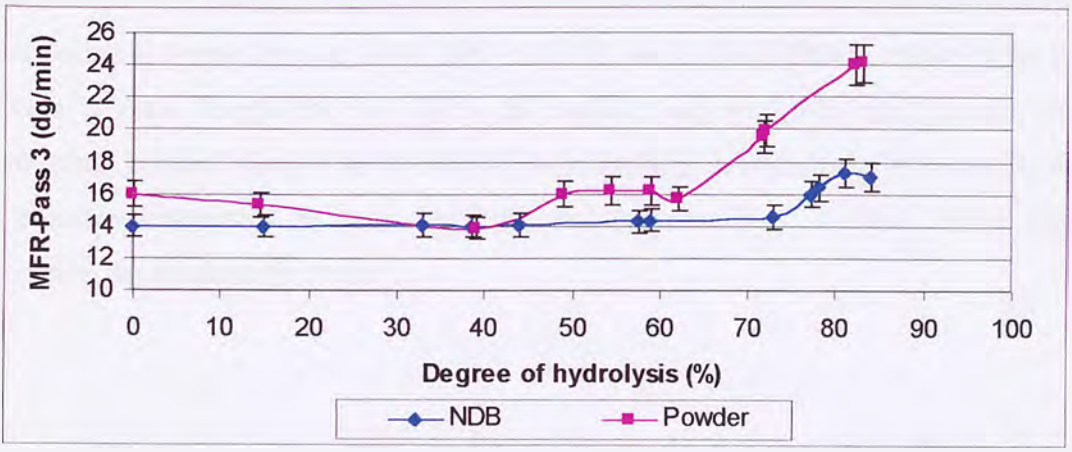


Figure 3.68. Degree of hydrolysis versus melt flow rate (third extruder pass) for Alkanox P-24/Anox 20/DHT-4A in poly(propylene).

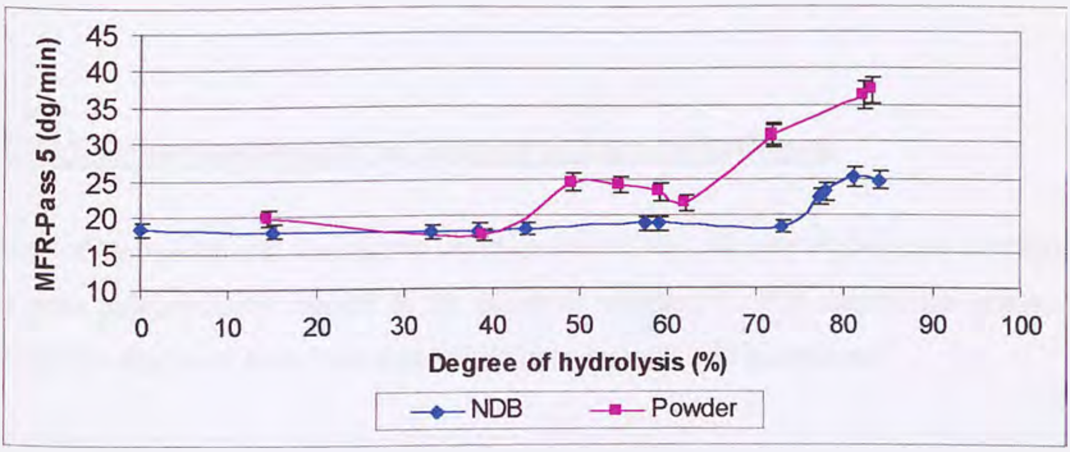


Figure 3.69. Degree of hydrolysis versus melt flow rate (fifth extruder pass) for Alkanox P-24/Anox 20/DHT-4A blend in poly(propylene).

From Figures 3.67, 3.68 and 3.69 it can be seen that an increase in the degree of hydrolysis of Alkanox P-24 gives an increase in the MFR of the polymer. At the early stages of hydrolysis there is no significant difference in the MFR of the NDB and powder blend. However, at a certain degree of hydrolysis, a significant increase in the MFR value is observed and a difference seen between the two physical forms. Theoretically, the same formulations for a given degree of hydrolysis should have the same performance independently of the physical form. In this case, this does not occur. After a certain level of degree of hydrolysis the performance in terms of melt flow protection is different for the NDB and powder blends. Higher MFR data are obtained for the powder blend showing that it performs worse than the NDB. This could be due to the diffusion rate of water in the different physical forms that will affect the stability and available concentration of the intermediate product thought to be active. The hydrolysis mechanism of Alkanox P-24 and the possible differences between both physical forms will be studied in the chapter concerning the mechanistic studies.

3.3.3.7. Colour performance as function of degree of hydrolysis

Degree of hydrolysis and the colour development of the Alkanox P-24/Anox 20/DHT-4A have been independently studied in the previous chapters. In this chapter the relationship between the degree of hydrolysis and colour development will be analysed.

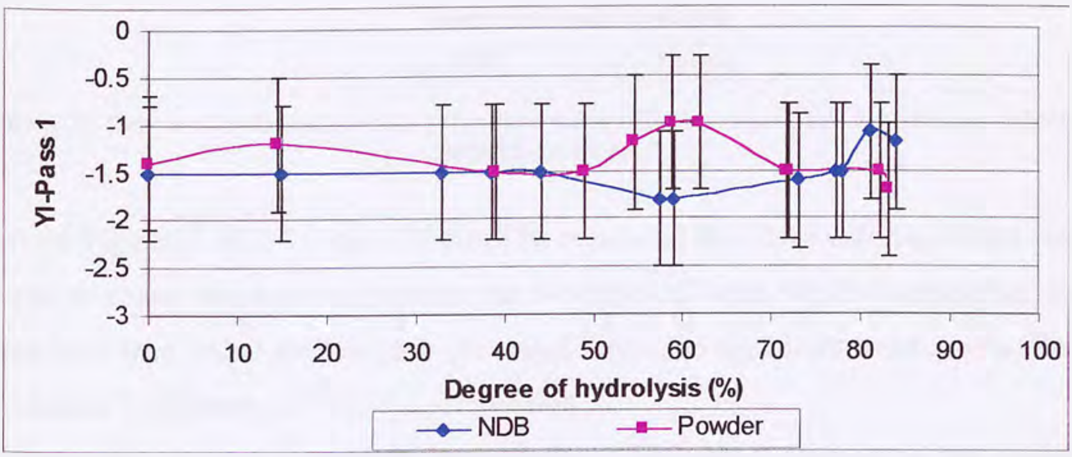


Figure 3.70. Degree of hydrolysis versus yellowness index (first extruder pass) for Alkanox P-24/Anox 20/DHT-4A blend in poly(propylene).

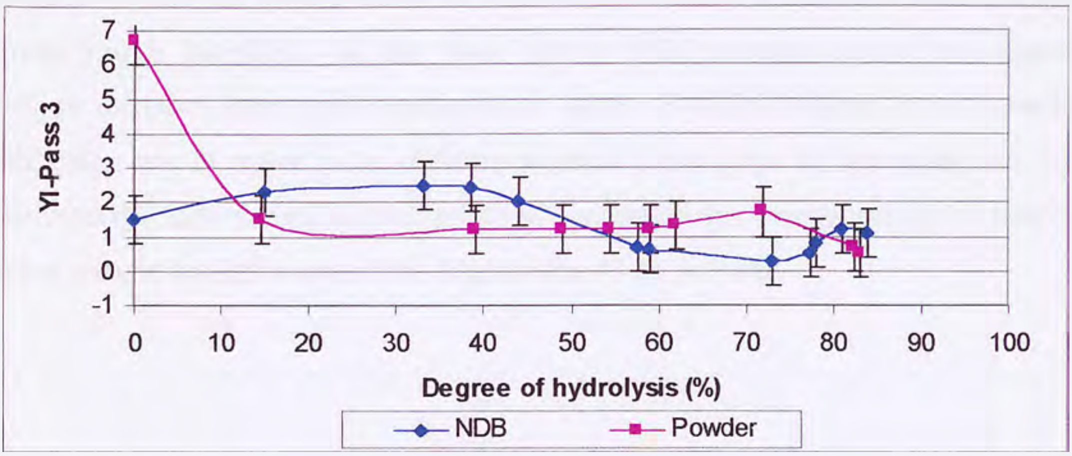


Figure 3.71. Degree of hydrolysis versus yellowness index (third extruder pass) for Alkanox P-24/Anox 20/DHT-4A blend in poly(propylene).

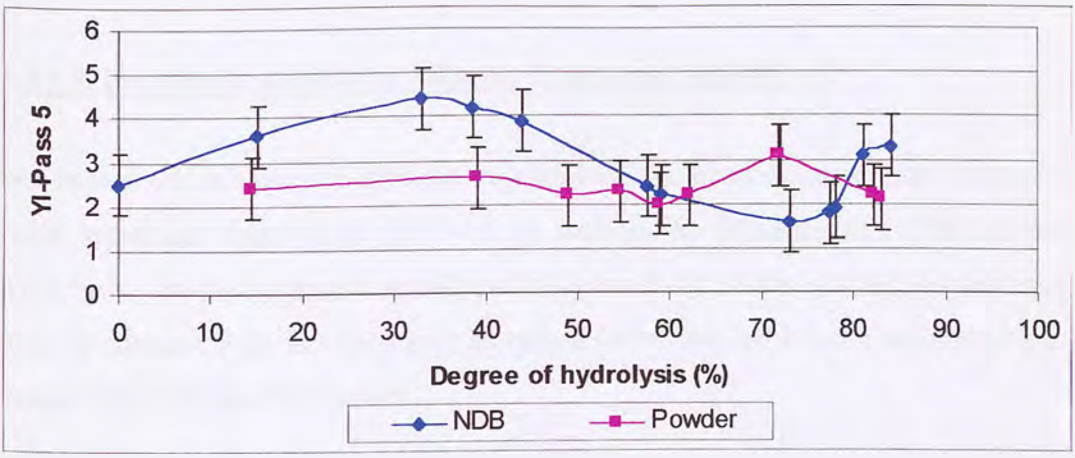


Figure 3.72. Degree of hydrolysis versus yellowness index (fifth extruder pass) for Alkanox P-24/Anox 20/DHT-4A blend.

From the Figures 3.70, 3.71 and 3.72 it can be concluded that there is no significant change in terms of colour development between the two physical forms for this formulation. These graphs have been added for reference. As stated before, no significant trend can be seen for the Alkanox P-24/Anox 20/DHT-4A formulation.

It is seen that the melt protection performance is not only a function of the degree of hydrolysis (measured as depletion of Alkanox P-24), but also a function of time and of physical form. For the powder blend an increase in the MFR is observed when the degree of hydrolysis is increased. On the hand, for the NDB initially even if the degree of hydrolysis increases there is no significance in terms of MFR Therefore, it is believed that the diffusion rate of water in the different physical forms plays an important role. In the NDB blend the intermediate species, which are generated as consequence of the hydrolysis reaction seem to be active against the degradation of the polymer.

3.3.3.8. Hydrolytic stability of Alkanox P-24/Anox 20/DHT-4A

In this section the influence of different co-additives, the phenolic antioxidant Anox 20 and the acid scavenger hydrotalcite DHT-4A as well as the influence of NDB and powder physical forms on the hydrolytic stability of Alkanox P-24 will be studied. In this case, the dilution of Alkanox P-24 has been kept as before (40%) but the relative amount of the acid scavenger DHT-4A has been halved.

Hydrolysis studies: [Alkanox P-24 + Anox 20 + DHT-4A] (40:40:20)
Physical forms: Powder and NDB

Compounding:
400 ppm Alkanox P-24
400 ppm Anox 20
200 ppm DHT-4A (hydrotalcite)

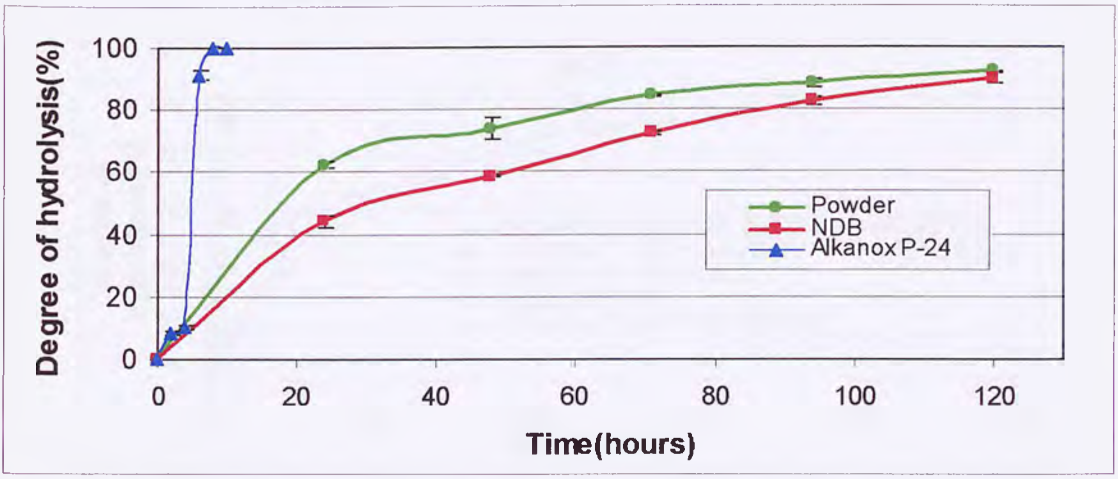


Figure 3.73. Effect of exposure time and physical form on degree of hydrolysis of Alkanox P-24. Sample exposed to 60 °C and 75 % R.H.

It is also observed that the hydrolysis rate of the phosphite Alkanox P-24 is retarded when the phosphite is part of a blend in the NDB form (Figure 3.73). Although the relative amount of acid scavenger DHT-4A has been halved (amount of phenolic antioxidant Anox 20 doubled) compared to the blend studied in the previous section a significant improvement is observed in terms of hydrolytic stability.

It is clear that the NDB concept has a positive impact on the hydrolysis rate of Alkanox P-24. The reaction rate of the phosphite with water would be partially controlled by the diffusion rate of the water into the pellet. The diffusion rate of the water into the pellet would be retarded due to the higher size of the NDB relative to the powder blend.

The hydrolysis performance of this blend is compared to the other blends and the degree of hydrolysis versus the exposure time is shown in Figures 3.74 and 3.75.

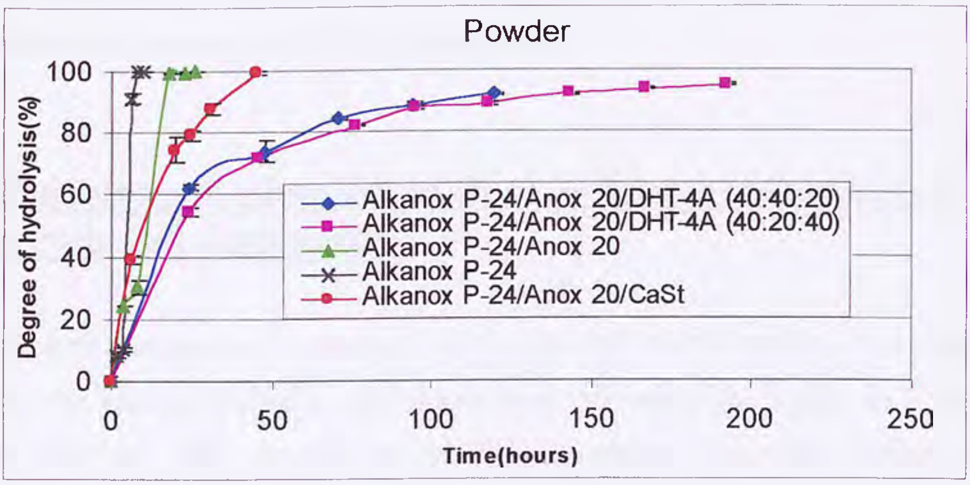


Figure 3.74. Effect of different co-additives on the hydrolysis of Alkanox P-24 (POWDER blend) when the samples were exposed at 60 °C and 75 % R.H.

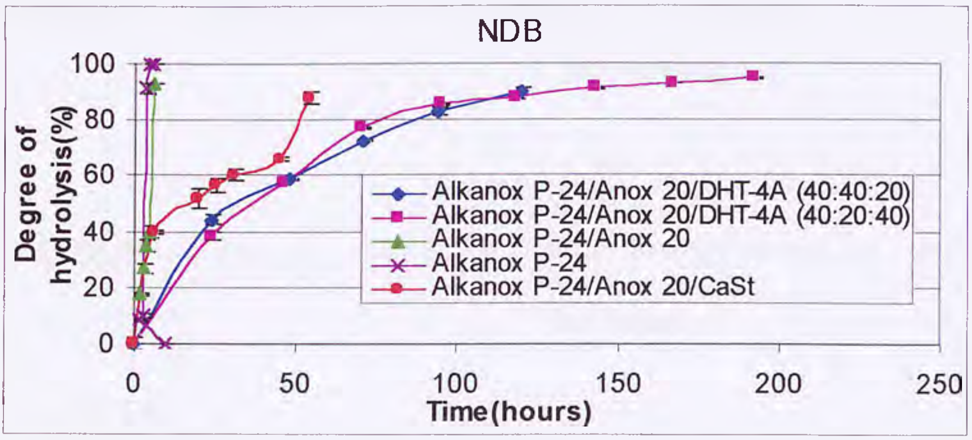
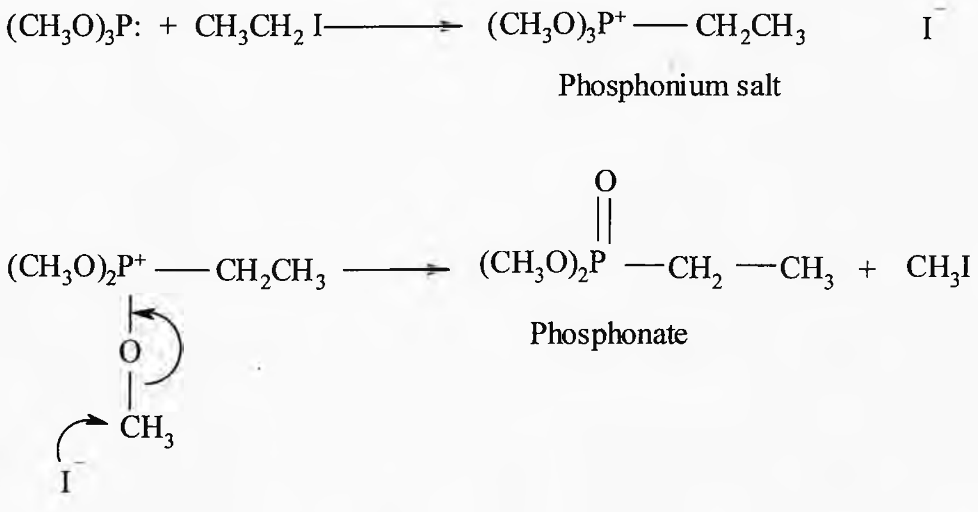


Figure 3.75. Effect of different co-additives on the hydrolysis of Alkanox P-24 (NDB blend) when the samples were exposed at 60 °C and 75 % R.H.

The formulations that have a more pronounced contribution to the hydrolytic stability of Alkanox P-24 are the ones containing the acid scavenger hydrotalcite, followed by the CaSt and then the phenolic antioxidant Anox 20. There is no significant difference between the two formulations containing the hydrotalcite acid scavenger. The same trend is observed for both powder and NDB physical forms.

3.4. Hydrolysis mechanism of Bis 2,4 (di-*tert*-butylphenyl) pentaerythritol diphosphite

The hydrolysis mechanism of Alkanox P-24 is studied in this section. According to the literature, the reaction between alkyl phosphites and water are similar to a Michaelis-Arbusov reaction. The reaction of trialkyl phosphites with alkyl halides to give phosphonites is known as Michaelis-Arbusov reaction[54].

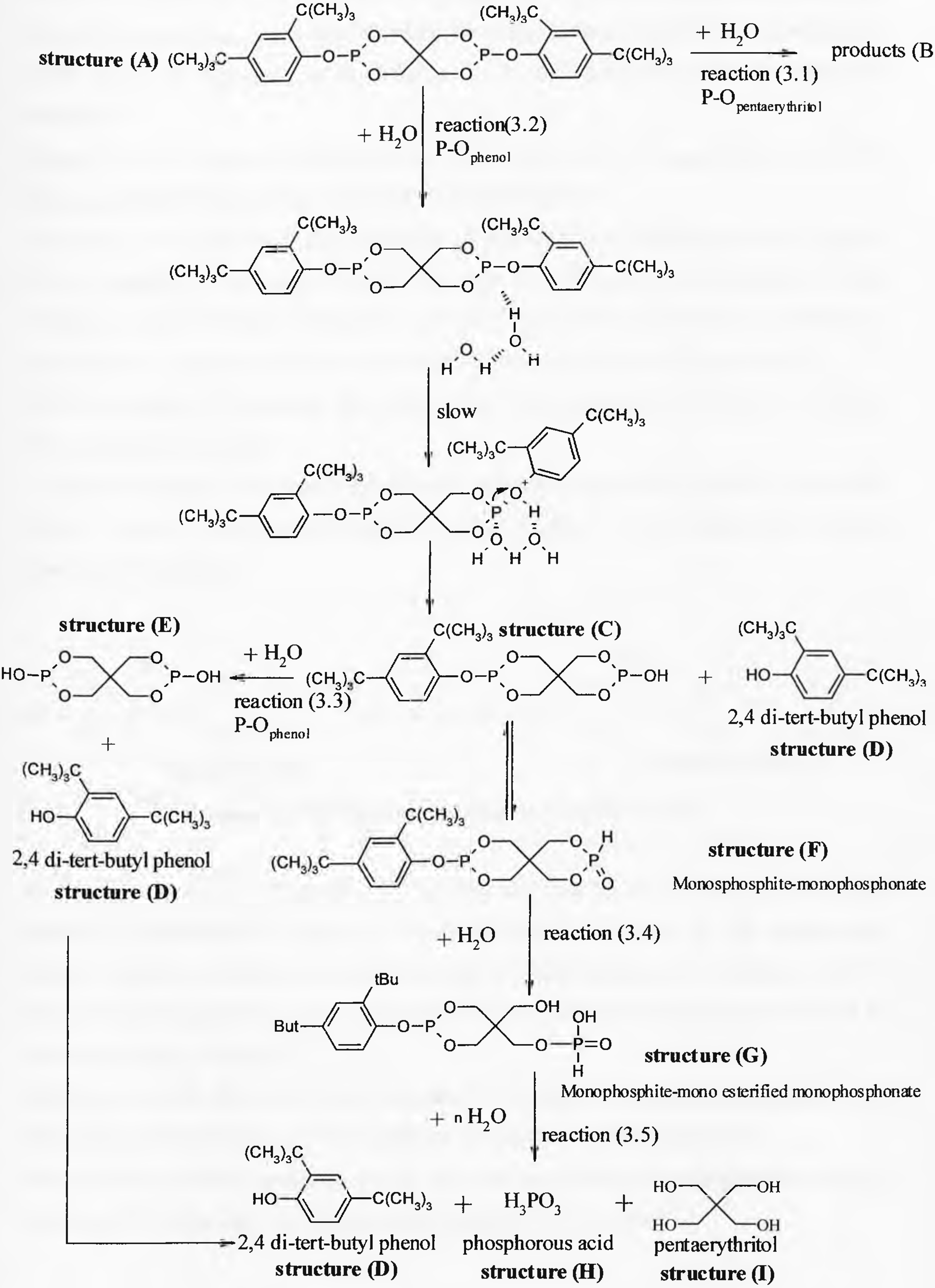


Scheme 3.1. Example of Michaelis-Arbusov reaction[54].

It is generally accepted that the reaction proceeds in two stages. First, alkyl halides undergo an initial substitution reaction with tryalkyl phosphites where a phosphonium salt is formed by nucleophilic attack on the halide. However, the salt is unstable in the presence of nucleophiles and is rapidly attacked by the iodide ion at one of the methoxy carbon atoms to give a phosphonate[54,55,103,104].

The rate-determining step in the Michaelis-Arbusov reaction of trialkyl phosphites with alkyl halides seems to be the first reaction, the formation of the phosphonium salt[105,106].

According to the literature the hydrolysis mechanism of Alkanox P-24 is:



Scheme 3.2. Hydrolysis reaction mechanism of Alkanox P-24.

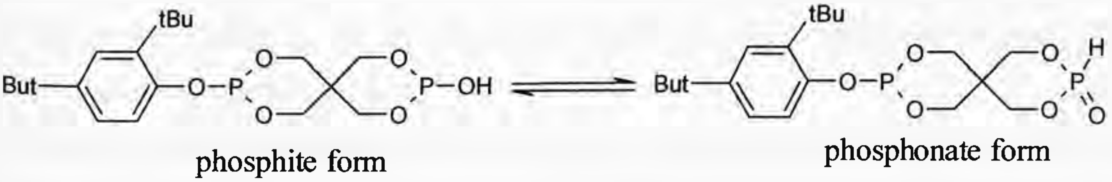
The great strength and stability of the phosphoryl P=O linkage dominates a considerable part of the phosphorus chemistry, but when the oxygen atom is involved in a bridge as in P-O-P or P-O-C linkages, as in Alkanox P-24, this generally results in hydrolytic instability[103].

Alkanox P-24 is a symmetrical di-phosphite that contains two P-O_{phenol} bonds and four P-$O_{pentaerytrhitol}$ bonds that could be vulnerable to hydrolysis attack.

According to the literature, the hydrolysis of Alkanox P-24 during storage at normal ambient humidity of air begins with the cleavage of a P-O_{phenol} bond (reaction 3.2) and initially proceeds with the cleavage of a second P-O_{phenol} bond (reaction 3.3), resulting in the release of 2,4 di-tert-butylphenol (structure D) from the Alkanox P-24 molecule[34].

In the initial stage of hydrolysis, cleavage via the P-$O_{pentaerythritol}$ bond (reaction 3.1) seems to be of minor importance[34].

As mentioned before, the reaction between the phosphite and water is similar to Michaelis-Arbusov reaction. The hydrolysis reaction should proceed via the phosphonium salt and would lead to structure C.



Scheme 3.3. Tautomerism involving the phosphoryl group.

The above tautomerism (Scheme 3.3) between the two species is well known in the literature. Spectroscopic evidence is overwhelmingly in favour of the phosphonate structure and the equilibrium constant for diethyl H-phosphonate, for example, is 10^7 in favour of the H-phosphonate form, and the P-OH form has never been directly detected by any spectroscopic technique[53,55].

Therefore, once the phosphite form (structure C) is formed the tautomeric equlibrium will take place and the phosphonate form (structure F) will be the main compound.

The hydrolysis reaction continues and in the subsequent stage the phosphorinane ring is opened and the mono esterified phosphonate (structure G) is formed[51].

Finally, the hydrolysis reaction will lead to the ultimate hydrolysis products of Alkanox P-24, which are reported to be, 2,4 di-tert-butylphenol, phosphorus acid (H_3PO_3) and pentaerythritol[34].

3.4.1. Verification of the hydrolysis mechanism

Different experiments and techniques have been used to verify the hydrolysis mechanism of the bis 2,4-(di-*tert*-butylphenyl) pentaerythritol diphosphite phosphite antioxidant.

It has been confirmed that the final hydrolysis products are 2,4-di-*tert*-butylphenol and pentaerythritol. During the hydrolytic stability studies (described in the previous chapters), samples were introduced in the oven at 60 °C and 75 % R.H. and they were periodically removed and analysed by High Performance Liquid Chromatography (HPLC) to follow the depletion of the phosphite and quantify the degree of hydrolysis.

When the samples of the phosphite were analysed with acetonitrile as a mobile phase the peak depletion appeared at a retention time of 5.2 minutes. At a retention time of 3 minutes a peak corresponding to the 2,4-di-*tert*-butyl phenol appeared, which was confirmed using 2,4-di-*tert*-butyl phenol standard.

During the same experiment, at the later stages of the hydrolysis, when the samples were dissolved in acetonitrile to be injected on the HPLC, an insoluble solid was observed. It was thought to be one of the hydrolysis products, 2,4 di-tert-butyl phenol, phosphorus acid or pentaerythritol. However, 2,4 di-tert-butyl phenol was discarded because of its solubility in acetonitrile and the visible peak in the HPLC chromatogram.

In order to determine the chemical structure of this unknown product an FTIR spectra was obtained, as shown in Figure 3.76, and it was confirmed to be pentaerythritol.

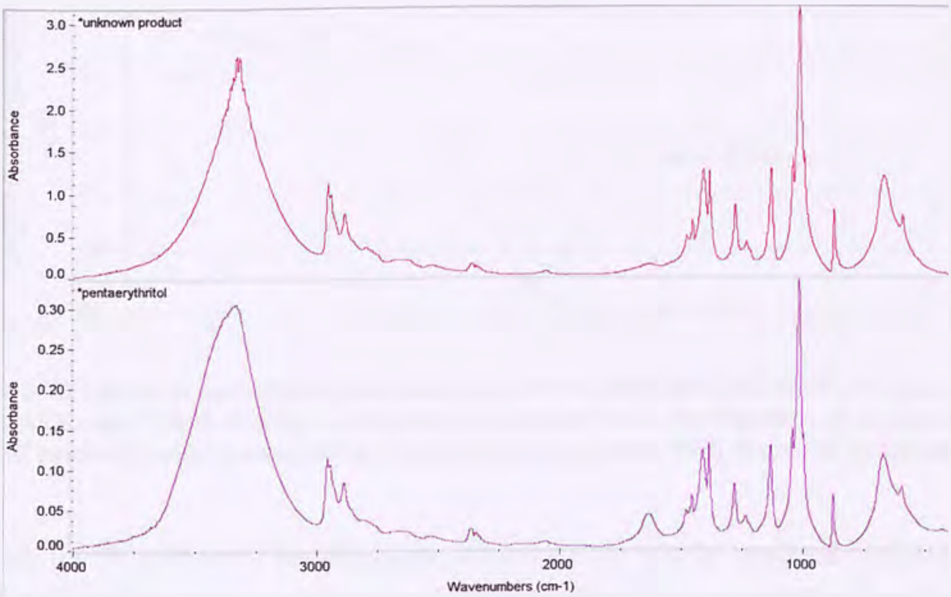


Figure 3.76. Infra-Red spectra for the insoluble product obtained during the hydrolysis studied and an spectra of pentaerythritol.

Therefore, it was confirmed that the pentaerythritol and 2,4-di-*tert*-butyl phenol are two of the hydrolysis reaction products as proposed by the literature.

The final products are known, however, the following step is to elucidate the intermediate products of the hydrolysis of Alkanox P-24. In order to study the intermediate products of the hydrolysis reaction, several experiments and different techniques were used, such as FTIR and mass spectrometry.

Firstly, a qualitative study was carried out, samples were introduced in the oven at 60 °C and 75 % R.H. and they were periodically removed and analysed by FTIR in order to analyse the disappearance or appearance of functional groups. Samples were removed after 2, 4, 6, 8 and 24 hours in the oven and the IR spectra were compared to the pure Alkanox P-24 spectra.

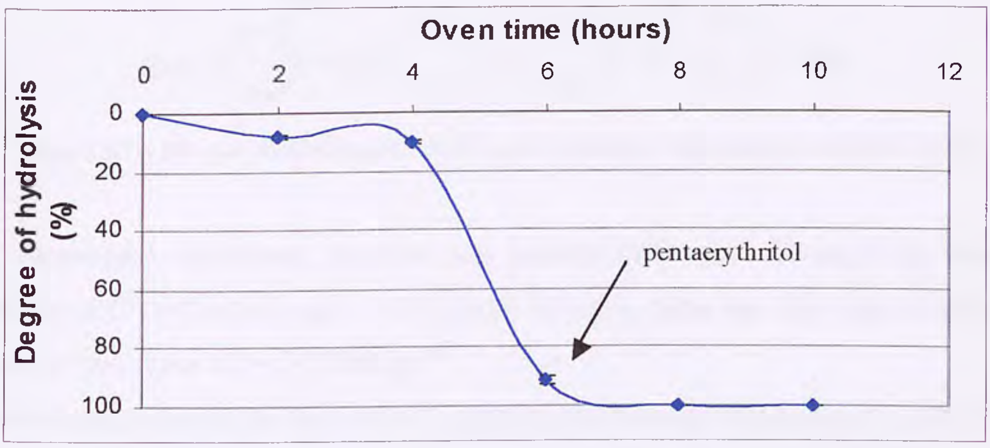


Figure 3.77. Degree of hydrolysis versus oven time for the phosphite Alkanox P-24 when is been exposed to 60°C and 75% R.H. Degree of hydrolysis is quantified as the depletion of Alkanox P-24. The first pentaerythritol is observed at 6 hours oven time (aprox. 90% degree of hydrolysis).

First of all, the IR spectra of the phosphite Alkanox P-24 will be analysed in depth in order to check the possible variations when exposed to the hydrolysis conditions.

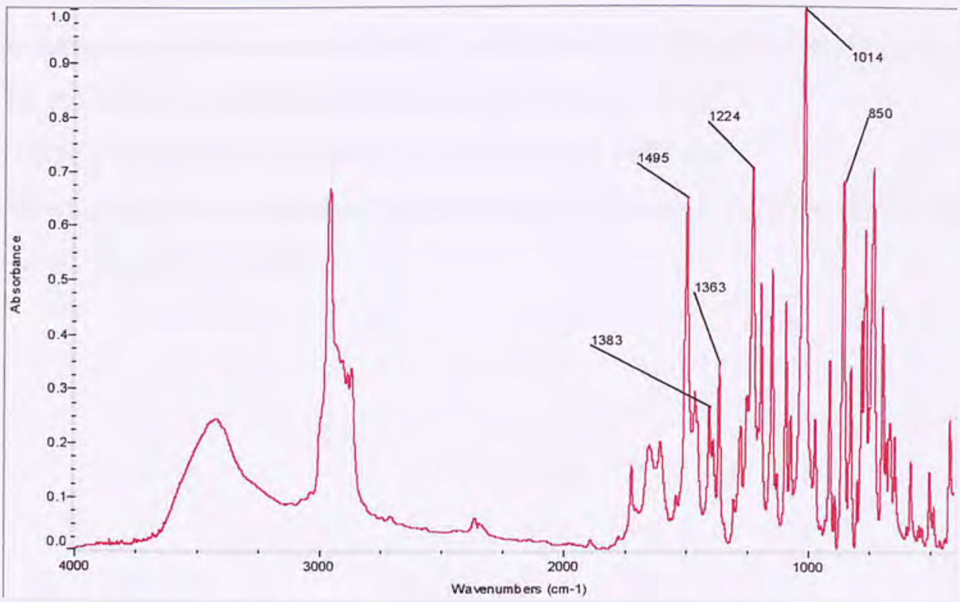


Figure 3.78. Infra-Red spectra of Alkanox P-24.

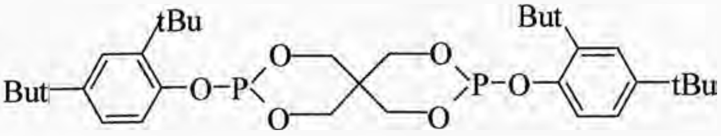


Figure 3.79. Bis 2,4 (di-tert-butylphenyl) pentaerythritol diphosphite (Alkanox P-24)

P-O-C (aromatic) vibrations. As there are marked differences between the absorption frequencies of C-O-C (alkyl) and C-O-C (aryl) linkages, there are also marked differences between the two types of P-O-C linkage[107].

The overall range found for the P-O-C (aromatic) stretching vibrations is 1240-1190 cm^{-1}[107,108]. The peak corresponding to this vibration in the case of Alkanox P-24 appears at 1224 cm^{-1}.

P-O-C (alkyl) vibrations. The stretching vibrations for P-O-C (alkyl) are found in the range of 1050-995 cm^{-1}[107,108]. The peak corresponding to this vibration in the case of Alkanox P-24 appears at 1014 cm^{-1}.

There are aromatic groups in the molecule, which give C-H stretching bands near 1600 cm^{-1} and 1500 cm^{-1} that are observed in the spectra of Alkanox P-24.

The tert-butyl groups have their bands at 1363 cm^{-1} and 1383 cm^{-1}.

In the following spectra the changes in the structure of Alkanox P-24 are shown after being exposed to 60 °C and 75 % R.H.

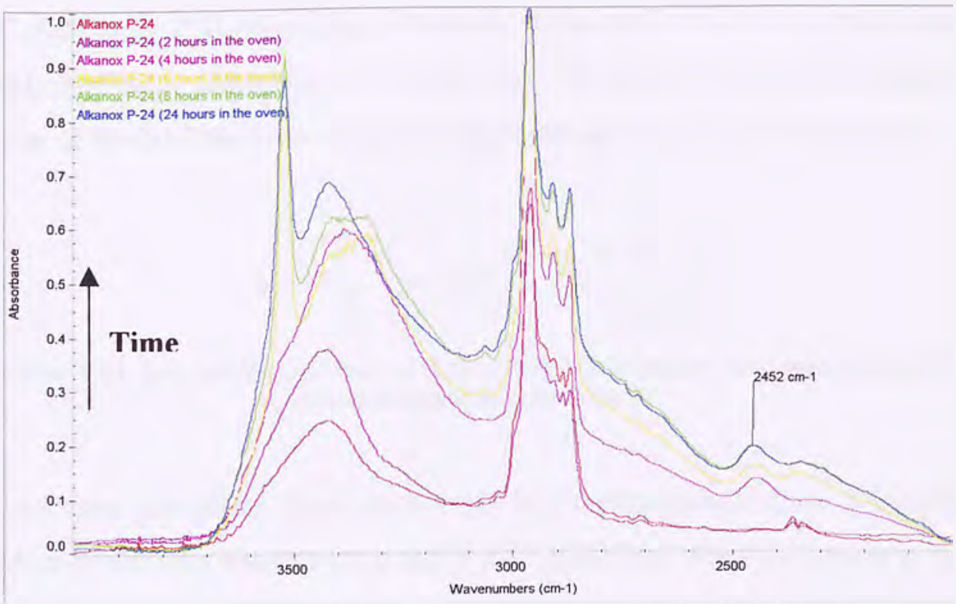


Figure 3.80. IR spectra(1600 cm^{-1} to 4000 cm^{-1}) of Alkanox P-24 after being exposed to 60 °C and 75 % R.H. Samples were periodically removed and the IR spectra was carried out.

Two important observations can be made in this region of the spectra. Firstly, above 3000 cm^{-1} is a common region for the stretching vibration of the O-H group. The value of the O-H stretching frequency has been used as a measure of the strength of hydrogen bonds[84]. The stronger the hydrogen bond, the lower the vibration frequency and the broader and the more intense the absorption band[84]. When the O-H groups are not forming hydrogen bonds, a sharp O-H stretching band is observed at 3650-3590 cm^{-1} and when the O-H groups are forming hydrogen bonds a broad band is usually observed at 3200-2500 cm^{-1}[84]. In the experiment a sharp band is observed together with a broad one. The sharp band is due to the O-H stretching of the 2,4-di-*tert*-butyl phenol, which is one of the final products of the hydrolysis of Alkanox P-24. This group is not forming hydrogen bonds due to the steric hindrance created by the *tert*-butyl groups. The broad band could be due to the O-H stretching vibration of the pentaerythritol or it is also possibly to be because of the crystallization of water in the KBr discs. Before carrying out the spectra the samples has been exposed to humidity. Water in trace amounts in KBr discs shows a broad band at 3450 cm^{-1}.

The second observation to be made is that at 2452 cm^{-1} there is another band that appears as consequence of the hydrolysis of Alkanox P-24. According to the literature,[107] the P-H stretching vibration of different phosphorus compounds have a sharp absorption band of medium intensity in the range of 2440-2350 cm^{-1}. The band observed in the IR spectra is probably due to a P-H stretching vibration. This could be due to the intermediate compound, hydrogen phosphite or phosphonate (Structure F) or the phosphorus acid H_3PO_3, one of the final products of the hydrolysis, which has a P-H bond as well.

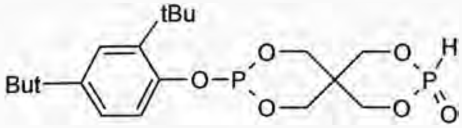


Figure 3.81. Intermediate product of the hydrolysis of Alkanox P-24; monophosphite-monophosphonate (Strucure F).

Dialkyl hydrogen phosphites (exist exclusively in the phosphonate form ($(RO)_2PHO$)have been studied by infrared spectroscopy and a P-H stretching vibration occurs in the region 2400 to 2450 cm^{-1} for aliphatic open chain esters and for cyclic esters[53]. P-H bending vibrations have been assigned to the region 970 to 980 cm^{-1}[53].

It has been mentioned before that the pentaerythritol was observed when the degree of hydrolysis was 90 % or after 6 hours of exposure time. Looking at the spectra (Figure 3.80) it can be seen that after 6 hours of exposure time the sharp peak above 3000 cm^{-1} of the 2,4-di-*tert*-butyl phenol can be seen clearly.

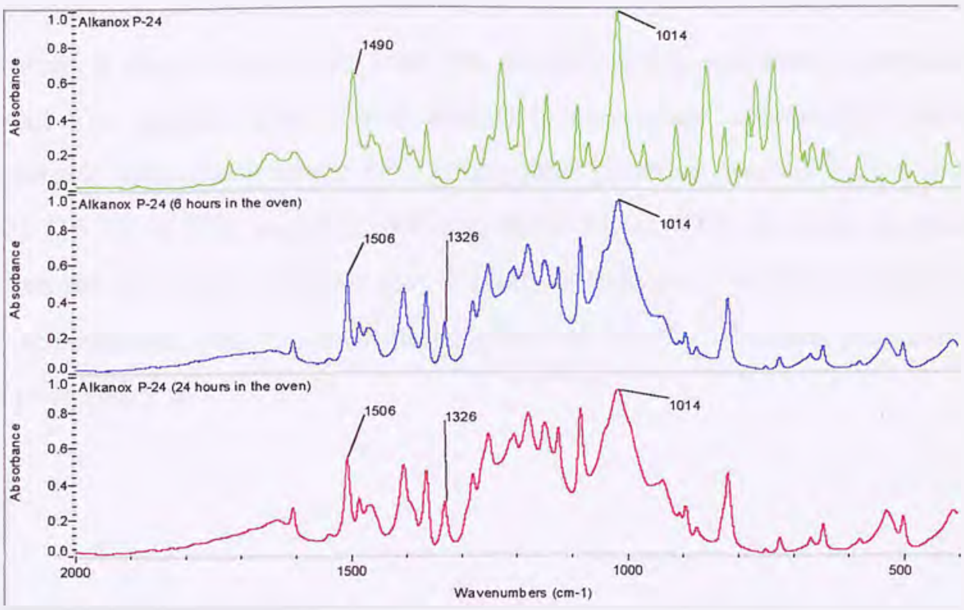


Figure 3.82. IR spectra (from 400 cm^{-1} to 1770 cm^{-1}) of Alkanox P-24 when the sample was exposed at 60 °C and 75 % R.H. Samples were removed periodically. Due to the quantity of the peaks in this area only some of the exposed times are shown.

In this area it is seen that the peak that belongs to the aromatic ring at 1494 cm-1 occurs at a higher wavenumber, 1506 cm^{-1}. A new peak appears at 1326 cm^{-1} which could be due to the P=O stretching vibration, that it is present in the organophosphorus acid and the intermediate products of the hydrolysis of Alkanox P-24. The peak at 1014 cm^{-1} (P-O-C) has not disappeared with the hydrolysis of Alkanox P-24 but this is because a vibration at the same wavenumber is observed for the pentaerythritol.

It can be concluded that this experiment confirmed the pentaerythritol and 2,4-di-*tert*-butyl phenol as final products. Due to the peak observed at 2452 cm^{-1} a P-H stretching vibration has been observed which could be due to the final phosphorus acid or an intermediate product containing this bond.

Mass spectrometry experiment was also carried out in order to investigate the intermediate products of the Alkanox P-24 hydrolysis.

The Alkanox P-24 that was used for the hydrolytic stability studies was stored in the laboratory in the aluminium bag where the sample was received under normal humidity and temperature conditions.

The product was stored in the aluminium bag (resealed) for a period of one year under normal temperature and humidity conditions. In order to study the intermediate products of the hydrolysis a sample was taken from the aluminium bag and mass spectrometry was carried out. The samples were diluted initially in isopropanol followed by methanol. A triple-quadruple mass-spectrometer with atmospheric pressure photoionization source was used (API-365 PE SCIEX, supplied by Glaxo Smith-Kline). The following conditions were used to run the spectrum; nebulizer gas: 8 l/min, curtain gas: 10 l/min, ionspray voltage: 1500 V, temperature: 500 °C, declustering potential: 24.7 V, focusing potential: 180 V, entrance potential: 9.0 V.

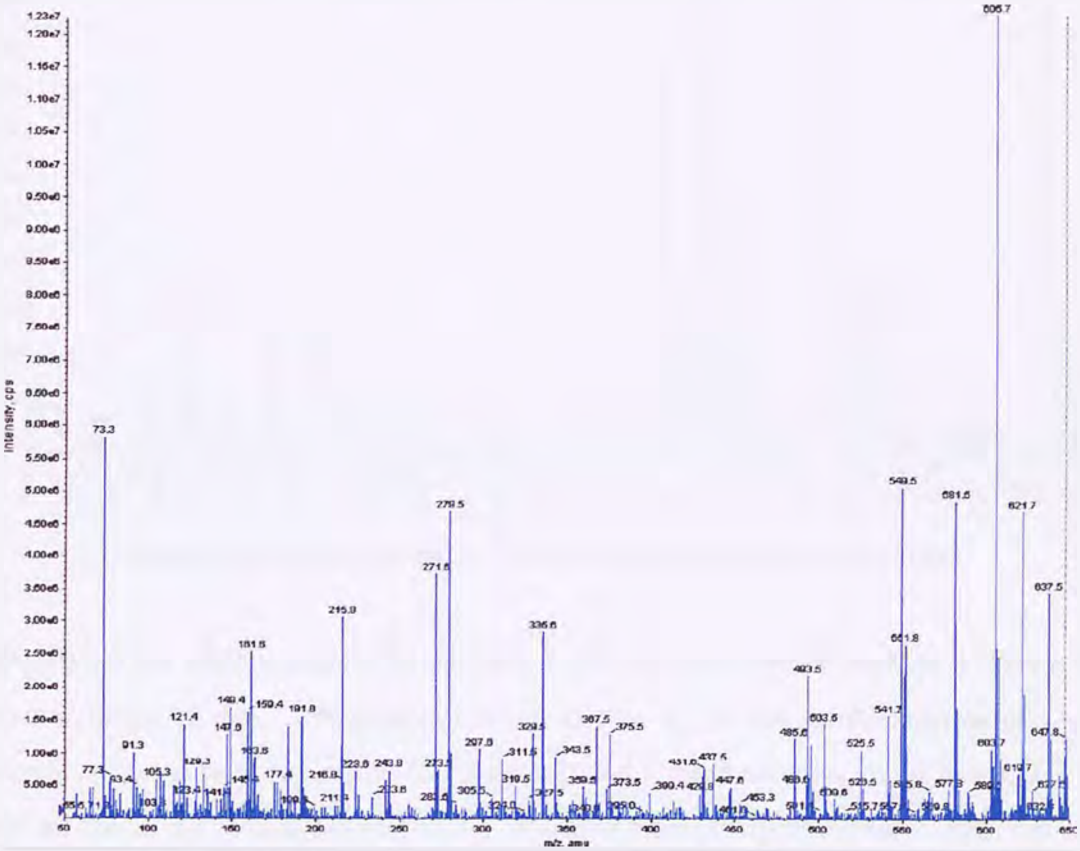


Figure 3.83. Mass spectrum of Alkanox P-24. The spectrum was carried out after one year of storage in an aluminium bag under normal humidity and temperature conditions.

In Figure 3.83 the spectrum of Alkanox P-24 is shown. It can be observed that the fragment ion at m/z 605.7 corresponds to the Alkanox P-24.

The structure (F), Monophosphite-monophosphonate compound shown is Scheme 3.2 has a molecular mass of 416 g/mol and the structure (G), monophosphite-mono esterified monophosphonate has a molecular mass of 434.5 g/mol. The final products 2,4-di-*tert*-

butylphenol, phosphorus acid and pentaerythritol have been already identified by HPLC and FTIR.

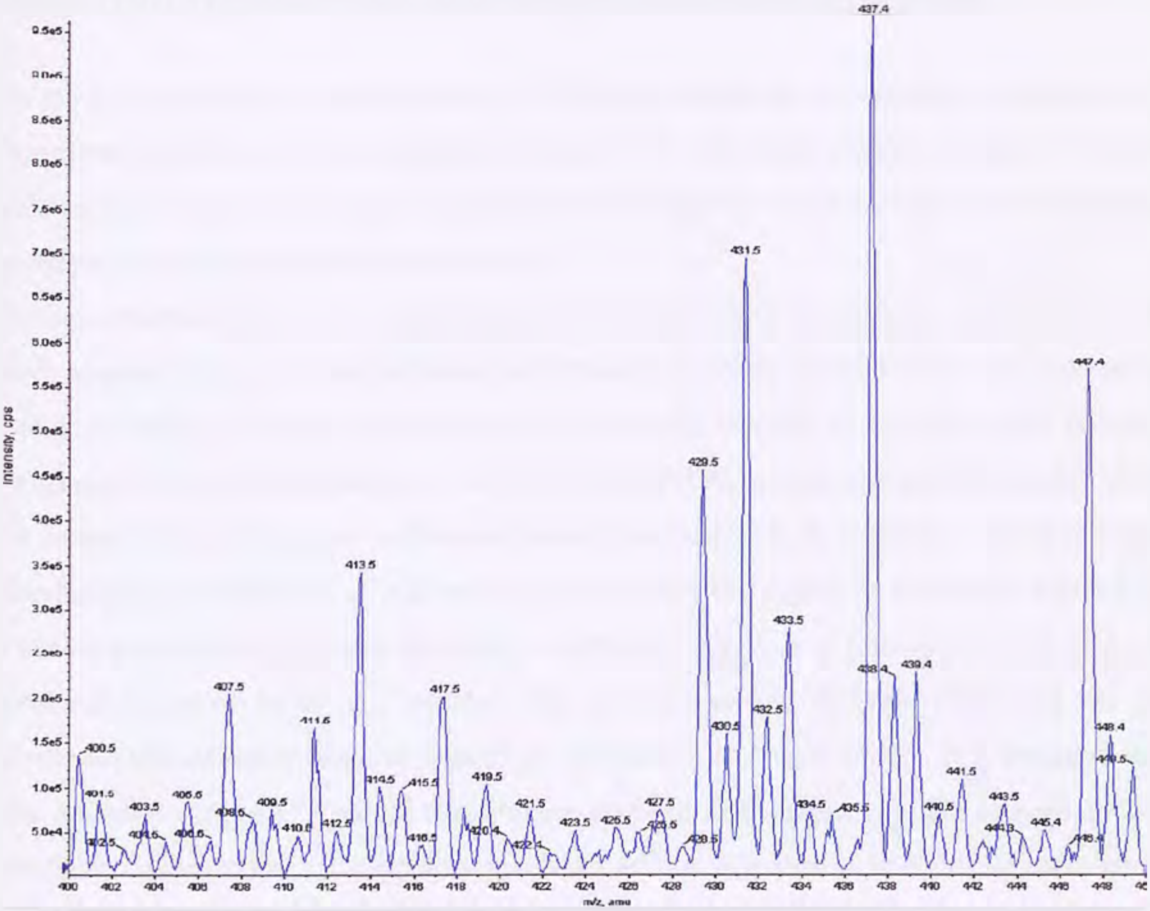


Figure 3.84. Mass spectrum of Alkanox P-24 in a narrower range of m/z.

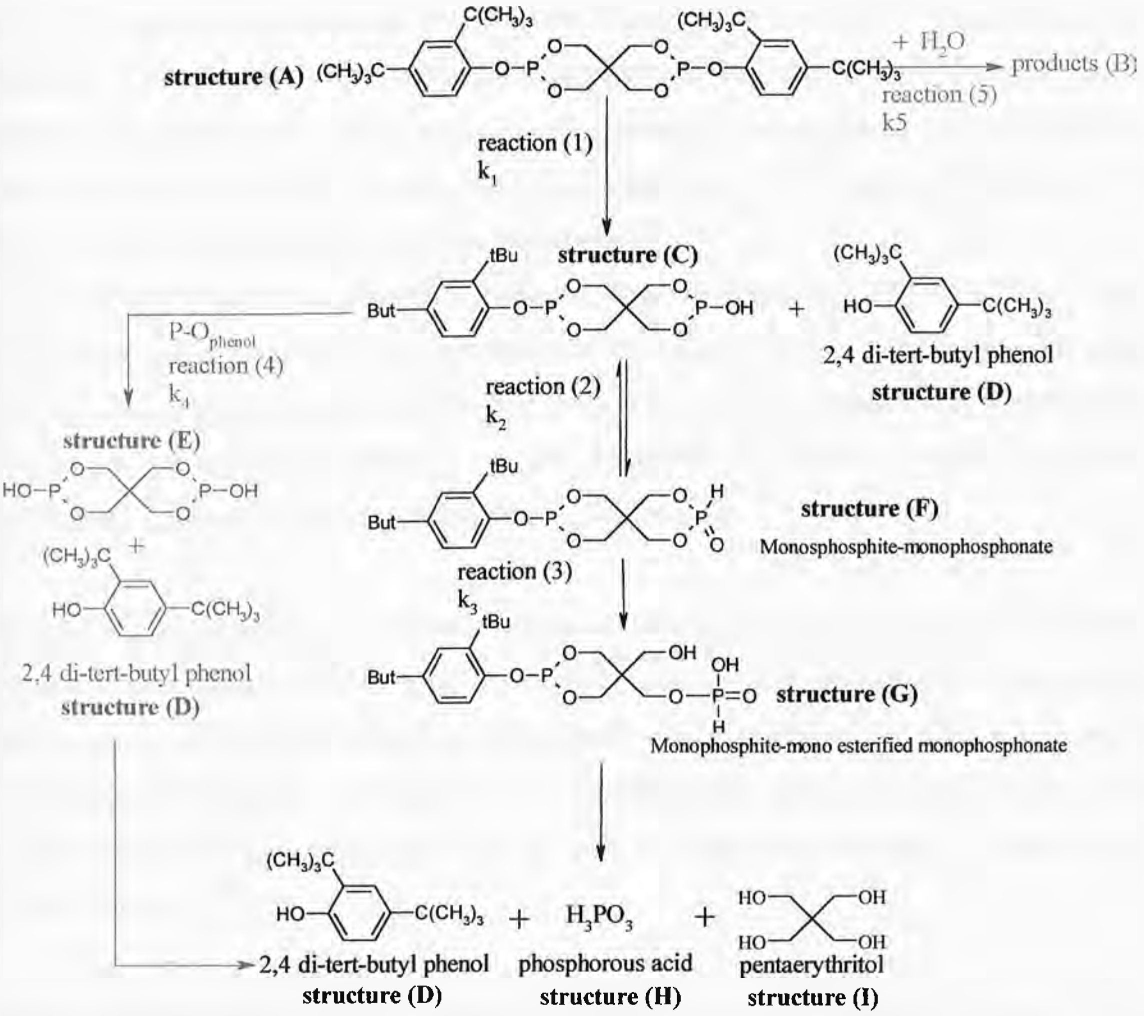
In Figure 90 the mass spectrum of Alkanox P-24 after one year of storage is shown in a narrower range of m/z. A fragmentation ion at m/z 417.5 that could correspond to the monophosphite-monophosphonate (Scheme 3.2) and a fragmentation ion at m/z 435.5 that could be due to the monophosphite-mono esterified monophosphonate were observed. This would confirm the hydrolysis pathway shown in Scheme 3.2 and these species might be active species that would contribute to the stabilisation of the polymer.

3.4.2. NDB versus powder. Hypothetical hydrolysis mechanism

In the previous chapter, the influence of different co-additives and physical forms upon the hydrolytic stability of the phosphite Alkanox P-24 has been studied together with the relationship between the degree of hydrolysis of Alkanox P-24 and the melt stability of poly(propylene) has also been investigated.

It was observed that above approximately 30 % hydrolysis the polymer containing NDB and powder blends showed different performance in terms of melt flow and yellowness index protection. It was also seen that at the same amount of hydrolysis the polymer processed with the formulations in the NDB physical form outperforms the powder blend in terms of melt flow and yellowness index protection. It is therefore considered that measurement of depletion of Alkanox P-24 to monitor the degree of hydrolysis may not be entirely appropriate. Different kinetically controlled hydrolysis is followed for the different physical forms of NDB and powder. The mechanisms are different depending on the concentration of water (relative humidity), diffusion control and acidity. It is assumed that the diffusion control of water in the different physical forms affects the life expectancy and available concentration of a highly active intermediate. The relatively high concentration in the partial hydrolysis pathway of the Alkanox P-24 NDB blend seems to be responsible for the differences in performance of NDB and the powder blend.

In Scheme 3.4 the hydrolysis pathway of the phosphite Alkanox P-24 is shown.



Scheme 3.4. Hydrolysis mechanism of Alkanox P-24.

Alkanox P-24 (Structure A) is a di-phosphite containing two identical P-O_{phenol} bonds and four P-$O_{pentaerythritol}$ bonds that are vulnerable to hydrolytic attack. However, the hydrolysis of Alkanox P-24 in air at ambient humidity begins with the cleavage of P-O_{phenol} bond (Reaction 1 in Scheme 3.4)[34]. This reaction results in the release of structure C and 2,4-di-*tert*-butyl phenol (Structure D).

Structures C and F are tautomers. The structure F is monophosphite-monophosphonate. The chemistry of phosphonates is complicated by the presence of this tautomeric equilibrium with the presence of P-OH form (structure C), which although in only tiny amounts, can play a critical role as a reactive intermediate[55].

Many studies over the years have delved into this equilibrium; spectroscopic evidence is overwhelmingly in favour of the phosphonate (structure F) form[53,55,104]. According to the literature[55], phosphonates have a multitude of practical uses, including additives in various plastics formulations, lubricants and fuel oils. Phosphonates seems to be antioxidatively active by them and, like the phosphorus acid (H_3PO_3) give synergistic mixtures with hindered phenols in higher-temperature oxidations[109].

It is believed that monophosphite-monophosphonate (Structure F) is a very active component and that this product contributes to the colour and melt stabilisation. Assuming that this monophosphite-monophosphonate is the major contributor to colour and melt flow protection the following reasoning on rate constants k_1 and k_5 explain performance differences between NDB and powder blends (Scheme 3.4).

Powder blend: (Scheme 3.4) It is believed that under given conditions k_1 does not depend on the concentration of H_2O and is relatively fast. In this case the poor processing performance of partly hydrolysed powder blend can be explained by only a low steady state concentration of the structure F. This could imply that k_3 has to be at the same order or is even much bigger than k_1: structure F would be depleted at least with the same rate as it was formed.

NDB: (Scheme 3.4) At the same degree of hydrolysis, the same amount of Alkanox P-24 is depleted which indicates that k_1 in both cases is identical. On the other hand, in contrast to the powder blend it is assumed that the k_3 is much smaller than k_1 and that a relatively high steady concentration of structure F is formed. Therefore, this indicates that the rate of the Reaction 3 in Scheme 3.4 would be a function of the H_2O concentration and diffusion (diffusion control of hydrolysis).

Therefore, it is believed that in both cases the structure F is formed quickly. However, in the NDB, the concentration of this compound remains stable over a certain time, as not enough moisture is present to carry on with the hydrolysis reaction further to the monophosphite-mono esterified phosphonate (Structure G).

In the powder blend the relatively large surface area for interaction of particles with moisture and the lack of diffusion barrier makes enough moisture available to carry on with the hydrolysis reaction to the structure G at any point in time.

It is also believed that due to the positive performance observed at low degrees of hydrolysis of the phosphite, k_4 and k_5 (Reaction 4 and 5, Scheme 3.4) are very low compared to k_1 and k_3. Therefore, at low degrees of hydrolysis the Reactions 4 and 5 (Scheme 3.4) would not play a significant role.

3.5.Stabilisation of High density poly(ethylene)

In this chapter the main effects and interactions of different additives used in polymer stabilisation (the influence of these additives upon the hydrolytic stability of the phosphite Alkanox P-24 was studied in previous chapters) was studied in Cr-catalysed HDPE. A full factorial experiment was carried out to study five factors, (in this case five polymer additives). Responses of interest were melt flow rate (MFR), yellowness index (YI) and long-term thermo-oxidative stability of the polymer. Due to the physical changes that can occur during the fabrication step, melt processing stability was an important factor to consider. Discoloration is usually associated with degradation processes due to processing, but this is not always the case, discoloration can be also due to the additives or interaction of additives in the stabilisation package. For each combination of the additives, the MFR, YI and long-term heat performance were measured.

3.5.1.Polymer and additives studied

Chromium catalysed HDPE and the different additives used for this study are described previously (section 2.1) in the experimental part.

It is well known that the main processing stabilisers are phenolic and phosphite antioxidants. Sterically hindered phenols are powerful stabilisers for the melt processing of polyolefins. The combination of a sterically hindered phenol and a phosphite is more effective in many cases. Suitable stabilisation of poly(ethylene) during processing is achieved by using appropriate combinations of phenol and phosphite antioxidants. Therefore, *phenolic antioxidant Anox 20* and *phosphite antioxidant Alkanox P-24* were chosen to study the effect of these antioxidants at different ratios in the melt stabilisation of HDPE.

Calcium stearate(CaSt) was chosen as lubricant additive. It is common to add a lubricant in conjunction with the phenolic and phosphites antioxidants in Cr-HPDE in order to ease processing. According to the literature[60] for Cr-catalysed HDPE the usual concentration of CaSt is 0.02-0.05 % and in this case the level of CaSt is 0-0.05 %.

Atmer 129 antistatic was chosen to study its influence during melt processing in terms of melt flow protection and colour development. Electrostatic charges are commonly generated by frictional contact between two materials with different susceptibilities to electron loss. The presence of charged polymer surfaces can have serious consequences during production, forming operations and service life. Problems caused by static electricity will be reduced or eliminated by using an antistatic agent[110]. In this case the level of Atmer 129 used was 0.1 %.

Palmarole, micronised sodium benzoate was chosen as the nucleating agent. Although HDPE has a high crystal growth rate and the polymer is very difficult to nucleate some moderately effective nucleating agents have been identified. Sodium benzoate was able to reduce almost fivefold the average spherulite size[71].

The polymer was initially dry blended with the additives and each dry blend was then extruded on a Betol® BTS 30 laboratory co-rotating twin-screw compounding extruder at a melt temperature of 230 °C and a screw rotation speed of 80 rpm.

Interactions between additives are likely to occur due to the diversity of additives involved on a stabiliser package. These interactions may be synergistic or antagonistic.

3.5.2. Design Expert. Two level factorial design

Factorial designs are widely used in experiments involving several factors where it is necessary to study the combined effect of the factors on a response. There are several special cases of the general factorial design that are important because they are widely used in research work and also because they form the basis of other designs of considerable practical value. The most important of these special cases is that of k factors (such as temperature, pressure, time, machines, variables that have impact on the response studied) each at only two levels. These levels can be quantitative, such as two levels of temperature, pressure, or time; or can be qualitative, such as two machines, etc. A complete replicate of such a design requires 2^k observations and is called a 2^k factorial design.

In this experiment, a 2^5 factorial design was carried out. Five factors were studied each at two levels. In Table 3.8 the chosen factors and the two levels for each factor are represented.

Table 3.8. Factors and its concentration levels studied.

Factor	Level (%)	
	Low	High
Alkanox P-24	0	0.1
Anox 20	0	0.05
CaSt	0	0.05
Atmer 129	0	0.1
Palmarole	0	0.1

The effect of a factor is defined to be the change in response produced by a change in the level of the factor. This is frequently called a main effect because it refers to the primary factors of interest in the experiment. If the design factors are quantitative then a regression model representation of a two-factor factorial experiment could be written as (Equation 3.1):

Equation 3.1. Equation of main effects and interaction terms of a two-factor factorial.

$$y = \beta_0 + \beta_1\chi_1 + \beta_2\chi_2 + \beta_{12}\chi_1\chi_2 + \in$$

Where y is the response, the β's are parameters whose values are to be determined, x_1 is a variable that represents one of the factors, x_2 is a variable that represents the other factor, and ε is a random error term. The variables x_1 and x_2 are defined on a coded scale from –1 to +1 (the low and high levels of the factors) and x_1x_2 represents the interaction between x_1 and x_2.

It is important to take into consideration that a potential concern in the use of two-level factorial designs is the assumption of linearity in the factor effects. It has been noted that if interaction terms are added to a main effects or first-order model (Equation 3.2), then there is a model capable of representing some curvature in the response function.

Equation 3.2. Equation for a first-order model.

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j\chi_j + \sum\sum_{i<j} \beta_{ij}\chi_i\chi_j + \in$$

There are going to be situations where the curvature in the response function is not adequately modelled by the equation above.

In such cases a logical model to consider is the following one.

Equation 3.3. Equation of a second-order response surface model.

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j \chi_j + \sum_{i<j}\sum \beta_{ij} \chi_i \chi_j + \sum_{j=1}^{k} \beta_{jj} \chi_j^2 + \in$$

where the β_{jj} represent pure second-order or quadratic effects. Equation 3.3 is called a second-order response surface model.

In running a two-level factorial experiment, it is usually anticipated fitting the first order model in the first equation, but it is important to be aware of the possibility that the second order model in Equation 3.3 is really more appropriate. There is a method of replicating certain points in a 2^k factorial that will provide protection against curvature from second-order effects as well as allow an independent estimate of error to be obtained. The method consists of adding centre points to the 2^k designs[111]. Data from centre points provides; estimates of pure error and estimates of curvature[112].

Four centre points were added in the experiment carried out to study the influence of different additives (Alkanox P-24, Anox 20, CaSt, Atmer 129, Palmarole) on the thermo-oxidaive stabilisation of Cr-catalysed HDPE.

There are many situations in which it is impossible to perform all of the runs in a 2^k factorial experiment under homogeneous conditions. The design technique used in these situations is blocking. If it is not possible to carry out all the runs in one day, it is very useful to create some blocking in the design because any day-to-day variation will be removed by blocking. The different studied formulations divided into four blocks are shown in Tables 3.9, 3.10, 3.11, 3.12.

In the experiment carried out, four blocks have been created.

Table 3.9. Different formulations studied in the first block.

RUN	Block	Alkanox P-24(%)	Anox 20(%)	CaSt(%)	Atmer 129(%)	Palmarole
1	Block 1	0.05	0	0.05	0	0.1
2	Block 1	0.025	0.05	0.025	0.05	0.05
3	Block 1	0.05	0	0.05	0.1	0
4	Block 1	0	0.1	0.05	0	0
5	Block 1	0	0	0	0.1	0.1
6	Block 1	0.05	0.1	0	0	0.1
7	Block 1	0	0.1	0.05	0.1	0.1
8	Block 1	0.05	0.1	0	0.1	0
9	Block 1	0	0	0	0	0

Table 3.10. Different formulations studied in the second block.

RUN	Block	Alkanox P-24(%)	Anox 20(%)	CaSt(%)	Atmer 129(%)	Palmarole
10	Block 2	0	0.1	0	0	0
11	Block 2	0.05	0.1	0.05	0.1	0
12	Block 2	0.05	0	0	0.1	0
13	Block 2	0.025	0.05	0.025	0.05	0.05
14	Block 2	0.05	0	0	0	0.1
15	Block 2	0	0	0.05	0	0
16	Block 2	0	0	0.05	0.1	0.1
17	Block 2	0	0.1	0	0.1	0.1
18	Block 2	0.05	0.1	0.05	0	0.1

Table 3.11. Different formulations studied in the third block.

RUN	Block	Alkanox P-24(%)	Anox 20(%)	CaSt(%)	Atmer 129(%)	Palmarole
19	Block 3	0	0	0	0	0.1
20	Block 3	0	0.1	0.05	0	0.1
21	Block 3	0.05	0	0.05	0	0
22	Block 3	0.05	0.1	0	0.1	0.1
23	Block 3	0.025	0.05	0.025	0.05	0.05
24	Block 3	0.05	0	0.05	0.1	0.1
25	Block 3	0.05	0.1	0	0	0
26	Block 3	0	0	0	0.1	0
27	Block 3	0	0.1	0.05	0.1	0

Table 3.12. Different formulations studied for the fourth block.

RUN	Block	Alkanox P-24(%)	Anox 20(%)	CaSt(%)	Atmer 129(%)	Palmarole
28	Block 4	0	0	0.05	0.1	0
29	Block 4	0	0.1	0	0	0.1
30	Block 4	0	0	0.05	0	0.1
31	Block 4	0	0.1	0	0.1	0
32	Block 4	0.05	0.1	0.05	0.1	0.1
33	Block 4	0.025	0.05	0.025	0.05	0.05
34	Block 4	0.05	0	0	0.1	0.1
35	Block 4	0.05	0.1	0.05	0	0
36	Block 4	0.05	0	0	0	0

3.5.3. Results and discussion

In the current section the results that were obtained for the experiment are presented and discussed. Table 3.13 shows the design summary for the MFR and YI response.

Table 3.13. Design summary for melt flow rate and yellowness index

	Unit	Model	R^2
MFR-Pass 1	dg/min	Linear	0.95
MFR-Pass 3	dg/min	2FI	0.96
Colour-Pass 1	YI	2FI	0.86
Colour-Pass 3	YI	Linear	0.85

3.5.3.1. Standard deviation on melt flow data

The centerpoints were prepared four times. MFR was measured after the first and the third pass.

The centerpoints contain:

0.025% Anox 20
0.005% Alkanox P-24
0.025% CaSt
0.05% Atmer 129
0.05% Palmarole

The mean, standard deviation and RSD of the four centre points are presented in Table 3.14. These results show that MFR measurements of the centre point replicates are comparable within the normal error range of ±5%. For the analysis of the design results, a relative error of 5% on MFR measurements was therefore considered as standard error.

Table 3.14. Standard deviation on melt flow data.

	Mean (dg/min)	Stdev	RSD (%)
MFR-Pass 1	9.0	0.44	4.6
MFR-Pass 3	5.8	0.3	5.5

3.5.3.2. Measured values versus predicted values for melt flow rate data from the Experimental Design Models.

It is important to check if the predicted values from the software are in concordance with the actual values measured experimentally.

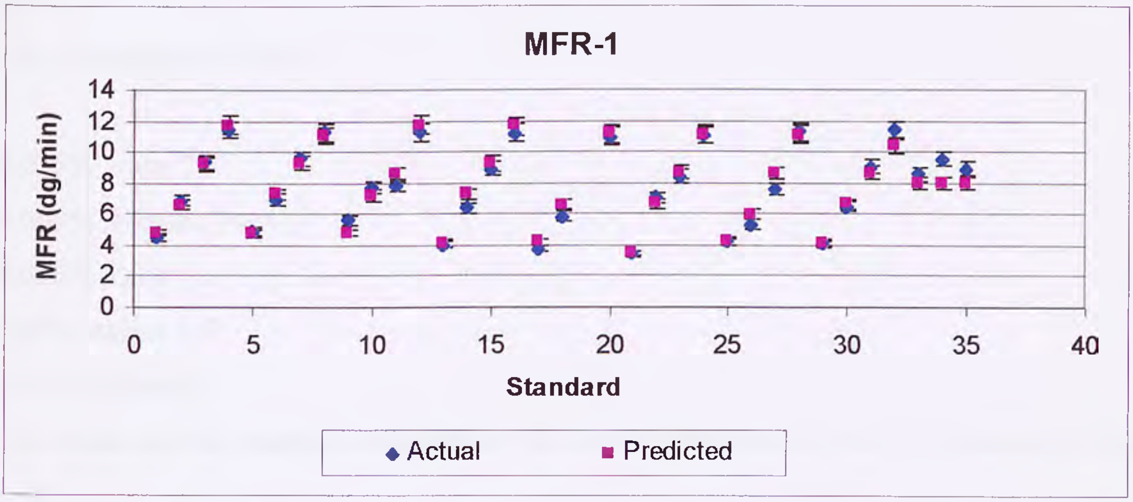


Figure 3.85. Measured versus predicted for melt flow rate for the first pass.

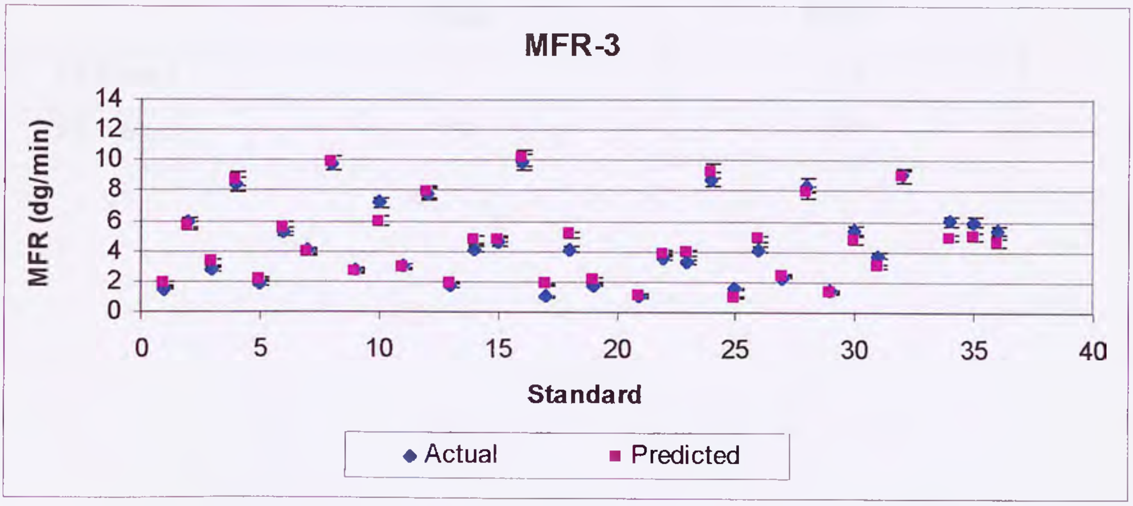


Figure 3.86. Measured versus predicted for melt flow rate for the third pass.

From Figures 3.85 and 3.86, it may be concluded that the MFR values for the actual and predicted for first and third extrusion are similar. There is a good fit to the model, which confirms what R-square values shown. There are some points where the actual and the predicted values are not within the 5% error. If these points are relevant when making final conclusions these differences should be taken into consideration in order not to reach wrong conclusions.

3.5.3.3. Standard deviation on colour measurements

The centrepoints were prepared four times. YI was measured after the first and the third pass.

The centrepoints contain:

0.025% Anox 20
0.005% Alkanox P-24
0.025% CaSt
0.05% Atmer 129
0.05% Palmarole

The mean and the standard deviation of the four centrepoints for the YI is shown in Table 3.15.

Table 3.15. Standard deviation on colour.

	Mean	Stdev
YI-Pass 1	2	0.4
YI-Pass 3	7.1	0.5

Measured values versus predicted values for colour data.

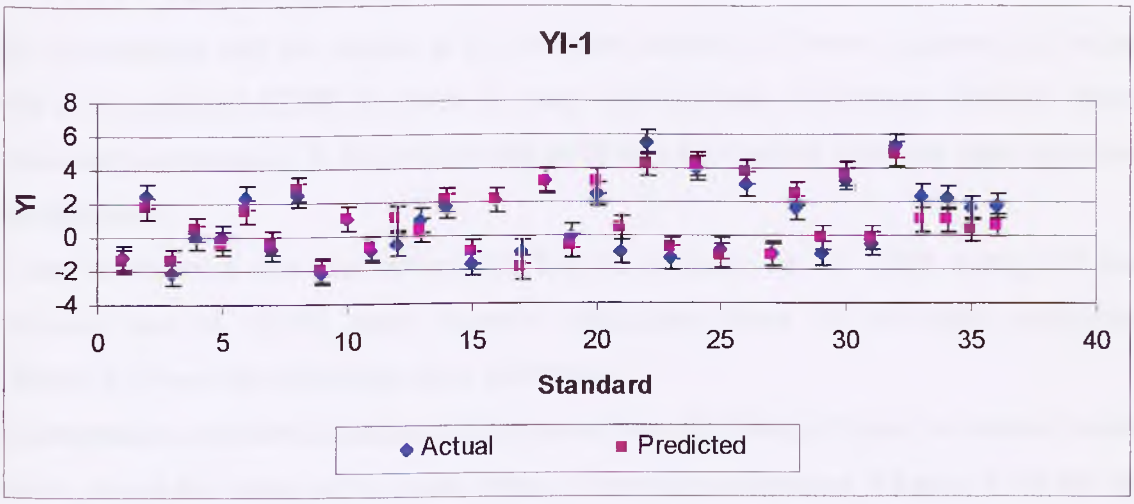


Figure 3.87. Measured versus predicted values for YI-Pass 1.

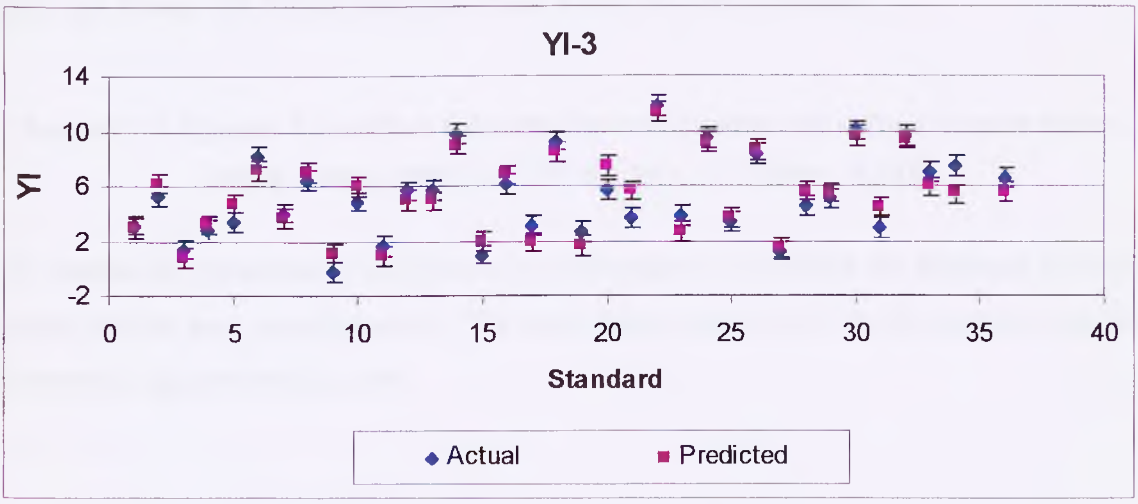


Figure 3.88. Measured versus predicted values for YI-Pass 3.

From Figure 3.87 and 3.88 it can be concluded that the yellowness index values for the actual and predicted for first and third extrusion are similar. There is a good fit of the model, which confirms what R-square values shows. There are some points where the actual and the predicted values are not within the ±0.7 units error. If these points are relevant when making final conclusions these differences should be taken into consideration not to reach wrong conclusions.

3.5.3.5. Melt Flow Data

3.5.3.5.1. Melt flow rate-Pass 1

The formulations that are shown in the previous section (5.2) were prepared and mixed with a Cr-catalysed HDPE in order to study the influence of different additives during processing performance. In this section the MFR data for the first extrusion pass are shown and discussed.

It can be observed that the factors that had an influence on the MFR during the first extrusion pass of HDPE were: phenolic antioxidant Anox 20, phosphite antioxidant Alkanox P-24 and the nucleating agent Palmarole.

The regression equation (Equation 3.4) obtained from the Design Expert, in terms of coded factors shows the nature of the main effects. Phosphite antioxidant Alkanox P-24 had the most pronounced effect out of the three mentioned before. It is also seen that the nucleating agent Palmarole has a negative effect during the first extrusion of the polymer.

CaSt and Atmer 129 did not have any effect during the first extrusion.

Equation 3.4. Equation for melt flow index after the first extrusion pass in terms of coded factors.

$$\mathbf{MFR\ (10kg,\ 190^{\circ}C) = 7.77 + 1.23A + 2.23B + -\ 0.31E}$$

The results are presented in the form of a perturbation plot, where the influence of all the factors can be seen simultaneously. The main factors highlighted in the equation are also observed in the perturbation plot.

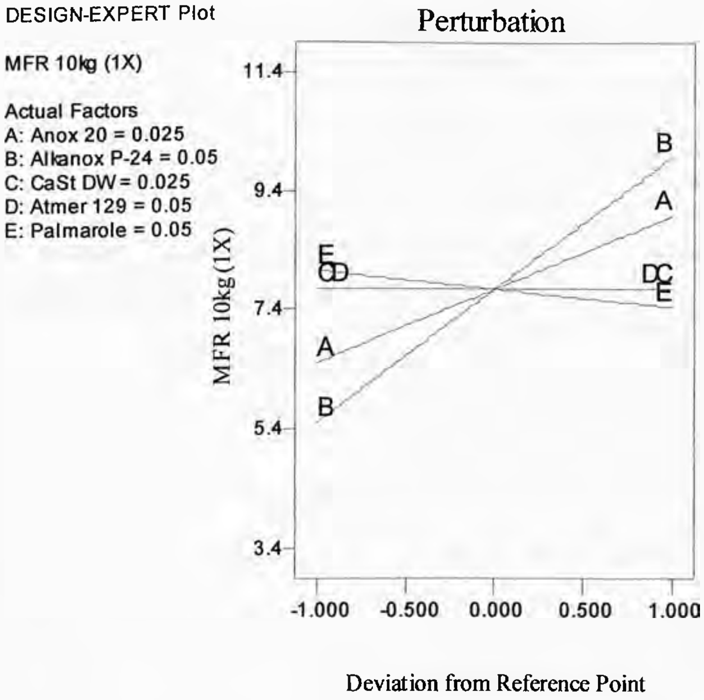


Figure 3.89. Perturbation plot for the influence of the individual factors on themelt flow index after the first extrusion pass; A = Anox 20; B = Alkanox P-24; C = CaSt; D = Atmer 129; E = Palmarole. Reference point: Anox 20 = 0.025, Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05.

Figure 3.89 shows how the MFR values change when one single factor is varied and the rest are kept constant at the reference point. It is clearly seen that the phosphite Alkanox P-24 (factor B) is the most influential factor after the first extrusion pass. Increasing the level of the phosphite Alkanox P-24 reduces the degradation of the polymer. The phenolic antioxidant also plays a significant role in the melt stabilisation of the polymer. However, the nucleating agent Palmarole contributed negatively to the melt stabilisation of the polymer.

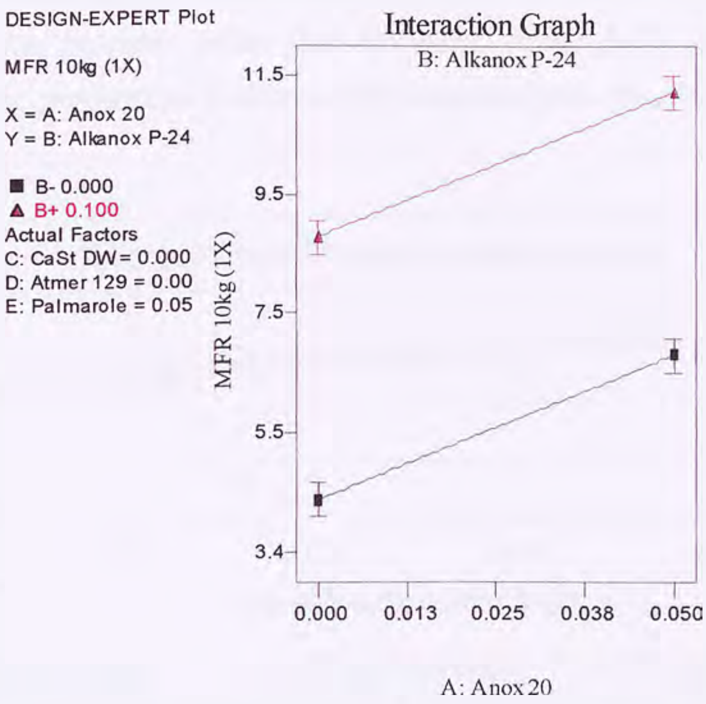


Figure 3.90. MFR-Pass 1. Interaction graph for Anox 20 and Alkanox P-24.The rest of the factors were kept constant. CaSt = 0.0, Atmer 129 = 0.0, Palmarole = 0.05

It is known from the literature that Alkanox P-24 is a very good processing stabiliser[113]. The main contribution of the phosphite to the stabilisation of the polymer melt is its action as a hydroperoxide decomposer[115].

Different polymers, such as poly(propylene), HDPE (prepared with different kind of catalyst systems), LLDPE, etc does not behave in the same way under processing conditions. During processing, due to degradation of the polymer, poly(propylene) undergoes chain scission, where the molar mass of the polymer decreases. On the other hand, during degradation of poly(ethylene), chain scission, chain crosslinking and branching phenomena takes place. HDPE can undergo crosslinking as well as chain scission during processing and significant changes in the molar mass distribution can result.

In Figure 3.90, it can be observed that Alkanox P-24 (1000 ppm) in combination with Anox 20 has more pronounced effect and is able to stabilize the polymer better than the phenolic antioxidant Anox 20 alone during the first extrusion.

A higher MFR value and consequently less crosslinking is observed when the Alkanox P-24 is taken into consideration.

The effect of increasing the concentration of Anox 20 has a positive effect in the stabilisation of the polymer during first extrusion. Although in terms of melt flow protection a better performance is observed with combinations of Anox 20 and Alkanox P-24.

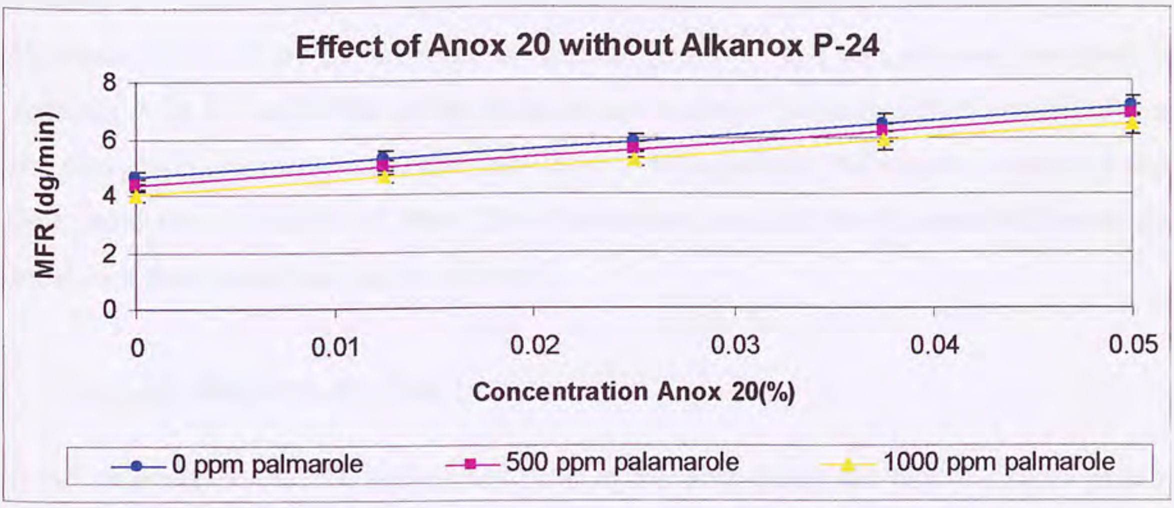


Figure 3.91. Effect of Anox 20 without Alkanox P-24 at different levels of Palmarole.

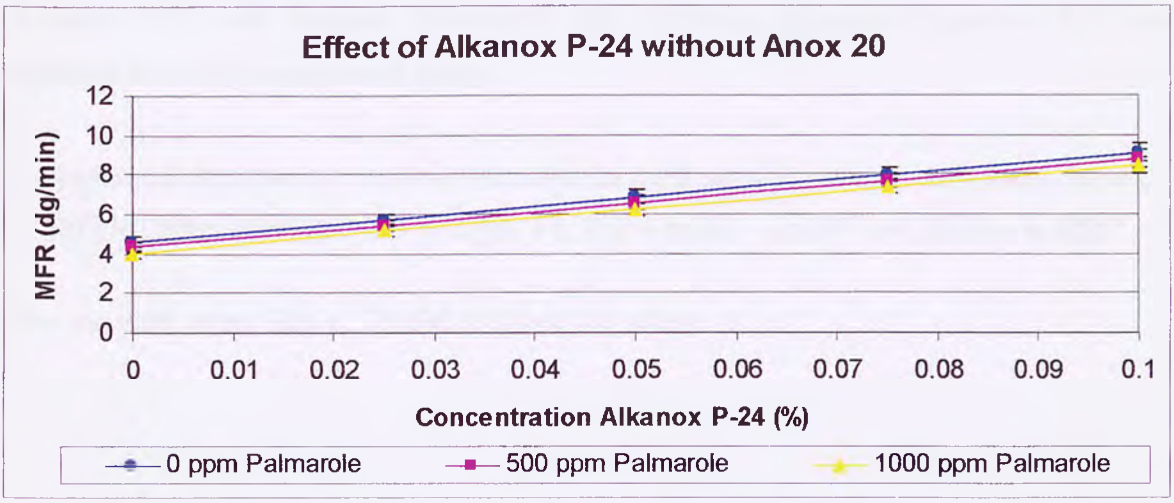


Figure 3.92. Effect of Alkanox P-24 without Anox 20 at different levels of Palmarole.

Observing the performance of Anox 20 alone it can be concluded that an increasing the levels of Anox 20 there is an improved melt flow protection (Figure 3.91). The same conclusion can be achieved observing the performance of Alkanox P-24 alone (Figure 3.92), where an increase in the concentration of the phosphite gives an improvement in terms of melt flow protection.

An increase in the level of Palmarole shows a decrease in the melt flow index values, although this is not a significant decrease. From previous graphs (Figure 3.91 and 3.92) a better performance in terms of melt flow protection with Alkanox P-24 is observed, because it is able to get a higher MFR value than the phenolic antioxidant Anox 20. However, the level of the stabiliser is another factor to take into account, the level of Alkanox P-24 is double that of the phenolic antioxidant. Comparing both antioxidants at the same level, it can be concluded that there is no significant difference in terms of melt flow protection. At 0.05% of Anox 20 in the polymer or 0.05% or Alkanox P-24 alone the same melt flow protection can be achieved.

3.5.3.5.2. Melt flow rate-Pass 3

It can be observed that the factors that have an influence during the third extrusion pass of HDPE are: phenolic antioxidant Anox 20, phosphite antioxidant Alkanox P-24, calcium stearate, the nucleating agent Palmarole and interactions are observed between Anox 20-Alkanox P-24 and Alkanox P-24-CaSt. The following equation (Equation 3.5) was obtained from the experimental design.

Equation 3.5. Equation for melt flow index after the third extrusion pass in terms of coded factors.

$$\mathbf{MFR\ (10kg,\ 190^{\circ}C) = 4.70 + 2.20A + 1.31B + 0.26C - 0.44E + 0.52AB + 0.48BC}$$

The antistatic agent Atmer 129 did not have any effect.

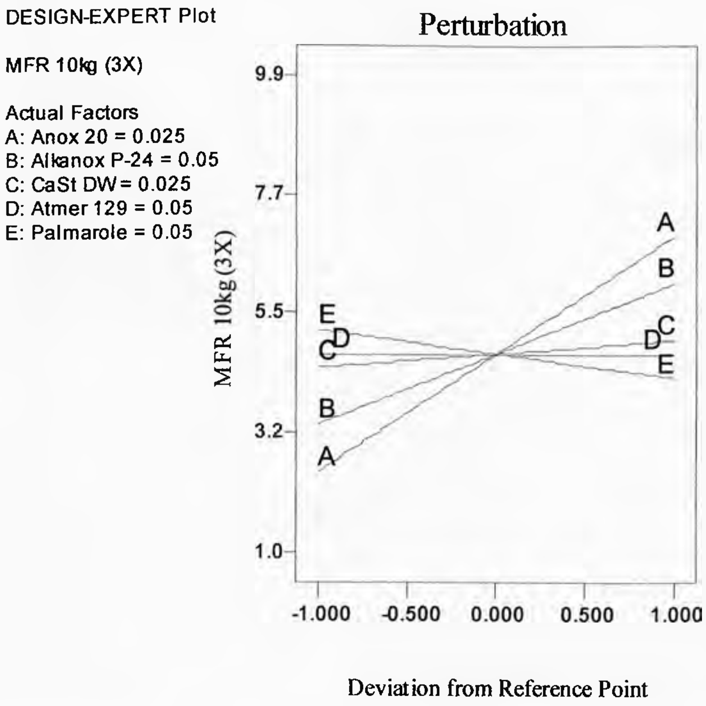


Figure 3.93. Perturbation plot for the influence of the individual factors on themelt flow rate after the third extruder pass; A = Anox 20; B = Alkanox P-24; C = CaSt; D = Atmer 129; E = Palmarole. Reference point: Anox 20 = 0.025, Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05.

The same conclusions were drawn from the perturbation graph (Figure 3.93) where the phenolic antioxidant Anox 20 has the more pronounced influence on the MFR value after the third extrusion pass, followed by the phosphite antioxidant Alkanox P-24. CaSt also has a positive influence on the melt flow protection under processing conditions. The nucleating agent Palmarole has a negative effect.

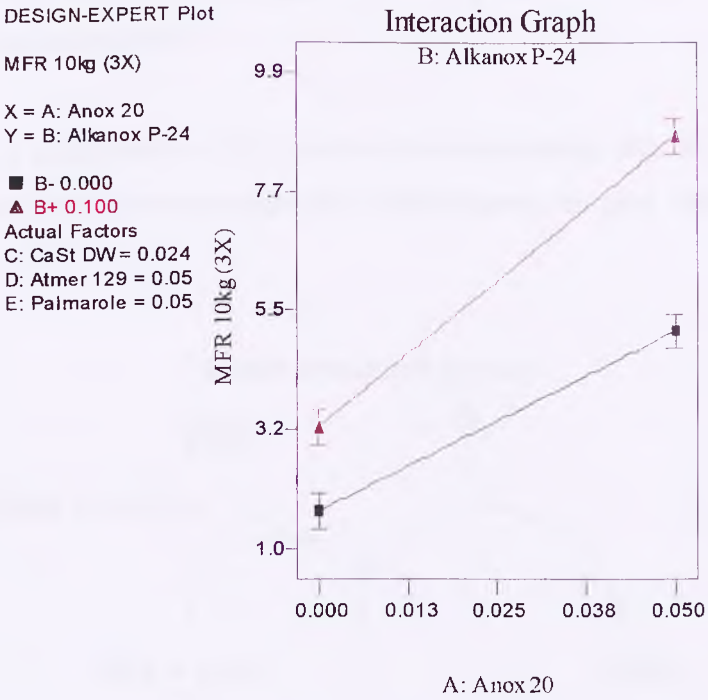


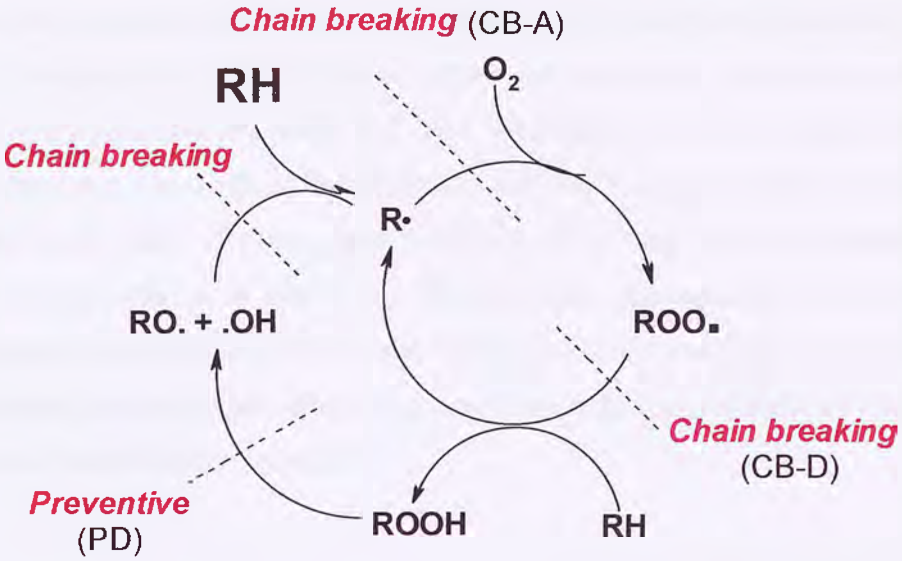
Figure 3.94. MFR-Pass 3, Interaction graph for Anox 20 and Alkanox P-24.The rest of the factors were kept constant. CaSt = 0.024, Atmer 129 = 0.0, Palmarole = 0.05

In the interaction graph (Figure 3.94) it can be observed that a better performance is obtained with a combination of Alkanox P-24 (1000 ppm) and Anox 20 than with the Anox 20 alone. The synergistic combination of phenol/phosphite antioxidants could be observed. An increase in the level of phenolic antioxidant Anox 20 gave a better performance in terms of melt flow protection and the addition of 1000 ppm Alkanox P-24 improves the melt flow protection. In the literature, processing stability strongly improves with increasing stabiliser content[114]. It is well known that the combination of phenolic antioxidants and phosphite antioxidants exhibit synergistic effects in polyolefin stabilisation [15,21,25,57,65,66,115,116].

During extrusion the highly reactive free radicals that are formed react with oxygen to form peroxyl radicals, which can remove a hydrogen atom from another carbon on the polymer chain to form a hydroperoxide and another macroalkyl radical. The hydroperoxide groups once formed can undergo decomposition to give peroxyl and hydroxyl radicals.

All phosphites are mainly considered as preventive antioxidants, decomposing hydroperoxides in a non-radical manner. However, depending on their structure, the nature of polymer to be stabilized and the aging conditions, phosphites may act both as preventive and chain breaking antioxidants[117].

This results in a suppression of the radical chain-branching step in the auto-oxidation mechanism where the hydroperoxides are decomposed to give alkoxyl and hydroxyl radicals.



Scheme 3.5. Oxidative degradation processes and antioxidant mechanism.

However, the reactions where hydroperoxides decompose to give alkoxy and hydroxyl radicals have no influence on the rate of auto-oxidation at the low temperatures at which hydroperoxides do not homolytically decompose[27]. On the other hand, at high temperatures, because of the rapid decomposition of hydroperoxides, their ionic decomposition by phosphites is too slow to efficiently prevent this reaction[27,56]. During auto-oxidations at higher temperatures, homolytic decomposition of the hydroperoxides formed takes place, given rise to reactive radicals that cause auto-initiation and chain branching of the oxidation reaction.

Under such conditions, the hydroperoxide decomposing ability of phosphites becomes effective in suppressing chain branching and so inhibiting oxidation. For aliphatic phosphites this is the only way of acting. This is responsible for the relatively low efficiency of these phosphites and for their synergistic action in combination with phenols[24].

Aromatic phosphites, may act by chain breaking in addition to hydroperoxide decomposition at higher temperatures. They could react with peroxyl and alkoxyl radicals, releasing aryloxyl radicals[24]. In low temperature oxidations they are poorer primary antioxidants than hindered phenols because of a lower reactivity towards peroxyl radicals[118]. Phenolic antioxidants, scavenge the peroxyl radicals to yield phenoxy radicals and hydroperoxides[119].

According to the literature,[69] the synergism between a phenol and phosphite is only possible when the hydroperoxide decomposing action of the phosphite affects the rate of oxidation, at temperatures where hydroperoxides homolytically decompose. At low temperatures, hydroperoxides are stable and have no influence on the oxidation process. An additive effect was found when the experiment was carried out in cumene solution at 65 °C for the combination of phenol and phosphite (BHT and tri-n butylphosphite)[69]. However, in poly(propylene), at 140 °C the hydroperoxide decomposition by phosphites made a pronounced contribution to the overall stabilisation and synergism was observed[69]. Phosphites enhance the antioxidant effect of phenols and reduce discoloration of polymers caused by phenol transformation products[120].

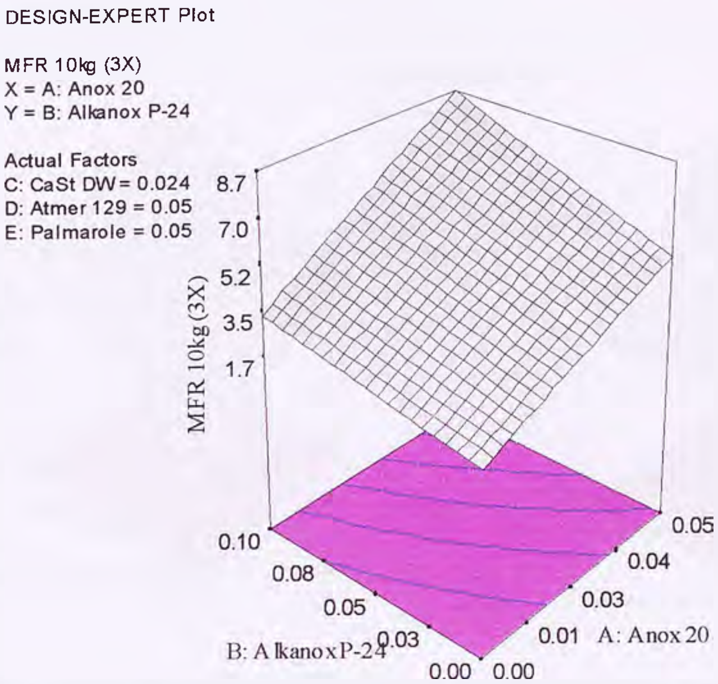


Figure 3.95. 3D surface plot, MFI-Pass 3, Interaction Alkanox P-24-Anox 20. The rest of the factors are kept constant; CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05.

The same result it is observed in the 3D surface plot, where the simultaneous influence of phenol and phosphite antioxidant concentrations on MFR after the third extruder pass is presented (Figure 3.95). The best melt flow protection is achieved with the maximum levels of the phosphite and the phenolic antioxidant. Phenolic antioxidant Anox 20 contributes to HDPE processing stabilization, where an increase in the concentration of the phenolic antioxidant shows an increase MFR, and avoiding crosslinking. It is very important to take into consideration that the performance could change from one additive package and to a different polymer.

The combination of a sterically hindered phenol and a phosphite is more effective than a phenol alone[15].

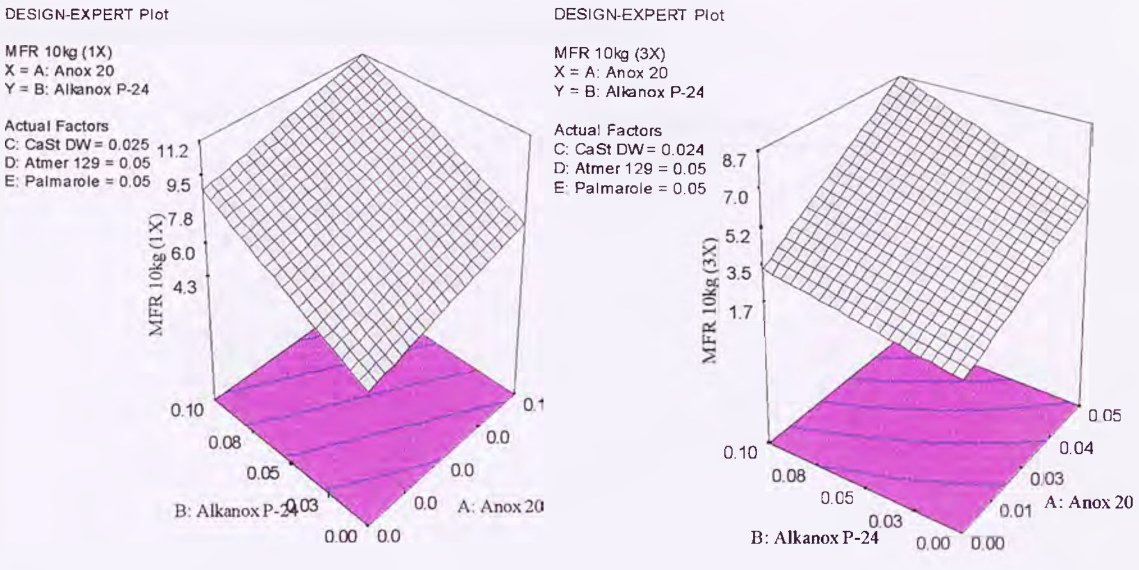


Figure 3.96. 3D surface plot for the first and third extrusion passes.

It is observed from the different plots (Figure 3.96) and the equations that the effect of the phosphite Alkanox P-24 on the stabilisation of the Cr-catalysed HDPE is more pronounced during the first extrusion than during the third extrusion. On the other hand, the phenolic antioxidant Anox 20 shows a greater effect during the third extrusion. It seems that during the first extrusion the phosphite Alkanox P-24 plays a major role. According to the literature, when Irgafos 168 is used in chromium-catalysed HDPE, a significant amount of the phosphite is consumed in the initial compounding step[121].

Although Irgafos 168 is a different phosphite from Alkanox P-24 it is possible that the same behaviour could be observed for Alkanox P-24. Initially the Alkanox P-24 would be consumed, however during the third extrusion, due to the consumption of the Alkanox P-24, the phenolic antioxidant would show more significant.

Another factor that has an impact on the third extrusion pass is the acid scavenger CaSt. CaSt-Alkanox P-24 was another interaction observed.

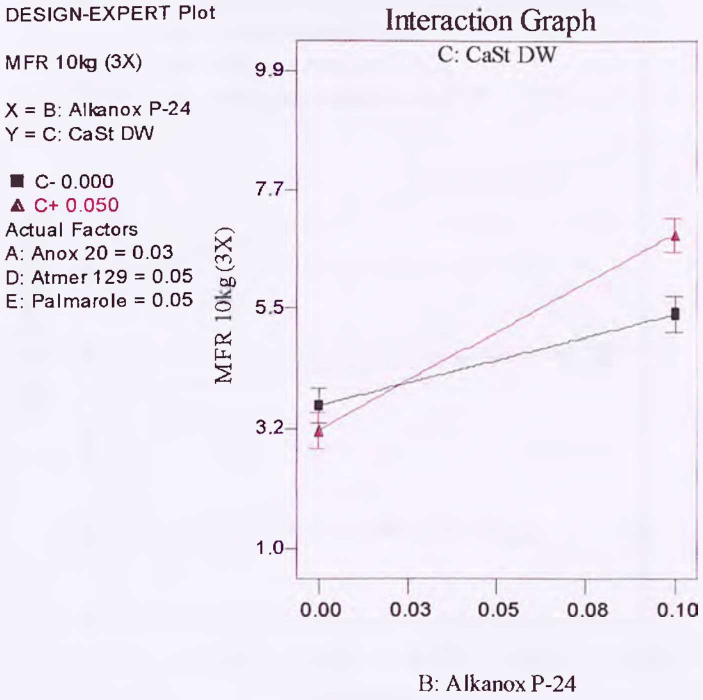
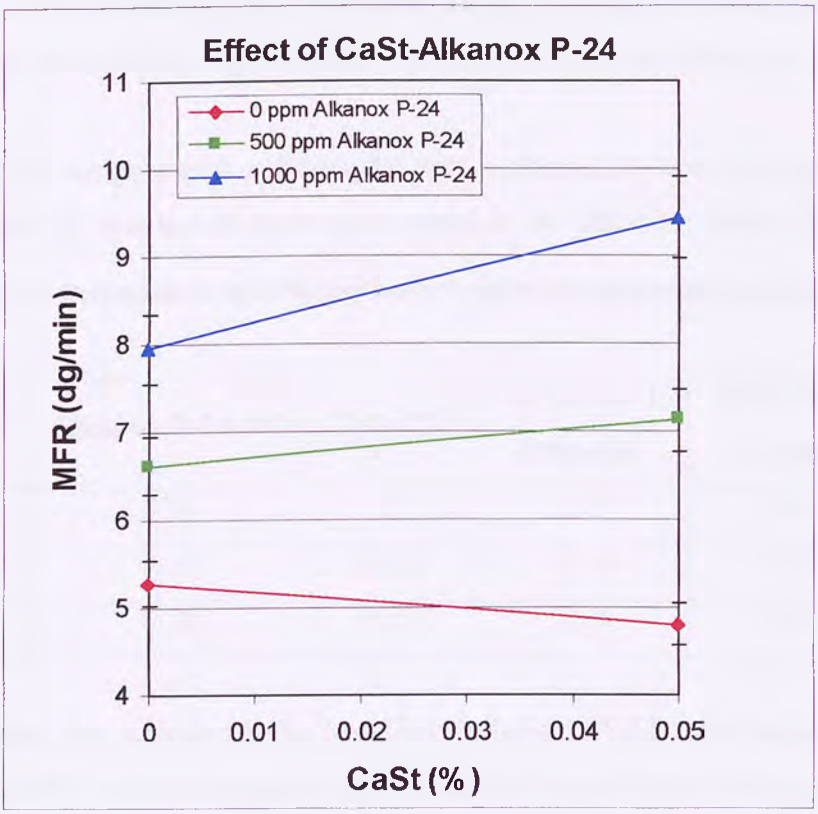


Figure 3.97. Interaction graph Alkanox P-24-CaSt, Experimental Design.

According to the interaction graph (Figure 3.97) the combination of Alkanox P-24 with CaSt gave a better performance in terms of melt flow protection than the Alkanox P-24 alone. It can be concluded that the addition of the CaSt is beneficial in terms of melt flow protection. Although it is important to take into consideration that the CaSt could act as a lubricant during melt blending and therefore reduce the level of mechanical chain scission.

-Interaction graph CaSt-Alkanox P-24



In the above graph the interaction CaSt-Alkanox P-24 is studied. Other stabilisers are kept constant at the following levels, Anox 20 = 0.05%, Atmer 129 = 0.05% and Palmarole = 0.05%. Increasing the level of the phosphite Alkanox P-24, improves the performance of the polymer in terms of melt flow protection. It can be observed that CaSt alone (without the phosphite antioxidant) has a negative effect on the stabilisation of the polymer.

An increase in the CaSt content gives a lower MFR value than the sample without any CaSt when the level of Alkanox P-24 = 0. It is important to take into consideration that the calcium stearate is known to be a lubricant for polymers[60]. It could be possible that the increase in the MFR when the concentration of acid scavenger is increased could be due to the lubricity of the CaSt.

3.5.3.5.3. Conclusions

It can be concluded that the main factors that had influence on the MFR were the phenolic antioxidant Anox 20 and the phosphite Alkanox P-24. Alkanox P-24 showed a significant stabilisation effect during the first extruder pass, whereas Anox 20 showed greater performance during the third extrusion. CaSt had a positive impact during the third extruder pass. The nucleating agent Palmarole showed a negative effect under processing conditions and the antistatic agent Atmer 129 did not have any effect on the processing stability.

According to the design expert software the best performance, where the maximum MFR was obtained for the first and third extrusion would be the following blends (Table3.16):

Table 3.16. Formulations and different concentrations giving maximum performance.

Anox 20 (%)	Alkanox P-24 (%)	CaSt (%)	MFI-Pass-1 (dg/min)	MFI-Pass 3 (dg/min)
0.050	0.10	0	11.5	8.43
0.050	0.10	0.025	11.5	9.13
0.05	0.10	0.05	11.5	9.90

Nucleating agent and antistatic agent were not included in Table 3.16 because the former had a negative effect on the processing stability and the latter did not show any effect.

3.5.3.6. Colour development data

Under processing conditions and when the polymer is stabilized with different additives, discolouration of the polymer occurs. Several sources of colour formation have been identified; catalyst residues, differences in colour formation characteristics during polymer processing are observed due to differences in both the concentration and reactivity of the various catalyst residues. Furthermore, the oxidation products of phenolic antioxidant are generally coloured quinoid compounds that impart colour to the polymer.

In this chapter the influence of the studied additives on the colour development during processing of the Cr-catalysed HDPE will be studied.

3.5.3.6.1. Yellowness index-Pass 1

It was observed that the factors that had an influence on the colour development during the first extrusion pass of HDPE were phenolic antioxidant Anox 20, CaSt and the nucleating agent Palmarole. An interaction between the phenolic antioxidant and the nucleating agent is observed as well.

The following equation (Equation 3.6) is obtained from the Design Expert software, which shows that the phenolic antioxidant has the most pronounced effect on colour development out of the three mentioned before.

Equation 3.6. Equation for yellowness index after the first pass; A = Anox 20, C = CaSt, E = Palmarole

$$\mathbf{YI\ (Pass\ 1) = 0.95 + 1.71A + 0.54C + 0.56E + 0.48AE}$$

In this case, the experimental data for yellowness index obtained after the first extrusion pass can be fitted well by a reduced two-factor interaction model. A factorial model is composed of a list of coefficients multiplied by associated factor levels. Where, A = Anox 20; C = CaSt; E = Palmarole.

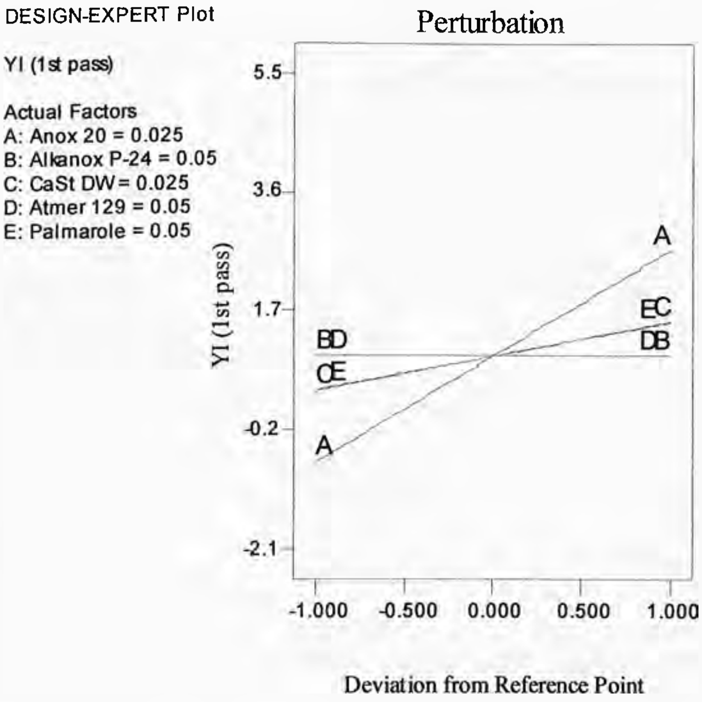


Figure 3.98. Perturbation plot for the influence of the individual factors on the yellowness index after the first extrusion pass; A = Anox 20; B = Alkanox P-24; C = CaSt; D = Atmer 129; E = Palmarole. Reference point: Anox 20 = 0.025, Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05.

The results from the Design Expert are presented in the form of a perturbation plot (Figure 3.98), which shows the influence of all the factors simultaneously.

As was observed in the equation of the yellowness index (Pass-1) the phenolic antioxidant Anox 20 was the additive that had a more pronounced negative influence on the colour development of the Cr-catalysed HPDE polymer under the given conditions. Although less pronounced, the nucleating agent and the CaSt had a negative influence on colour development after the first extrusion pass.

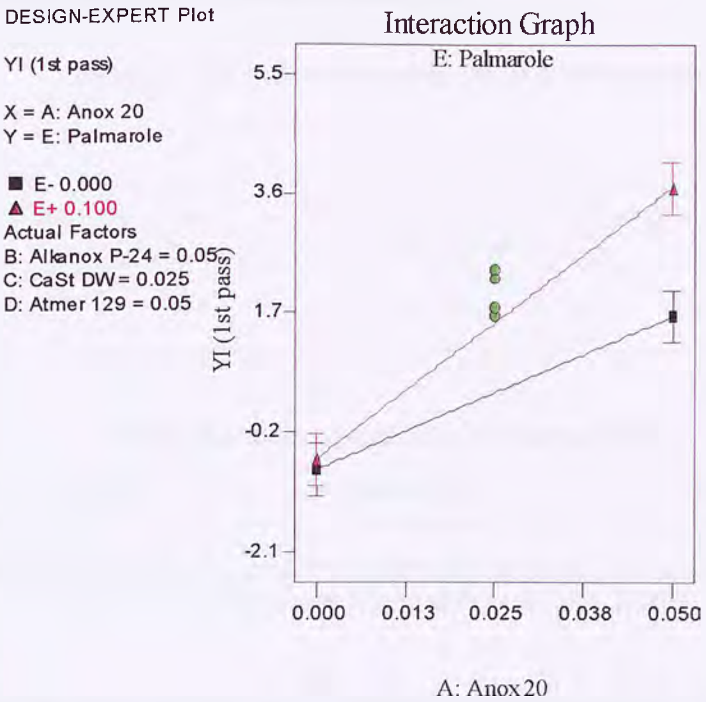


Figure 3.99. Interaction graph Anox 20-Palmarole; Constant concentration; Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05.

It is seen from Figure 3.99 that an increase in the concentration of Anox 20 imparts more colour to the polymer and the same effect is observed when increasing the nucleating agent Palmarole. When the level of Anox 20 is zero the yellowness index value does not differ from the one obtained with 0.01 % nucleating agent Palmarole. When the concentration of the phenolic antioxidant is increased the interaction between the two antioxidants is more perceptible.

Another factor imparting colour is the CaSt. Therefore, in order to analyse the whole effect, the influence of CaSt in the interaction between the phenolic antioxidant Anox 20 and the nucleating agent Palmarole will be discussed.

-Effect of CaSt in the interaction Anox 20-Palmarole

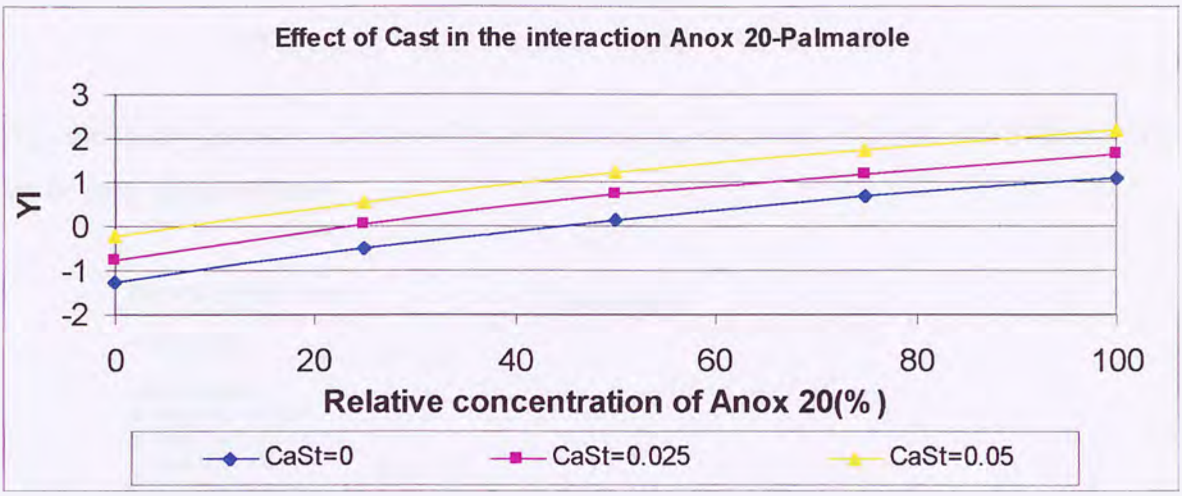


Figure 3.100. Yellowness index-Pass 1 versus the relative concentration of Anox 20 at total load level of Anox 20 + Palmarole of 0.1 % at different levels of CaSt

In order to study the effect of CaSt on the interaction between Anox 20 and Palmarole, the total load level of Anox 20 + Palmarole was 0.1%. It is observed (Figure 3.100) that an increase in the concentration of Anox 20 imparts more colour to the polymer and the phenolic antioxidant has a more pronounced impact than the nucleating agent. On the other hand, the CaSt had a negative impact in terms of yellowness index. An increase on the concentration of the CaSt showed a higher yellowness index, which means more colour development in the polymer.

3.5.3.6.2. Yellowness index-Pass 3

The experimental data for yellowness index obtained after the third extruder pass can be fitted well by a linear model (Equation 3.7). The factors that have influence on the yellowness index after the third pass were: the phenolic antioxidant Anox 20, phosphite antioxidant Alkanox P-24, CaSt and the nucleating agent Palmarole.

Equation 3.7. Equation for yellowness index after the third pass; A = Anox 20, B = Alkanox P-24, C = CaSt, E = Palmarole

$$YI\ (Pass\ 3) = 5.29 + 2.26A - 0.80B + 1.19C + 0.79E$$

The results are presented in form of perturbation plot, where the influence of all the factors can be seen simultaneously.

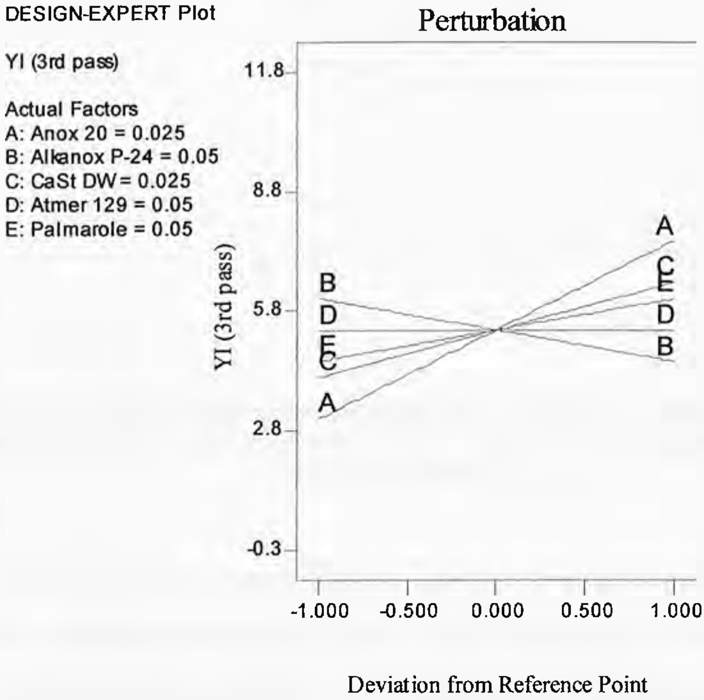


Figure 3.101. Perturbation plot for the influence of the individual factors on the yellowness index after the third extrusion pass; A = Anox 20; B = Alkanox P-24; C = CaSt; D = Atmer 129; E = Palmarole. Reference Point: Anox 20 = 0.025, Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05

The situation has changed after the third extruder pass relative to the first pass. The factor that had a more pronounced influence on the yellowness index, the phenolic antioxidant, was observed for the first extrusion pass. CaSt and nucleating agent Palmarole had a negative effect in terms of colour development after the third extrusion pass. However, the phosphite Alkanox P-24 had a positive effect. Phosphites are known to retard the discoloration of HDPE[113].

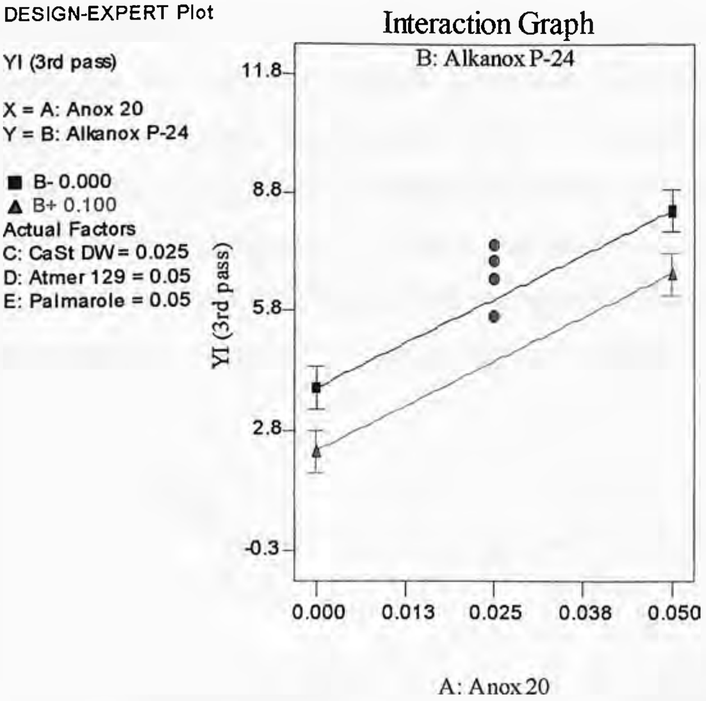


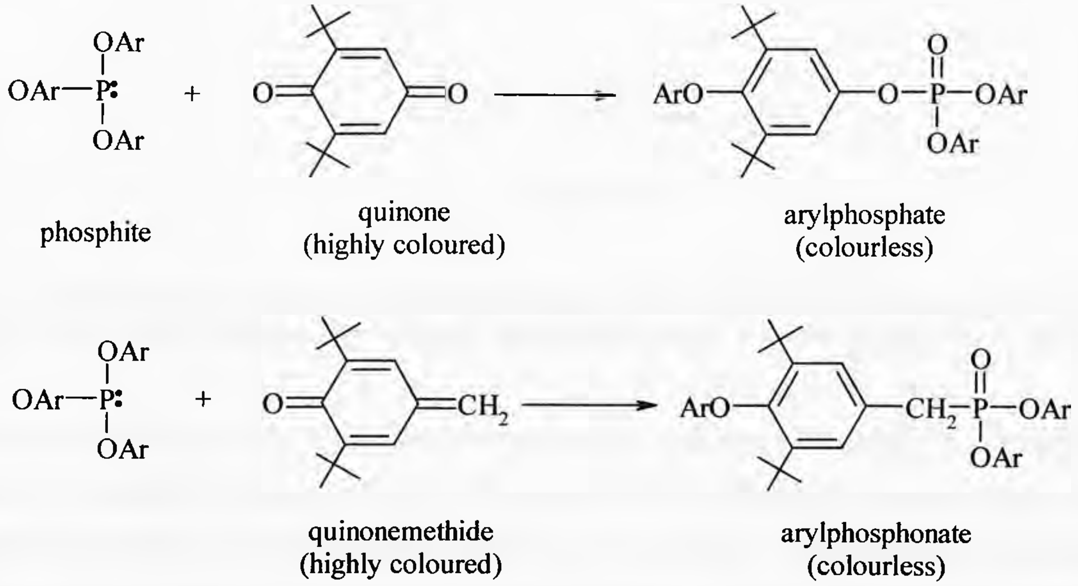
Figure 3.102. Interaction graph where the influence of Alkanox P-24 is observed. Constant factors; CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05. Two levels of the phosphite are shown; Alkanox P-24 = 0 and Alkanox P-24 = 0.1.

The first observation to be made (Figure 3.102) is that an increase in the concentration of the phenolic antioxidant Anox 20 gave a higher yellowness index value, therefore more colour development in the polymer. It is widely known that the oxidation products of some phenols may cause discoloration of the polymer. The formation of chromophores is a direct consequence of the structure of the phenol involved.

Choosing a phenolic antioxidant with a specific structure and the use of suitable co-stabilisers can minimize the discoloration[15].

Phosphite stabilisers can be effective colour suppressors in the processing of HDPE containing phenolic antioxidants as primary stabilisers[47].

The chromophoric products of the oxidation of phenolic antioxidants, mainly quinonoid compounds play a significant role in the colour development in the stabilisation of polymers by phenols. The introduction of organic phosphites also leads to the elimination of colour from the polymer, which is associated with the conversion of the coloured quinonoid compounds into colour-less non-conjugated benzene structures. A remedy for many types of discoloration in polyolefins is often a suitable phosphite or phosphonite[15]. Phosphite stabilisers may also react with unsaturated atoms and thereby disrupt the polyene sequences in the backbone of oxidized PE to minimize discoloration[99,58].



Scheme 3.6. Reaction of an aromatic phosphite with quinone and quinonemethid, which are highly coloured compounds[58].

According to the literature, the discoloration of HDPE with phenolic antioxidants in chromium oxide catalysed polymers suggests that chromium phenolates may be formed[122].

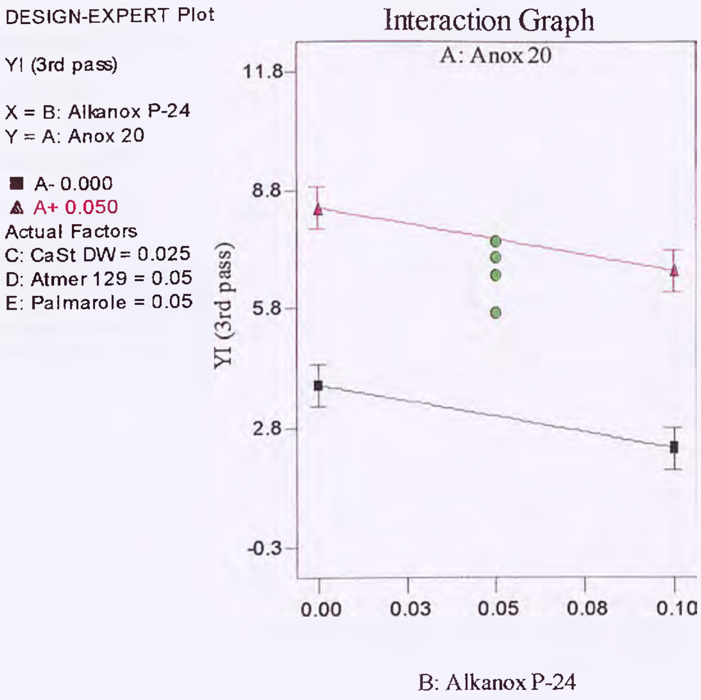


Figure 3.103. Interaction graph for Anox 20 and Alkanox P-24; Constant concentrations, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05. Phenolic antioxidant Anox 20 is shown at two levels, 0 and 0.05

In Figure 3.103 the effect of the phenolic antioxidant is shown when added in combination with the phosphite Alkanox P-24. As observed in the literature a positive effect was observed in terms of colour protection when the concentration of the phosphite antioxidant was increased under the studied processing conditions. In the absence of the phenolic antioxidant the colour development is reduced, which shows once again the negative contribution of the phenolic antioxidant to colour formation during processing.

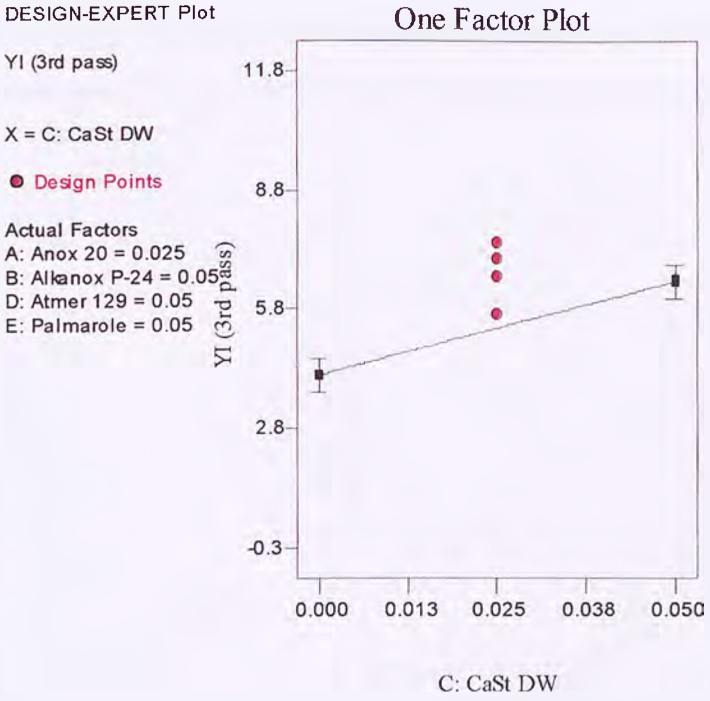


Figure 3.104. Effect of the acid scavenger CaSt in the yellowness index. Constant factors; Anox 20 = 0.025, Alkanox P-24 = 0.05, Atmer 129 = 0.05, Palmarole = 0.05

As observed in the equation and the perturbation plot for the third extrusion pass, the CaSt had a negative effect and imparts some colour to the polymer during processing.

The influence of various acid scavengers of discoloration of poly(ethylene) depends very much on the resin used[15]. According to the literature, the performance in terms of colour development of the acid scavenger CaSt in a Cr-catalysed HDPE is negative, which is in agreement with the results obtained[15]. On the other hand, it has also been observed that due to the CaSt that it tends to discolour over time at high temperatures, the calcium stearate becomes a yellow coloured compound.

In order to check this fact, a CaSt sample was heated at 200 °C in an air oven and FTIR spectra were measured periodically when the sample was removed from the oven.

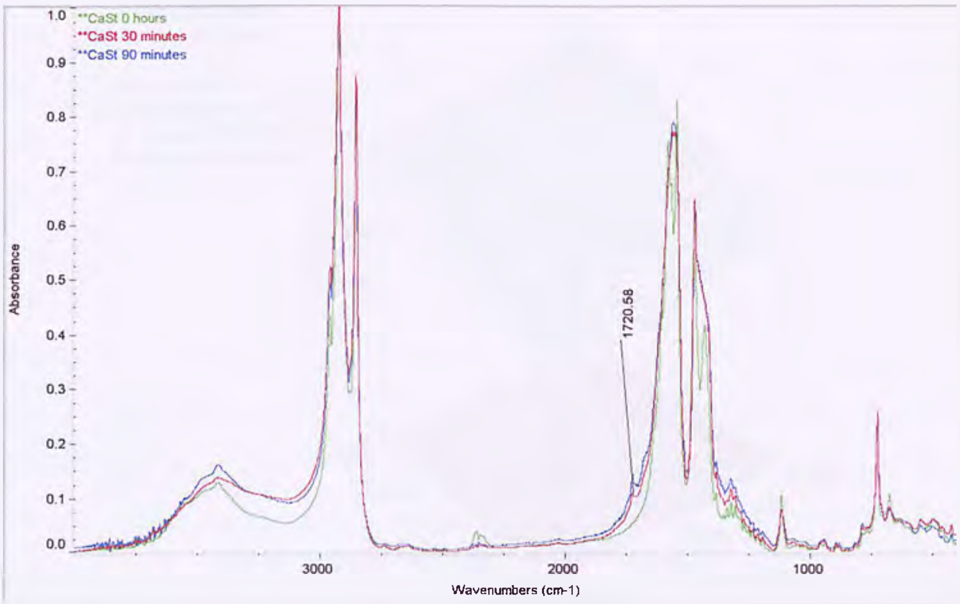


Figure 3.105. FTIR spectra of CaSt without oven ageing and after 30 and 90 minutes at 200°C.

As it can be observed in Figure 3.105 formation of carbonyl group occurs when the CaSt sample is aged at 200°C. Furthermore, it has been observed [123] that this grade of CaSt (Faci DW) contains unsaturation impurities. Therefore, the combination of conjugated systems such as unsaturation and carbonyl groups may contribute to the discolouration observed.

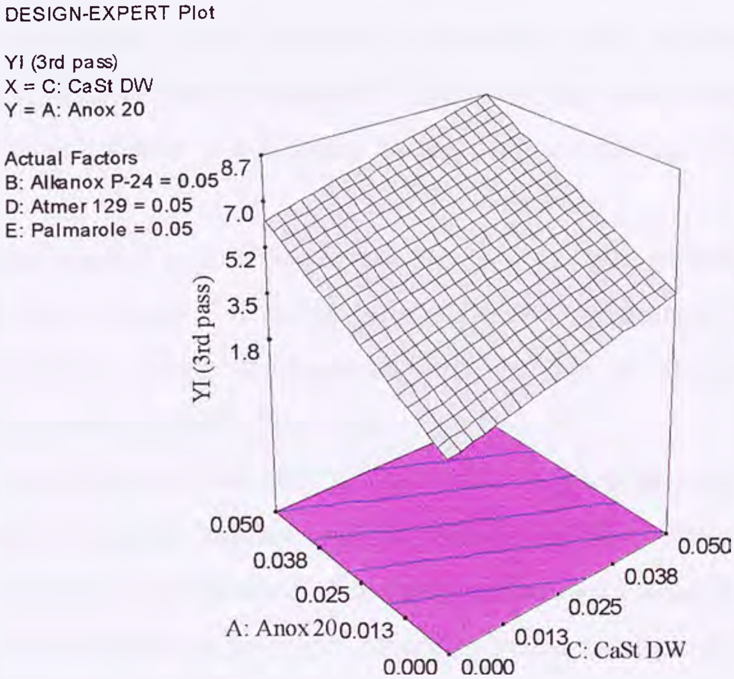


Figure 3.106. 3D-surface plot for Anox 20 and CaSt, Alkanox P-24, Atmer 129 and Palmarole are kept constant.

Figure 3.106 shows another method of observing the effects of CaSt and the phenolic antioxidant. An increase in both additives has a negative effect in terms of colour protection. As can be observed, the effect of the phenolic antioxidant is more pronounced than the acid scavenger. The highest yellowness index is obtained with the maximum levels of both additives.

According to the literature, in poly(propylene), adding acid scavengers significantly reduces the colour introduced to the polymer by the phenolic antioxidant as part of the base stabilisation package[60]. On the other hand, it has been observed that the interaction of titanium residues (due to the catalyst) in poly(propylene) with the phenolic antioxidants results in the formation of coloured metal phenolates[122].

Calcium stearate is commonly added to all poly(propylene)s with the primary purpose of neutralizing acid residues resulting from the Ziegler-Natta catalyst. The acidity of the catalyst residues contributes to colour formation by producing hydrogen chloride, which reacts with the phenolic antioxidant. It is found that the addition of calcium stearate reduced the colour in the polymer[62].

Cr-catalysed HDPE does not contain acidic residues because the chromium catalyst residues are neutral and the discoloration is due to the formation of chromium phenolates[122]. Nevertheless, metal stearates, particularly ZnSt, reduce colour in many HDPE polymers containing these compounds[62]. However, the colour suppression effect of zinc stearate in these systems is not linked to the acid neutralizing characteristic of the stearates.

Since the polymer studied is a Cr-catalysed HDPE it is not surprising that the acid scavenger CaSt has a negative effect in terms of colour protection. In this case, the contribution of CaSt to colour development could be due to structural imperfections (unsaturation, etc) in the alkyl part of the CaSt.

It can be seen from Figure 3.106 that at high levels of phenolic antioxidant Anox 20, increasing the level of calcium stearate leads to increase the discoloration. This confirmed previous results regarding the influence of calcium stearate with antioxidants[123]. Indeed, it was found that the presence of peroxide impurities in the calcium stearate investigated (CaSt DW, Faci SpA) promoted excessive consumption of the phenolic antioxidant investigated (Anox 20), hence additional generation of oxidative conversion of quinone derivative products, and therefore greater discoloration in the presence of calcium stearate.

Another factor that has influence on the yellowness index after the third extrusion pass is the nucleating agent Palmarole.

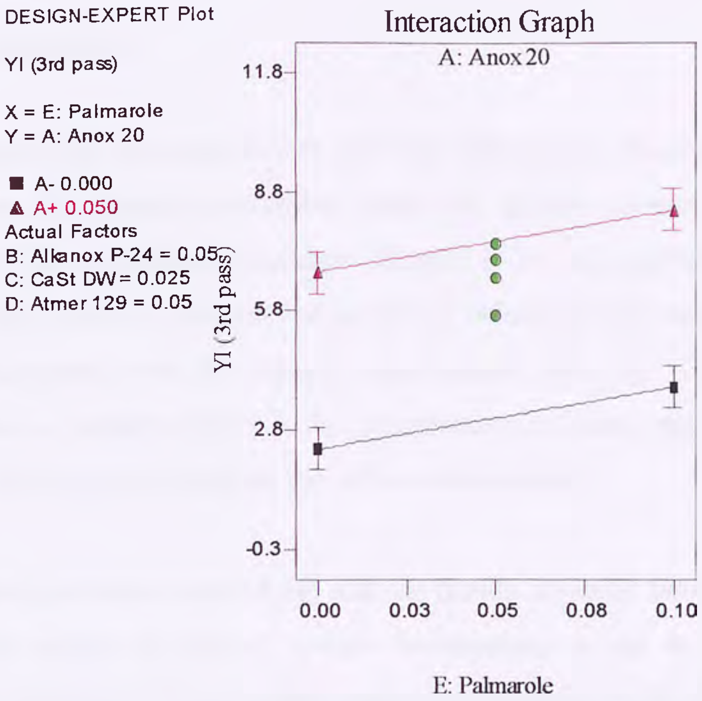


Figure 3.107. Interaction graph for Anox 20 and Palmarole. Constant concentrations, CaSt = 0.025, Atmer 129 = 0.05, Alkanox P-24 = 0.05. Phenolic antioxidant Anox 20 is shown at two levels, 0 and 0.05

It can be seen (Figure .107) that an increase in the concentration of the nucleating agent Palmarole increases the colour development in the polymer under processing conditions.

It is important to consider the following possibility; CaSt interferes with the nucleating agent sodium benzoate (Palmarole) by rendering it useless or at least less effective by forming sodium benzoate and calcium benzoate. The calcium benzoate formed does not act as a nucleating agent[60].

3.5.3.6.3. Conclusions

It can be concluded that the main factors that had influence on the colour development of the polymer were the phenolic antioxidant Anox 20, calcium stearate and the nucleating agent Palmarole. The phosphite antioxidant Alkanox P-24 had a positive effect during the third extrusion pass, where it contributed to colour reduction. The main factor responsible for colour development was the phenolic antioxidant Anox 20. The nucleating agent Palmarole showed a negative effect under processing conditions and the antistatic agent Atmer 129 did not have any impact on the colour development.

According to the experiments carried out and the results obtained from the design the best yellowness index value, the lowest colour development would be achieved with the formulation that contains 0.1% phosphite antioxidant Alkanox P-24. However, this would not be practical because the Anox 20 antioxidant is essential for protecting the polymer against degradation during processing and higher dosage of Anox 20 are needed.

3.5.3.7. Long-term thermo-oxidative stability

In this chapter the influence of the additives (Anox 20, Alkanox P-24, CaSt, Atmer 129, Palmarole) on Cr-catalysed HDPE will be studied during long-term thermo-oxidative stability. Different formulations described in the previous sections were extruded and 100 µm films were prepared by compression moulding. Compression moulded films of high-density poly(ethylene) were cut into strips and they were aged in a thermostatted air-circulating oven at 110°C. Induction times were measured when the corresponding carbonyl index reached a value of 0.1 ($t_{0.1}$CI).

The design summary is shown in Table 3.17.

Table 3. 17. Design summary. Unit, Model and R-squared to the long-term thermo-oxidative stability experiment.

	Unit	Model	R^2
Long-term thermo-oxidative stability (Induction time)	Hours	2FI	0.97

3.5.3.7.1. Standard deviation on long-term thermo-oxidative stability data

The centerpoints were prepared four times.

Table 3.18. Standard deviation on long-term thermo-oxidative stability

	Mean (hours)	Stdev	RSD (%)
Induction time	1953	137.1	7 %

For the analysis of the experimental design results and a relative error of 7 % on long-term thermo-oxidative will be considered as standard error.

3.5.3.7.2. Measured versus predicted values for long-term thermo-oxidative data

The plot that represents the actual values versus the predicted values of the design for induction times is shown in Figure 3.108

Considering the relative error of ±7 % for induction time, it can be concluded that the predicted values fit the experimental data very well.

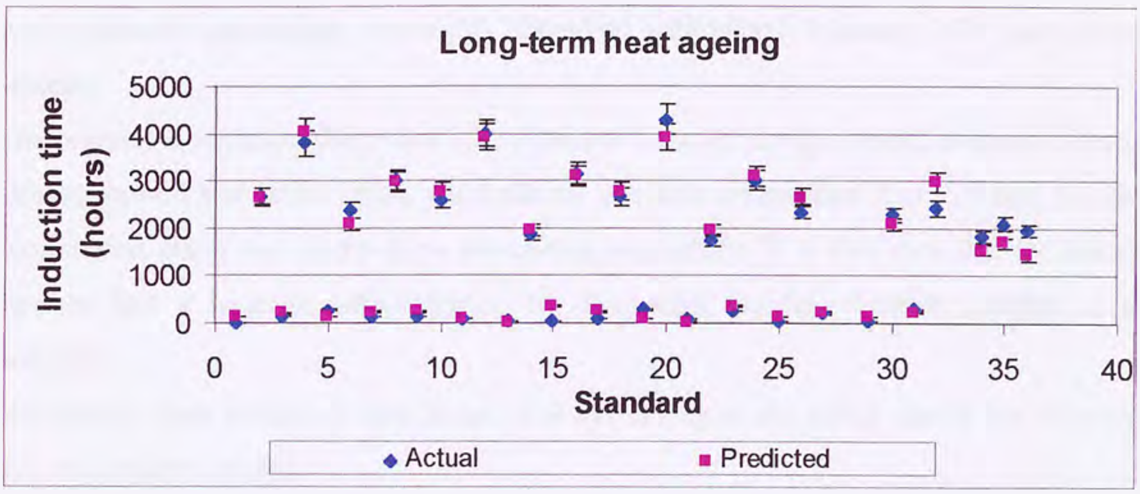


Figure 3.108. Actual versus predicted values for long-term thermo-oxidative stability. The vertical bars represents the standard error of 7%.

3.5.3.7.3. Long-term thermo-oxidative data

Oven ageing is one of the simplest accelerated tests for measuring antioxidant effectiveness. Polymer compositions are oven-aged at selected temperatures and examined periodically. Changes in visual appearance, mechanical properties and chemical composition have been used to follow the course of degradation[15].

In the current chapter the influence of the studied additives on long-term heat ageing of Cr-catalysed HDPE will be studied and discussed.

All the formulations studied in the previous chapters were compression moulded and the films were introduced in the oven at 110 °C.

Carbonyl index measurements were carried out and the time required to reach 0.1 carbonyl index was recorded.

It can be observed that the factors that had influence of the long-term heat ageing of HDPE were: phenolic antioxidant Anox 20, phosphite antioxidant Alkanox P-24 and calcium stearate.

The regression equation (Equation 3.8) obtained from the design expert, in terms of coded factors showed the nature of the main effects. Phenolic antioxidant Anox 20 had the most pronounced effect out of the three mentioned additionaly. It is also seen that the calcium stearate had a negative effect during the long-term thermo-oxidative stability of the polymer.

Nucleating agent Palmarole and Atmer 129 did not have any effect during the long-term thermo-oxidative stability.

Equation 3.8. Equation for long-term heat ageing; A = Anox 20, B = Alkanox P-24, C = CaSt

$$\textbf{Induction time (hours)} = 1550.11 + 1380A + 310.80B - 201.99C + 262.43AB - 208.74AC$$

A positive interaction was observed with the phenolic antioxidant Anox 20 and the phosphite antioxidant Alkanox P-24. A negative interaction was observed with the phenolic antioxidant Anox 20 and the calcium stearate.

In this case, the experimental data for long-term thermo-oxidative degradation can be fitted well by a reduced two-factor interaction model.

The results from the Design Expert are presented in the form of a perturbation plot (Figure 3.109), which shows the influence of all the factors simultaneously.

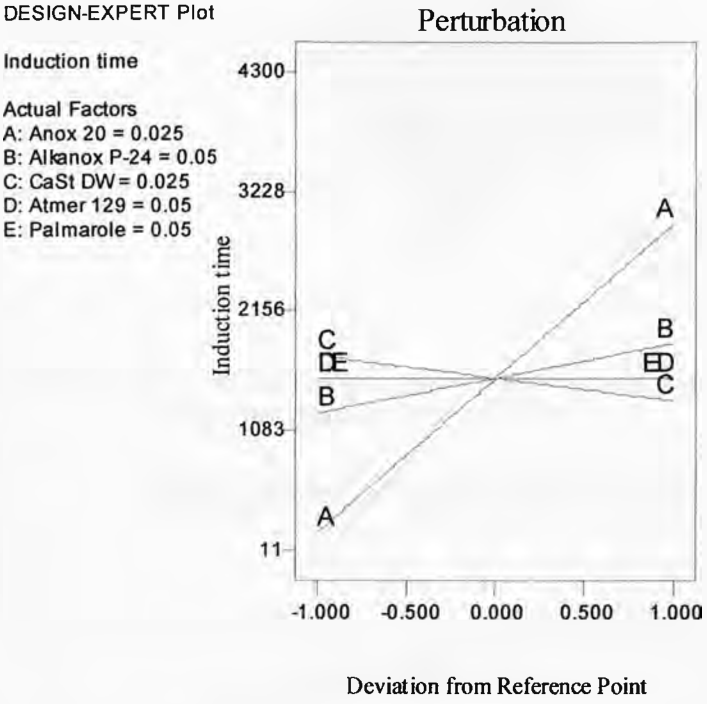


Figure 3.109. Perturbation plot for the influence of the individual factors on the long-term heat ageing; A = Anox 20; B = Alkanox P-24; C = CaSt; D = Atmer 129; E = Palmarole. Reference point: Anox 20 = 0.025, Alkanox P-24 = 0.05, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05.

It can be seen clearly that the factor that had a more pronounced influence on the long-term heat ageing stability was the phenolic antioxidant Anox 20.

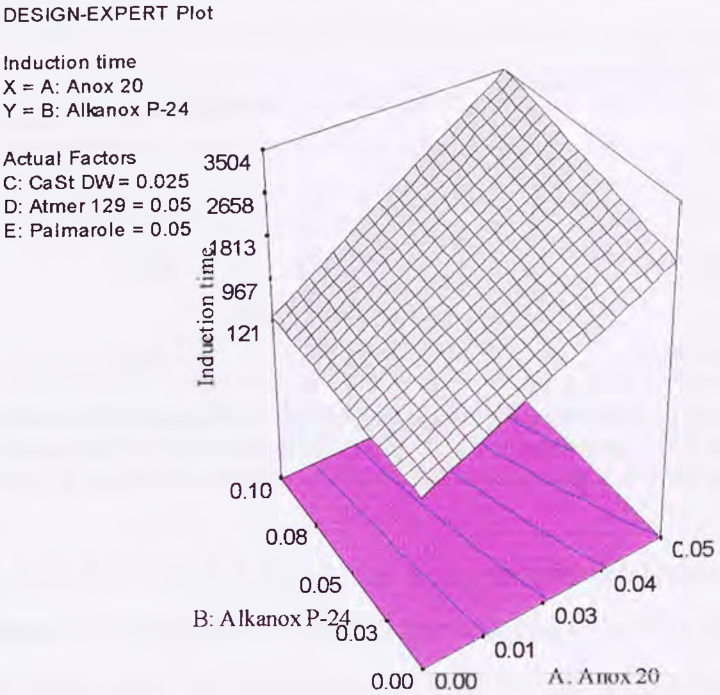


Figure 3.110. 3D surface plot where the interaction between Anox 20 and Alkanox P-24 is observed for long-term thermo-oxidative stability.

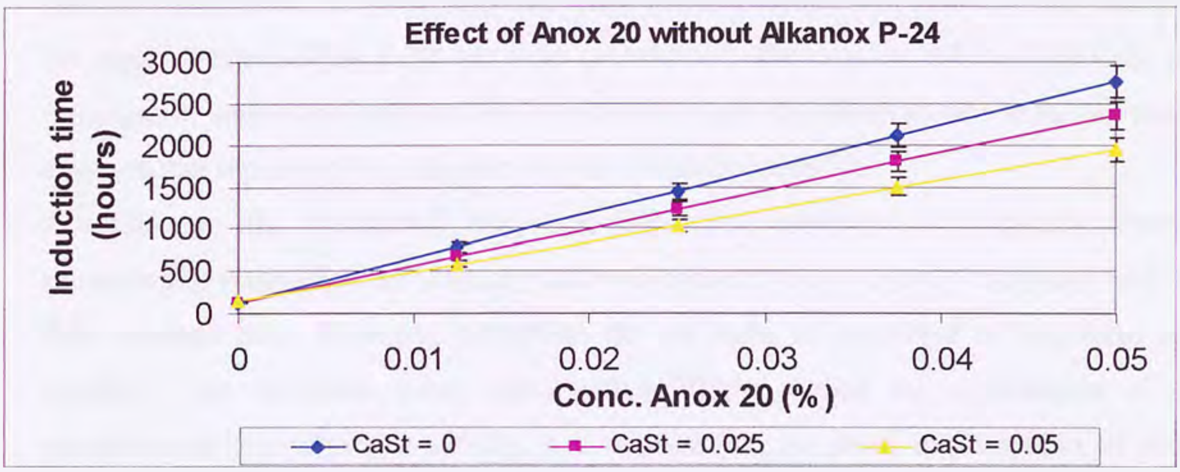


Figure 3.111. Effect of Anox 20 without Alkanox P-24 at different level of calcium stearate and when the Palmarole and Atmer 129 are kept constant at 0.05 %. Oven ageing at 110°C and induction time (hours) is recorded when the carbonyl index has reached a value of 0.1.

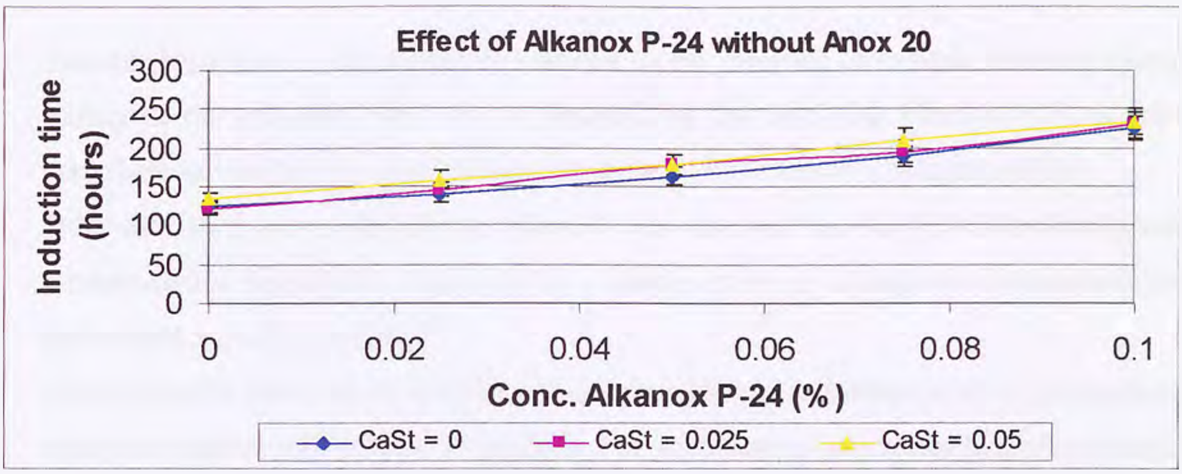


Figure 3.112. Effect of Alkanox P-24 without Anox 20 at different level of CaSt and when the Palmarole and Atmer 129 are kept constant at 0.05 %. Oven ageing at 110°C and induction time (hours) is recorded when the carbonyl index has reached a value of 0.1.

From Figures 3.110, 3.111 and 3.112 it can be seen that the factor that had a more pronounced influence on long-term thermo-oxidative stability was the phenolic antioxidant Anox 20. At the same level of antioxidant, at 0.05 %, the long-term thermo-oxidative stability is substantially higher with the inductions time being approximately 10 times that with 0.05 % of the phosphite. On the other hand, the calcium stearate had a negative effect in the long-term thermo-oxidative stability of the polymer in combination with the phenolic antioxidant. It can be seen that when the concentration of Anox 20 was increased the negative effect of the CaSt was more pronounced. The negative effect of the CaSt and the negative interaction between the Anox 20 and CaSt was observed also in the regression equation that represents the long-term thermo-oxidative stability.

According to the literature,[15] the most important stabilisers for long-term thermal protection of polyolefins are sterically hindered phenols; this is entirely consistent with the data obtained here. However, phosphites do not seem to contribute to long-term heat stability[15]. On the other hand, some authors[102]have studied the contribution of the phosphites to long-term heat stability. It is believed that the ability of phosphites of acting as long-term heat stabilisers is conditioned by the presence of a suitable hindered phenol moiety and the ability to release it[102].

These authors carried out long-term heat ageing experiments in poly(propylene) and found that the phenolic antioxidant exhibited the best long-term heat ageing stability relative to the phosphites. Although the majority of the phosphites assessed did not exhibit any (or negligible) long-term thermo-oxidative stabilisation activity in isolation, it has been shown in the literature, the phosphite bis (2,4-di-*tert*-butylphenol) pentaerythritol diphosphite was to a limited extent capable of performing as long-term heat stabiliser[102]. They concluded that this behaviour of the phosphite was due to the presence of suitable hindered phenolic moiety in the phosphite that can be released. In this case, the Alkanox P-24 seems to contribute as well to long-term heat ageing stability and releases a hindered phenol.

Other authors found similar results, where it was observed that bis (2,4 di-tert-butylphenol) pentaerythritol diphosphite could act, to a certain extent as a long-term thermo-oxidative antioxidant in poly(propylene)[34].

Due to specific break-down reactions of certain additives and differences in polymerisation catalysts residues and method of catalysis it is important to appreciate that generalisations regarding the effects of additives and combinations therefore are not always possible to make.

Synergism is observed with the combination of phenolic antioxidant Anox 20 and the phosphite Alkanox P-24 in terms of long-term heat ageing stability.

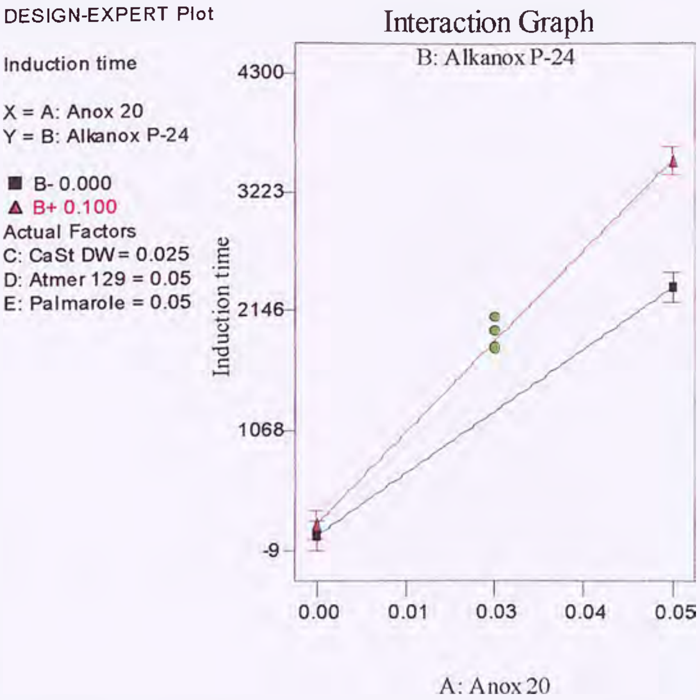


Figure 3.113 Interaction graph for Anox 20 and Alkanox P-24; Constant concentrations, CaSt = 0.025, Atmer 129 = 0.05, Palmarole = 0.05. Phosphite antioxidant Alkanox P-24 is shown at two levels, 0 and 0.05

It can be observed from Figure 3.113 that an increase on the phenolic antioxidant Anox 20 contributes positively to the long-term heat ageing stability of the HDPE. The addition of the phosphite antioxidant Alkanox P-24 shows an enhanced long-terms heat ageing stability. A phenol/phosphite synergism during long-term thermo-oxidative stability was observed also in Cr-catalysed HDPE by other authors[124].

CaSt had a negative influence on the long-term themo-oxidative stability of the Cr-HDPE studied. A negative interaction occurs also between the phenolic antioxidant Anox 20 and the CaSt.

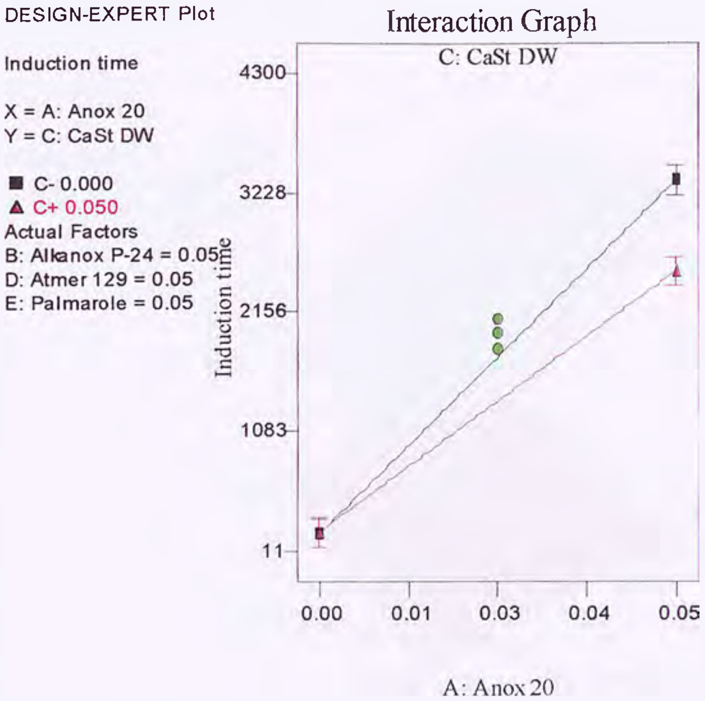


Figure 3.114. Interaction graph for Anox 20 and CaSt: Constant concentrations, Alkanox P-24 = 0.05, Atmer 129 = 0.05, Palmarole = 0.05. CaSt is shown at two levels, 0 and 0.05

An increase in the concentration of the phenolic antioxidant Anox 20 gave a better long-term thermo-oxidative stability (Figure 3.114). However, when 0.05 % of CaSt is added to the formulation, the long-term thermo-oxidative stability of the polymer decreases for a given concentration of Anox 20. Therefore, the CaSt influences the phenolic antioxidant during long-term thermo-oxidative stability reducing its ability to stabilize the polymer. Some authors also found that the presence of CaSt exhibited an interaction, significantly accelerating the rate of thermal decomposition of the phenolic antioxidants[124]. It is believed that the acid scavengers interact with the phenolic antioxidants and reduce the initial levels in the polymer[124].

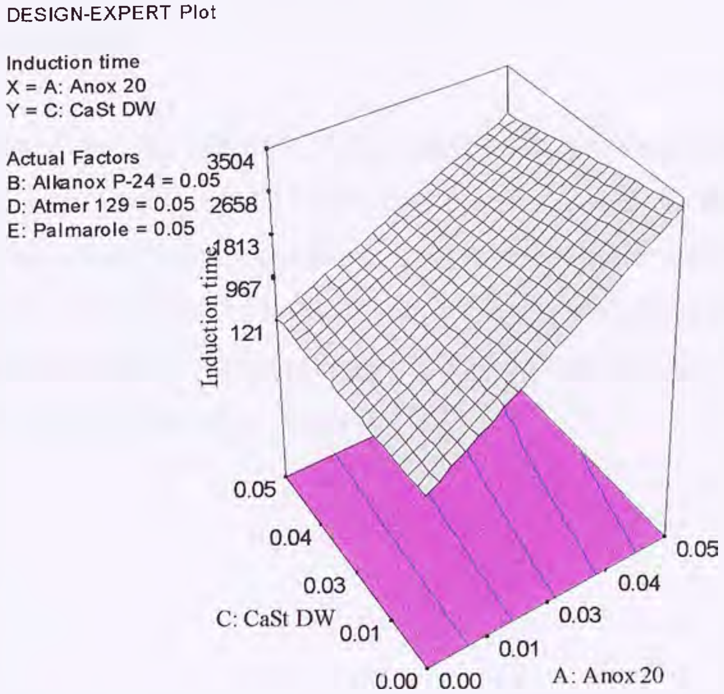


Figure 3.115. 3D-surface plot of the interaction between Anox 20 and CaSt. Rest of the factors are kept constant. Alkanox P-24 = 0.05, Atmer 129 = 0.05 and Palmarole = 0.05.

In the 3D surface plot (Figure 3.115) for the long-term thermo-oxidative stability of the Cr-HDPE the negative effect of the CaSt is highlighted together with the positive effect of the phenolic antioxidant. Maximum performance is obtained when the concentration of Anox 20 is a maximum and the concentration of the CaSt is a minimum. Combination of both additives at 0.05 % each shows a worst performance than 0.05 % of the phenolic antioxidant Anox 20, showing the influence of the calcium stearate on the Anox 20.

3.5.3.7.4. Conclusions

It can be concluded that the additives, which contributed more significantly to the long-term thermo-oxidative stability of the Cr-HDPE at 110 °C, were the phenolic antioxidant Anox 20 (with the more pronounced influence) and the phosphite antixoidant Alkanox P-24. According to the numerical optimisation carried by the design expert software, on the best performance, the additives combination that would give maximum long-term stability would be 0.05 % Anox 20 and 0.1 % Alkanox P-24.

CONCLUSIONS

Comparative hydrolysis studies (60 °C and 75 % relative humidity) of different commercial phosphites showed that Alkanox P-24 (bis 2,4-(di-*tert*-butylphenol) pentaerythritol diphosphite) was one of the most hydrolytically unstable phosphites. Alkanox 28 was the most hydrolytically stable phosphite followed by Alkanox 240, ADK STAB HP-10, Alkanox 24-44, ADK STAB PEP-36, Ultranox 641 and Alkanox P-24.
Internal or external addition of a basic component to the phosphite, increase of stearic hindrance around the phosphorus atom and the reduction of electron density on the phosphorus atom are the factors that affect the hydrolytic stability of the phosphites[92]. Alkanox 28, ADK STAB PEP-36 and Alkanox P-24 are pentaerythritol-based phosphites. The different substitution on the aromatic ring makes them different. Alkanox 28 has a greater steric hindrance around the phosphorus atom than the other two phosphites, which makes hydrolysis more difficult. On the other hand, Alkanox P-24 has the lowest steric hindrance around the phosphorus atom and this makes it hydrolytically unstable.

Hydrolysis reaction of Alkanox P-24 is an autocatalytic reaction. Initially, an induction period is observed, however, after a certain time the hydrolytic stability of the phosphite decreases dramatically. Acid or bases have an influence on the rate of hydrolysis reaction of phosphites. Indeed, it is known that in the presence of acidic species an acceleration of the hydrolysis reaction is observed[36]. During the hydrolysis reaction of Alkanox P-24, acidic species are formed, such as, phosphorus acid that would accelerate the hydrolysis reaction that would create the autocatalytic pattern.

In order to study the influence of different co-additives and the possible improvement on the hydrolytic stability of the phosphite Alkanox P-24 different binary blend and ternary blend were studied at 60 °C and 75 % R.H.

Therefore, to investigate the effect of the phenolic antioxidant Anox 20, the acid scavengers CaSt and DHT-4A on the hydrolytic stability of Alkanox P-24, binary blends of each of these compounds were prepared by melt blending at different ratios.

It could be concluded that the co-additive that had a more pronounced influence on the hydrolytic stability of Alkanox P-24 was the acid scavenger hydrotalcite like compound DHT-4A. Firstly, it is believed that the improvement on the hydrolytic stability of Alkanox P-24 in the presence of the acid scavenger hydrotalcite was due to a dilution effect. An increase in the concentration of the acid scavenger in the blend showed an improvement on the hydrolytic stability of Alkanox P-24. On the other hand, due to the acid scavenging ability of the hydrotalcite a chemical effect should be taken into consideration. Indeed, due to the acid scavenging nature of the hydrotalcite the acidic species formed during hydrolysis reaction of Alkanox P-24 would react with the acid scavenger and the autocatalytic reaction would be avoided. According to the literature, the hydrolysis of tripropyl phosphite in water with acetonitrile was significantly retarded using a small amount of a tertiary base[36].

The hydrolytic stability of Alkanox P-24 was improved also in combination with CaSt. The improvement was due to a dilution effect and a chemical effect. An increase on the CaSt concentration in the binary blend showed a positive effect on the hydrolysis of Alkanox P-24. A chemical effect was observed due to two factors, acid scavenging capacity of CaSt and the content of water. Initially because of the water content (3 %) on the CaSt the hydrolysis reaction was accelerated. However, at the latter stages of hydrolysis an improvement on the hydrolytic stability of Alkanox P-24 could be noticed. This could be attributed to the acid scavenging capacity of the CaSt, which would react with the acidic products generated as consequence of the hydrolysis reaction of Alkanox P-24 and also due to the dilution effect.

In the presence of Anox 20 an improvement is also observed. In combination with the phenolic antioxidant Anox 20 a longer induction time was observed before the autoacceleration pattern. The improvement in the hydrolytic stability of Alkanox P-24 is due to a dilution effect.

It is well known that the phenol and phosphite antioxidants are used in synergistic combinations to avoid polyolefin degradation during melt processing. Therefore, the improvement of the hydrolytic stability of Alkanox P-24 in combination with Anox 20 is a positive aspect.

The hydrolysis behaviour of binary and ternary blends containing Alkanox P-24 was evaluated at 60 °C and 75 % R.H. together with the effect of partially hydrolysed Alkanox P-24 on the processing stability of poly(propylene). Alkanox P-24/Anox 20 (50:50), Alkanox P-24/Anox 20/CaSt (40:20:40), Alkanox P-24/Anox 20/DHt-4A (40:20:40) blends were studied in two possible physical forms, powder and Non Dust Blends (NDB). The influence of the physical form on the hydrolysis rate of Alkanox P-24 was also considered.

It is concluded that the hydrolysis rate of Alkanox P-24 could be efficiently retarded by various blending procedures. Three main mechanisms of hydrolysis protection could be identified; a dilution effect, when Alkanox P-24 was blended with another product the hydrolysis was slowed down. A chemical effect provided by specific acid scavengers CaSt and hydrotalcite like compound (DHT-4A). The most efficient acid scavenger delaying the hydrolysis reaction of Alkanox P-24 is the DHT-4A due to its ability to react with the acidic products formed as a consequence of the hydrolysis of the phosphite. As was also observed for the binary blends, CaSt was found to have a dual effect, in the early stages of hydrolysis the water content in the CaSt plays an important role and the hydrolysis of Alkanox P-24 is accelerated. However, at the latter stages, the acid scavenging capacity of the CaSt had a positive effect slowing down the hydrolysis reaction. A physical form effect was observed also due to the difference on the hydrolytic stability of Alkanox P-24 when it was part of a powder blend or when it was part of a NDB. The hydrolysis reaction of Alkanox P-24 is clearly slower in the NDB physical form compared to the powder form. This is attributed to a diffusion control of the reaction, as the water has to diffuse through the pellet.

Hydrolysis of Alkanox P-24 has an effect on melt processing performance. Both melt flow protection and colour protection were affected when the blends Alkanox P-24/Anox 20, Alkanox P-24/Anox 20/CaSt and Alkanox P-24/Anox 20/CaSt were exposed to 60 °C and 75 % R.H. and periodically removed in order to be processed with poly(prolyene) at 275 °C.

Melt flow protection depends on exposure time to moisture. The same behaviour in terms of melt flow protection was observed for the blends. Initially, no loss of performance, a linear behaviour was observed and at a certain point in time a steep increase on melt flow rate occurred.

Colour protection also depends on the exposure time to moisture and temperature. In the early stages of hydrolysis the Alkanox P-24/Anox 20 became more efficient in protecting the colour development than in the later stages. For the Alkanox P-24/Anox 20/CaSt blend there is no significant difference in yellowness index with the exposure time although in early stages of hydrolysis a tendency to decrease the yellowness index is observed. Alkanox P-24/Anox 20/DHt-4A did not show any significant difference in terms of colour protection with exposure time. Therefore, it was observed that in early stages of exposure time the performance of the poly(propylene) in terms of melt flow and colour protection is comparable to the sample that was not exposed to moisture and temperature conditions. This suggests that partially hydrolysed Alkanox P-24 is able to perform as an efficient antioxidant. This could be due to the active intermediate products generated as consequence of the hydrolysis reaction that could protect the polymer from degradation during melt processing.

Another important observation is that depending on the physical form (NDB or powder) the loss of melt and colour protection was not the same at a given degree of hydrolysis. It was also seen that at the same amount of hydrolysis the polymer processed with the formulations in the NDB physical form outperforms the powder blend in terms of melt flow and yellowness index protection. This suggests that in the sequence of hydrolysis reaction of Alkanox P-24 there are intermediates that become more efficient in antioxidant activity. It is believed that the hydrolysis mechanism could be different for the NDB and powder blends.

Different techniques were used to verify the hydrolysis mechanism of Alkanox P-24. Final products were, phosphorus acid, 2,4-di-*tert*-butylphenol and pentaerythritol that were confirmed by HPLC and FTIR. The intermediate product monophosphite-monophosphonate and the monophosphite-mono esterified monophosphonoate (Scheme 3.2) were detected by mass spectrometry.
It is assumed that depletion of Alkanox P-24 in order to measure the degree of hydrolysis is not the proper measurement in order to study the different behaviour in performance of the two physical blends. Different kinetically controlled hydrolysis is followed for the different physical forms NDB and powder. The mechanisms are different depending on the concentration of water (percentage of relative humidity), diffusion control and acidity. It is assumed that particularly the diffusion control of water in different physical forms affects the life expectancy and available concentration of a possible highly active intermediate. The relatively high concentration in the partial hydrolysis pathway of the Alkanox P-24 NDB blend seems to be responsible for the differences in performance of NDB and powder blend. It is believed that the monophosphite-monophosphonate generated as a consequence of the hydrolysis reaction of Alkanox P-24 is an active product that could contribute to the melt and colour stabilisation. It is assumed that this intermediate is formed in the hydrolysis of Alkanox P-24 NDB and powder. However, in the NDB the concentration of this compound remains stable over a certain time, as not enough moisture is present to carry on the hydrolysis reaction due to the diffusion control of H_2O. In the powder blend, there was no such diffusion control, due to the much lower size of the powder particles and higher surface area. The poorer performances in terms of melt flow and colour protection of the partly hydrolysed blend could be explained by a low steady state concentration of this compound.

Finally, the two level factorial experimental design proved to be a very useful tool to investigate the simultaneous effects of each additive and the possible interaction between the additives present in the stabiliser system studied. Alkanox P-24 and the phenolic antioxidant Anox 20 were the most significant stabiliser that had influence on the melt flow protection of the Cr-HPDE.

A synergistic effect was observed for the third extrusion pass between the phenolic antioxidant Anox 20 and the phosphite Alkanox P-24 that is in accordance with the literature. It was thought that the phosphite Alkanox P-24 was sacrificially consumed towards the phenolic antioxidant Anox 20 up to the third extrusion pass. CaSt had also a positive effect on the melt flow protection of the polymer after the third extrusion pass. This positive effect was thought to be due to the lubricating properties of the fatty acid salt. Furthermore, a synergistic effect was observed with the phosphite antioxidant Alkanox P-24. The nucleating agent Palmarole showed a negative effect under processing conditions and the antistatic agent Atmer 129 did not have any impact on the melt processing stability. Regarding the discoloration during processing it was confirmed that the phenolic antioxidant had the more pronounced influence due to the formation of high coloured conjugated quinone derivatives. CaSt had also a negative influence in terms of discoloration that was attributed to its structure. At processing temperatures, CaSt becomes yellow due to the generation of carbonyl groups in the molecule. The nucleating agent Palmarole had a negative impact due to its contribution to colour development. The phosphite antioxidant Alkanox P-24 had a positive effect on the colour development. Finally, the phenolic antioxidant Anox 20 was the main additive that contributed to the long-term thermo-oxidative stability of Cr-HDPE. Phosphite antioxidants also showed a positive effect, which has also been observed by other authors. It was seen that Alkanox P-24 could act, to a certain extent as a long-term thermo-oxidative antioxidant in poly(propylene)[34]. Synergism was observed with the combination of Alkanox P-24 and Anox 20. CaSt had a negative effect on the long-term-thermo-oxidative stability of Cr-HDPE and an interaction was observed with the phenolic antioxidant Anox 20.

FURTHER WORK

The influence of different co-additives on the hydrolytic stability of Alkanox P-24 has been studied. It has been observed that the acid scavenger DHT-4A (hydrotalcite like compound) had a pronounced effect retarding the hydrolysis of the phosphite. The effect of DHT-4A should be studied in depth in order to analyse its outstanding performance. It was believed that the phosphite might be able to intercalate between the DHT-4A layers. X-Ray analyses should be carried out to study possible changes in the layered structure of the acid scavenger.

CaSt also showed an improvement on the hydrolytic stability of Alkanox P-24 although in the early stages of the hydrolysis seemed to accelerate the reaction. This effect was attributed to the presence of water in CaSt. Different CaSt with different water content should be taken into consideration in order to evaluate the effect of the water content in the early stages of the Alkanox P-24 hydrolysis reaction.

The hydrolysis mechanism of Alkanox P-24 has been studied. The products identified by mass spectroscopy could be the intermediate species generated as consequence of the hydrolysis reaction of the phosphite. However, LC-MS spectrometry should be carried out to confirm the intermediate products of the Alkanox P-24 hydrolysis. The hydrolysis reaction of Alkanox P-24 should be studied more in depth. It was believed that different kinetically controlled hydrolysis is followed for the different physical forms NDB and powder. Kinetic studies for both physical forms should be undertaken and compared to verify the hypothesis mentioned before.

It was suggested that the partially hydrolysed Alkanox P-24 was able to perform as efficient antioxidant. The intermediate products generated as consequence of the hydrolysis reaction could protect the polymer during melt processing. These intermediates should be synthesized and the performance during multiple pass extrusion (melt flow and colour protection) analysed in order to study their antioxidant activity.

It is known from the literature [35,38] that synthesizing a phosphite with a piperidine group (HALS) could also improve the hydrolytic stability of the phosphites. Alkanox P-24 is a symmetric molecule with two phosphite groups. It would be interesting to synthesize the phosphite with a piperidine moiety in order to evaluate its hydrolytic stability and melt processing performance.

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