Reduction of Organic Compounds Leached to Extractive Media from Polymers through Improved Polymer Processing

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Reduction of Organic Compounds Leached to Extractive Media from Polymers through Improved Polymer Processing

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requirements of Manchester Metropolitan University
for the degree of Doctor of Philosophy

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Department of Natural Science – Chemistry

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Testimony

I herewith confirm that all literature reviews and interpretation of literature knowledge was decided, initiated and done by me. All experimental designs were generated by me and all interpretation of the corresponding data conducted by me personally.

Experimental work was carried out on my behalf at TIC (SONGWON, South Korea), PCE (USA), CERTECH (B) and last but not least at MMU (UK).

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In Memory of Maurizio Butti …

This all began with a question to **Maurizio** whether he would fund my PhD study at the age of 50 …

I would like to thank this inspiring and charismatic person for this opportunity … something I was not able to do when I was young due to financial reasons.

When this PhD started in summer 2014, my industrial sponsor Songwon was a great place to work and accommodated and funded this research. For this I thank the acting CEO **Jongho Park**.

Of course, I am glad that Manchester Metropolitan University accepted me as a part-time student. Specifically, I appreciate the effort and guidance of **Michele Edge**. Thanks and again apologize for all the inconveniences caused by the constant lack of time on my side. **Lindsey Munro** helped out several time.

I appreciate a lot the help of some of my former Songwon colleagues in South Korea, namely **Sua Kim** and **Jaeyong Lee**, which in the meantime have become friends. The termination of my employment at Songwon end of June 2020 was a major interruption of this research work. By the “helping hands” of **Beatrice Iuorno** this was turned into a transition and allowed me to finish this PhD work.

Last but not least, a big thanks and a very big hug to my partner-in-life **Antonella**, who had to cope 3 months and another 6 months 2 years later with a lot of stress … an immensely valuable moral support.

Together we can achieve a lot.

Je suis fier de Mélanie et Marlene Charlotte.

Abstract

This research work was sparked by the initial publication of Professor Eric Arvin for the Department of Environmental Engineering of the Technical University of Denmark in Lyngby in 2002. He reported several organic fragments in drinking water which is transported via “plastic” pipes. The fragments seemed to originate from protective chemicals present in the organic pipe substrate. In the last 20 years several other publications have reported similar fragments. Whilst these studies have been useful in identifying this issue, there has not been a systematic approach to the polymeric substrate and its intentionally added ingredients.
This study intends to add the knowledge on which conditions cause protective chemicals in polyolefins (stabilisers, antioxidants, modifiers) to produce specific structures and concentrations of water-extractable fragments It further examines how factors other than protective chemicals in a PO determine water-extractable fragments.

PO (as a thermoplastic material) cannot be melt-processed at ~250°C without the formation of a very high concentrations of oxidised-aliphatic fragments. Addition of protective chemicals to suppress these fragments, results in additional fragments of an oxidised-aromatic nature. The total number and concentration of fragments, as well as the ratio between oxidised-aliphatic and oxidised-aromatic fragments, is an optimum function between the two opposing effects. Optimum stabilisation packages to reduce water-extractable fragments optimum can be identified by this systematic approach, by clustering the different fragments based on their mechanism of formation. Five different mechanisms of leading to fragments are proposed, which require different strategies to inhibit them. The strategies proposed in this study have shown that a significant reduction in fragments, in the range of ~90%, can be achieved. The extraction temperature has a major impact on type, number, and concentration of fragments. A temperature of approximately 40°C has been chosen as characteristic of extraction in service-life applications for water containment (e.g., pipes and packaging). Different migration behaviour of organic fragments above and below this temperature has been examined.

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Abbreviations

CB-A	**C**hain **b**reaking **a**cceptor
CB-D	**C**hain **b**reaking **d**onor
CERTECH	**Ce**ntre de **R**essources **T**echnologiques **e**n **Ch**imie (Seneffe, B)
ECHA	**E**uropean **Ch**emical **A**gency
EFSA	**E**uropean **F**ood **S**afety **A**uthority
ELiSANA	**E**uropean **Li**ght **S**tabilizer and **An**tioxidant **A**ssociation
GC	**G**as **c**hromatography
GC-MS	**G**as **c**hromatographer coupled with a **m**ass **s**pectrometer
HDPE	**H**igh **d**ensity **p**oly**e**thylene
HDT	**H**eat **d**istortion **t**emperature
HMW	**H**igh **m**olecular **w**eight
HALS	**H**indered **a**mine **l**ight **s**tabilizer
HAS	**H**indered **a**mine **s**tabilizer
HP	**H**indered **P**henol
IAS	**I**ntentionally **a**dded **s**ubstance
LD	**L**imit of **d**etection
LMW	**L**ow **m**olecular **w**eight
LQ	**L**imit of **q**uantification
LTTS	**L**ong **t**erm **t**hermal **s**tability
MDPE	**M**edium **d**ensity **p**oly**e**thylene
MFI	**M**elt **f**low **i**ndex
Min / min	**Min**utes
MMU	**M**anchester **M**etropolitan **U**niversity (Manchester, UK)
MOSH	**M**ineral **o**il **s**aturated **h**ydrocarbons
MS	**M**ass **s**pectrometer
MTC	**M**aximum **t**olerable **c**oncentration
MTC$_{\text{tap}}$	**M**aximum **t**olerable **c**oncentration at the **tap**
MW	**M**olecular **w**eight
MWD	**M**olecular **w**eight **d**istribution
NIAS	**N**one **i**ntentionally **a**dded **s**ubstance
NOR-HAS	**H**indered **A**mine **S**tabilizer with an amino ether functional group
PDMS	**P**oly**dim**ethyl **s**iloxane
PB	**P**oly**b**utylene
PE	**P**oly**e**thylene
PE-X (PEX)	Crosslinked **p**oly**e**thylene
PO	**P**oly**o**lefin
POSH	**P**oly**o**lefin **s**aturated **h**ydrocarbons
PP	**P**oly**p**ropylene
PP-H	**P**oly**p**ropylene **h**omopolymer
PP-R	**P**oly**p**ropylene **r**andom copolymer
PVC	**P**oly**v**inyl**c**hloride
SML	**S**pecific **m**igration **l**imit
TIC	**T**otal **i**on **c**hromatogram (MS analysis)
TTC	**T**hreshold of **t**oxicological **c**oncern
UBA	**U**mwelt **B**undes**a**mt (German federal environmental agency)
YI	**Y**ellowness **i**ndex
Z/N	**Z**iegler/**N**atta metalorganic catalyst for the synthesis of polyolefins

Glossary

6.5D Thermal death curve	FDA cooking recommendations which are set to reach a reduction level of 6.5D (where D stands for "decimal" or a factor of 10), which corresponds to killing 99.99997% of pathogens
Additive	A chemical added to a polymeric substrate in order to either help synthesize or process it respectively to modify or preserve the properties of the polymeric substrate. The additive is in general initially not chemically bound (via covalent bonds) to the polymeric substrate.
Anti-blocking agents	Polyolefin films often stick together and the different layers cannot be separated. This adhesion is called blocking. Anti-blocking agents lower the force needed to separate 2 layers of a (polyolefin) film. Anti-blocking agents can be divided into inorganic (silica, zeolite, talc) and organic (behenamide & ethylene-bis-stearamide).
Antiozonant	Organic additive which slows down the degradation of unsaturated (macro-) molecules caused by ozone (O_3) instead of oxygen (O_2). Antiozonants are mainly used in (poly-) butadiene based rubbers. Antiozonants are sub-categorized into chemical and physical antiozonants.
ARVIN fragments	Organic aromatic compounds discovered by the research group of Prof. Arvin in drinking water transported through polyethylene pipes. The fragments constitute reaction products of commercially available synthetic preservative chemical (antioxidants).
B-blend (concept)	B-blend for binary blends. Concept introduced in the mid 1980s by CIBA-GEIGY for the processing and thermal stabilisation of organic (mainly polymeric) substrates. The concept is based on the combination of a Hindered Phenol with a Phosph(on)ite and exploits the synergism between these two classes of protective chemicals.
CAS#	A unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open literature
Chromophore	A chromophore is the part of an (organic) molecule which is responsible for its colour. It absorbs in the wavelength range of visible light.
Controlled rheology	Controlled rheology PP (often referred to as PP-CR) is PP which is intentionally and in a controlled manner degraded during melt-processing via the addition of (mainly) peroxides. This reactive extrusion results in a decrease in molecular weight and a narrowing of molecular weight distribution.
CRAMER class	One of several alternative classification schemes to estimate the **T**hreshold of **t**oxicological **c**oncern TTC for a chemical substance based on its chemical structure. 3 CRAMER classes exists which correspond to a maximal recommended daily intake of a chemical.
E number	Code for substances (additives) used as direct food additives within the European Union EU and the European Free Trade Association EFTA. The letter "E" stands for "Europe".
General purpose (PP) grade	A polypropylene grade (defined by melt flow index, density and comonomer type & amount) which can be used in various extrusion or moulding applications. It has not one defined specific end use or processing technology.
Hindered Phenol	One out of several chemical classes which act as preservatives against oxidative degradation of organic materials. Major mechanism of action chain breaking donor CB-D.
Log K_{ow}	Logarithmic expression of the ratio of the solubility of a chemical compound in n-octanol and water. Log K_{ow} is used as a relative indicator for a substance to adsorb into soil and living organic matter. It is proportional to its molecular weight and invers proportional to its water solubility.
Log K_{ow} – Aldehyde equivalence scale	Approximative Log K_{OW} calculated for aliphatic (mainly mono-) oxygenated fragments on the basis of Equation 1 (of Figure 8) based on linear aldehydes
Masterfluff	A powder mixture of the just synthesized polyolefin and solid additives at final concentration. This masterfluff is added to the compounding extruder. The approach is not possible with liquid additives.
Melt flow index	A very simple rheological measurement at a given temperature and with one shear rate only. The shear rate is determined by a weight. The melt index expresses the weight of (polymeric) material pushed through a die at a given temperature and a given weight. Example for the conditions for PP: MFI $_{230°C/2.16Kg}$
Metilox	Intermediate developed by CIBA-GEIGY out of which many high molecular weight Hindered Phenols HP are synthesized. Metilox (CAS # 6386-38-5) is chemically 3-(3, 5-di-tert-butyl-4-hydroxyphenyl) methyl propanoate. It is also referred to as drinking water impurity ARVIN 9.
Molar activity of Hindered Phenols	A measure for the amount of functional groups (phenolic OH groups) present in a preservative chemical of the class of Hindered Phenols. It is expressed in [mol OH/Kg of additive].
Molar activity of Phosph(on)ites	A measure for the amount of functional groups (trivalent phosphorus) present in a preservative chemical of the class of Phosph(on)ites. It is expressed in % phosphor of the molecule.

Mould release agent	Separation of the surface layer of a plastic part from the metal mould during the conversion process of (mainly) injection moulding via the formation of a separation layer. Mould release agents can be compounded into the polymeric substrate (calcium stearate or glycerol monostearate for PP) or only applied topically (e.g. silicon oil).
Phosph(on)ite	One out of several chemical classes which act as preservatives against oxidative degradation of organic materials. Major mechanism of action is the decomposition of unstable peroxides into none-radical species.
PP-originating fragment	Any water-extractable fragment which can be associated directly with polypropylene
Protective chemical	Generic term for any chemical which inhibits, stops or slows down aging
Protective chemical-originating fragment	Any water-extractable fragment which can be associated directly with one of the present protective chemicals
Slip agent	Organic additives used as surface modifiers for polyolefins. Polyolefin have in general a high coefficient of friction and films therefore tend to adhere to themselves and (hot) metal surfaces and do not slide along those surfaces. Slip agents reduce the coefficient of friction. Typical slip agents for polyolefins are erucamide, oleamide and ethylene-bis-oleamide.
Substrate-originating fragment	Any water-extractable fragment which can be associated directly with the (organic) substrate
Thermal stabilizer	Scientifically not completely correct term to describe protective chemicals which slow down (not just oxidative) degradation during the use of a plastics (in a temperature range well below its melting or softening range). This term may not be confused with PVC processing stabilizers which slow down the thermal degradation pathway of dehydrochlorinations (mainly during melt-processing).
Thermoplastic(s)	A polymeric material constituted of mainly linear macromolecules (e.g. PO) which can be softened or molten and in this state shaped and subsequently re-solidified. This feature of thermoplastics is not present with duromers and crosslinked elastomers (rubbers).
Thermoset	A polymeric material constituted of a 3-dimentional network of macromolecules. Thermosets are not meltable and in general not soluble.
Yellowness index	One out of several ways to quantify the colour of a sample against an ideal white standard.

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1 Background and Introduction

1.1 Background

Thermoplastic polymeric materials have the advantage over other polymer classes (thermosets and elastomers) because they can be melt-processed and shaped repeatedly at lower temperatures (180-300°C) than glass and metals (600-3500°C). Despite this advantage, it became apparent during mid-20th century industrialization that most thermoplastic polymers are not intrinsically stable enough to survive the elevated temperatures of melt conversion without degradation. Even at lower temperatures, the three major polymer classes lack intrinsic stability and are unable to maintain their initial properties for a prolonged (service) lifetime of several months or even several years. This makes them unsuitable for end applications of intermediate and long-term durability without further modification.

To address this issue, a broad variety of protective chemicals ("antioxidants, stabilisers, preservatives") were introduced from the mid-1950s onwards by plastics processors. **Throughout this report the term 'protective chemicals' is used** to avoid confusion (since subtle differences exist for the widely used terms 'antioxidants' when applied to biological systems and plastics; with the term 'preservatives' applying mainly to prevention of microbiological deterioration).

Essentially, plastics consist of a polymer matrix to which several compounds (including protective chemicals) are added (polymer formulation), to give the desired properties. The addition of protective chemicals to the polymer matrix proved very effective in polyolefins (PO) and many different combinations of antioxidants were in use. The development of this technology peaked in the late 1970s and in the 1980s and a tendency to 'industry standardisation' reduced use to relatively few commercial antioxidants; leading to the "workhorse" formulation (termed the "B-blend concept"), which has been used almost universally by the polyolefin industry for the last 45 years.

For many (melt-) processing and service life conditions, this technology is still sufficient. At present, the protective packages used exhibit good technical performance properties (the dominant requirement during their development) and broad global regulatory approval (of the ‘intact’ protective chemical structures). The continuous development of formulations of protective structures, coupled with expiration of corresponding intellectual property, means that the “relatively few” commercial antioxidants can be offered by various suppliers at attractive market prices.

Unfortunately, over the last 15 years, it became apparent that typical formulations of protective chemicals show a tendency to fragment into a variety of smaller molecules when used under certain conditions. While the literature has shown that this is not necessarily detrimental, and indeed may even enhance antioxidant activity, some fragments are of low molecular weight and could be physically lost from the PO matrix by volatilization or extraction. This becomes an issue in specific PO applications (for example, potable water containers (pipes and bottles) or food packaging) where antioxidant fragments could contaminate drinking water or food.

Often, the concentrations, range and toxicological profile of antioxidants and their transformation products (including fragments) has not been assessed. Consequently, legislative bodies (in particular, European authorities: ECHA, UBA) are concerned that the actual (total) exposure of the population to harmful chemicals has not been fully evaluated. To address these concerns, selected antioxidant manufacturers, via their European industry association ELiSANA (European Light Stabilizer & Antioxidant Association) are attempting to establish the nature and toxicological profile of the major fragmentation products of the main antioxidants used in the PO industry. The research presented in this thesis is an integral part of this initiative, the main aim being to identify the range of fragmentation products from protective chemicals and, to modify formulations to reduce the number of fragments that constitute an environmental hazard.

1.2 The Use of Polyolefin Plastics as Construction and Packaging Materials

Polymeric materials have been used since the beginning of mankind in the form of natural polymers (such as wood, fibres, skin, etc). With the emergence of metals as construction materials the use of polymers declined, until *c.*1870 when semi-synthetic polymers were discovered. From the mid-1960s, the development and industrialisation of synthetic polymers resulted in polymers regaining their importance as construction materials [1-3]. Today synthetic polymers have extended their applications to a range of industry segments, that also include packaging, automotive and electrical applications [6]. The major uses of polymers as plastics in Europe in 2014 are illustrated in **Figure 1**.

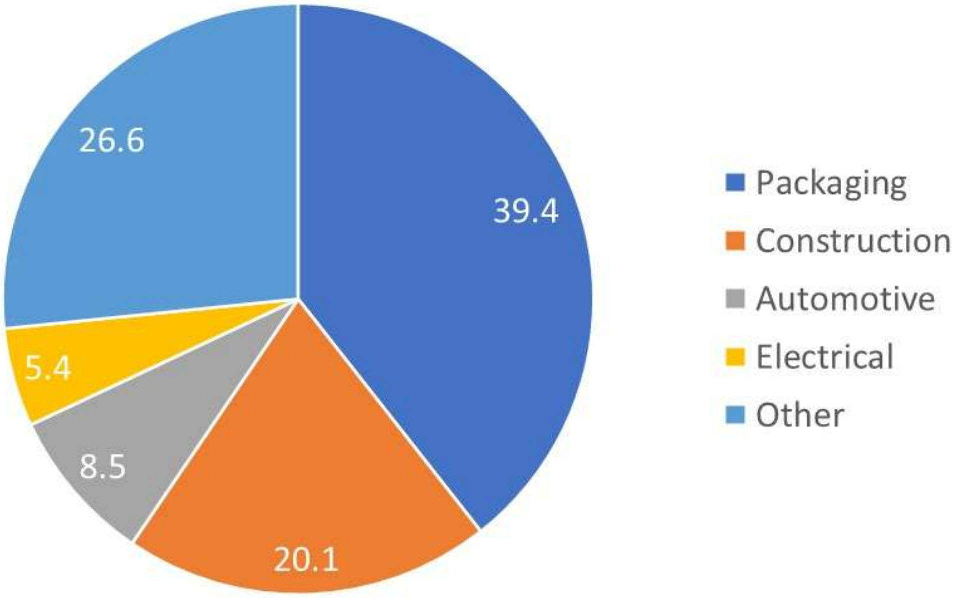

Figure 1: Use of plastics in Europe in 2014 [6]

In general, the advantageous properties of the material class that is (synthetic) polymers can be described as follows [4,5]

- Low density
- Relatively high chemical resistance

- Good electrical insulators
- Toughness
- Strongly varying mechanical properties (which can be tailor-made from fibre-reinforcing over impact modification to plasticizing)
- Limited temperature resistance
- Varying degree of solubility and swelling
- Transparency of selected thermoplastics and/or thermosets
- Low processing temperatures (for thermoplastics only)

Nevertheless, this material class exhibits some obvious disadvantages as well, such as

- Low elastic modulus (E)
- Brittleness at low temperatures

In the construction industry sector that (thermo-) plastics have found use in (drinking) water pipes, and in particular polyvinylchloride (PVC), high density polyethylene (HDPE), medium density polyethylene (MDPE), polybutylene (PB) and crosslinked polyethylene (PE-X or PEX). In this application, thermoplastic pipes compete with pipes manufactured out of other construction materials such as steel, iron, copper, concrete or clay. Of these materials, PO-based pipes offer the following advantages [7-9]

- Lower material cost
- Lower installation cost (due to lower density)
- Flexible material (ease of installation via horizontal direct drilling)
- Inert against many chemicals
- Corrosion resistant (and hence service lifetimes exceeding 50 years)

Despite these advantages thermoplastics in general are not inert enough (intrinsically) to withstand the oxidation effects which take place (during melt conversion at elevated temperature) and in-service-use of the solid plastic product (at moderate temperatures). Long durability applications of PO are only possible due to use protective chemicals, but these can be the source of organic compounds leaching out of PO into water under extractive conditions. Additionally, it should be noted that while pipes only represent a fraction of the use of thermoplastics (less than 5% in **Figure 1**), packaging applications represent 40% with most of this being related to (indirect) food packaging. The same type of protective chemicals is used in PO packaging applications; hence the danger exists of organic compounds leaching out of PO under extractive conditions.

1.3 Synthesis of Polyolefins

Polyolefins are polymers which are derived from simple alkenes (such as ethylene, propylene, butene, isobutene and 4-methyl-1-pentene), though this study is limited to ethylene and propylene only. Both the properties and stability of PO materials are determined by the chemical structure of the monomers from which they are made, as well as the shape, size, order, and secondary valences of the resultant polymer chains (macromolecules). Given that these features are controlled by the polymerisation process the following sections highlight key mechanisms and technologies and, their implications for properties and stability.

1.3.1 Chemistry of Polymerisation

The chemical reactions available for the build-up of synthetic high molecular weight (HMW) organic polymers depends on the chemical identity of the corresponding low molecular weight (LMW) raw materials (monomer). Monomers with functional end or side groups (e.g., alcohol-, carboxyl-, isocyanate-, amine-) proceed via condensation or addition step reactions (**Figure 2** [3,10,11]). Unsaturated monomers (e.g., ethylene and propylene) react in general via an addition chain reaction. The chain reaction can be initiated in a radical, anionic, cationic, or in a stere-regular manner. The substituent on the unsaturated carbon atoms, along with its ability to donate or withdraw electrons, determines which of the initiation types is possible. The polymerization of ethylene can be initiated in a radical or stereo-regular manner, while propylene can only be initiated in a stereo-regular manner. Stereo-regular initiation can be further subdivided by catalyst system (Ziegler/Natta (Z/N), Chromium-based (Cr) and metallocene (m) or single site catalysts (SSC)).

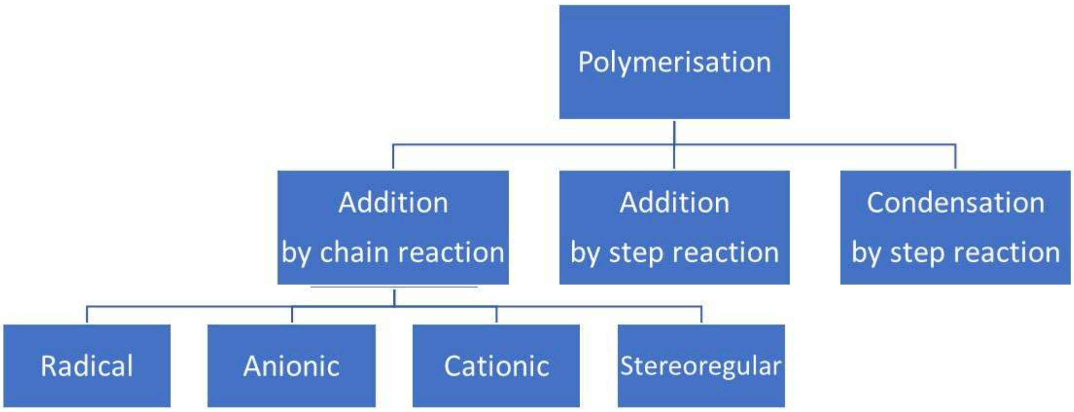

Figure 2: Summary of key mechanisms used in the polymerisation process [3]

1.3.2 Technology of Polymerisation

Various process technologies are suitable to carry out a polymerisation reaction. The principal choices are [3,12]

- Substance or mass polymerisation
- Solution polymerisation
- Precipitation from solution
- Precipitation from mass
- Emulsion polymerisation
- Suspension polymerisation
- Precipitation from suspension

The selection of the process technology impacts the quality and purity of the resulting polymer. Solution and slurry processes carry the risk that LMW organic compounds (LMW alkanes or LMW aromatics) are not eliminated completely from the polymer and remain as impurities. Depending on the details of the finishing section and work-up of the industrial polymerisation procedure, LMW aromatic structures (e.g., benzene, styrene, ethylbenzene) can be present in the final polymer. The amount tends to vary from one batch to the other. The possibility to de-volatise the polymer later-on in the melt-compounding step also varies with the individual industrial plant design.

1.3.3 Effect of Polymerisation Chemistry and Technology on Polymer Properties

The combination of polymerisation chemistry and polymerisation technology defines for ethylene and propylene derived polymers the molecular weight distribution (MWD), dominant (oxidative) degradation mechanism and, need for scavengers for acidic species (**Table 1** [3,13-17]). All three parameters have an influence on organic compounds which could potentially leach out of PO. The catalyst system determines the MWD distribution of polymer chains and hence the type and amount of LMW hydrocarbons (aliphatic) compounds (from any LMW tail in the distribution) which could be extracted from PO [18]. Acidic residues of the catalyst system (e.g., Z/N catalyst supports) require the presence of acid scavengers. Acid scavengers are modifiers, different in chemical nature to required protective chemicals and constitute an additional source for the origin of extractable compounds. For the combination Cr-catalyst and slurry process (due to a limited hydrogen response for the termination reaction) the dominant oxidative degradation reaction below a (processing) temperature of ~ 230 to 240 °C is crosslinking (re-combination of macromolecular radicals [19]). Processing temperature and vinyl concentration determine whether the major (net) oxidative degradation pathway is chain scission (molecular weight reduction), or crosslinking (molecular weight increase) [20]. Few LMW aliphatic compounds are formed under these conditions. In contrast, in Z/N catalysed PO in general chain scission dominates. The frequency of chain scission (β-scission) in PO determines the amount of LMW aliphatic compounds which could be formed and potentially be extracted.

More detailed descriptions of PO synthesis and mechanisms are available elsewhere [3,13,21-24]. Where high mechanical strength and/or service life operating temperatures, close to the softening range of PO are required, the thermoplastic PO can be concerted via an intentional crosslinking reaction into a thermoset.

Table 1: Chemistry and technology of polymerisation of ethylene (a) and propylene (b) [3,17]

<table>
<tr><th colspan="2">Polymerization Chemistry</th><th colspan="4">Polymerization Technology</th></tr>
<tr><th></th><th>Catalyst / Initiator</th><th>Solution</th><th>Slurry</th><th>Mass (gasphase)</th><th>Mass (liquid)</th></tr>
<tr><td>Radical</td><td>Peroxide, Oxygen</td><td></td><td></td><td></td><td>Very broad MWD
LSC Recombination</td></tr>
<tr><td>Stereo-Regular</td><td>Z/N</td><td colspan="3">Medium MWD
Chain scission (β-scission)
Acid scavenger</td><td></td></tr>
<tr><td></td><td>Cr</td><td></td><td colspan="2">Broad MWD
Crosslinking</td><td></td></tr>
<tr><td></td><td>m / SSC</td><td>Narrow MWD
Chain scission
Acid scavenger ?</td><td></td><td>Narrow MWD
Chain scission
Acid scavenger</td><td></td></tr>
</table>

(a)

<table>
<tr><th colspan="2">Polymerization Chemistry</th><th colspan="4">Polymerization Technology</th></tr>
<tr><th></th><th>Catalyst / Initiator</th><th>Solution</th><th>Slurry</th><th>Mass (gasphase)</th><th>Mass (liquid)</th></tr>
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<tr><td></td><td>Cr</td><td></td><td></td><td></td><td></td></tr>
<tr><td></td><td>m / SSC</td><td></td><td></td><td colspan="2">Narrow MWD
Chain scission
Acid scavenger</td></tr>
</table>

(b)

1.4 Modification of the Properties of Polyolefins

Most synthetic thermoplastic polymers, including PO, are not used in the form they exit the polymerisation reactor. Major modifications take place in post-synthesis operations, adding additional complexity to the final material. These can be subdivided into intentional (and hence wanted) modifications and un-intentional (but unavoidable) changes which must be balanced against them [3,25]. Intentional modifications can be achieved via additional modification of MW (e.g. crosslinking reactions [26]), orientation of macromolecules during melt-processing [27,28] and addition of chemicals (modifiers) which alter the properties of the organic substrate [29,30]. A further sub-division into modification of bulk and surface properties is possible. Selected examples of surface modifications are

- Appearance (e.g., pigmentation, texture)
- Surface conductivity
- Slip and anti-block properties
- External lubrication and mould release

Selected examples of bulk property modifications are

- Mechanical properties (via orientation of the macromolecules or via nucleating agents, fibre re-enforcement and fillers)
- Transparency (of the plastic article)
- Internal lubrication and plasticisation
- Flammability
- Controlled rheology
- Crosslinking

Most intentional modifications are optional and not mandatory. Intentional modifications can therefore be avoided in case of a negative impact onto the purity of the polymer. In contrast, the sum of all non-intentional chemical, physical and mechanical modifications over time is referred to as aging [25] and cannot be avoided.

1.5 Aging of Polyolefins

Among the non-intentional modifications of polymers are structural modifications, often constituting an irreversible change [33]. Such chemical changes can be subdivided into oxidative, thermal (in the absence of oxygen), solvolysis, mechanical and biological degradation (or aging as a function of time) (**Figure 3** [32]).

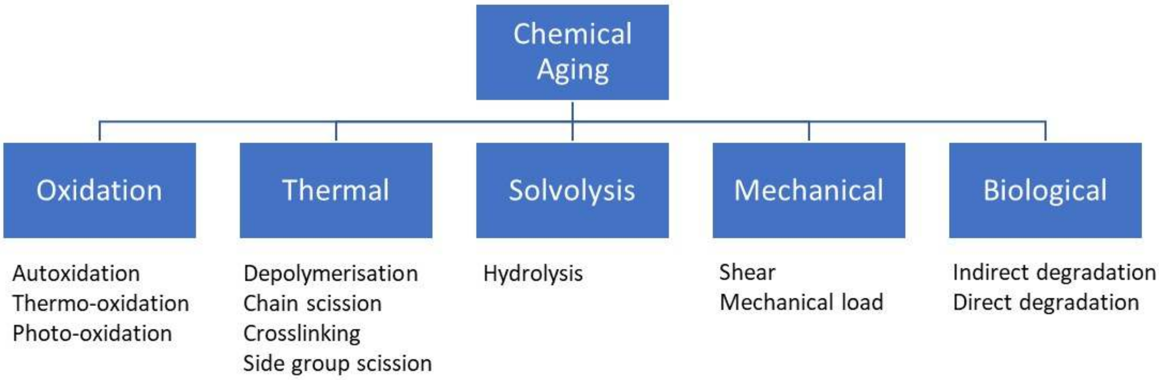


Figure 3: Chemical aging of polymer materials [32]

Each of these aging mechanisms leads to the scission of covalent bonds, either in the backbone of the macromolecule or in any side chains. Observable consequences are

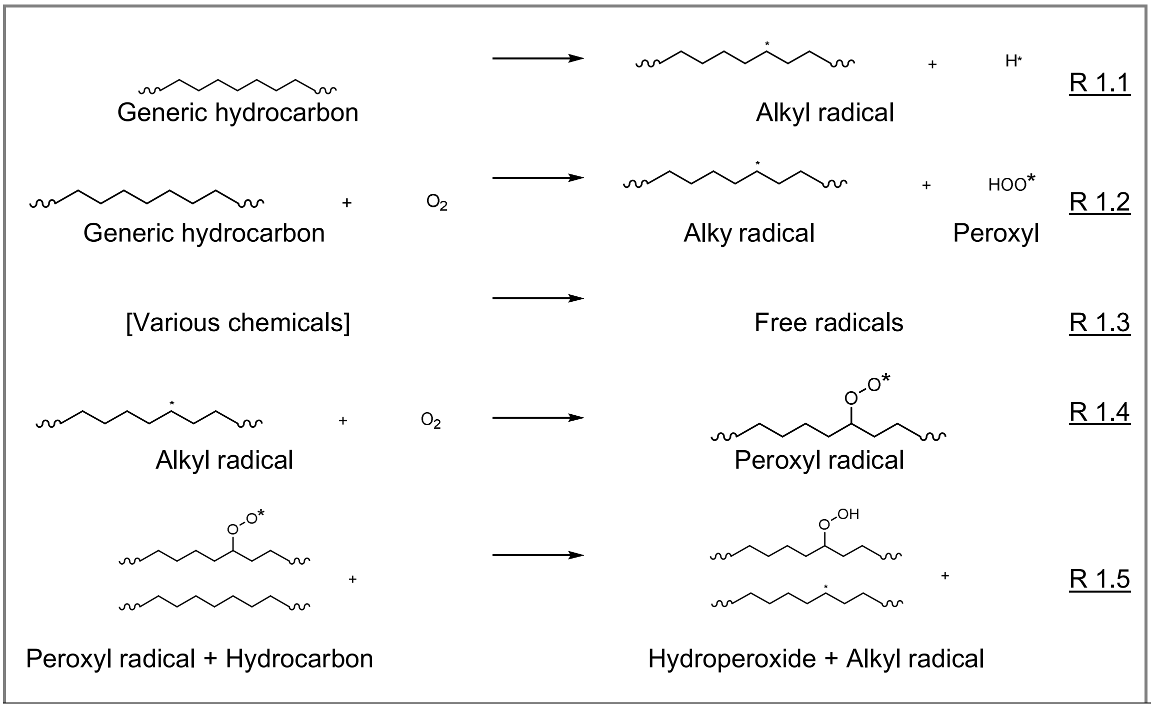
- Changes in molecular weight (MW)
- Formation of functional groups
- Formation of low molecular weight products

In contrast to many other organic (polymeric) substrates, PO ages mainly by oxidative (radical chain degradation) routes with varying initiation mechanisms [34].

1.5.1 Basic Principles of Autoxidation

Oxygen is a triplet in the ground-state and readily participates in free-radical reactions with organic substrates. The reactive oxygen species generated propagate further radical reactions, so the process is often referred to as auto-oxidation (**autoxidation**). It was initially described by Bolland and Gee, who studied rubber oxidation[33] and later refined to encompass organic polymers in plastic applications[33,35,36], coatings & adhesives[37,38], as well as LMW or HMW lubricant & fuel oxidation[39,40] and preservation of lipids in food[41] and cosmetics[42].

Significant differences do exist in the concentration profiles of oxygenated species formed in autoxidation and in the rate of oxidation reactions. This is due to the specific structure and physical form of an organic material, along with oxygen pressure and temperature profile. Despite this, the generic radical chain mechanism of autoxidation can be divided into four stages: chain initiation, chain propagation, chain branching or transfer, and chain termination (represented in **Scheme 1**).



Scheme 1: General description of autoxidation[33]

1.5.1.1 Chain initiation

Various reactions can lead to the abstraction of a hydrogen from the polymer chain and the formation of an alkyl radical (R 1.1, R 1.2 and R 1.3, **Scheme 1**). This reaction is relatively slow [43,44] unless catalysed by metal ions [45].

The site of the hydrogen abstraction depends on the strength of the C-H bond and the probability of abstraction increases from left to right in **Figure 4**.

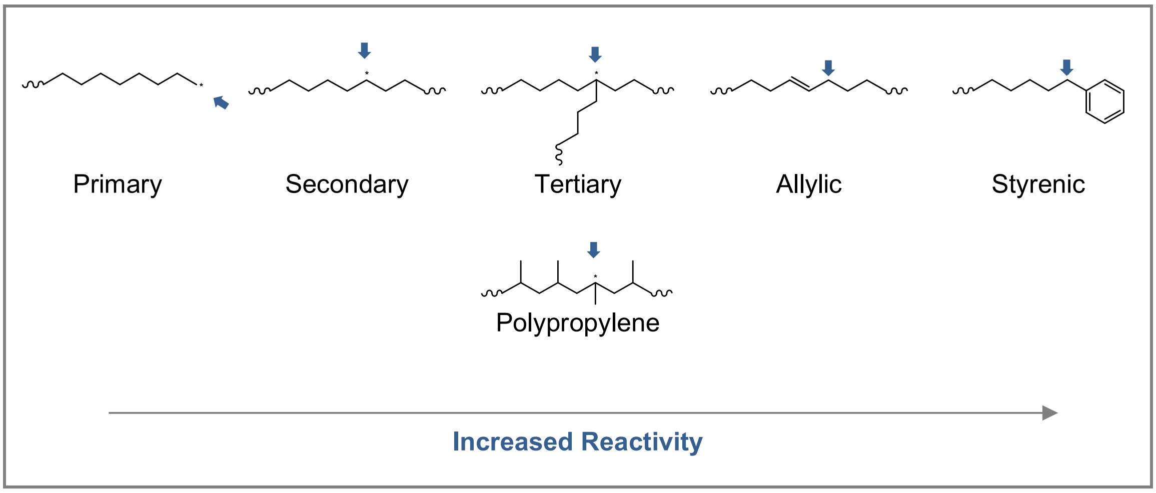


Figure 4: Reactivity of hydrocarbons towards hydrogen abstraction [40]

1.5.1.2 Chain propagation

The alkyl radical reaction with oxygen is very fast (large rate constant) resulting in the formation of an alkyl peroxyl radical (R 1.4, **Scheme 1**).

The specific kinetics depend on the substituents of the carbon atom carrying the radical site and increases in **Figure 5** from left to right. The alkyl peroxy radical abstracts a hydrogen from another hydrocarbon (R 1.5) to result in a hydroperoxide and another alkyl radical (which can further react according to R 1.4). Reaction R 1.5 is relatively slow and constitutes therefore the rate determining step of the oxidation reaction. Due to the low reactivity and energy level of peroxyl radicals, a selective reactivity of peroxyl radicals is observed.

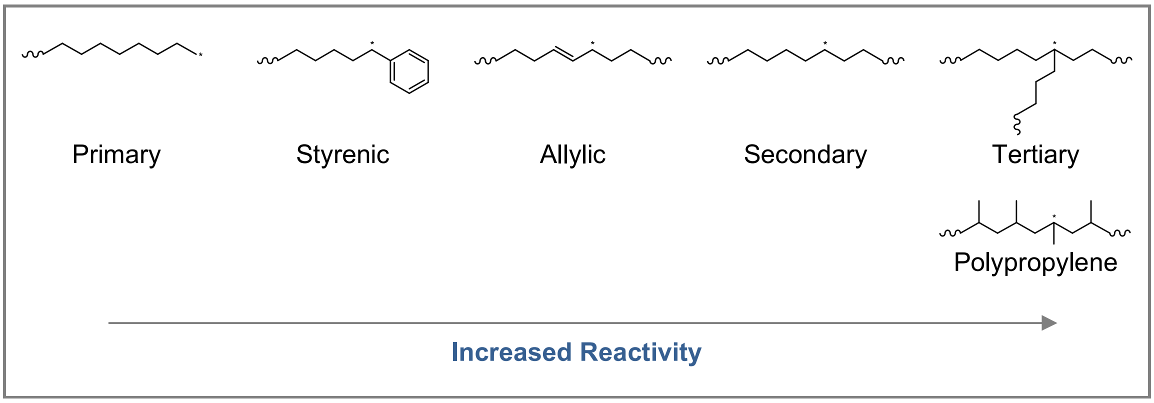
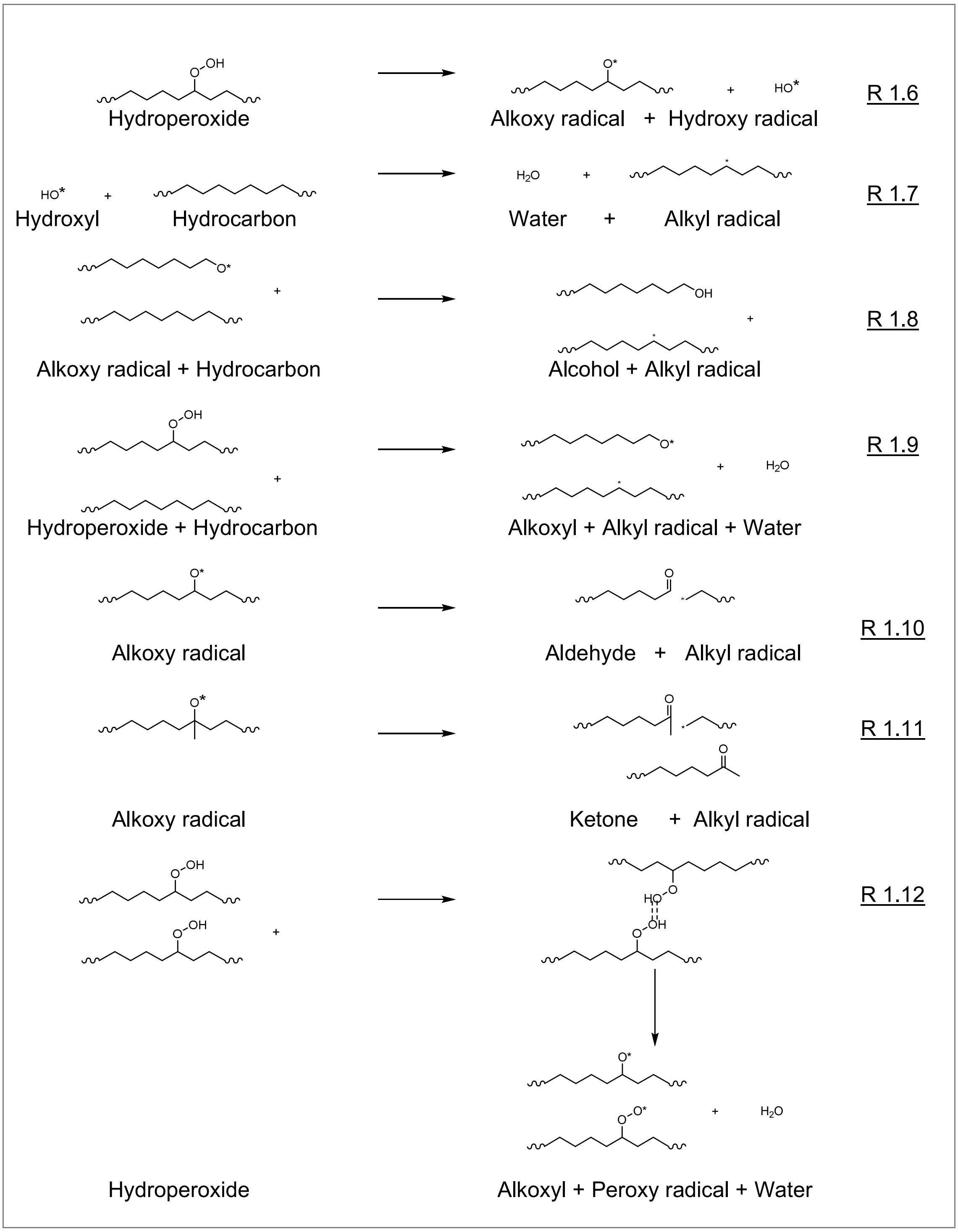


Figure 5: Reactivity of alkyl radicals with oxygen

1.5.1.3 Chain branching or transfer (**Scheme 1b**)

Hydroperoxides can decompose by homolytic scission to form alkoxy radicals and hydroxy radicals (R 1.6). The moderate speed of the reaction is significantly accelerated at elevated temperature, under the influence of high energy radiation, and in the presence of selected metal ions. The highly reactive hydroxy and primary alkoxy radicals abstract further hydrogens from other chains in a random manner (R 1.7 to R 1.9). Primary alkoxy radicals R 1.8 produce hydrocarbons with an alcohol end-group. In contrast, secondary alkoxy radicals yield mainly aldehydes (R 1.10); while tertiary alkoxy radicals result in ketones (R 1.11 [46-49]). At high peroxide concentrations, an additional bi-molecular reaction is possible (R 1.12). Continued formation of hydroperoxides and their corresponding cleavage leads, after an induction period, to an exponential increase in radicals in an auto-catalytic and hence self-accelerated chain reaction. This phenomenon is depicted in **Figure 6**.



Scheme 1b: Chain branching and transfer steps in autoxidation (extension of **Scheme 1**) [33]

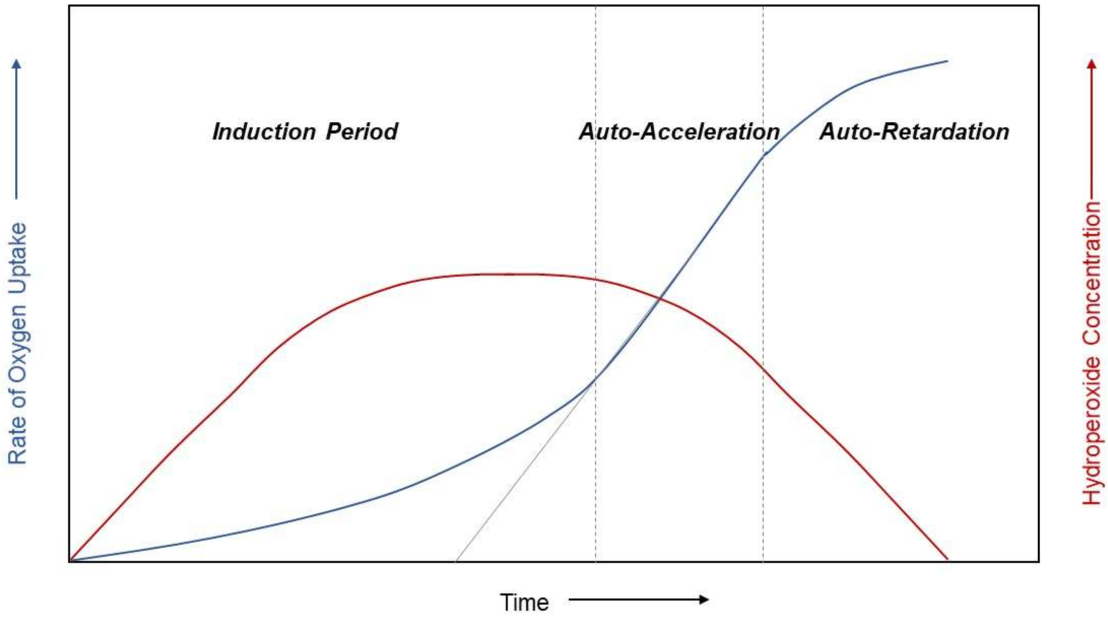
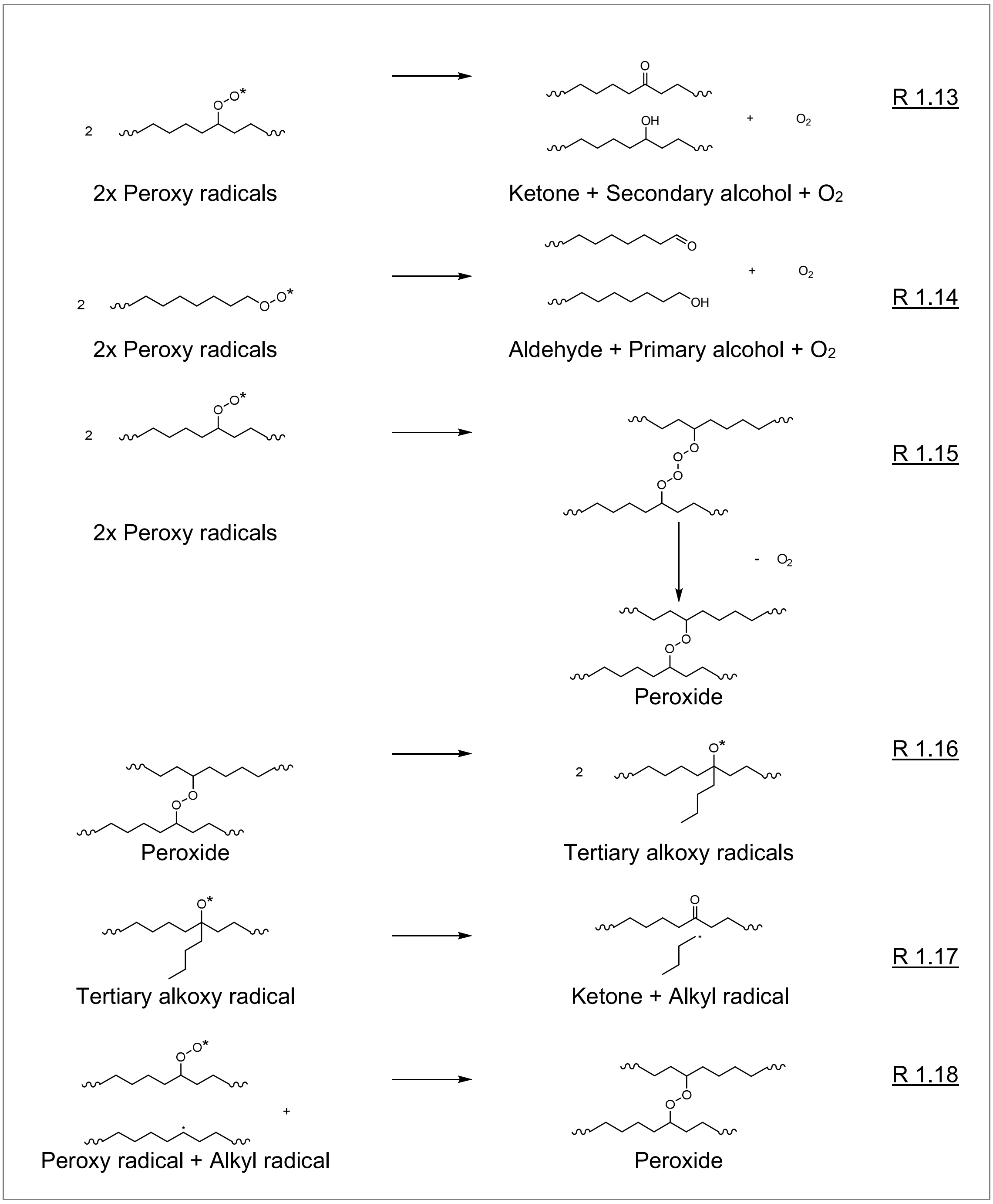


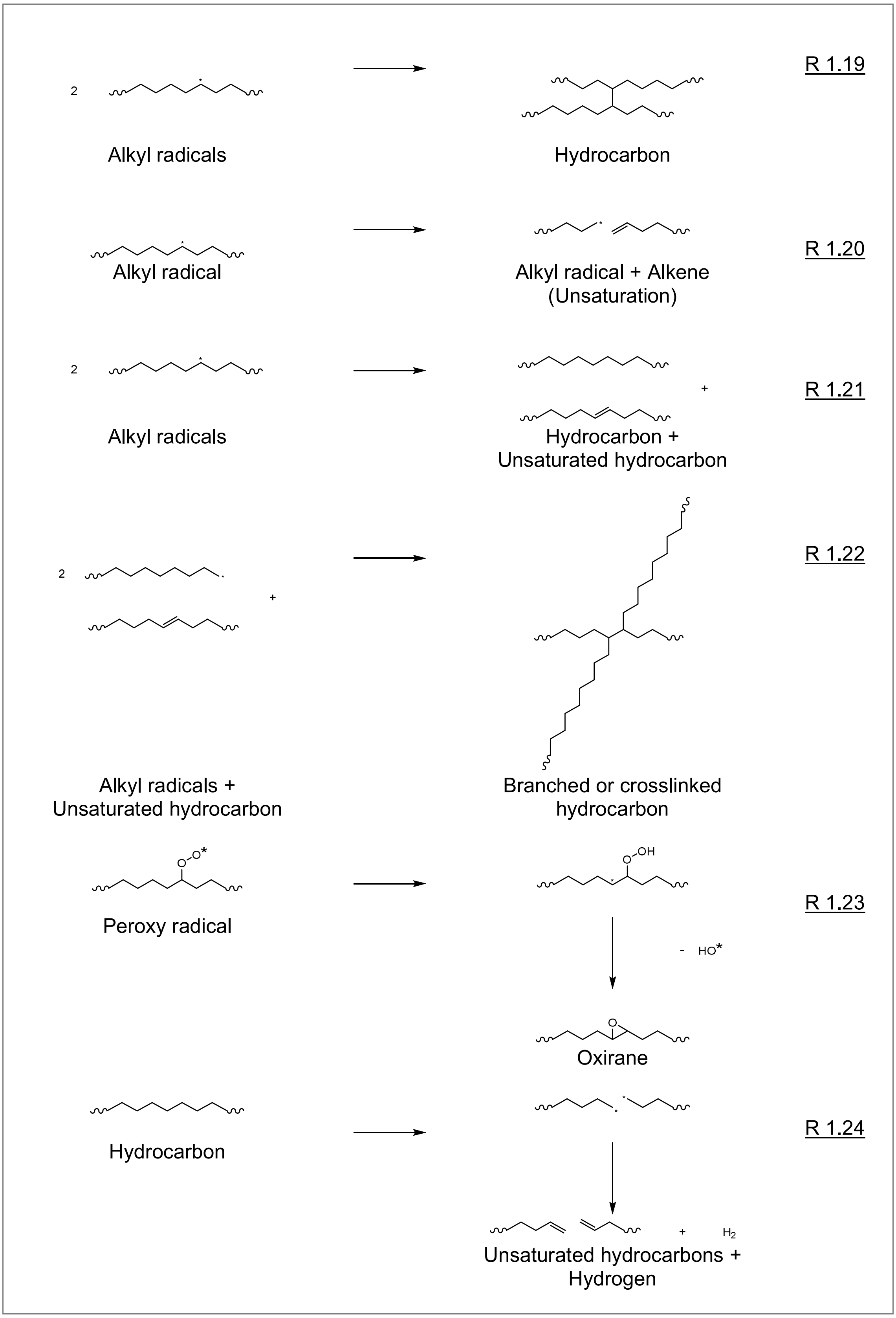
Figure 6: Conceptual visualisation of oxygen uptake and hydroperoxide concentration in an organic matter during oxidative aging [40]

1.5.1.4 Chain termination (**Scheme 1c** and **Scheme 1d**)

At high concentrations of radicals, recombination reactions of radicals become more important, ultimately in a slowing down of the oxidation reaction. The recombination of primary (R 1.13) and secondary alkylperoxy radicals (R 1.14) generates non-radical products; among which are aldehydes and primary alcohols (R 1.13); as well as ketones & secondary alcohols. In contrast, tertiary alkylperoxy radicals either recombine (under oxygen elimination) to peroxides (R 1.15 & R 1.16) or alternatively yield ketones and alkyl radicals (R 1.15 & R 1.17). Under oxygen deficiency, alkyl peroxy radicals can recombine with alkyl radicals (instead of another oxygenated radical; R 1.18) or two alkyl radicals can recombine (R 1.19). Alkyl radicals can under conditions of oxygen deficiency and limited mobility undergo additional reactions, such as fragmentation into an alkyl (olefin) and an alkyl radical (R 1.20), disproportionation into a saturated & an unsaturated hydrocarbon (R 1.21), as well as a branching reaction with an alkene (R 1.22). At temperatures above 120°C, initiation and propagation steps occur in a similar manner but with an increased rate of reaction and reduced selectivity. Reaction (R 1.6) becomes the most important reaction. Under high temperature and diffusion-controlled conditions, ethers or oxiranes can the formed (R 1.23). Under the same conditions, thermal cleavage of a hydrocarbon is possible and yields unsaturated hydrocarbons (R 1.24).



Scheme 1c: Termination steps of oxygen species in autoxidation (extension of **Scheme 1**) [33]



Scheme 1d: Other termination steps in autoxidation (extension of **Scheme 1**) [33]

Table 2 summarizes the different reactions of the oxidation process for polymers. Chain initiation and propagation reactions result mainly in an increase of radicals and hydroperoxides in the organic substrate. Primary, secondary and tertiary alkyl peroxyl radicals are responsible for the appearance of functional groups (alcohol, aldehyde and ketone) via branching and chain transfer reactions. Termination reactions significantly impact MW and result in a further functionalisation of the polymer chains (alcohol, aldehyde, ketone, ether, oxirane & unsaturation). Several branching and termination reactions can potentially lead to LMW radicals, depending on the specific location of the reaction site on the backbone of the hydrocarbon molecule.

Table 2: Reaction products of oxidation reactions

Reaction	*Radicals*	*(Hydro-) Peroxide*	*Functional Groups*	*Molecular Weight*
R 1.1	↗			
R 1.2	↗			
R 1.3	↗		?	
R 1.4				
R 1.5		↗		
R 1.6	↗	↘		LMW radical
R 1.7				
R 1.8			Primary Alcohol	
R 1.9	↗	↘		
R 1.10			Aldehyde	↘ & LMW radical
R 1.11			Ketone	↘ & LMW radical
R 1.12	↗	↘		
R 1.13			Ketone & Secondary Alcohol	
R 1.14			Aldehyde & Primary Alcohol	
R 1.15	(↗)	(↘)		(↗)
R 1.16	(↗)	(↘)		(↗)
R 1.17			Ketone	↘ & LMW radical
R 1.18	↘	↗		↗
R 1.19	↘			↗
R 1.20			Unsaturation	↘ & LMW radical
R 1.21	↘		Unsaturation	
R 1.22	↘			↗
R 1.23	↘		Ether or Oxirane	
R 1.24	↘		Unsaturation	↘

The location of the oxidised functional groups can in some cases (e.g., reactions R 1.10, R 1.11 & R 1.12) determine the MW of the oxygenated hydrocarbon (oxygenated aliphatic molecule) and for MW below approx. 300 g mol^{-1} (or Dalton) significantly influence physico-chemical properties. This relationship is illustrated for melting point (**Figure 7**) and solubility in n-octanol and water (Log K_{ow}; **Figure 8**). It is evident that the melting behaviour of aldehydes increases significantly with increasing MW for MW below approx. 200 g mol^{-1} and then starts to level off around 300 g mol^{-1}. Solubility in n-octanol and water shows the same behaviour but displays a linear relationship due to the logarithmic function (Log K_{ow}). With increasing Log P_{ow}, aldehydes formed in the hydrocarbon and hence present in, or on, the surface of it will not be soluble anymore in the polar medium "water". The same relationship is valid for other functional groups, such as ketone and alcohol or the corresponding branched isomers. Hydrocarbons with broad MWD may contain, from the beginning, very mobile LMW molecules which after oxidation are rather polar (Log K_{ow} approx. < 5) and hence water soluble.

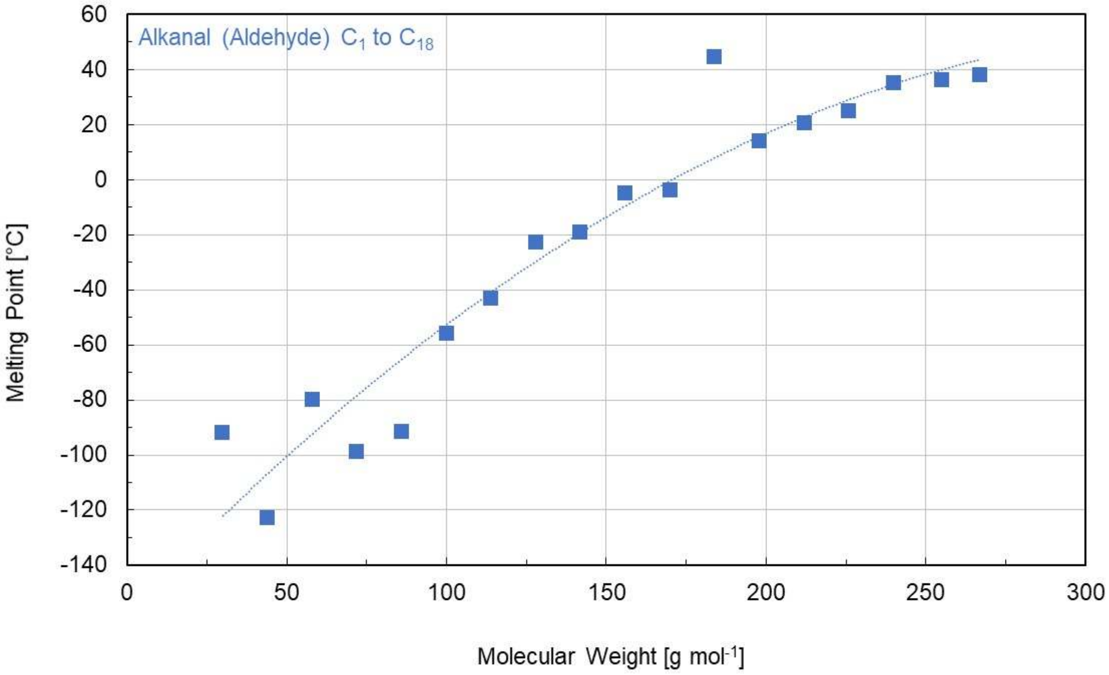


Figure 7: Melting point versus molecular weight of aldehydes

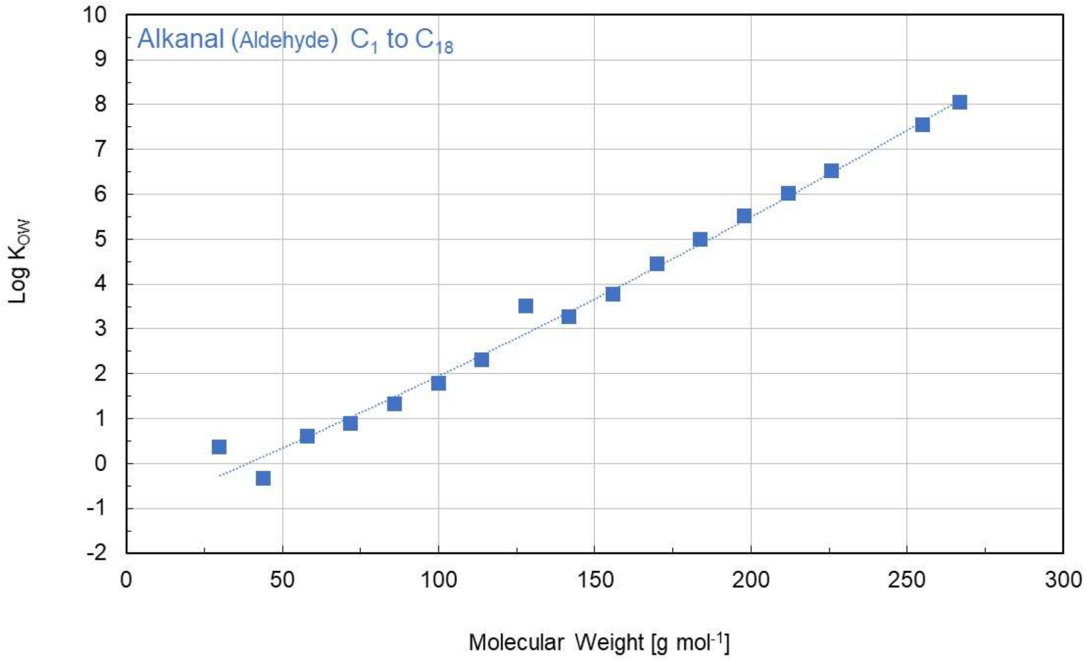


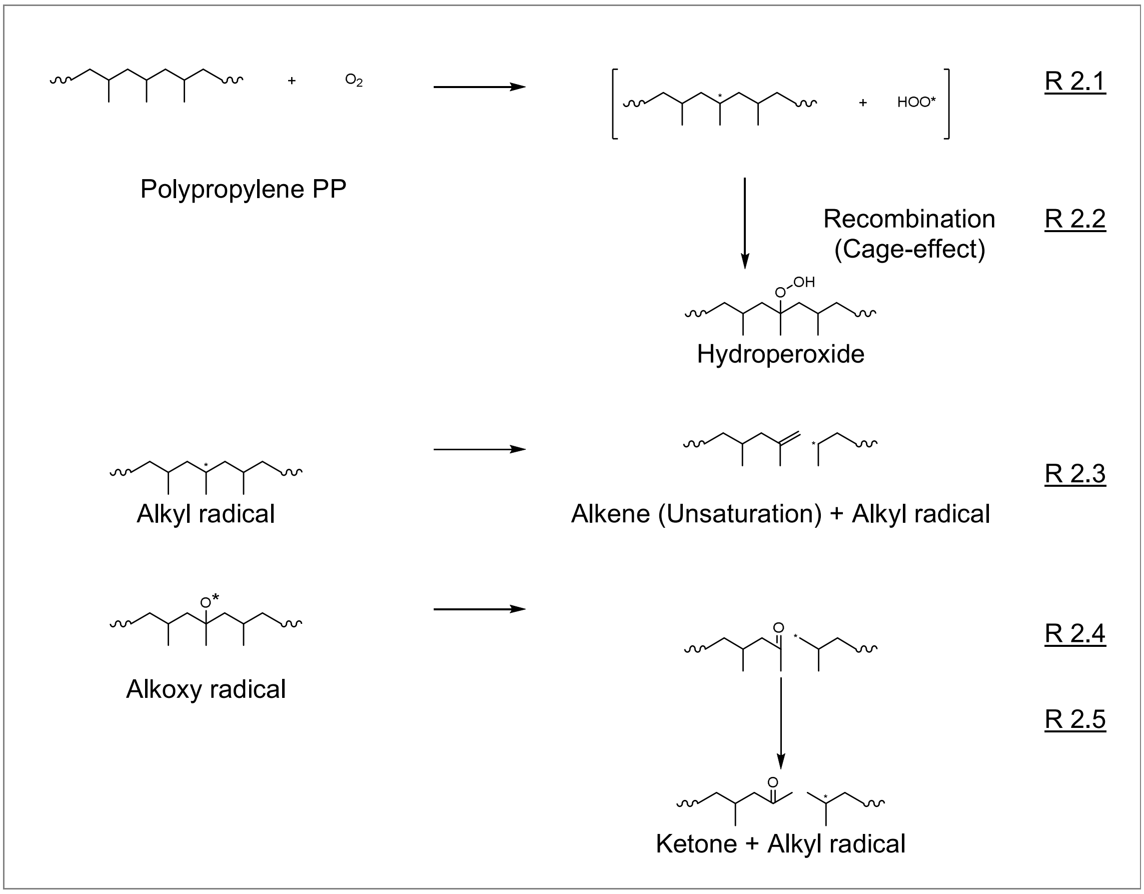
Figure 8: Log K_{ow} versus molecular weight of aldehydes

1.6 Specific Aspects of the Oxidation of Polypropylene

PP is a specific representative of hydrocarbons, characterized by a high molecular weight and a medium-broad MWD. Every second carbon in the main chain is a tertiary carbon due to the presence of the methyl side groups. It is a thermoplastic material and hence mixed and shaped in the molten state around 190 to 250 °C and useable up to a service life temperature of ~ 90°C (HDT Heat distortion temperature) to 110°C.

Therefore, the basic principles of autoxidation also apply to PP with some adjustment for the high number of tertiary carbons in the hydrocarbon, MWD and the two physical states of high viscosity melt (and corresponding shear; resulting from the HMW) and solid state under the use condition of the plastic article. The limited mobility of the PP macromolecule allows an additional chain initiation reaction (R 2.1 & R 2.2 in Scheme 2). Molecular oxygen can abstract a hydrogen from the PP macromolecule. Due to a cage effect an immediate recombination is possible which yields a macromolecular peroxide. This peroxide will feed into reaction R 1.6.

Recombination reactions of carbon-centred or oxygen-centred PP macroradicals (R 1.15 to R 1.19) are disfavoured due to the steric hinderance of the methyl side groups. Therefore, the dominant reaction which impacts the MW of PP and result in a decrease of MW is the β-scission of a carbon-centred (R 1.18) tertiary alkoxy macro radical (R 1.11). Both these generic reactions, depicted specifically for PP, are given in **Scheme 2** (R 2. 3 & R 2.4).



Scheme 2: Selected (auto-) oxidation reactions characteristic for PP

Scheme 1 and **Scheme 2** relate to the theoretical chemistry of oxidation. However, in practice, the oxidation of PP is rather complex, and the type and concentration of oxidation and degradation products formed depends on many factors. Principally the stage in the life cycle of the PP (e.g., monomer, polymerisation, or the melt-processing of PP or, even later-on the service life, with or without exposure to UV light is considered). In addition, parameters like physical state, temperature, exposure time and certainly oxygen availability can vary significantly (**Table 3**). In consequence, the speed of the chain initiation rate, the preferred type of radical formed as well as the concentration and decomposition rate of peroxides will vary significantly (**Table 4**).

Table 3: Various conditions during the life cycle of polypropylene [50]

				Service Life		
	Monomer	*Polymerisation*	*Processing*	*Heat Ageing*	*Outdoor*	*Fatigue*
Physical State of the Polymer	Liquid/Gas	Various	Melt	← Solid →		
Temperature [°C]	Room temp.	70 - 320	150 - 320	-30 - 150	≤ 60	≤ 80
Exposure Time	Hours/Months	Minutes	Minutes	← Hours/Years →		
Oxygen Availability	?	← Deficiency →		Saturation Equilibrium (“Excess”)		

Table 4: Various conditions during the life cycle of polypropylene [50]

				Service Life		
	Monomer	*Polymerisation*	*Processing*	*Heat Ageing*	*Outdoor*	*Fatigue*
Rate of Initiation	Low	Low	High	Low	High	High
Initiation Species			Shear	Heat	Peroxide Photolysis	Shear
Radical Species			[R*] > [ROO*]	[ROO*]>>[R*]	[R*] = [ROO*]	[R*] = [ROO*]
[ROOH] Concentration			Low	← High →		
[ROOH] Decomposition			Fast	Moderate [$f_{(T)}$]		

According to **Table 1**, a PP manufactured with Z/N catalyst results in a medium (to broad) molecular weight distribution MWD. For this type of polymeric hydrocarbon, the occurrence of chain scission increases with the severity of melt-processing (time, temperature and shear) and the MW. At the higher end of the MWD, the largest macromolecules preferentially undergo chain scission; while on the LMW side, chain scission occurs randomly [51]. As a result, in Z/N PP random oxidation and subsequent β-scission of LMW hydrocarbons cannot be avoided. The resulting oxidized aliphatic compounds (see **Table 2**) are more likely to show a low(er) Log P_{OW}, independent of the exact location of the oxygen attack.

The ***oxidative degradation mechanism outlined here occurs not only within the PP matrix but with any organic-based additives incorporated into the matrix*** (such as metal soaps or amides of fatty acids, fatty acid alcohols, fatty acid glycerols, etc.).

1.7 Prevention of Oxidative Degradation in Polypropylene

Many strategies exist to prevent or at least slow down the oxidation of a (polymeric) organic substrate (**Figure 9**). Some are related to the exclusion of oxygen, reduction of diffusion rate of oxygen and the general reduction of the reaction rate of all chemical reactions. One fundamental stabilization strategy is to offer *alternative reaction pathways* by incorporating organic additives that react more quickly (compete) with polymer radical species (in this report these are referred to as protective chemicals). Given that oxidative degradation mechanisms occur not only within the PP matrix but with additives incorporated into the matrix, an appreciation of the mechanisms by which protective chemicals act and any transformations of their structure is given in this section.

The specific stabilisation strategies involving protective chemicals are

- Removal of alkyl (macro) radicals
- Removal of alkyl peroxy (macro) radicals
- Removal of hydroperoxides

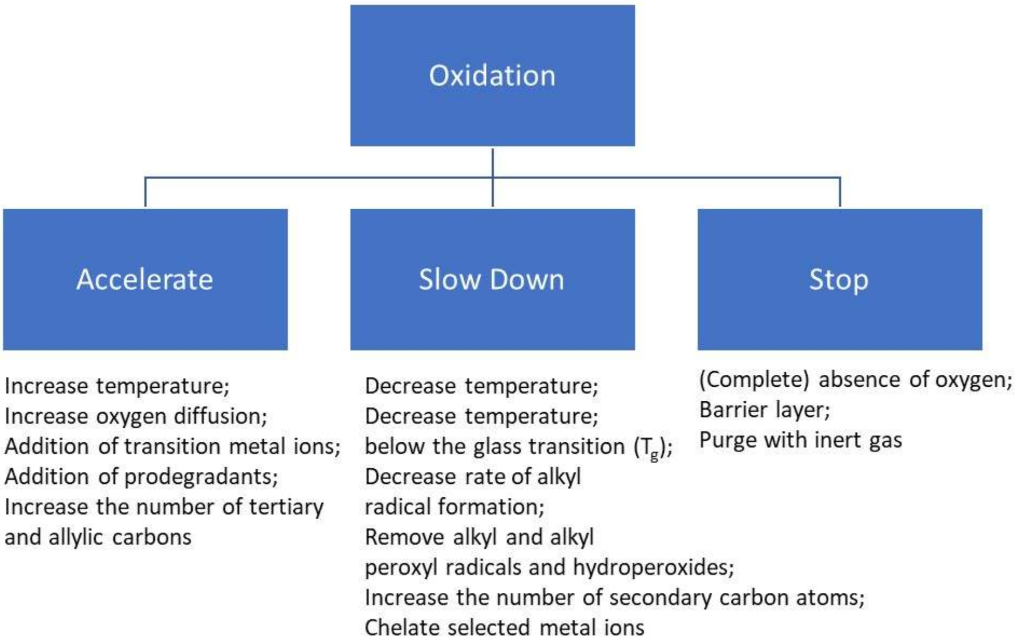
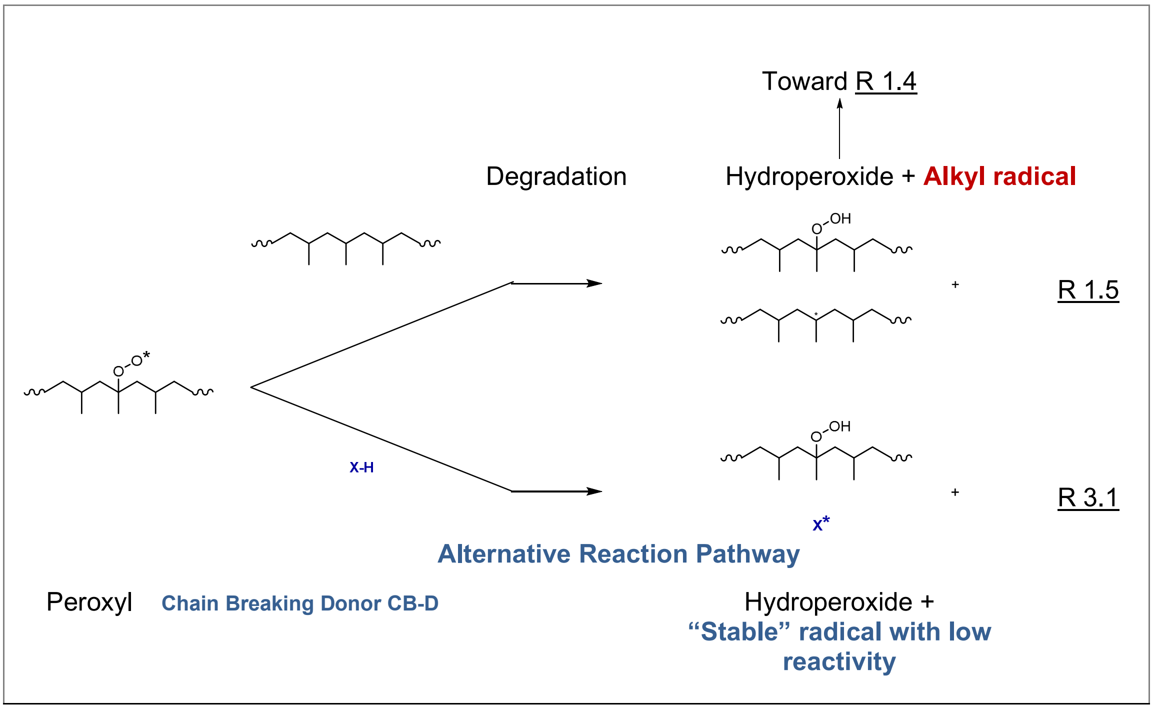


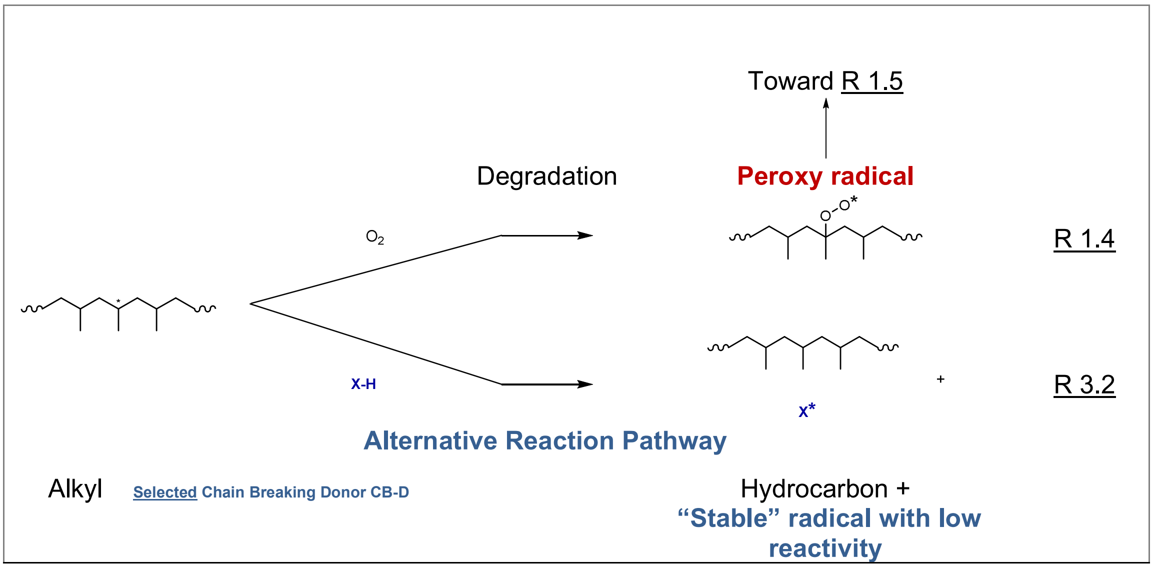
Figure 9: Strategies to influence the oxidation of polymeric organic matter [31]

Removal of alkyl peroxy (macro) radicals is considered a (degradation) *chain breaking* mechanism, as it slows down the rate determining chain propagation reaction R 1.5 via an alternative reaction pathway. This is achieved via the addition of a (protective) chemical which can donate a labile hydrogen, which subsequently forms a radical with low reactivity. The corresponding mechanism is referred to as *chain breaking donor CB-D* mechanism (Reaction R 3.1 in **Scheme 3** [50,52]). The protective chemical competes with (many) tertiary carbons on the polypropylene backbone for the reaction with the alkyl peroxy (macro) radical. In the presence of specific structural features of the CB-D protective chemical, the bond dissociation energy of the "labile" hydrogen is so low, that the alternative reaction R 3.2 can compete with the very fast reaction of an alkyl (macro) radical with oxygen (R 1.4). In this case, the protective chemical competes with oxygen for the reaction with an alky (macro) radical. Reactions R 3.1 & R 3.2 can be favoured over reactions R 1.5 & R 1.4 by [53]

- Early addition of CB-D protective chemical
- Fast homogenisation of CB-D protective chemical throughout the PP matrix
- High concentration of CB-D
- High molar activity of CB-D
- Very labile hydrogen (very low bond dissociation energy)
- Low reactivity of resulting radical (inverse proportional to above statement)

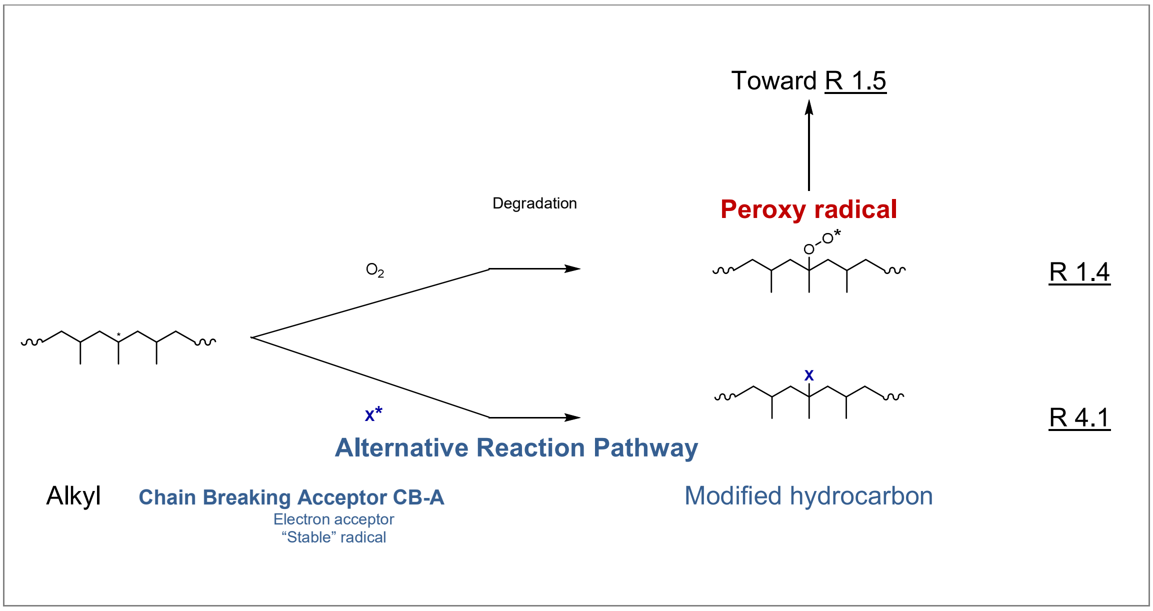


Scheme 3: Alternative reaction pathway with CB-D (modified from [53])

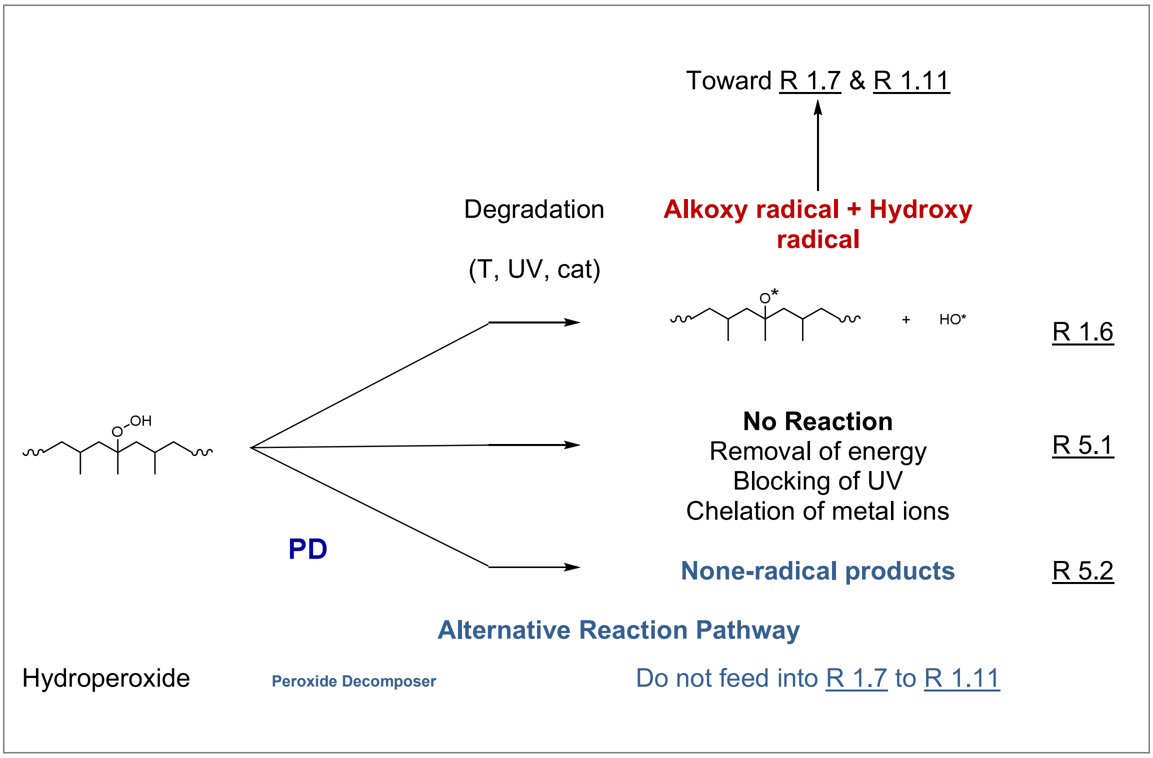


Scheme 3b: Alternative reaction pathway with selected CB-D (modified from [53])

Alternatively, alkyl (macro) radicals can be removed by reaction with an electron acceptor, and hence is referred to as *chain breaking acceptor CB-A* mechanism. This mechanism is favoured under conditions of high concentration of alkyl radicals and oxygen deficiency. Typical representatives are (strong) oxidizing agents and stable radicals. CB-A protective chemicals compete with oxygen (reaction R 1.4) for reaction with alkyl radical (R 4.1) (**Scheme 4**). The CB-A mechanism is favoured by the same parameters as the CB-D mechanism and additionally by oxygen deficiency, which results in alkyl radicals dominating over alkyl peroxy radicals. Reaction R 1.6 (and to a certain degree R 1.12) lead to a significant increase of oxygen-centred radicals in the organic substrate. Any compound which pro-actively removes either hydroperoxides or decomposes hydroperoxides without the formation of free radicals will slow down reaction R 1.6. This mechanism is referred to as *preventive peroxide decomposition PD*. The available alternative reaction pathways are outlined in **Scheme 5**.



Scheme 4: Alternative reaction pathway with CB-A (modified from [54])



Scheme 5: Alternative reaction pathway with PD (modified from [55])

A large variety of classes of protective chemicals which can provide alternative reaction pathways (**Scheme 3**, **Scheme 4**, and **Scheme 5**) has been proposed in the literature. An overview over selected classes is given in **Table 5** [39-41,50,56-60]. Due to regulatory restrictions, this study focuses initially on only four classes of protective chemicals

- Hindered Phenols (HP)
- Hindered Amine Stabilizers (HAS)
- Phosph(on)ites (P)
- Hydroxylamine (HYA)

Table 5: Stabilisation mechanisms provided by selected classes of protective chemicals

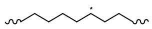
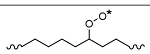
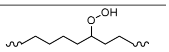
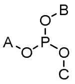
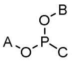
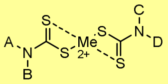
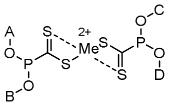
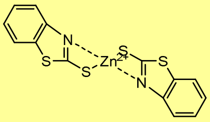
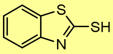
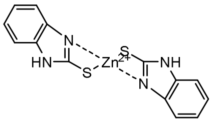
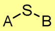
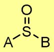
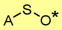
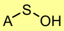
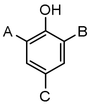
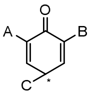
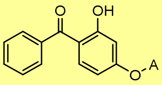
Class	*Generic Structure*	*#*	*CB-A*	*CB-D*	*PD*
					
Phosphite Ester				● Aromatic	●
Phosphonite Ester				● Aromatic	●
Metal Dithiocarbamate					●
Metal Dithiophospate					●
(Metal) Mercapto-Benzotiazole				●	●
					●
(Metal) Mercapto-Benzimidazole				●	●
Sulfide Thioester					●
					●
			● “Stable” radical		
				●	
Hindered Phenol HP			● Selected molecules	●	
				●	
Benzophenone				● Secondary effect (UV filter)	

Table 5b: Stabilisation mechanisms provided by selected classes of protective chemicals

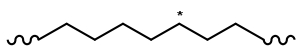
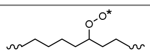
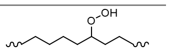
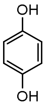
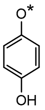
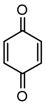
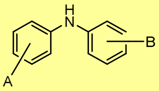
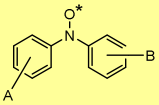
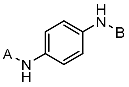
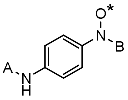
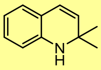
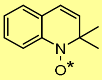
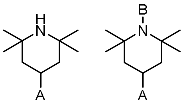
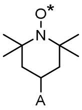
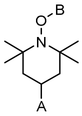
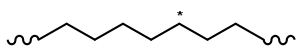
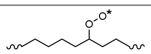
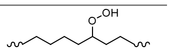
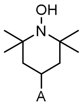
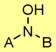
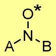
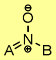
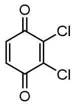
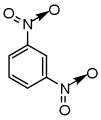
Class	*Generic Structure*	*#*	*CB-A*	*CB-D*	*PD*
					
(Hindered) Hydroquinone				●	
			●		
			●		
Diphenylamine DPA			●	●	
			●		
Paraphenylene- Diamine PPD			●	●	
			●		
Trimethyl- Hydroquinoline TMQ				Must be activated	
			●		
Hindered Amine Stabilizer HAS				Must be activated	
			●		
	 NOR-HAS		●		

Table 5c: Stabilisation mechanisms provided by selected classes of protective chemicals

Class	Generic Structure	#	CB-A	CB-D	PD
					
Hindered Amine Stabilizer HAS				●	●
Hydroxylamine				●	●
			●		
			●		
(Selected) Oxidizing Agents			●		
			●		
	…				
Selected Metal ions Cu^{+}/Cu^{2+} Organo copper				●	
Organo molybdenum				●	● Mo-Dithiocarbamate
Organo boron Boric acid ester				● Aromatic	●
Carotenoids	Carotenes			● Secondary effect (Addition to unsaturation) (Singlet oxygen scavenger)	
	Xanthophylls			●	
	…				

The four classes of protective chemicals warrant a more detailed discussion. **Figure 10** shows the window-of-operation related to temperature of the four classes of protective chemicals [61]. Considering a typical PP melt processing range of 190 to 250°C [62] and a service life temperature range between -25 to 70°C (depending on the end application [63]), only the class of HP covers the entire temperature range, so is suitable as protective chemical during melt processing and service life. As such, HP must be able to cope with the *contradicting requirements for protective chemicals* which result directly from the different oxidation conditions (outlined in Table 3 and 4 [50]). Note, HAS is not able to interfere with the oxidation reaction at temperatures above 120°C. However, in contrast, the classes of P & HYA do interfere with the oxidation reaction under melt processing conditions.

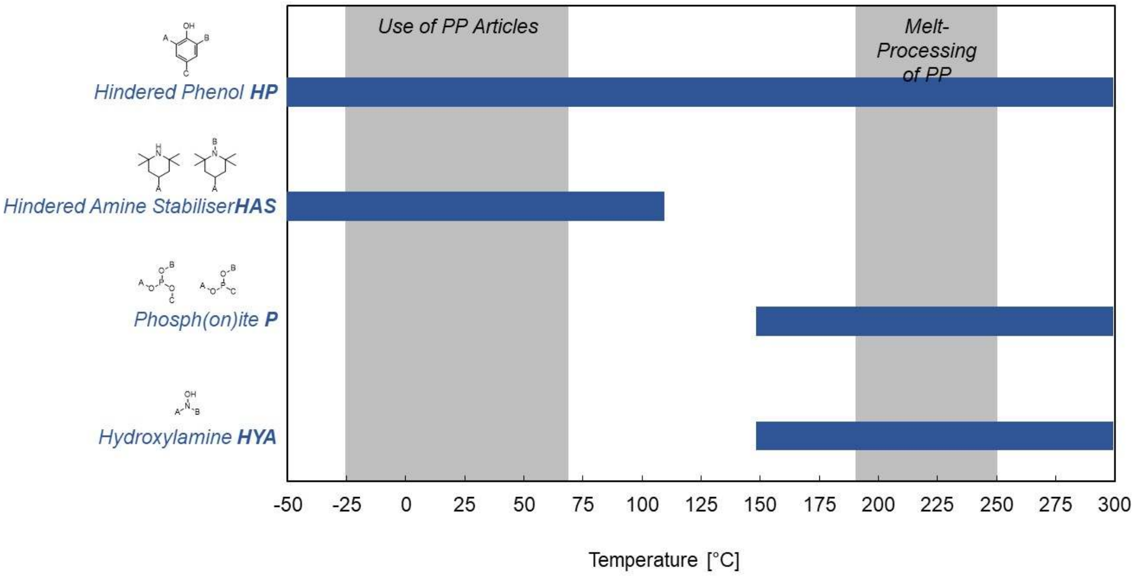
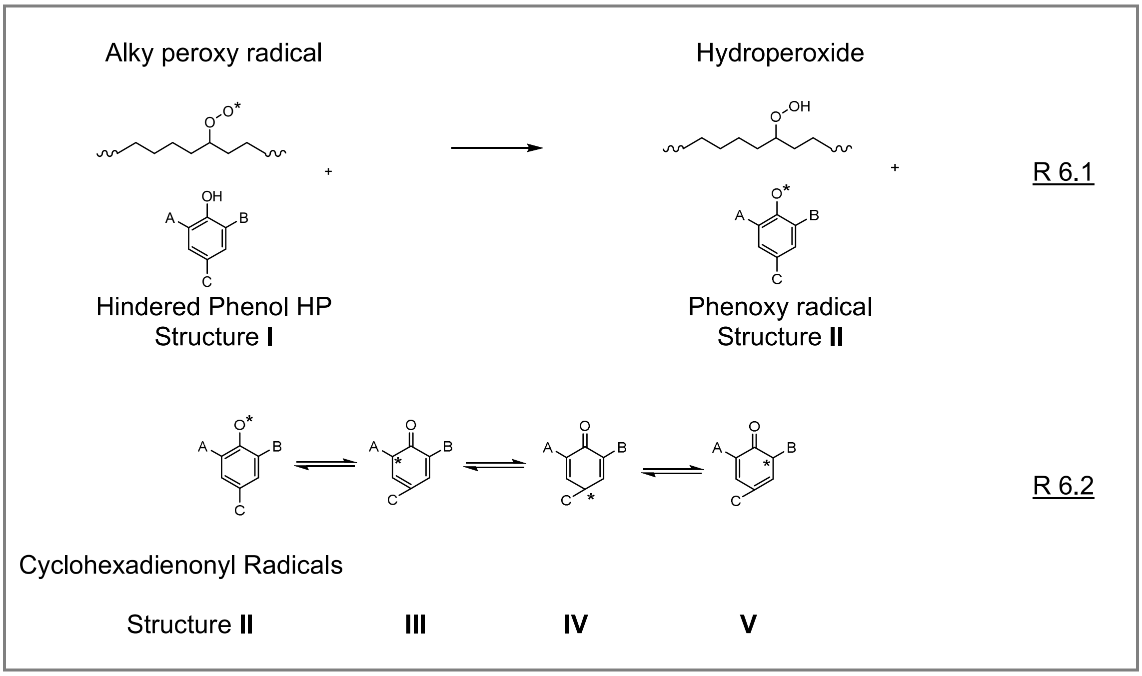


Figure 10: Temperature range of selected stabilizer classes [61]

1.7.1 The Chemistry of Hindered Phenols (HP)

The principal reaction of a CB-D with an alkyl peroxy radical (R 3.1) is reprinted in **Scheme 6** as R 6.1 for the class of protective chemicals of HP. The transfer of a hydrogen results in a phenoxyl radical (Structure II) which is subsequently stabilised via a mesomeric effect; respectively the formation of cyclohexadienonyl radicals (Structures II to V; R 6.2). The kinetics of reaction R 6.1 and the magnitude of the mesomeric effect via R 6.2 is influenced by the nature of the substituents A and B in ortho position of the phenolic group [64-66]. The substituent in the *para*-position influences additionally the range of *primary and secondary reaction (or transformation) products of HP* [67]. Four different cases are possible

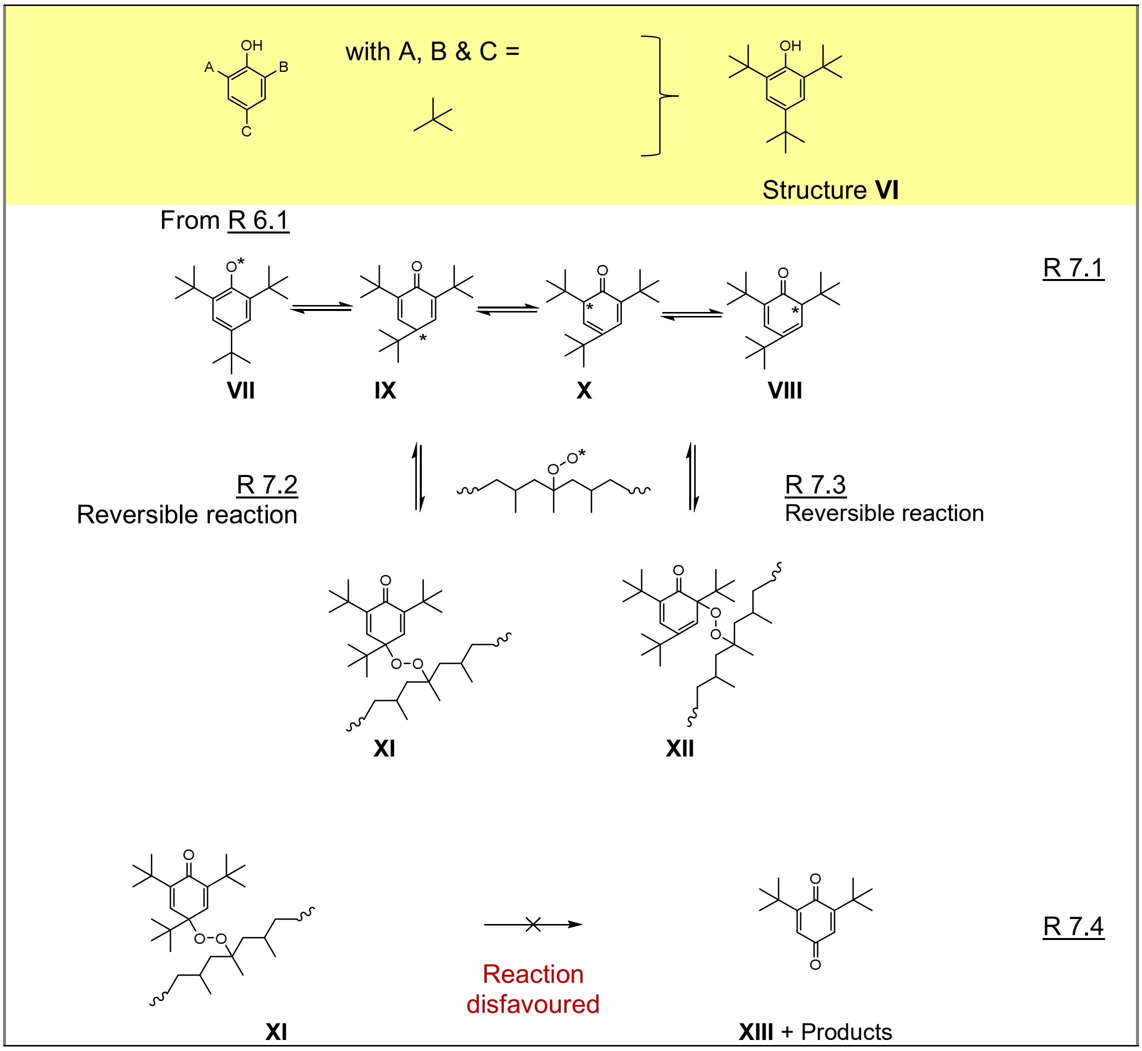
- Fully hindered phenol (no α-carbon in ortho or para position has H- bond)
- Non-hindered phenol (no substituent in para position)
- Partially hindered phenol (at least a 2^{o} C-atom adjunctant to *para*-position)
- Partially hindered phenol bases on “Metilox” (AO-39) intermediate



Scheme 6: Mechanism of action of Hindered Phenols HP as CB-D

1.7.1.1 Fully hindered phenol

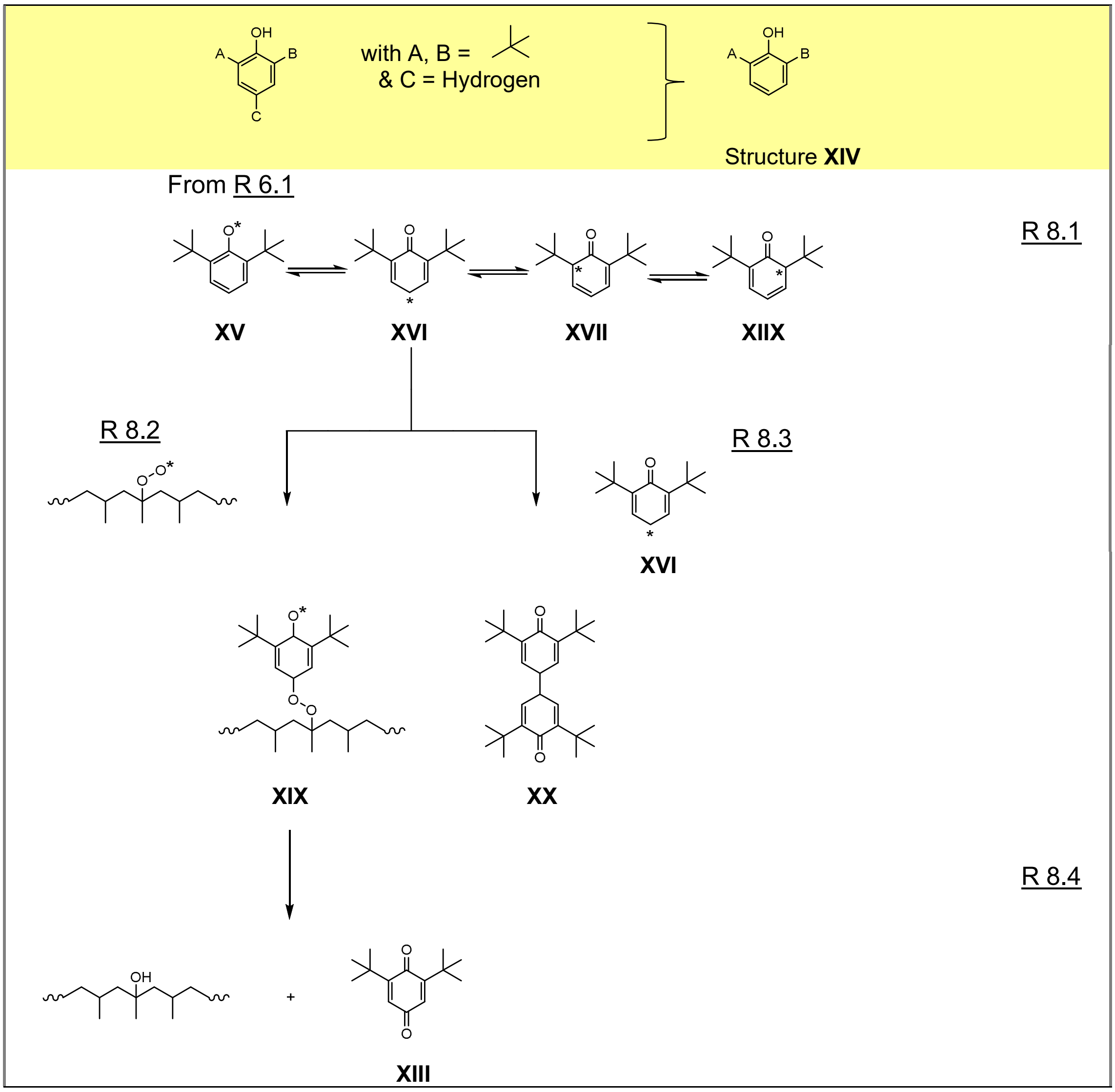
Fully hindered phenols are defined as HP which are fully hindered in the para position (as well as in the ortho positions); meaning the *α-carbon to the phenol ring does not contain a hydrogen bond*. This is exemplified in **Scheme 7** by *tert*-butyl substitients. During the reaction of the phenoxy radical with the second peroxy macro radical, mainly *reversible* C-O coupling products are formed (R 7.2 & 7.3). The formation of para-benzoquinone structures is not favoured (R 7.4). The stabilisation activity of this sub-class of HP is limited to the stoichiometric reaction between the initial hindered phenol and a peroxy macro radical.



Scheme 7: Reactions and primary transformation products of fully hindered phenols [67-70]

1.7.1.2 Non-hindered phenol

Hindered phenols *without substituents in the para position* are of low molecular weight and hence not very suitable for thermoplastic processing due to their high volatility. Upon reaction as CB-D, mono-quinones (**Structure XVI**) and the corresponding dimer (**Structure XIIX**) are formed easily [71]. In the example of a 2,6 di-*tert*-butyl hindered phenol, the reaction path is illustrated in **Scheme 8** R 8.1, R 8.2 & R 8.3. Reaction R 8.4 is favoured compared to fully hindered phenols and yields para-benzoquinone (here, MW of 220 g mol^{-1}, while dimer is > 400 g mol^{-1}).

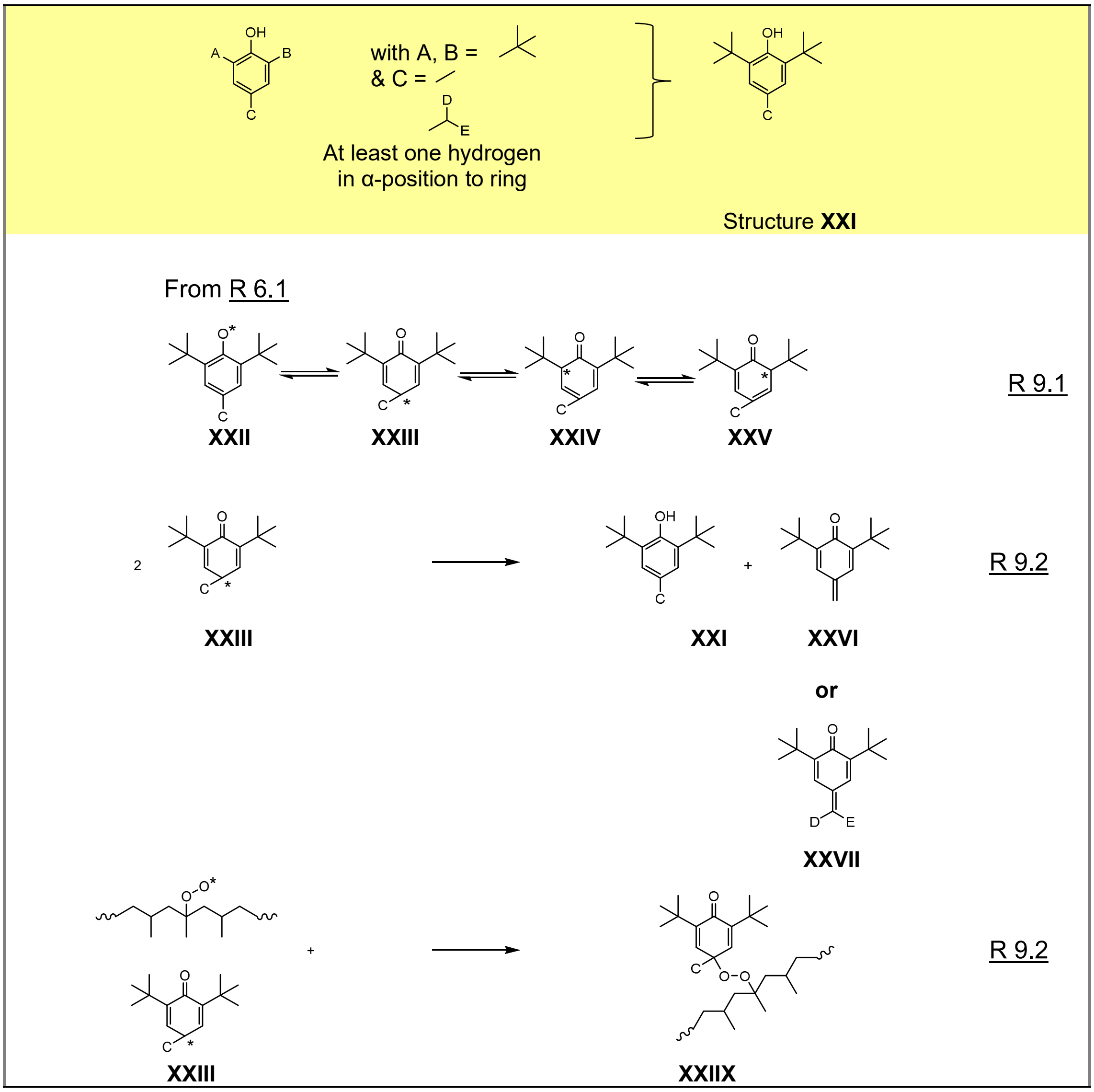


Scheme 8: Reactions and primary transformation products in *para*-position of non-hindered phenols [71]

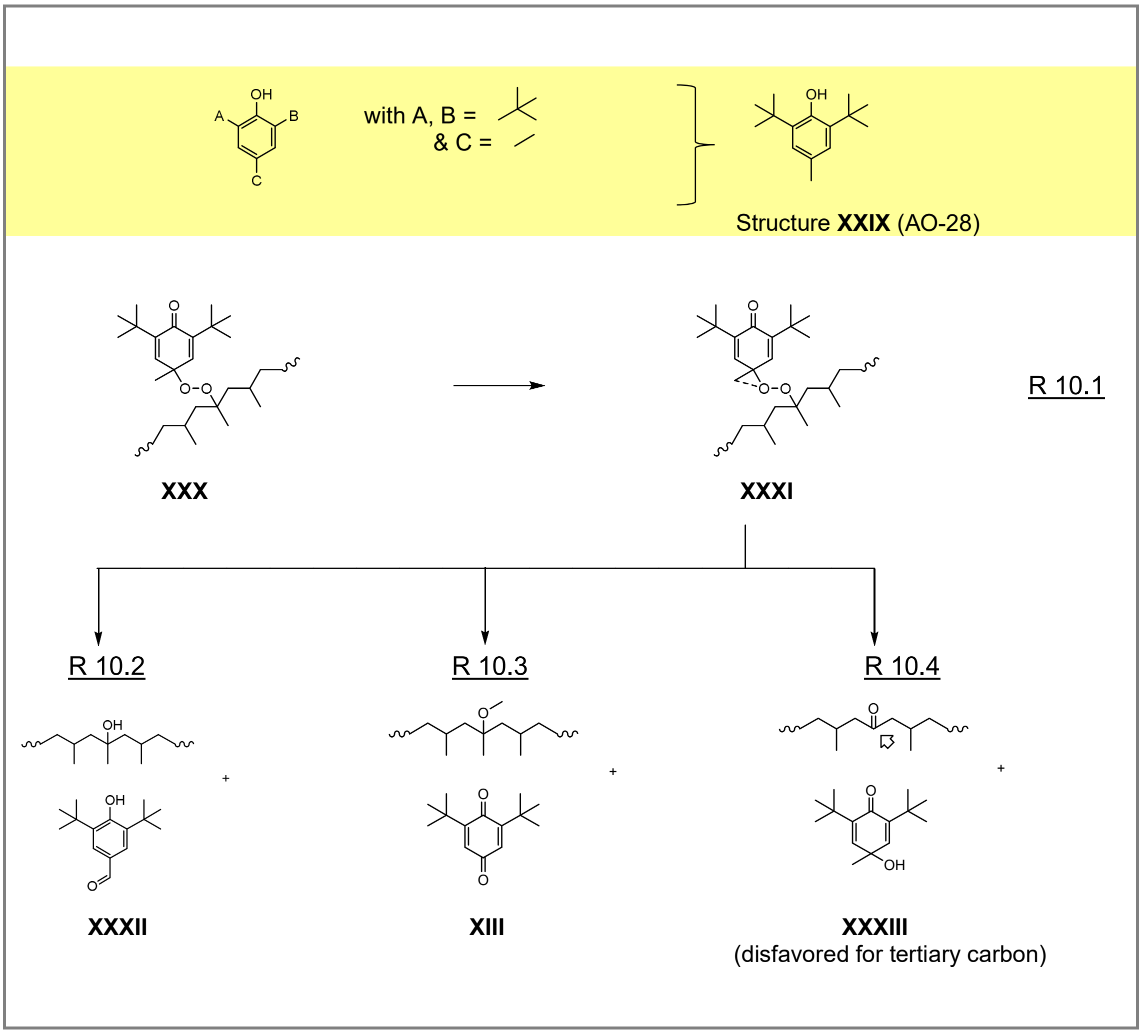
1.7.1.3 Partially hindered phenol

Partially hindered phenols are defined as phenols with *at least one hydrogen on the α-carbon atom in the para, or alternatively in the ortho, position* (Note, this category does not include "Metilox"-based partially hindered phenols, since this will be discussed later). This subclass is caracterised by the the ability to reconstitute the initial phenol in a disproportioning reaction which leads as well to the formation of the coresponding quinone methide (**Structure XXI** and **Structure XXV**; see **Scheme 9** R 9.2 [67]). The stabilisation activity of this sub-class is therefore over-stoichiometric. Reaction R 9.3 of the cyclohexadienonyl radical (**Structure XXIII**) with a peroxy macro radical is similar to R 8.2 for non-hindered phenols. However, the subsequent formation of secondary transformation products resulting from the thermally unstable *para*- alkylperoxy cyclohexadienone (**Structure XXIIX**) depends on the exact constitution of the substituent in *para*-position [71,72]. For the simple case of a methyl group as the para-substituent, various single ring products in a molecular weight range around 200-300 g mol^{-1} are formed including *p*-benzoquinine (**Structure XIII**) and benzaldehyde (**Structure XXXII**; **Scheme 10** [74]). In early model studies, the formation of acetone and related ketones were reported as secondary transformation products [72,75,76]. The dimerization of primary transformation products leads to highly coloured molecules in the range of 400 g mol^{-1}. In the case of an ethyl group in the para-position (AO-37) similar reactions lead to the formation of para-benzoquinone and acetophenone (**Scheme 11** [71]) without dimerization. When there is an aromatic system in the β-position to the phenolic ring (AO-61), an alternative reaction pathway to form secondary transformation products is reported via hydrogalvinoxyl (**Scheme 12**, **Structure XXXXI** [71]). As well as *p*-benzoquinone and benzaldehyde, a benzoic acid derivative (**Structure XXXIII**) is reported as a low molecular weight fragment, though the reaction pathway is unclear in the presence of oxygen.

For the specific example of AO-4 more than 20 transformation products have been identified [73,77]. Only two of these have a molecular weight below 300 g mol^{-1} and correspond to para-benzoquinone (**Structure XIII**) and benzaldehyde (**Structure XXXII**). Here oxidation of the methylene group in the *para*-position to form the corresponding carbonyl group is proposed in the literature [78] and accords with reaction R 10.2. To explain the formation of a benzaldehyde, a further cleavage of the α-carbon from the mesitylene backbone would have to take place. For additional HMW representatives of this sub-class (AO-3 & AO-5), only five transformation products are reported [77]. Both HMW Hindered Phenols HP are structurally related and contain an iso-cyanurate ring as their backbone. All transformation products were above 500 g mol^{-1}; however, in each case the version with the lowest molecular weight is missing a substituent on the ring nitrogen.

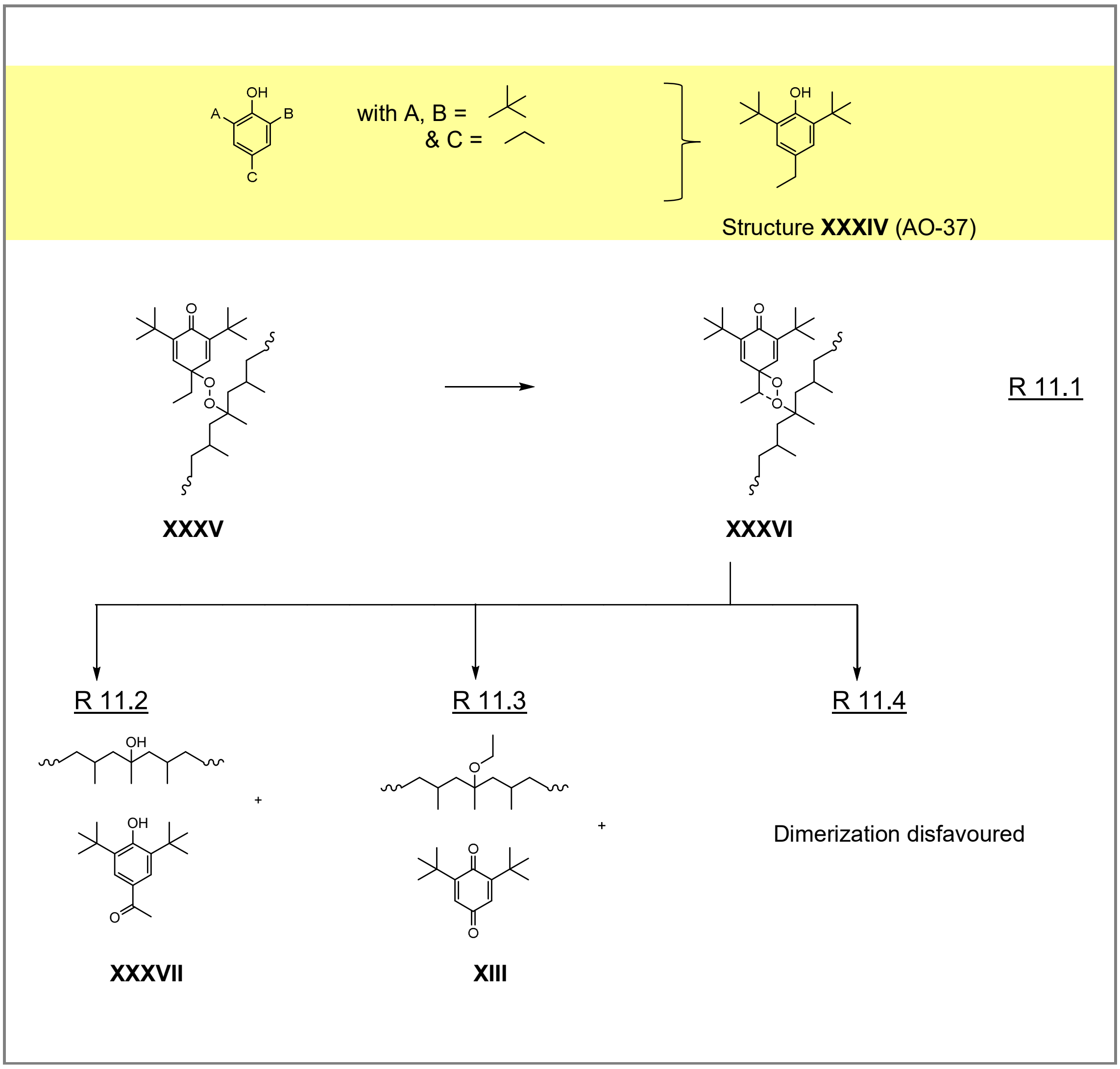


Scheme 9: Reactions and primary transformation products in *para*-position of partially hindered phenols [71]

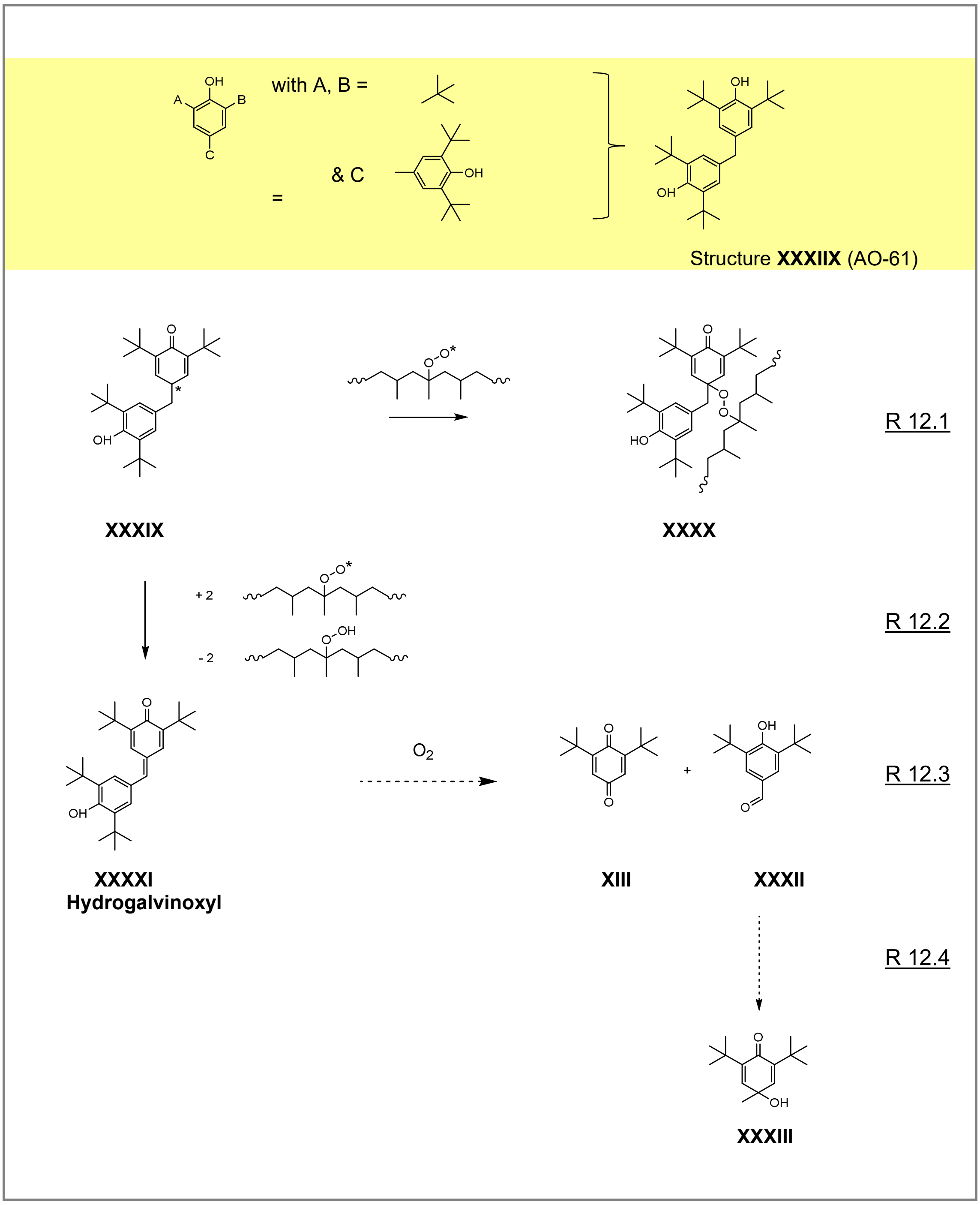


Scheme 10: Selected secondary transformation products of AO-28

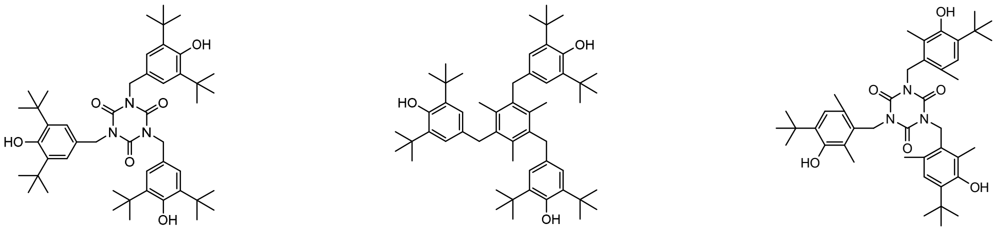
Depending on the oxidation state, the ‘missing’ substituent could correspond to a HP (like AO-28), a *p*-benzoquinone (**Structure XII**) or a benzaldehyde (**Structure XXXII**). In fact, several LMW mainly aromatic-oxygenated structures are reported in the same study (**Table 6** 77).



Scheme 11: Selected secondary transformation products of AO-37



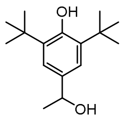
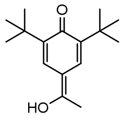
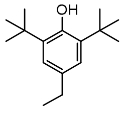
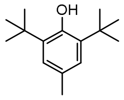
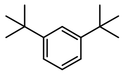
Scheme 12: Selected secondary transformation products of AO-61



AO-3 AO-4 AO-5

Figure 11: HMW Hindered Phenols AO-3, AO-4 & AO-5

Table 6: Low molecular weight fragments potentially from AO-3, AO-4 and/or AO-5 [77]

Fragment Number	***Chemical Name***	***Chemical Structure***	***Remark***	***Reference***
	2,6-Di-tert-butyl-4-(-1-hydroxyethyl) phenol ***14681-20-0*** 250 Dalton $C_{16}H_{26}O_2$			**77**
	2,6-Di-tert-butyl-4-(-1-hydroxyethylidene) cyclohexa-2,5-dienone ***14681-20-0*** 248 Dalton $C_{16}H_{26}O_2$			**77**
	2,6-Di-tert-butyl-4-ethyl phenol ***4130-42-1*** 234 Dalton $C_{16}H_{26}O$			**77**
	2,6-Di-tert-butyl-4-methyl phenol ***128-37-0*** 220 Dalton $C_{15}H_{25}O$			**77**
	1,3-Di-tert-butyl benzene ***1014-60-4*** 190 Dalton $C_{14}H_{22}$			**77**

1.7.1.4 Partially hindered phenols based on AO-39 (Metilox)

“Metilox” based Hindered Phenols HP are a specific category of the sub-class of partially hindered phenols. This category is based on the intermediate “Metilox”; namely 3-(3,5-di-tert-butyl-4-hydroxypheyl) methyl propanoate (**Figure 12** [79,80]). All reactions of **Scheme 10** and **Scheme 11** are valid, however the quinone methide can rearrange to a cinnamate (**Scheme 13**, R 13.2, **Structure XXXXV**). This reaction reconstitutes an active HP functionality and subsequently improves the activity of this class of HP [81], as it further increases the stoichiometric reaction factor of HP [82,83]. The category contains by definition at least one carboxylic acid ester functionality per molecule, which is potentially subject to hydrolysis [Scheme 14 R 14.1 [84]. Reaction R 14.2 for the specific example of AO-2 yields 3-(3,5-di-*tert*-butyl-4-hydroxypheyl) propanoic acid (**Structure XXXXVI**). **Structure XXXXVI** is an active protective agent and can react according to **Scheme 13** and **Scheme 15** R 15.1; forming additional tertiary transformation products (**Structure XXXXVII**, **Structure XXXXIIX** and **Structure XXXXIX** [85]). The kinetics of the hydrolysis reaction R 14.1 is reported to be significantly accelerated above 50°C [85]. For the specific “Metilox”-based HP AO-1, AO-2 & AO-17, many transformation products are reported [77]. The vast majority are above 400 g mol^{-1} and are primary transformation products or result from (partial) dealkylation of the substituent(s) in ortho position. However, several transformation products of AO-1 are additionally missing a phenolic moiety according to R 14.1. The corresponding (analytically identified) LMW HP are listed in **Table 7**.

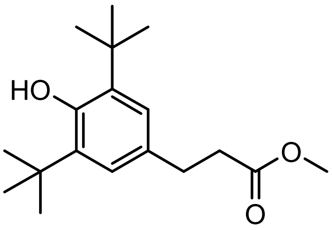
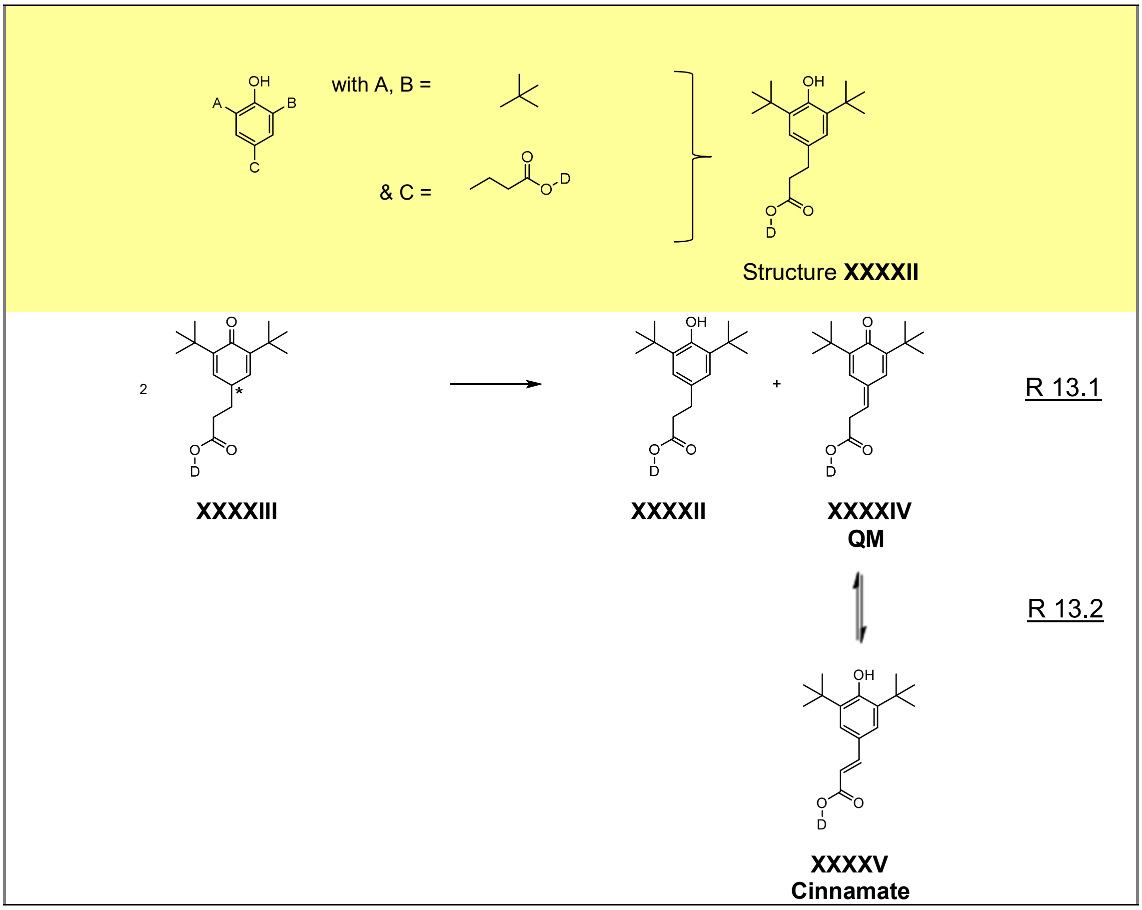
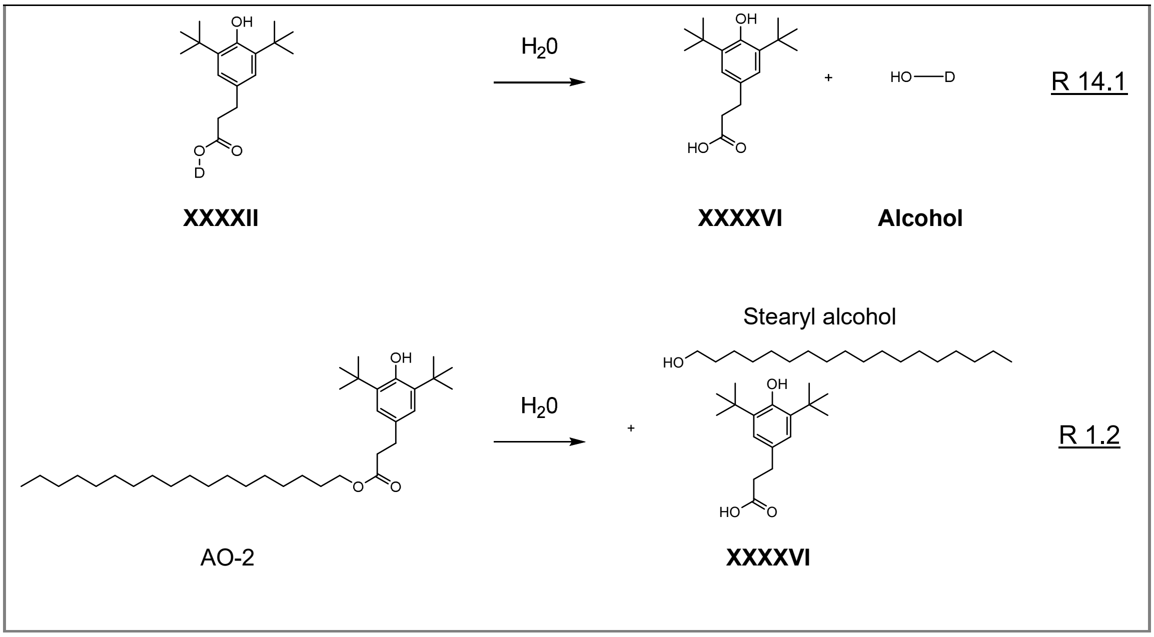


Figure 12: “Metilox” intermediate; also referred to as AO-39

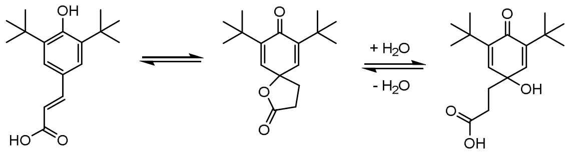


Scheme 13: Additional transformation products of “Metilox”-based HP



Scheme 14: Hydrolysis products of “Metilox”-based HP

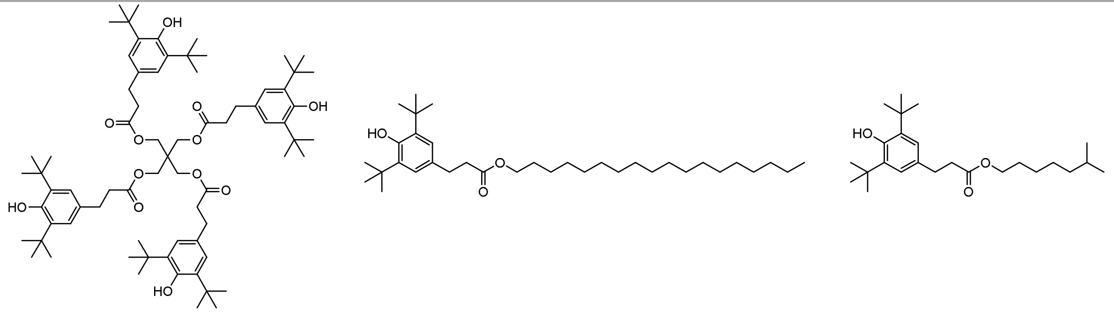
From R 13.2



R 15.1

XXXXVII XXXXIIX XXXXIX

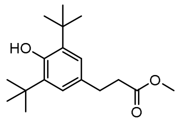
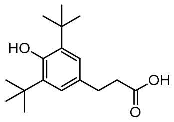
Scheme 15: Further hydrolysis transformation products of “Metilox”-based HP



AO-1 AO-2 AO-17

Figure 13: “Metilox”-based HMW Hindered Phenol AO-1, AO-2 & AO-17

Table 7: LMW molecules from “Metilox”- based HP [77]

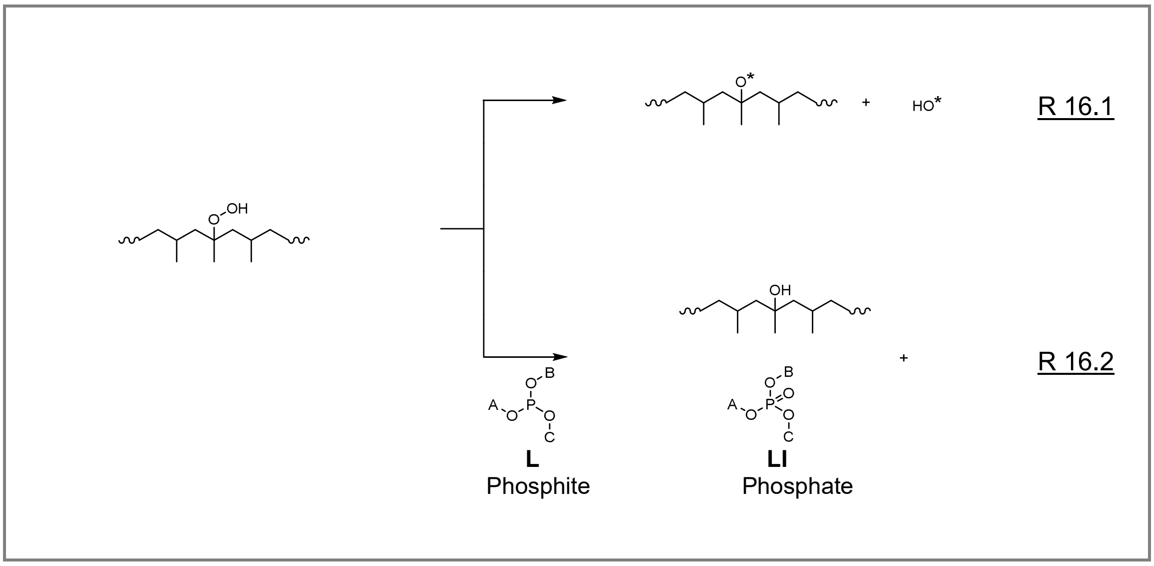
Fragment Number	*Chemical Name*	*Chemical Structure*	*Remark*	*Reference*
	3-(3,5-Di-tert-butyl-4-hydroxyphenyl) methyl propanoate ***6386-38-5*** 292 Dalton $C_{18}H_{28}O_3$		**Hydrolysis**	**77**
	3-(3,5-Di-tert-butyl-4-hydroxyphenyl) propanoic acid ***20170-32-5*** 278 Dalton $C_{17}H_{26}O_3$		**Hydrolysis**	**77**

1.7.2 The Chemistry of Phosph(on)ites P

In a pre-emptive step, peroxide decomposers PD react with peroxides to form non-radical products and prevent peroxides forming peroxy and hydroxy radicals via reaction R 1.6. In the case of tri-valent organo-phosphorous structures, referred to as phosph(on)ites, this is accomplished via a stoichiometric oxidation of phosphorus III to phosphorus V (phosph(on)ate) and the formation of an alcohol (**Scheme 16** R 16.1 [67,86]. The dominance of R 16.1 over R 1.6 is determined by the molar activity of the phosph(on)ite, which is easily quantifiable by the phosphorus III content of a specific molecule, and the nature of the substituent. The relative reaction rate with hydroperoxides is illustrated in **Figure 14** [87,88]. For aromatic phosph(on)ites, direct reactions with peroxy (**Scheme 17** R 17.1) and alkoxy radicals (R 17.2) are also reported [89,90]. In addition, direct reactions with oxygen, which is dissolved in the polymer melt, are reported (R 17.3) [91]. This reaction decreases the concentration of oxygen available during melt-processing for oxidative degradation of the polymer substrate. Additional reactions are reported which can contribute to the slow-down of oxidation [92,93]:

- Reaction with (para-) quinone (to yield colourless & higher MW aryl phosphate)
- Reaction with quinone methide (to yield colourless & higher MW aryl phosphonate)
- Deactivation of metal ions (potential catalysts for oxidation reaction)
- Addition to (polymeric) unsaturation

Phosph(on)ites do not interfere with the oxidation reaction below a temperature of ~150 °C (**Figure 10**). However, due to the activity of phosph(on)ites during melt-processing of PP at ~ 190 to 240°C, the class of protective chemicals of HP is not consumed to the same extent during this stage i.e., more (still intact) HP is available to extend the service life [91,94]. A lower degree of CB-D required reactions (**Scheme 3** as well as **Schemes 6 to 12**) should statistically result in less transformation products during melt-processing. A key feature of this class of protective chemicals is the tendency to hydrolyse. A certain degree of hydrolysis seems to enhance the performance of selected phosphites. This effect is utilized where water is intentionally added during post-synthesis reactor compounding [95,96]. Several other investigations concluded an increased activity of selected phosph(on)ites during the initial stage of hydrolysis. This effect is attributed to highly active intermediates [97] or auto-synergistic mixtures of oxidative reaction products with hydrolysis products [98].



Scheme 16: Principle peroxide decomposition pathway of phosph(on)ites P

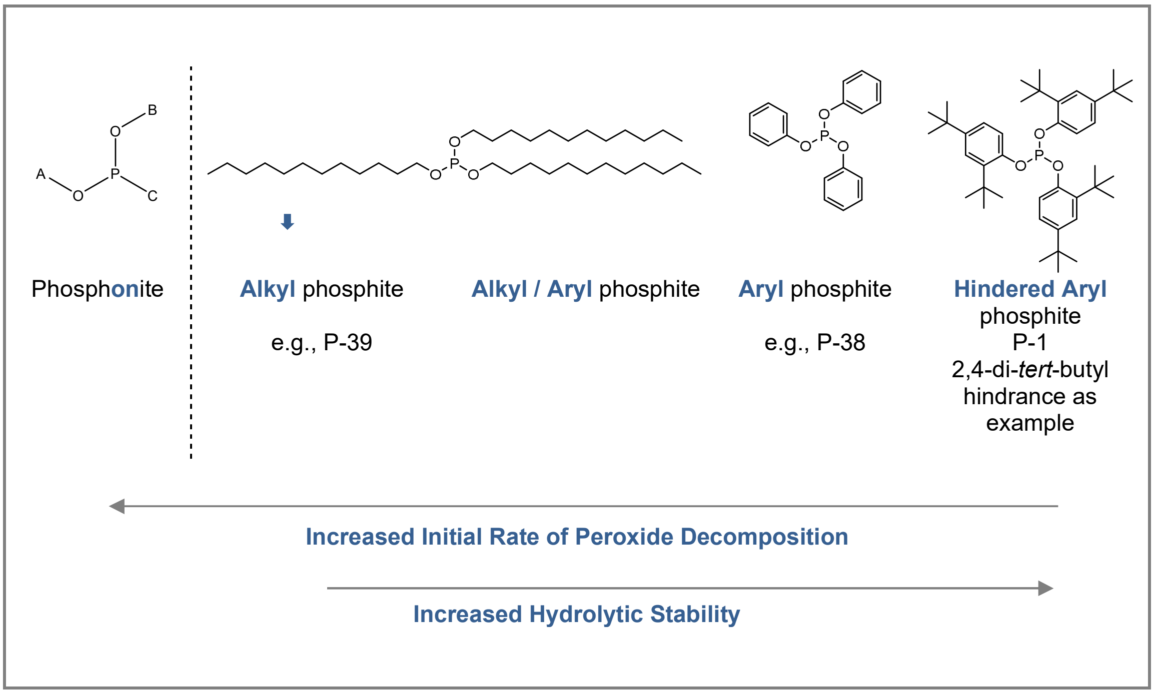
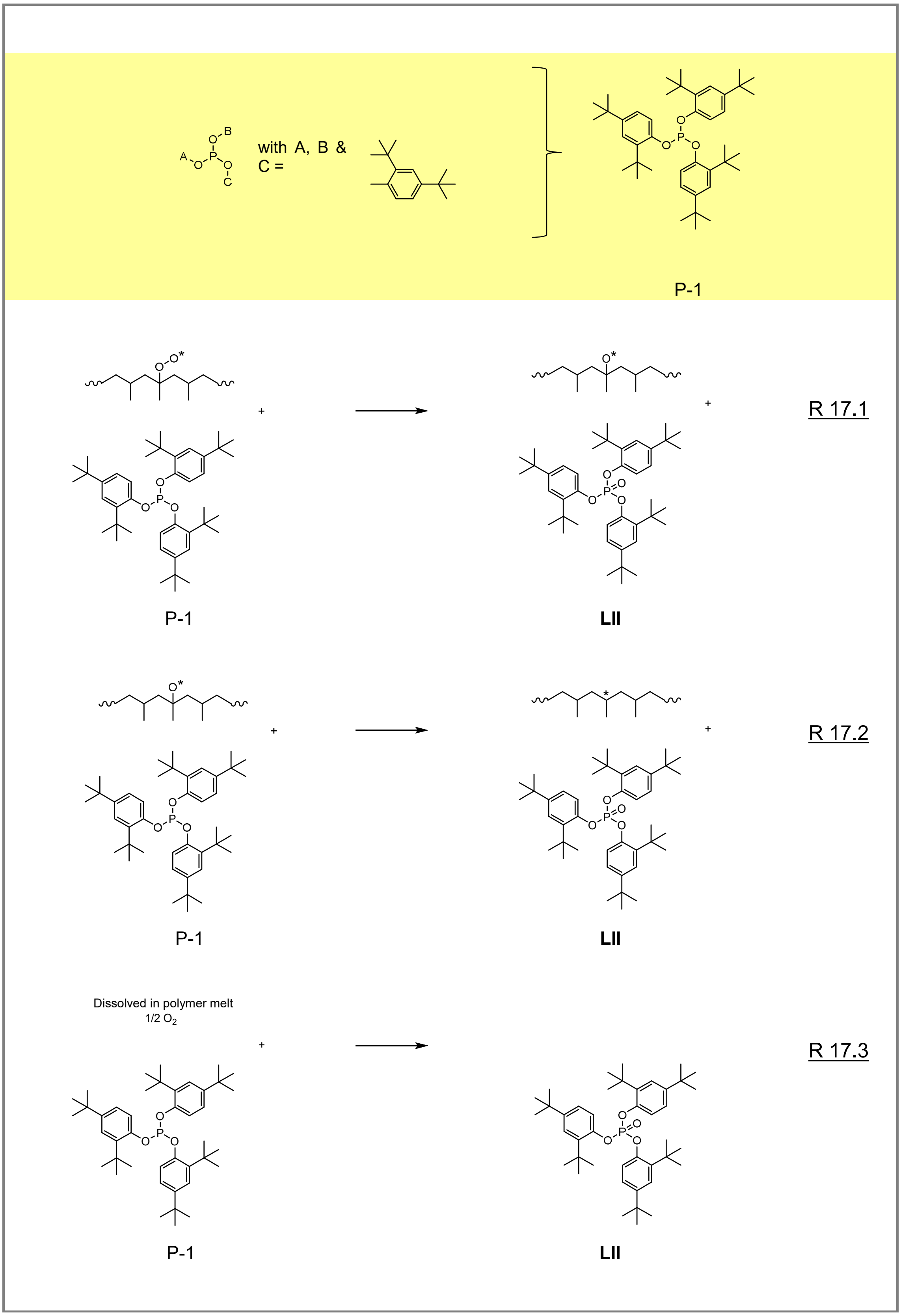
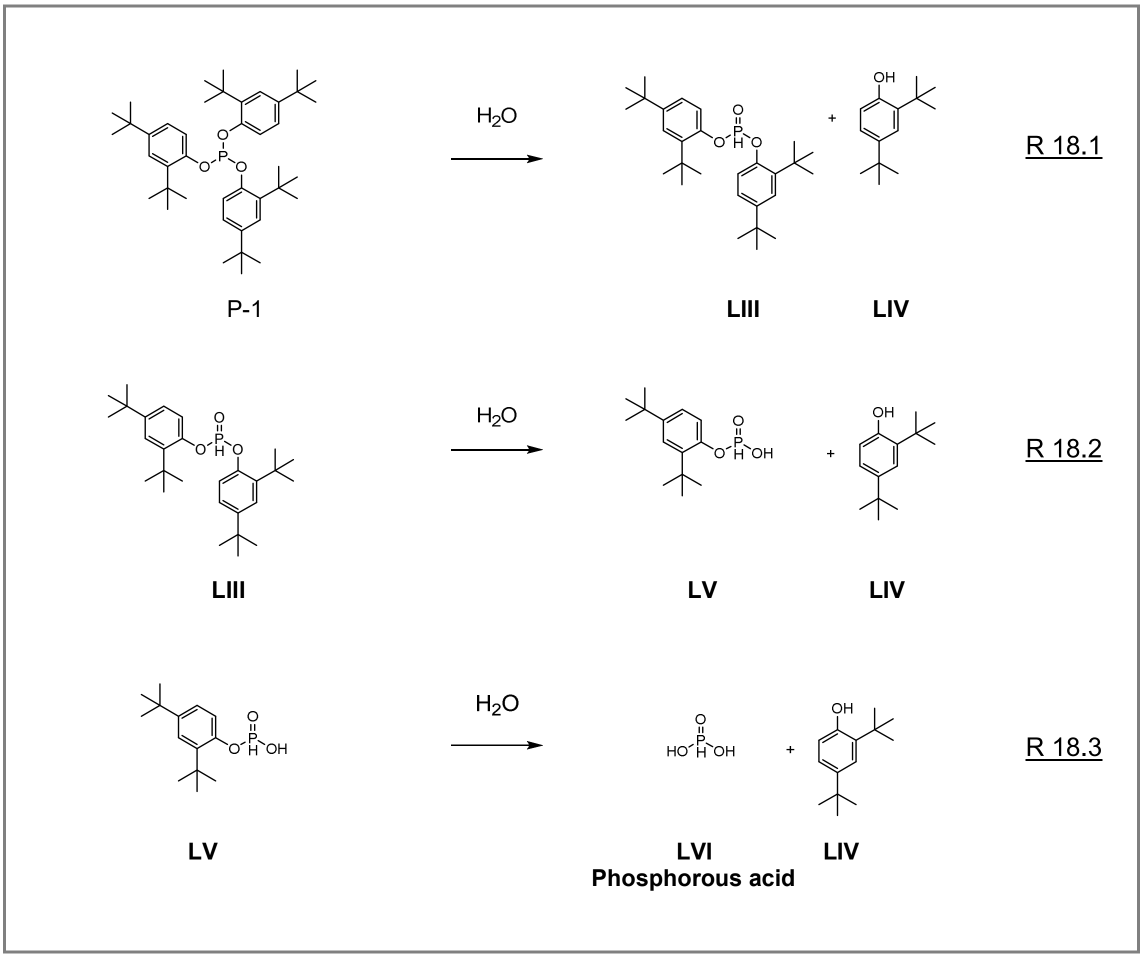


Figure 14: Relative reaction rates of phosphites with hydroperoxides depending on the substituents of phosphorus III



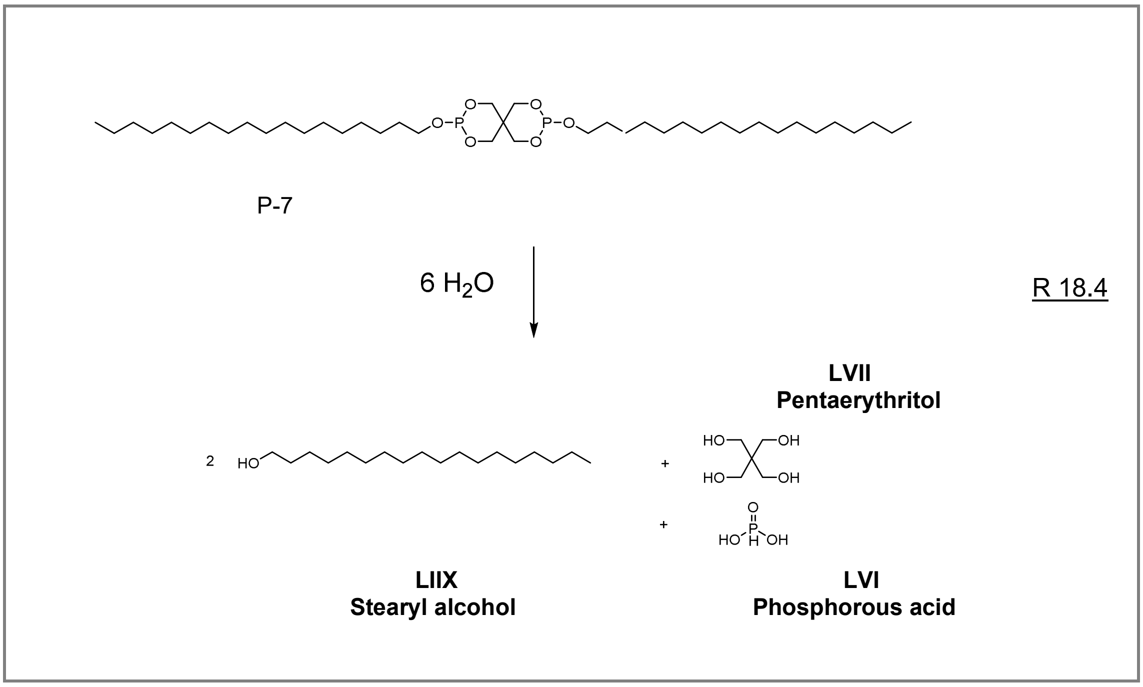
Scheme 17: Additional stabilization pathway of phosph(on)ites P

Excessive hydrolysis causes performance issues, due to a significant change of the physical form of the additive and the subsequent challenge to incorporate this form into PP[99]. Ultimately, reaction R 16.1 is suppressed due to the complete oxidation of phosphorus III to phosphorus V during hydrolysis. This alternative reaction is exemplified in **Scheme 18** for an aromatic and an aliphatic phosphite. R 18.3 and R 18.4, which describe the formation of phosphorous acid (responsible for the observed corrosion effects). All reactions of **Scheme 18** yield LMW alcohols, the exact chemical composition of which depend on the initial phosphite. The different physico-chemical parameters including Log K_{OW} for **Structure LIV** (Log K_{OW} = 5.19) and **Structure LIIX** (Log K_{OW} = 8.22) are noteworthy.



Scheme 18: Hydrolysis of phosph(on)ites P[81]

Hydrolytic stability of phosph(on)ites is influenced by the same parameters as already outlined in **Figure 14**; with (in this series) hindered aryl phosphites being the most stable. Various technologies have been proposed to increase insufficient hydrolytic stability of phosph(on)ites [99]. Hydrolysis is an auto-accelerating reaction in acidic and alkaline environment. The impact of onset of hydrolysis of a phosph(on)ite on the potential hydrolysis of another additive or protective chemical is not yet understood; but the former could trigger the latter.



Scheme 18b: Hydrolysis of phosph(on)ites P [81]

1.7.3 The Chemistry of Hindered Amine Stabilisers HAS

Hindered Amine Stabilisers HAS (initially referred to as Hindered Amine Light Stabilizer HALS in the literature) differ from other nitrogen-based CB-D and/or CB-A by greater hinderance of the nitrogen functionality and the absence of a neighbouring aromatic system for mesomeric stabilisation of the radical formed (**Figure 15**). The initial N-H, or N-R piperidine group must be activated according to **Scheme 19** to give the main reactive species, the nitroxyl radical. The kinetics of this oxidation typically do not allow an activation during conditions of melt-processing and oxygen deficiency. The class of protective chemicals of HAS is therefore not able to interfere with the oxidation reaction of PP at temperatures of ~190 to 240°C; but only below 110°C and hence in the solid state of PP. This can only be circumvented by prior oxidation of HAS, or intentional addition of a strong radical generator during melt-processing [100]. The activation of HAS to the corresponding cyclic hydroxylamine via peracids is also postulated (**Scheme 20** [101]). The main contribution of the nitroxyl radical at temperatures below 110°C is the reaction as CB-A with carbon-centred macro radicals (**Scheme 21** reaction R 21.1) to form an N-alkoxy piperidine moiety and the subsequent regeneration of the nitroxyl radical via a reaction with a peroxy macro radical (R 21.2) [102-109]. In addition, a parallel reaction allows the nitroxyl radical to react with a carbon-centred radical under formation of a hydroxylamine and an alkene (R 21.3). The regeneration of the nitroxyl radical is achieved via the subsequent reaction with a peroxy macroradical (R 21.4).

The efficacy of HAS as CB-A is determined by its molar activity, which can be quantified as the amount of piperidine-nitrogen, as well as the substituent on the piperidine-nitrogen. The ease of formation of the corresponding nitroxyl radical is illustrated in **Figure 16** [110]. An indirect effect of HAS on the decomposition of peroxides to none-radical products is via complexation of transition metal ions [111-113]. Removal of metal ions withdraws the catalytic effect of such metal ions (R 1.6) and subsequently disfavours it.

1.7.3.1 Comparison of HAS and HP as thermal stabilisers

According to **Figure 10**, both classes of protective chemicals, HAS and HP, are effective over the temperature range in which PP based articles are used (below 0°C to ~70°C). However, only HP maintain CB-D based peroxy radical trapping activity up to the maximum testing temperature for PP (homo) polymer of 150°C. The higher the testing temperature, the more defined the initial induction period of autoxidation (**Figure 6**), followed by a sharp decrease in mechanical properties of PP (which correlates with a fast decrease in MW; **Figure 17**). This sharp decrease is often referred to as “catastrophic failure”. In contrast, the (mainly) CB-A activity of HAS to scavenge carbon-centred and oxygen-centred macro radicals is more dominant at lower temperatures; especially below 100°C (approaching the actual service life temperatures of this polymer). The mechanical properties of PP show a continuous decline in the slope (**Figure 17**) as a function of aging temperature [106,113-115]. In contrast, the temperature dependency in an Arrhenius plot is more pronounced for HAS than for HP. This is illustrated in **Figure 18** [116,117]. HAS is not expected to yield a high number and concentration of transformation products during melt-processing. However, cleavage products and reaction products with HP are reported under long term exposure conditions [102].

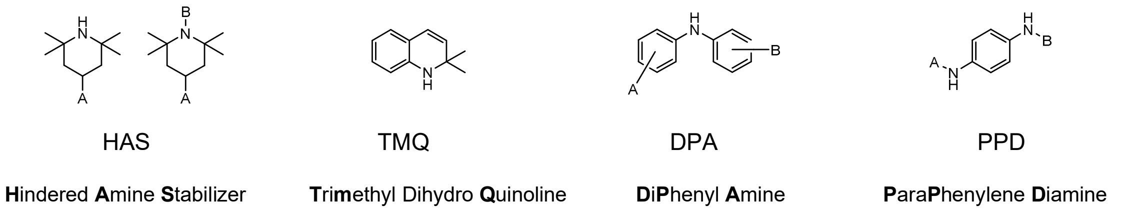
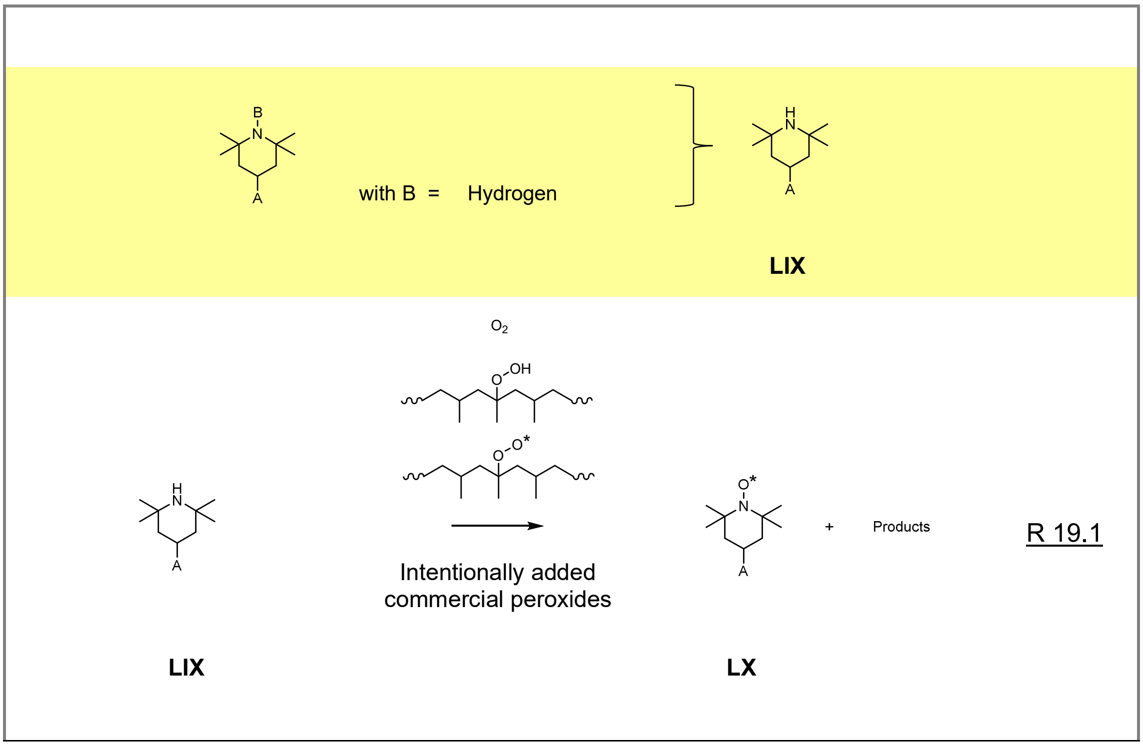
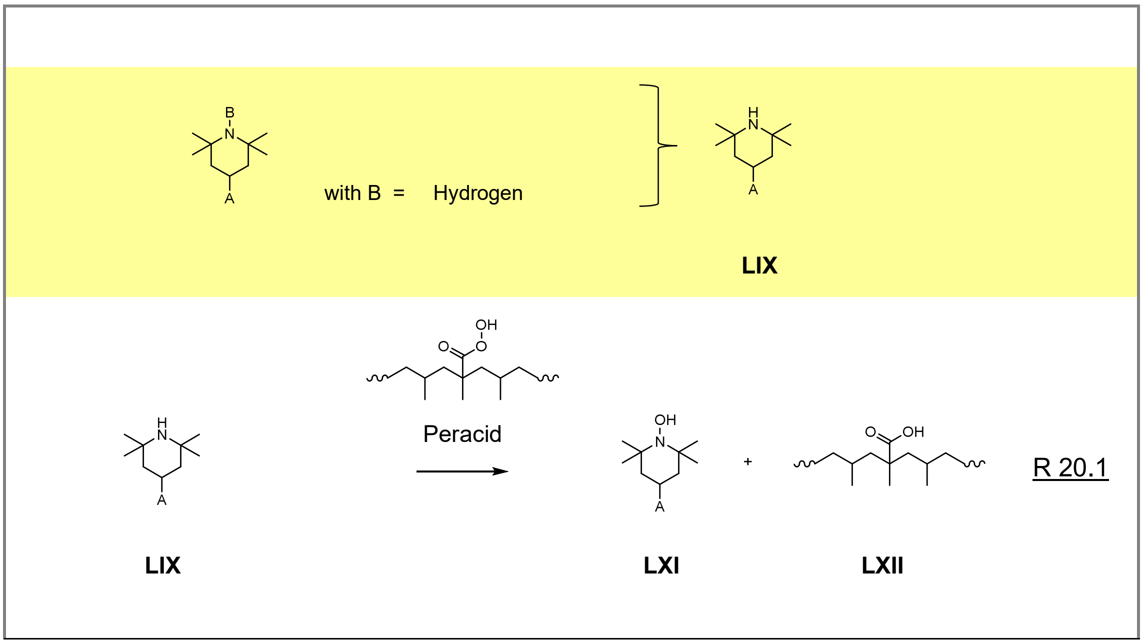


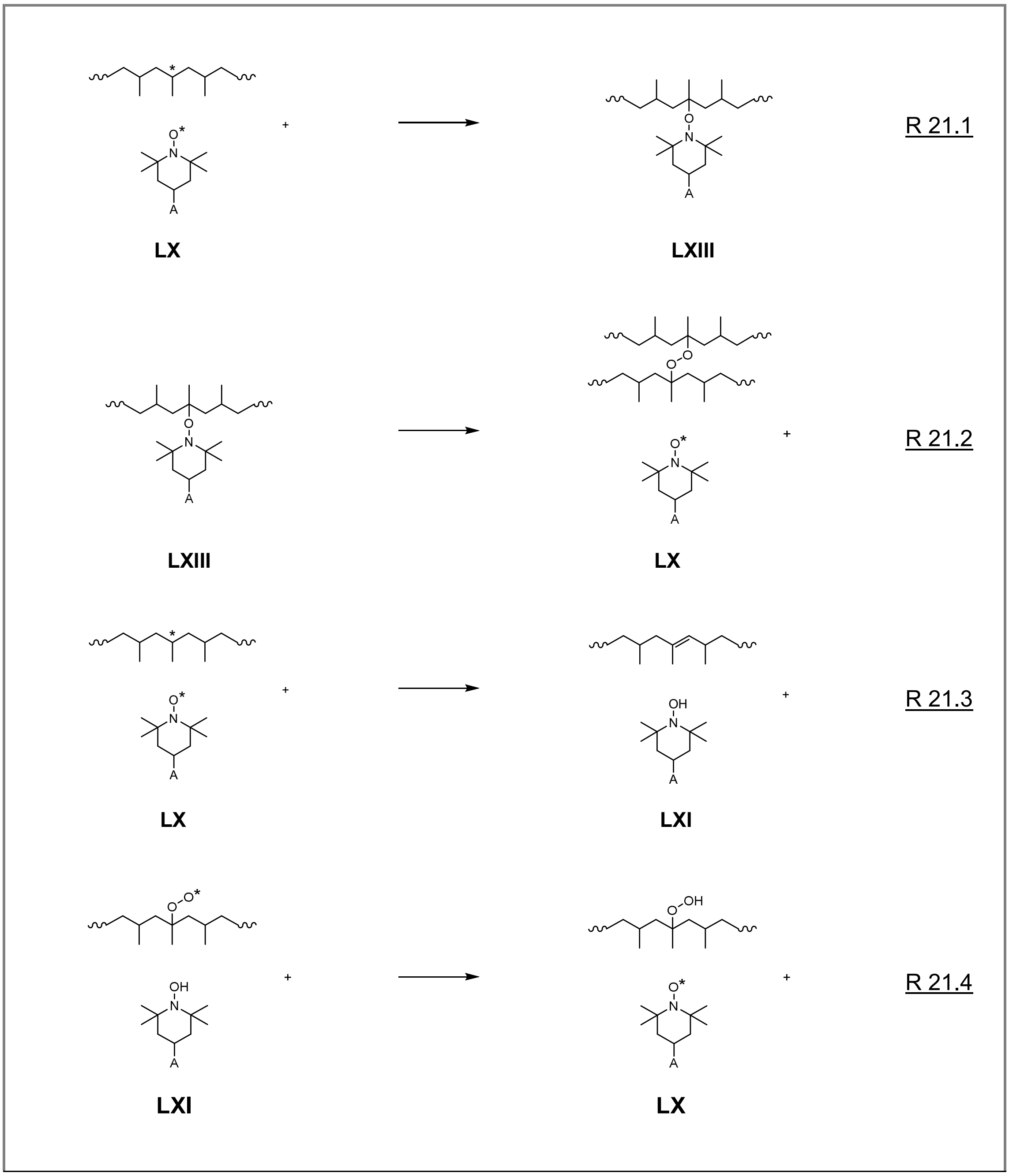
Figure 15: Various nirogen-based CB-D and CB-A



Scheme 19: Activation (oxidation) of HAS to the corresponding nitroxyl radical



Scheme 20: Activation (oxidation) of HAS to the corresponding hydroxylamine



Scheme 21: Regenerative CB-A activity of nitroxyl radical formed from HAS

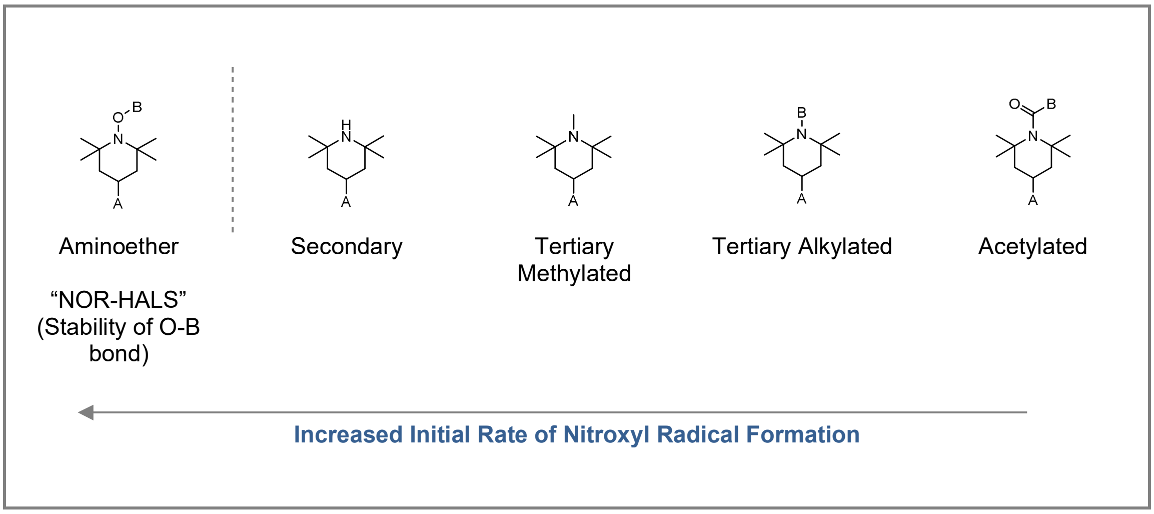


Figure 16: Kinetics of nitroxyl radical formation from HAS parent functionality [118]

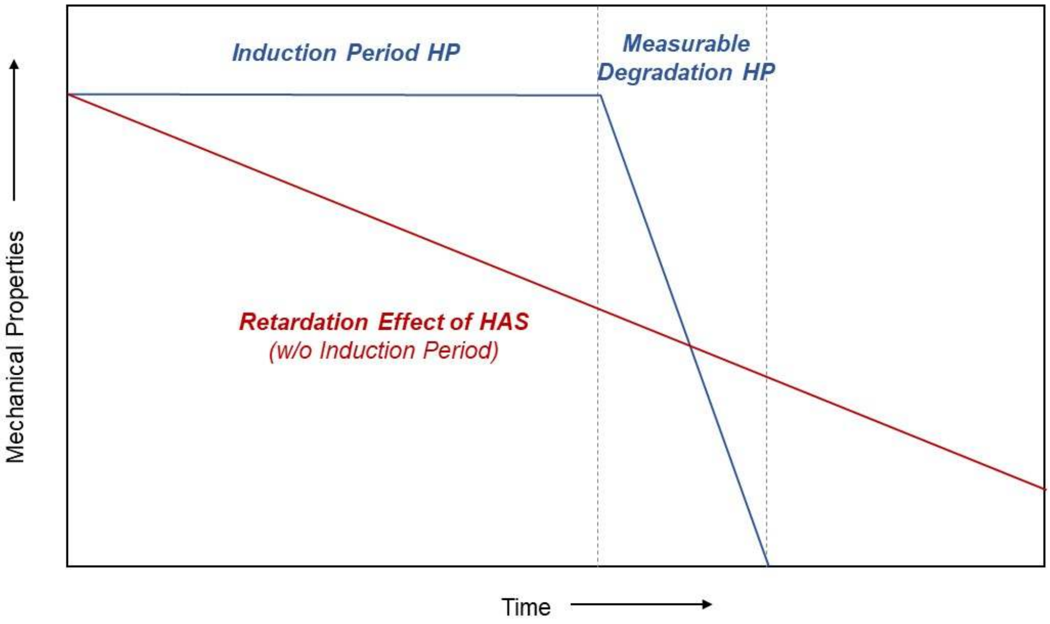


Figure 17: Degradation of PP samples containing HAS or alternatively HP as thermal stabiliser

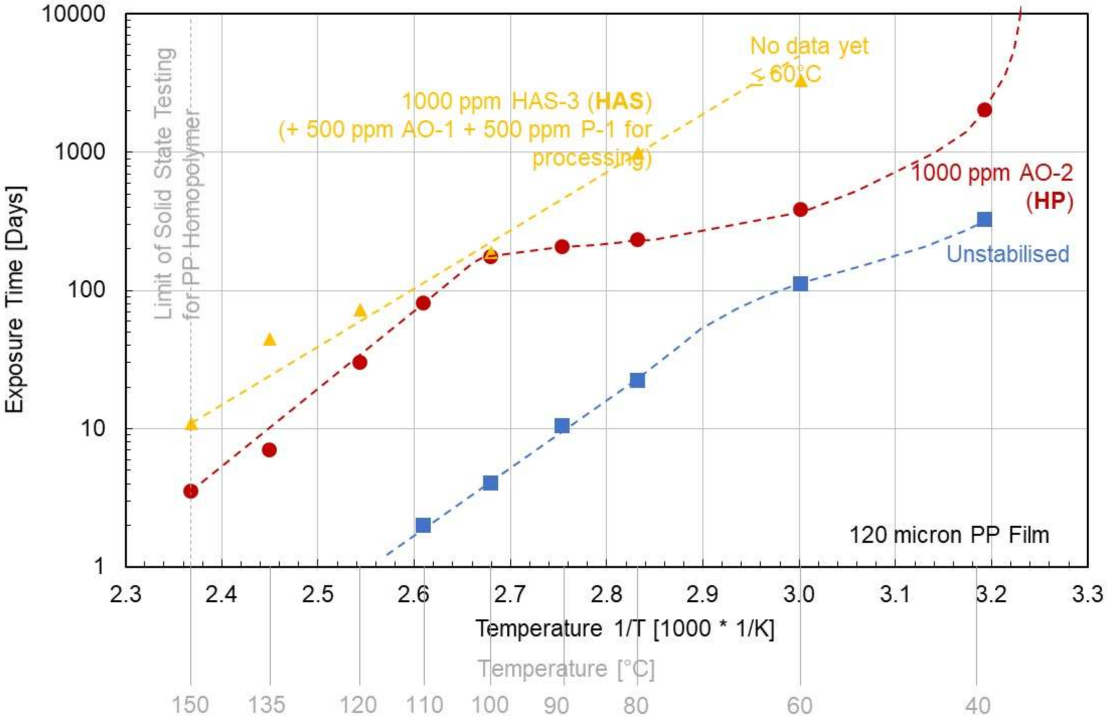
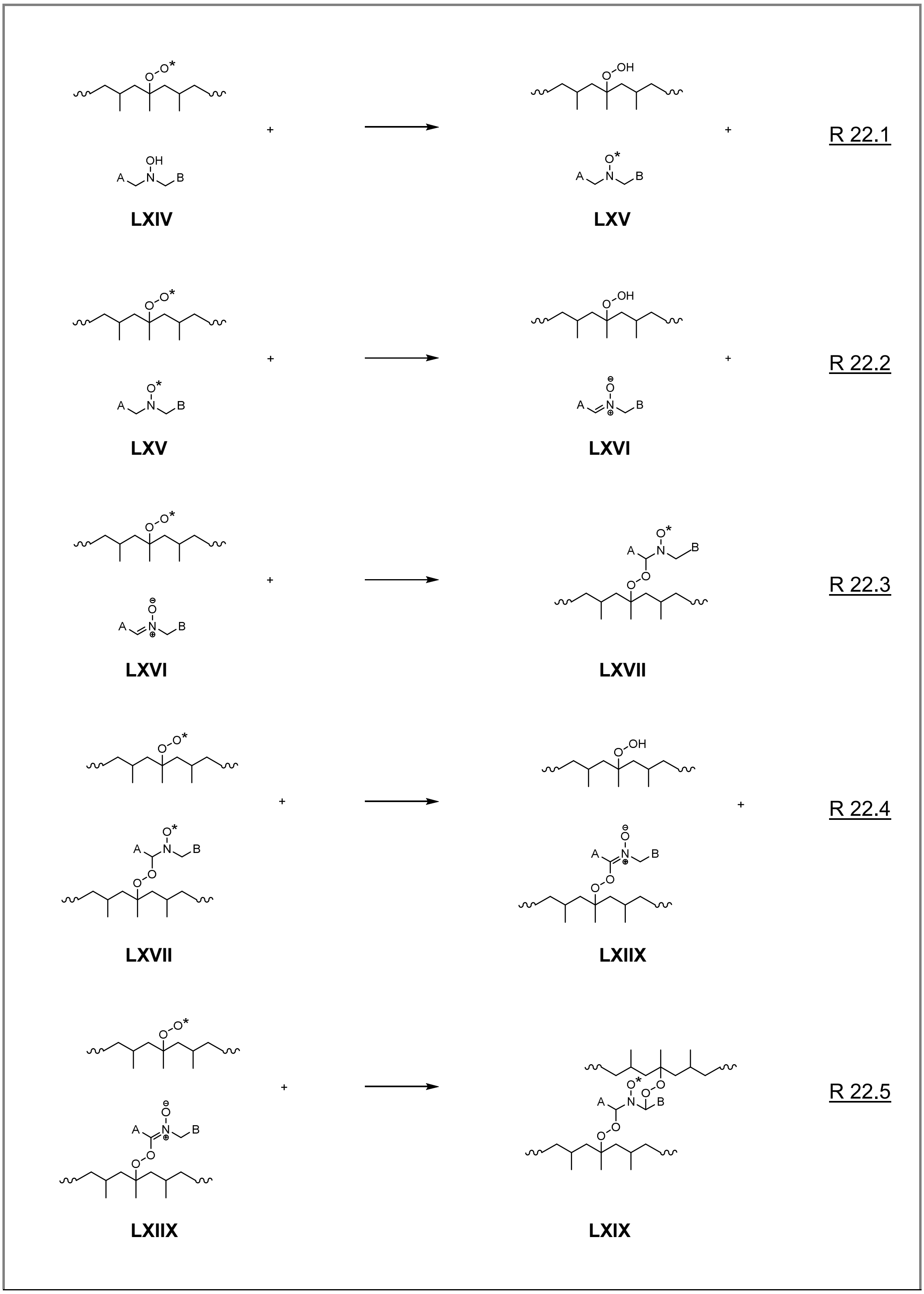


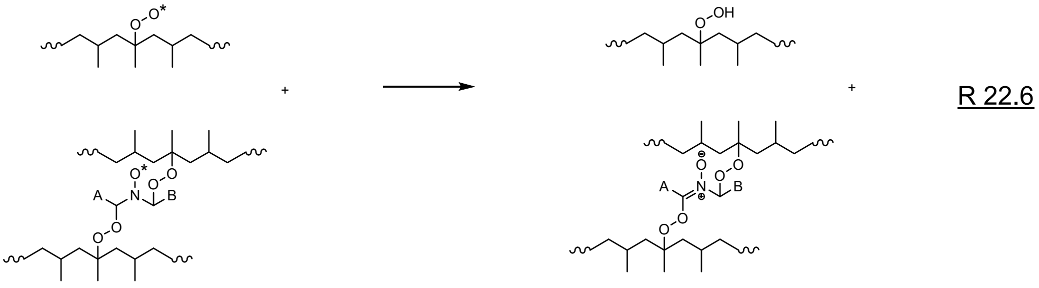
Figure 18: Temperature dependency of HP versus HAS – Note the slope and shape of curve of Arrhenius plot (modified from [117])

1.7.4 The Chemistry of Hydroxylamines (HYA)

The class of protective chemicals of hydroxylamines (HYA) functions according to three main mechanisms; CB-D, CB-A and PD. However, its ability to scavenge oxygen-centred macro radicals is less pronounced than its ability to decompose peroxides [118,119]. Trapping of radicals is accomplished via a series of CB-D and CB-A reaction steps, which all compete with reaction R 1.5 (**Scheme 22**). The key intermediates involved are the nitroxyl radical (**Structure LXV**) and the nitrone (**Structure LXVI**). Although a stoichiometric reaction, one HYA can scavenge ultimately eight peroxy radicals. **Scheme 23** describes the PD activity of HYA via the nitrone intermediate as alternative reaction pathway to R 1.6. HYA are reported to function mainly at elevated temperatures (**Figure 10**) with limited ability to reduce the rate of oxidation at PP use temperatures [120].

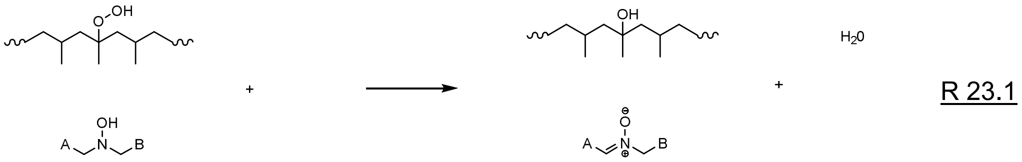


Scheme 22: Mechanism of action of HYA as CB-D and CB-A



LXIX **LXX**

Scheme 22b: Mechanism of action of HYA as CB-D and CB-A



LXIV **LXVI**

Scheme 23: Mechanism of action of HYA as PD

1.8 Emissions from Polyolefins

Industrially manufactured PO often contain LMW molecules within the polymer matrix [122]. The migration of LMW molecules is inverse proportional to their solubility and proportional to their diffusion coefficient. In turn, solubility and diffusion coefficient depends on the following characteristics of a LMW molecule [123,124]

- Molecular weight [125]
- Physical state (below T_m or T_g) [126]
- Specific volume (inverse density)
- Shape of the molecule [124]
- Concentration
- Interaction with the matrix or self-association with itself

The diffusion coefficient of a LMW molecule is additionally determined by

- Morphology of the matrix (especially for PP)
- Processing conditions and orientation of the macromolecules
- Segmental mobility of the macromolecule chain (mobility along the chain)
- Specific free volume

Hence for protective chemicals used in PP, the functional requirements are high solubility at temperatures during which the plastic article is used, along with high degree of homogenisation and optimum diffusion [127]. On migration to the surface of the plastic article, the LMW molecule can be lost from the matrix due to three different mechanisms [128]

- Evaporation into air
- Blooming
- Leaching / extraction by a solvent

1.8.1 Evaporation into Air

Below its solubility limit, a LMW additive at the surface is depleted due to evaporation in case where the polymer is only exposed to air (and no other solvent). The rate of evaporation depends on the contact surface, temperature, and volatility (which in turn depends strongly on the exact MW) of the LMW molecule. Aging (oxidation) of PP in air within typical processing temperatures ranges (250 °C down to 120 °C) results in the emission (evaporation) of LMW molecules up to MW of around 100 g mol^{-1} [129,130]. All molecules identified are oxygenated aliphatic compounds, with aldehydes dominating. Evaporation of protective chemicals with a MW below 300 g mol^{-1} is also reported [131,132,133,134]. For thick (PP) samples with slow diffusion of additives but fast evaporation, this effect is diffusion controlled. The opposite is true for thin samples, with fast diffusing additives and slow evaporation, such that the effect is evaporation controlled [123].

1.8.2 Blooming

The effect of blooming occurs in cases where LMW molecules with lower volatility accumulate at the surface of plastic articles due to their concentration in the bulk of the article being above solubility limit. The effect is diffusion controlled, even if at very high concentrations at the surface evaporation also occurs [123]. The effect is i used in an intentional manner in the rubber industry, for chemical and physical antiozonants [135,136] as well as for modifiers like antistatic agents [137], slip agents and antifogging agents. Blooming is often reported as undesired side effect where typical HMW protective chemicals are used at (very) high concentrations and above solubility limits to meet stringent (severe) durability requirements of plastic products [138,139].

1.8.3 Leaching / Extraction by a Solvent

If the vapor pressure of a LMW molecule at the surface of a polymer is low, it might dissolve significantly faster in an organic solvent or water (where both are in contact with the surface of the plastic part) rather than in air. The effect can be controlled either by the diffusion of the LMW molecule to the surface or by the rate of removal from the surface [123]. The rate of removal depends strongly on the chemical nature of the solvent, extraction temperature and stagnation versus replenishment of the solvent. Leaching and extraction of LMW molecules is in general an undesired effect, which often results in a depletion of additives in the polymeric matrix and in conjunction a loss in performance. Furthermore, contamination of the extractive media can occur by LMW fragments of the polymer such as POSH (polyolefin oligomeric saturated hydrocarbons), MOSH (mineral oil saturated hydrocarbons) or even MOAH (mineral oil aromatic hydrocarbons). Equally LMW additives including protective chemicals can leach out of PP. A major differentiation is made by the chemical nature of the extractive medium and corresponding test conditions (in different industry sectors) and regulatory standards. Based on this the following categories are proposed to account for different environments

- Water or water-based detergents [140,141,142,143,144]
- Food simulant liquids (FSL) [141,145,146]
- Liquid food [141,147]
- Solid food [141,148]

This study also proposes a further sub-division pertinent to the extraction of LMW molecules by water into

- Technical components
- (Drinking) water containers (some technical but not regulatory overlap to aqueous based foods)
- (Drinking) water pipes under pressure

In the first (technical compounds), the only concern is the depletion of the protective chemical and as direct consequence a premature failure of the plastic article.

Examples are washing machine and dishwasher parts made of (inorganic filler containing) PP [149,150,151,152] or PE wire and cable compounds [153].

The major differences between drinking water containers and drinking water pipes under pressure are the service life temperature, the durability requirement of the plastics part and the complexity of the manufacturing of the plastic part. Pressure-less drinking water containers experience a temperature range of approximately 5 to 30 °C, while drinking water supply (and sanitary) pipes experience temperatures of up to 65-70 °C. The reason for the high temperature is the suppression of pathogens in drinking water [155,156,157,158,159]. Requirements for durability and mechanical strength are opposites. For "packaging type" drinking water containers, only several weeks of service life are required, while for pipes beyond 50 years of service life are required. *The type and concentration of protective chemical recommended is proportional to the required service life* [160,161]. Hence, in PO pipe materials, significantly higher concentrations of protective agents are present. Due to the higher mechanical resistance of pressurized drinking water and sanitary water pipes, PE is often converted via an intentional crosslinking reaction from a thermoplastic into a thermosetting material (PEX). Depending on the crosslinking mechanism, additional LMW molecules can be generated [162,163,164]. *In both these cases, the major concern is a potential contamination of drinking water by LMW molecules and health risk associated with exposure and their bodily uptake*. **Figure 19** summarizes the temperature range for non-pressurized water containers compared with pressurised pipes. Note the typical generic testing temperatures for PO for long term thermal stability (LTTS) from approximately 90 °C to 150°C is just below the softening behaviour of the specific PO.

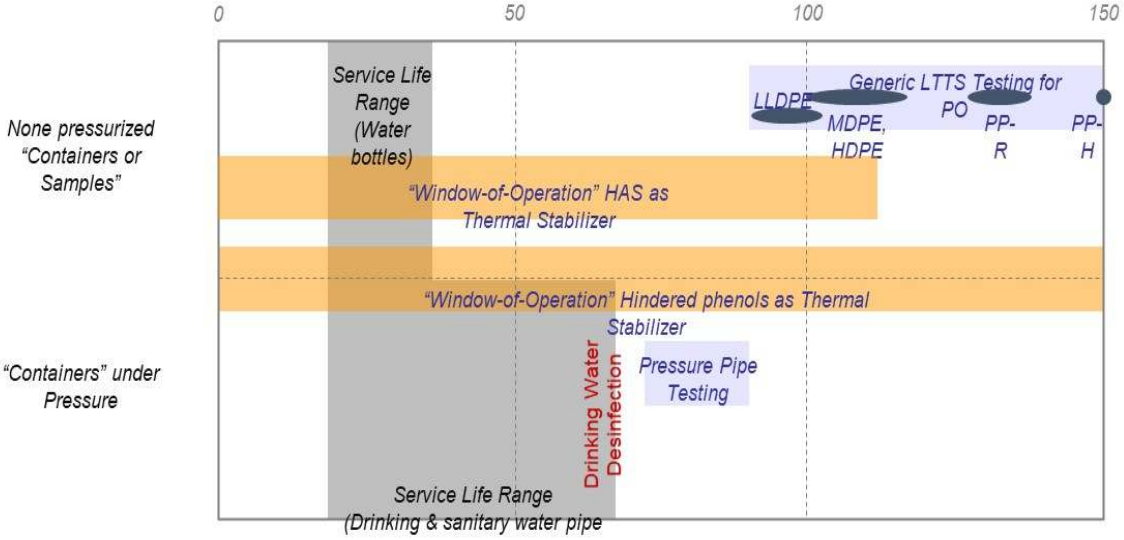


Figure 19: Temperature range during service life of PO articles and typical test & water extraction conditions (modified after [154])

The chemical nature of molecule emissions from PO can be clustered, as in **Table 8**. Apart from aliphatic, oxygenated aliphatic, aromatics and oxygenated aromatics as well still unidentified molecules exist, which therefore cannot be associated with any of the classes in **Table 8**. The origin of the four classes of LMW molecules varies and requires a differentiation into IAS (intentionally added substances) and **NIAS (non-intentionally added substances)**.

The idea of NIAS has been formally introduced as concept in the EU Plastic regulation for food contact materials in 2011 [166] and hence concerns only (indirect) food contact material and to a certain degree drinking water application. In this project the "spirit" of this regulation (i.e., to make sure that the final food contact article is safe and known migration or degradation substances identified) shall be evaluated. The ultimate legal obligation to ensure the safety lies with the manufacturer of the food contact article but can be delegated to manufacturers of components (for their part). The threshold and concern limit is fixed at 10 µg/kg food; hence 10 ppb (except for CMR Carcinogen, Mutagen, Reproductive substances, which have an even lower limit). A similar regulation exists in the USA [167].

Table 8: Classes of LMW molecules potentially emitting from PO [154]

Chemical Nature	*Classification*	*Origin*	*Reference*
Alkane, Alkene **Aliphatic** Hydrocarbon	IAS	Synthesis reactor Chemistry of polymerization Technology of polymerization Catalyst system Hydrogen response	Table 1 3, 17, 122, 154, 165
Oxygenated Aliphatic (Aliphatic with hetero atom)	NIAS	**Melt-processing and/or reactive extrusion** Oxidative degradation of PP Oxidative degradation of organic additives	Reaction R 1.8, R 1.11, R 1.13, R 1.14, R 1.17, R 1.25 122, 165
Aromatic Hydrocarbon **Aromatics**	IAS	Technology of polymerization Separation of polymer from reaction medium Catalyst deashing Monomer stripping **Work-up of none-commercial grades**	Table 1
Oxygenated Aromatics	NIAS	**Melt-processing**, LTTS Protective agents (HP, P, …)	140, 143, 144, 152

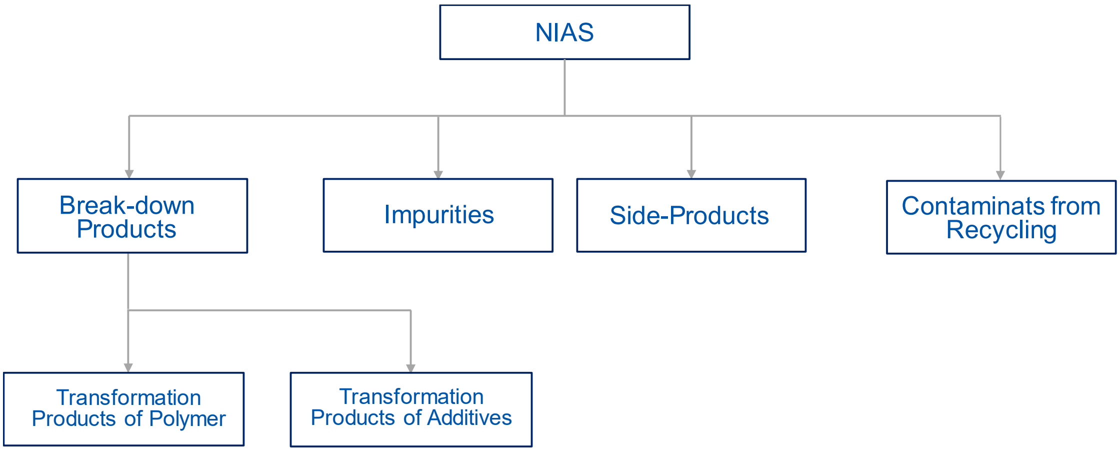


Figure 20: Definition & categorisation of NIAS [168]

Derived from **Table 8** is a further differentiation of the origin of NIAS in **Figure 20**. The potential health risk of NIAS increases in **Figure 21** from left to right; with the major concern being around "*known & not (yet) authorised*" substances. The lack of authorisation is though in general not due to an established toxicological (hazard) issue but related to the lack of a toxicological profile for the NIAS.

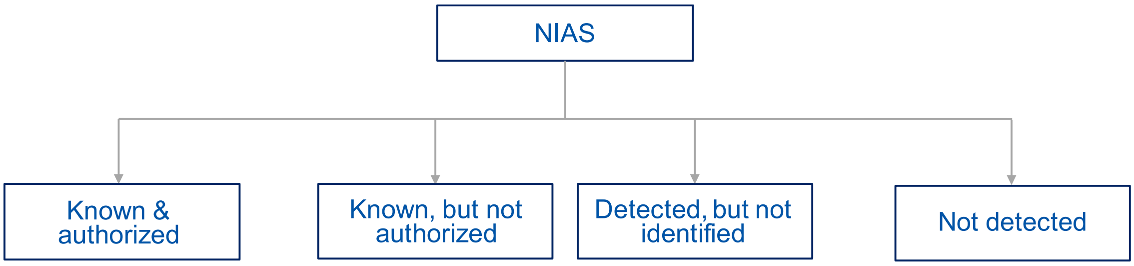


Figure 21: Health risk of NIAS [168]

A specific sub-class of NIAS are water extractable LMW fragmentation products of protective chemicals for PO, which are named after the work of Arvin *et al*. [139, 168]. Arvin *et al*. have identified 13 (thirteen) transformation products from protective chemicals, which can be extracted from PE pipes [170,171]. These fragments are identified in **Chapter 3**.

Meanwhile attempts are being made to assess the toxicological profile of fragments and agree on the maximum exposure limit (and hence maximum daily intake) [172,173].

1.9 Specific Aims and Objectives

As stated in Section 1.1, selected antioxidant manufacturers and industry associations are attempting to establish the nature and toxicological profile of the major fragmentation products of the main antioxidants used in the PO industry. Hence the wider aim of this research project is to understand the environmental impact of protective chemicals, which are intentionally incorporated into polyolefins to retard oxidative degradation, on the formation of NIAS under extractive conditions (into water).

Specifically, the working hypothesis (principal aim) of this research project is to identify NIAS from commercially available protective chemicals and demonstrate whether proper selection of protective chemicals during melt conversion (and service life) can reduce (or eliminate) the number and concentration of NIAS that leach into water (from either the protective chemical or a PO substrate).

Within this context the following objectives are required:

- Development of a simple extraction method to obtain leachates from various PO samples
- Development of an analytical method to identify leachates from polyolefin samples
- Development of an analytical method to (semi-) quantify leachates
- Evaluation of (for a range of protective chemicals) the structures which display fragmentation and compare the fragmentation products with databases of molecules of known eco-toxicity
- Determination of a polymer processing window that optimizes stabilisation efficiency whilst minimising Protective Chemical (stabiliser) fragmentation

Footnote: It is not an aim of this study to develop a standardised test with globally agreed upon experimental conditions (e.g., international standards for the testing of water pipes). Though it is an aim of this study to understand the importance of the selection of protective chemicals relative to other parameters (such as selection of pipe material class, processing conditions, extraction conditions respectively conditions of use and preparation of sanitary water). It is envisaged that this study could help to (re-)centre discussions on contaminants in drinking water which originate from protective chemicals, compared with other sources of contamination. It is a further aim of this study to determine whether such a phenomenon is limited to the processing and use of PO pipe material or spread to other areas such as food packaging.

2 Experimental

2.1 Rationale for adopted methodology

This research work aims to identify **NIAS (non-intentionally added substances) extract-able (into water) from PO**. The vast majority of studies attempting to identify leachable or extractable compounds from PO have used commercially available products of unknown provenance [140,232]. This has led to extensive variability in the types and concentrations of NIAS identified. Physical and chemical variations in the production of PO exist not only at the polymerisation and compounding stages, but more significantly downstream where different melt-processors convert the PO compound to final product. Because of this, it is not possible to ascertain whether NIAS have resulted from 'good' or 'poor' processing; a situation made more complex by difficulties in defining an appropriate 'processing window'.

During the production and service-life of a PO product in contact with water (for example pipes and packaging materials) the following parameters could influence the presence of extractable organic fragments:

- Synthetic process to produce PO
- Type and amount of protective chemicals
- Type and amount of modifiers and other additives
- Specific melt-processing conditions
- Specific processing operations (e.g., devolatilization or cleaning procedure)
- Service-life age of the plastic PO product

To understand how and why NIAS arise it is necessary to use known PO raw materials and melt-process them in a controlled manner, so that results obtained can be reliably compared. To enable this, the research undertaken here has been limited to identifying NIAS arising from organic compounds originating both from protective chemicals (antioxidants) and the polymer substrate (PO).

Furthermore, water extraction conditions should be relevant to end-use conditions. Often, studies have used water extraction conditions that exacerbate the situation to ‘force’ the detection of low concentrations of NIAS [140,232]. In this study water extraction temperatures ranging from 20°C to 60°C, together with the known type and amount of protective chemicals, allow a realistic assessment of the NIAS that may arise in water containment applications. Here conditions will simulate non-durable packaging applications (low water temperature and low concentrations of protective chemicals added) to durable sanitary pipe applications (high water temperature and high concentrations of protective chemicals).

2.2 Raw Materials

2.2.1 Polymer Substrates

Polyolefins (non-commercial grades, not cross-linked) without protective chemicals (or other additives) were obtained from Korea Petrochemical Ind. Co. Ltd. (**Table 9**). To obtain these PO powders, the procedure to discharge the polymers from the industrial synthesis reactors (before addition of modifiers) resulted in some variation between different batches of the same polymer. Where required, the polymers obtained were cryogenically ground to obtain a fine powder. The polymer powders were stored in a refrigerator (< 5°C) to minimize oxidation. No further purification of the polymers was undertaken.

Table 9: Physical characteristics of PO substrates as supplied

Polyolefin	**Code**	**Catalyst**	**Melt Flow Index MFI** (230°C/2.16 kg [g/10min])	**Density** (g cm^{-3})
Polypropylene	YUWHA PP 5014*			
Batch 1	**PP-A**	Z/N	~5-6	0.9
Batch 2	**PP-B**	Z/N	3.2	0.9
Batch 3	**PP-C**	Z/N	1.1	0.9

2.2.2 Protective Chemicals (and other additives)

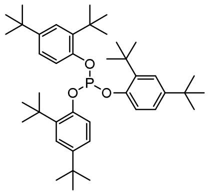
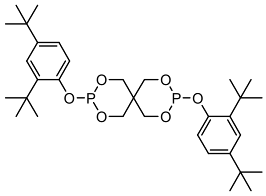
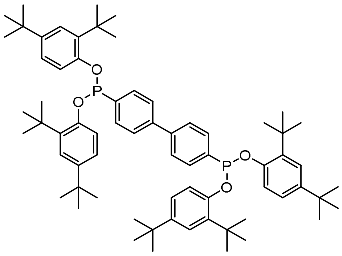
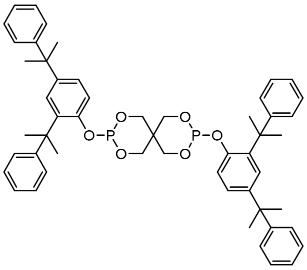
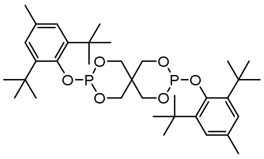
A total of twenty-six (26) organic additives and three (3) inorganic additives were evaluated for their contribution to water-extractable fragments. Twenty-four (24) of the organic additives are known to be protective chemicals, while the remaining two (2) organic and inorganic additives are known to be scavengers of low molecular weight LMW molecules. The additives were categorised primarily by their function in PO as:

- Protective chemicals during melt conversion
- Protective chemicals during service life
- Scavengers of selected low molecular weight LMW compounds

The additives were further categorised by chemical class (**Tables 10 to 13**]. The coding system is that adopted universally by the polymer additives industry [174]. The additives were incorporated into the polymeric substrates as received; no further purification took place.

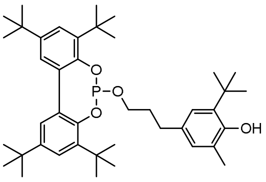
It is useful to note that the Phosph(on)ites constitute the major category of protective chemicals used as processing (co-) stabilizers for polyolefins. All six (6) phosph(on)ites are recommended for use in polyolefins [175-180]. An additional reason to select P-5, P-9 and P-19 is the definition of their Specific Migration Limit SML under European law. The migration limit of 5 mg/Kg food includes the total of the sum of the initial phosphite structure and selected reaction products [183,184].

Table 10: Phosph(on)ites protective chemicals added to PO during melt conversion

Code	Chemical Name	Chemical Structure	Class Description Reference
P-1	Tris (2,4-di-tert-butylphenyl) phosphite **31570-04-4*** 647 Dalton $C_{42}H_{63}O_3P$		**Mono-phosphite** Alkylated aryl phosphite Hydrolytically stable 4.8 % Phosphor content (medium molar activity) Workhorse of PO industry (supplied by Songwon Industrial)
P-3	Bis (2,4-di-tert-butylphenyl) pentaerythritol diphosphite **26741-53-7** 605 Dalton $C_{33}H_{50}O_6P_2$		**Di-phosphite** Alkylated aryl phosphite Very sensitive to hydrolysis 10.3 % Phosphor content (high molar activity) (supplied by Songwon Industrial)
P-4	Tetrakis(2,4-di-tert-butylphenyl)-4,4-biphenyldiphosphonite **119345-01-6** 1035 Dalton $C_{68}H_{92}O_4P_2$		**Di-phosphonite** Alkylated aryl phosphonite Sensitive to hydrolysis 6.0% Phosphor content (lo to medium molar activity) High initial rate constant for reaction with peroxides (supplied by Clariant International Ltd)
P-5	Bis (2,4-dicumyl phenoxy) penta-erythritol diphosphite **154862-43-8** 853 Dalton $C_{53}H_{58}O_6P_2$		**Di-phosphite** Di-cumyl aryl phosphite Hydrolytically stable 7.3 % Phosphor content (high molar activity) **EU SML covers selected reaction products** (supplied by Dover Chemical Corporation)
P-9	Bis(2,6-di-ter-butyl-4-methyl phenyl) penta- erythritol-diphosphite **154862-43-8** 633 Dalton $C_{35}H_{54}O_6P_2$		**Di-phosphite** Alkylated aryl phosphite Hydrolytically stable 9.8 % Phosphor content (high molar activity) (supplied by Adeka Corporation)

* numbers in bold type indicate the **CAS # of the chemical**

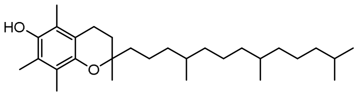
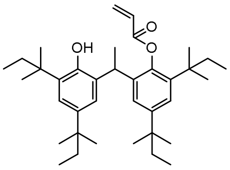
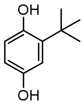
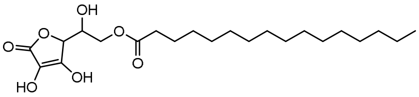
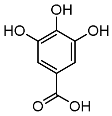
Table 10b: Phosph(on)ites protective chemicals added to PO during melt conversion

Code	Chemical Name	Chemical Structure	Class Description Reference
P-19	2-tert-butyl-6-methyl-4-[3-(2,4,8,10-tetratert-butylbenzo[d][1,3,2] benzodioxaphosphepin-6-yl)oxypropyl] phenol **203255-81-6** 661 Dalton $C_{42}H_{61}O_4P$		**Mono-phosphite** Alkylated aryl phosphite **Hybrid** **Dual function Hindered Phenol & Phosphite** Hydrolytically stable 4.7 % Phosphor content (low molar activity) **EU SML covers selected reaction products** (supplied by Sumitomo Chemical)

* numbers in bold type indicate the **CAS # of the chemical**

A second sub-category of five (5) protective chemicals during melt conversion was selected based on the chemistry of hindered phenols and derivatives (**Table 11**). Except for AO-6 [185], none of these chemicals is suggested for use in polyolefins. Three (3) of the selected chemicals are approved for use as protective chemical in food and have been assigned an “E number” under EFSA **E**uropean **F**ood **S**afety **A**uthority [186]. AO-60 was used as “representative” for the corresponding higher molecular weight gallic acid esters which constitute an additional range of protective chemicals for use in food. The substances were not available at the time of the experiments.

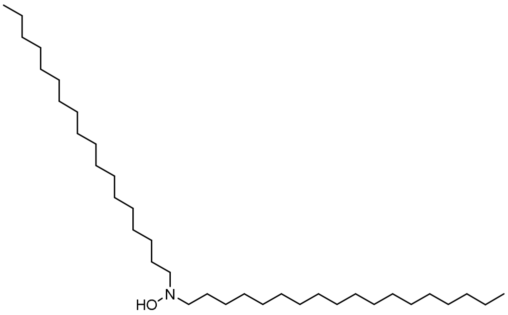
Table 11: Hindered Phenol protective chemicals added to PO during melt conversion

Code	Chemical Name	Chemical Structure	Class Description Reference
AO-6	α-Tocopherol **10191-41-0** 431 Dalton $C_{29}H_{50}O_2$		**Hindered Phenol Tocopherol** Natural antioxidant (mixture) Direct food contact additive E 306 E 306-E 309 (mixture) Molar activity 2.3 [mol OH/kg additive] Carbon-centred radical scavenger (purchased from Sigma Aldrich)
AO-36	2-(1-(2-Hydroxy-3,5-di-tert-pentyl-phenyl) ethyl)-4,6-di-tert-pentylphenyl acrylate **123968-25-2** 549 Dalton $C_{37}H_{56}O_3$		**Acryloyl-modified Hindered Phenol** Molar activity 3.6 [mol OH/kg additive] Molar activity 1.8 [mol acryloyl group/kg additive] Carbon-centred radical scavenger (supplied by Sumitomo Chemical)
AO-53	Tert-butylhydro-quinone **1948-33-0** 166 Dalton $C_{10}H_{14}O_2$		**Hydroquinone** TBHQ Direct food contact additive E 319 Molar activity 6.0 [mol OH/kg additive] (purchased from Sigma Aldrich)
AO-58	Ascorbyl palmitate **137-66-6** 415 Dalton $C_{22}H_{38}O_7$		**Fat soluble ester derivative of Vitamin C** Direct food contact additive E 304 Molar activity 2.4 [181] [mol OH/kg additive] (purchased from Sigma Aldrich)
AO-60	Gallic acid **149-91-7** 170 Dalton $C_7H_6O_5$		**"Functional group" of direct food additives E 310- E313** Molar activity 5.9 [182] [mol OH/kg additive] E 310 Propyl gallate E 311 Octyl gallate E 312 Dodecyl gallate E 313 Ethyl gallate (purchased from Sigma Aldrich)

* numbers in bold type indicate the **CAS # of the chemical**

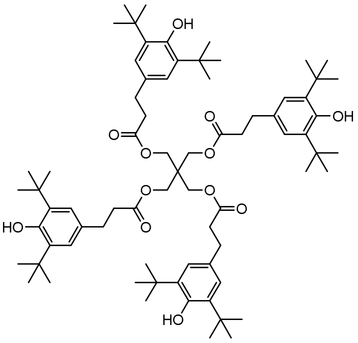
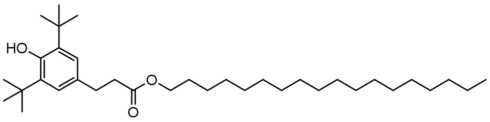
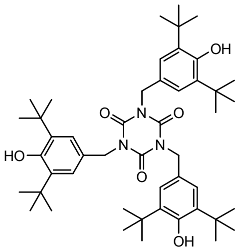
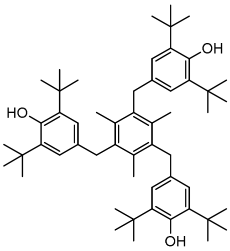
Table 12 lists additional protective chemicals during melt conversion which are based on a different chemistry. HYA-1 is recommended for use in polyolefins [187]; while L-2 is currently being evaluated in polyolefins. L-2 is the high molecular weight, oligomeric derivative of the original lactone L-1 [188-190].

Table 12: Additional categories of protective chemicals added to PO during melt conversion

Code	**Chemical Name**	**Chemical Structure**	**Class Description Reference**
HYA-1	N,N-Dioctadecyl-hydroxylamine **143925-92-2** 538 Dalton $C_{36}H_{75}NO$		**Hydroxylamine** Mixture-by-process (purchased from Sigma Aldrich)
L-2	Lactone Benzofuranone **No CAS# assigned** approx. 1000 Dalton	(chemical structure not identified by supplier)	Experimental high molecular weight lactone [188,189] (received from MILLIKEN Chemical, USA)

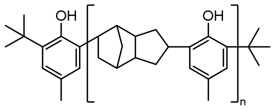
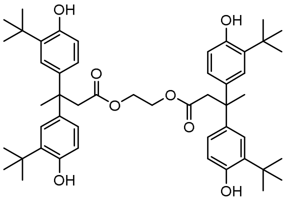
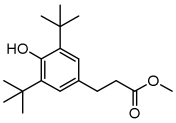
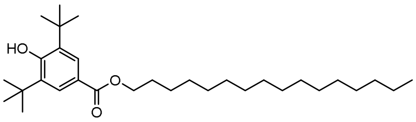
* numbers in bold type indicate the **CAS # of the chemical**

Table 13: Hindered Phenol protective chemicals added to PO for Service-Life protection

Code	Chemical Name	Chemical Structure	Class Description Reference
AO-1	Pentaerythritol tetrakis 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate **6683-19-8** 1178 Dalton $C_{73}H_{108}O_{12}$		**Hindered Phenol** 2,6-di-tert.butyl (DTB) hinderance Molar activity 3.4 [mol OH/kg additive] Medium molar activity 4 ester bonds/molecule High molecular weight (supplied by Songwon Industrial)
AO-2	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate **2082-79-3** 531 Dalton $C_{35}H_{62}O_3$		**Hindered Phenol** 2,6-DTB hinderance Molar activity 1.9 [mol OH/kg additive] Low molar activity 1 ester bond/molecule High compatibility in PO (supplied by Songwon Industrial)
AO-3	1,3,5-Tris (3,5-di-tert-butyl-4-hydroxy-benzyl) isocyanurate **27676-62-6** 784 Dalton $C_{48}H_{69}N_3O_6$		**Hindered Phenol** 2,6-DTB hinderance Molar activity 3.8 [mol OH/kg additive] Medium molar activity No ester bonds Reduced re-activity due to isocyanurate group in para position (supplied by Songwon Industrial)
AO-4	1,3,5-Trimethyl-2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl) benzene **1709-70-2** 774 Dalton $C_{54}H_{78}O_3$		**Hindered Phenol** 2,6-DTB hinderance Molar activity 3.9 [mol OH/kg additive] Medium molar activity No ester bonds (supplied by Songwon Industrial)

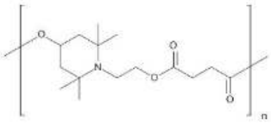
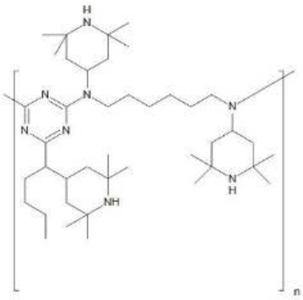
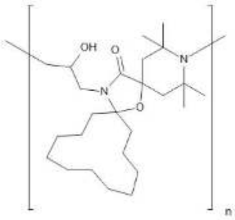
* numbers in bold type indicate the **CAS # of the chemical**

Table 13: Hindered Phenol protective chemicals added to PO for Service-Life protection (continued)

Code	Chemical Name	Chemical Structure	Class Description Reference
AO-7	*Reaction product of* Phenol, 4-methyl- with dicyclopentadiene-diene & isobutene **31851-03-3** Oligomer 700-900 Dalton $[270]_n$		**Hindered Phenol** 2,6-DTB hinderance & 2-TB hinderance Molar activity ~3.7 [mol OH/kg additive] Medium to high molar activity No ester bonds Mixture-by-process (supplied by Omnova Solutions)
AO-38	Bis [3,3-bis-(4'-hydroxy-3'-tert-butyl-phenyl)butanoic acid] glycol ester **32509-66-3** 795 Dalton $C_{50}H_{66}O_8$		**Hindered Phenol** 2-TB hinderance Molar activity 5.0 [mol OH/kg additive] High molar activity 2 ester groups (supplied by Clariant International Ltd)
AO-39	Benzenepropoanoic acid,3,5-bis (1,1-dimethylethyl)-4-hydroxy-, methyl ester **6386-38-5** 292 Dalton $C_{18}H_{28}O_3$		**Hindered Phenol** 2,6-DTB hinderance Molar activity 3.4 [mol OH/kg additive] Medium molar activity 1 ester group Intermediate for AO-1 & AO-2 (supplied by Songwon Industrial)
AO-54	Hexadecyl-3,5-bis-tert-butyl-4-hydroxybenzoate **67845-93-6** 474 Dalton $C_{31}H_{54}O_3$		**Hindered Phenol** **Hydroxybenzoate** 2,6-DTB hinderance Molar activity 2.1 [mol OH/kg additive] Low molar activity (supplied by Songwon Industrial)

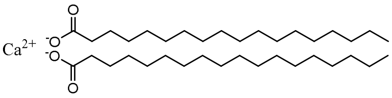
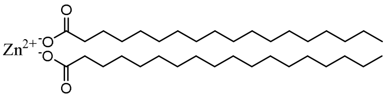
* numbers in bold type indicate the **CAS # of the chemical**

Table 14: Hindered Amine protective chemicals added to PO for Service-Life protection

Code	Chemical Name	Chemical Structure	Class Description Reference
HAS-5	Poly (4-hydroxy-2,2,6,6-tetramethyl-1-piperigine ethanol-alt-1,4-butanoic acid) **65447-77-0** Oligomer 3100-4000 Dalton $[283]_n$ [204]		**HAS** **Hindered Amine Stabilizer** Tertiary alkylated Molar activity ~3.2 [mol N-X/kg additive] Functional group in the backbone 2 ester groups/repeat unit (supplied by Sabo S.p.A.)
HAS-16	*Reaction material of* 1,6-hexanediamine; N,N'-bis (2,2,6,6-tetramethyl-4-piperidine-yl),2,4,6-trichloro-1,3,5 triazine; N-butyl-1-butylamine & N-butyl-2,2,6,6-tetramethyl-piperidine amine **192268-64-7** Oligomer 2600-3400 Dalton $[676]_n$		**HAS** **Hindered Amine Stabilizer** Secondary Molar activity ~4.4 [mol N-X/kg additive] Molecular weight distribution No fragments below 1000 Dalton [191] Triazine containing (supplied by Sabo S.p.A.)
HAS-25	*Polymer of* 2,2,4,4-tetramethyl-7-oxa-3,20-diaza-dispiro [5.1.11.2]-heneicosan-21-on & epichlorohydrin **78276-66-1** Oligomer > 1500 Dalton $[419]_n$		**HAS** **Hindered Amine Stabilizer** Mainly tertiary alkylated Molar activity ~2.4 [mol N-X/kg additive] Less than 20% of oligomers < 1000 Dalton (supplied by Clariant International Ltd)

* numbers in bold type indicate the **CAS # of the chemical**

Table 15: Scavengers of low molecular weight LMW compounds during melt-processing of PO

Code	**Chemical Name**	**Chemical Structure**	**Class** **Description** **Reference**
MS-1	Calcium stearate **1592-23-0** 607 Dalton $C_{36}H_{70}CaO_4$		**Metal soap** Organic (supplied by Songwon Industrial)
MS-2	Zinc stearate **557-05-1** 632 Dalton $C_{36}H_{70}ZnO_4$		**Metal soap** Organic (supplied by Songwon Industrial)
O-3	Synthetic Hydrotalcite SHT **11097-59-9** 604 Dalton $Mg_6Al_2(CO_3)(OH)_{16}$ * 4 H_20 (general formula) $Mg_{4.3}Al_2(CO_3)(OH)_{12.6}$ *m H_20 (specific quality used)		Layered aluminium-magnesium hydroxy-carbonate **Hydrotalcite** Inorganic (supplied by Kyowa Chemicals)
O-4	Zeolite **1318-02-1** $M^{n+}_{x/n}$ $[(AlO_2)^-_x\ (SiO_2)_y]$ * 2 H_2O		**Microporous alumino silicate** Inorganic (purchased from Sigma Aldrich)
O-5	Zinc oxide **1314-13-2** 81 Dalton ZnO		**Metal oxide** Inorganic Improved colour (purchased from Sigma Aldrich)

* numbers in bold type indicate the **CAS # of the chemical**

2.2.3 Reagents for extraction procedures

Water (deionised) was used for the water extraction experiments. Ordinary tap water was judged unsuitable due to varying type and concentration of contaminants depending on origin and timing of the batches [211]. Ethanol was purchased from Merk (grade: gas chromatography ECD and FID SupraSolv®)

2.3 Sample Preparation

Polyolefin PO powder (batch size 6 kg) was shaken by hand in a polyethylene bag with the corresponding amount of solid additive powders (betsenn 0 and 5000 ppm; see details in the different chapters). The purpose of this operation was to pre-distribute the additives in the PO matrix. Liquid additives were first adsorbed to a small quantity (10 g per 1000 g polymer) of PO powder, which was subsequently added to the remaining PO powder.

The mixtures were then homogenized by melt-compounding (melt-mixing), using a Toshiba TEM 37BS twin screw extruder with a temperature profile from 190°C to 215°C under nitrogen [198]. The powder mixture was added to a feeding hopper (3; **Figure 22a**) and melted by external heating (6; **Figure 22a**) as well as shear. The mixture was then compressed and conveyed towards the exit nozzle on the left by the screw(s) (1; **Figure 22a**). To improve homogenization, a high shear co-rotating twin screw extruder was generally used (**Figure 22b**). The operation was carried out under a nitrogen blanket to avoid contact of the PO with oxygen (contained in the ambient air). A cylindrical exit nozzle produced a (cylindrical) strand (of approximately 1 mm diameter) which was water-cooled and afterwards cut into lengths of 2-6 mm (**Figure 23**) to obtain PO granules. The exact dimension of the granules and subsequently the exact contact surface with extractive media depends on the type of cutter/granulator and the take-off speed.

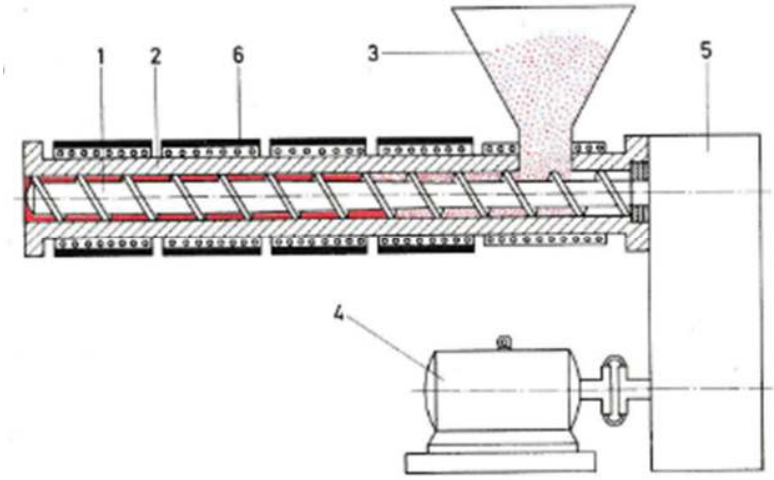


Figure 22a: Coumpounding twin screw extruder [4,197]

1 screw	2 Cylinder
3 Feeding hopper	4 Motor
5 Gear	6 Heating zone(s)

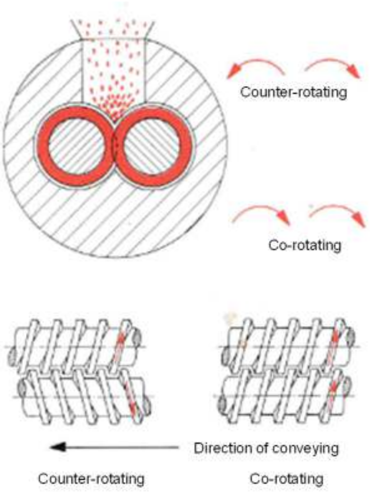


Figure 22b: Screw design of a compounding twin screw extruder [4,197]

Granulates are usually stored in plastic (polyethylene) bags but to prevent cross-contamination all samples prepared were stored in cleaned glass bottles [199].

Figure 23: Polyolefin granules after compounding

Multi-pass extrusion was then carried out in the laboratories of the Polymer Center of Excellence PCE (North Carolina, USA) on a Killion / Davis Standard single screw extruder in air with a temperature profile of 193°C to 255°C. The procedure is in accordance with the industry SOP given in the literature [200]. Multi-pass operation (5 passes) was undertaken according to specified extrusion conditions is just an *arbitrary* measurement of prolonged exposure of polymer melts to high temperature and high shear conditions as encountered during processing of thermoplastic polymers. There is *no exact correlation to actual production equipment and production conditions* (which may vary anyhow). Nevertheless, passing a PO through a laboratory extruder 5 times (multi-pass) represents approximately two industrial melt conversion operations (compounding and subsequent shaping of the plastic article). The selected processing conditions should therefore be considered as *generic conditions for PO processing* (i.e., provide a relative rather than absolute measure). The conditions are not specific to any particular conversion technology (e.g., extrusion of pipes or films, injection moulding) and/or end application (e.g. water transportation, construction or packaging).

Detailed parameters of the compounding operation (mixing) C-1 and the multipass extrusion M-1 are listed in **Table 16**.

Table 16: Conditions of PO preparation and processing

Condition	Laboratory	Equipment	Temperature [°C]	RPM [1/min]	Atmosphere	Feed Rate [kg/hour]
Compounding **C-1**	Songwon TIC SOP B26.3008	Toshiba TEM 37 BS Twin screw L/D 40	190/195/200/205/210/215	150	Nitrogen	10
Multi-pass **M-1**	PCE	1.5'' Single screw L/D 30	193/227/230/250/255	40	Air	

2.4 Sample Characterisation

The PO granules obtained from compound and multi-pass extrusion were characterised by the following techniques … melt flow index, yellowness index, extraction test and analyses of the leachates by GC-MS.

2.4.1 Melt Flow Index (MFI)

Melt flow index (MFI) is a very crude (but simple and practical) rheological measurement of the flow behaviour of polymer melts at a given temperature and for one single, given shear rate. It is proportional to the molecular weight of the polymer. An increase in melt flow index corresponds to a decrease in molecular weight due to chain scission, while a decrease in melt flow index corresponds to an increase in molecular weight due to crosslinking reactions. *Specifically for the highly linear macromolecules of PO, any change in MFI indicates a change in molecular weight MW and molecular weight distribution MWD.* The test conditions are determined by the weight of 2.16 (chosen for this study), 5, 10 or 21.6 Kg (respectively the corresponding shear rate) and the temperature which is typically 190°C for PE and

230°C for PP. The MFI value corresponds to the weight (in grams) of material pushed through the capillary nozzle within 10 minutes. The MFI measurement is illustrated in **Figure 24**.

MFI measurement was carried out in on a semi-automatic Ceasit 16412 [201]. Accepted industry standard operating procedure was followed according to ASTM D1238 and ISO 1133. The accuracy of the method is ± 0.1 [g/10 min], established for polypropylene.

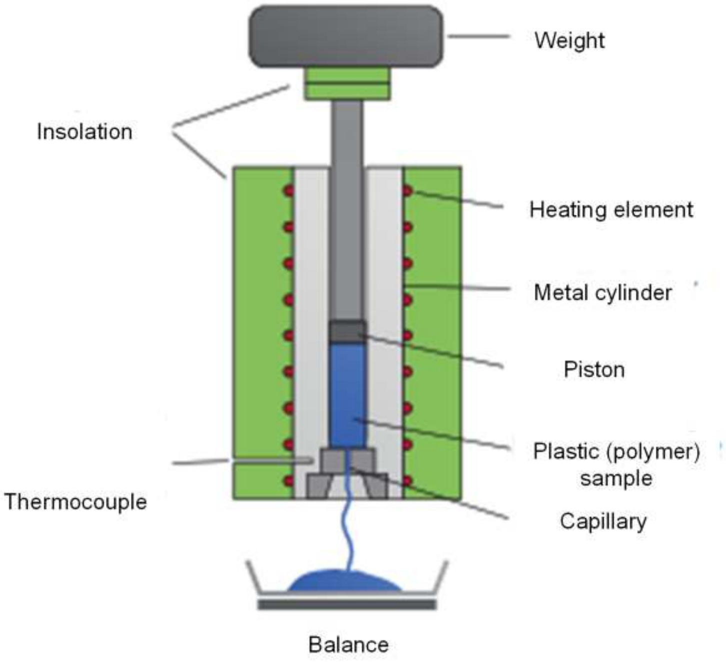


Figure 24: Illustration (cross-section) of MFI instrument [202]

2.4.2 Yellowness Index (YI)

The yellowness index is a measure of the discoloration of a (plastic) material with specific emphasis on yellowing (in contrast to Whiteness Index WI and total colour change E). It is calculated according to the equation:

Yellowness Index YI = 100 * (0.72a + 1.79b) / L

This equation emphasises change of the parameter ‘b’ in CIELAB colour space. In the 3-dimensional colour space of the CIELAB model, the coordinate ‘b’ represents the blue-yellow colour axis, while ‘a’ represents the red-green colour axis and ‘L’ the black-white colour axis or brightness [203]. The CIELAB colour space is illustrated in **Figure 25**.

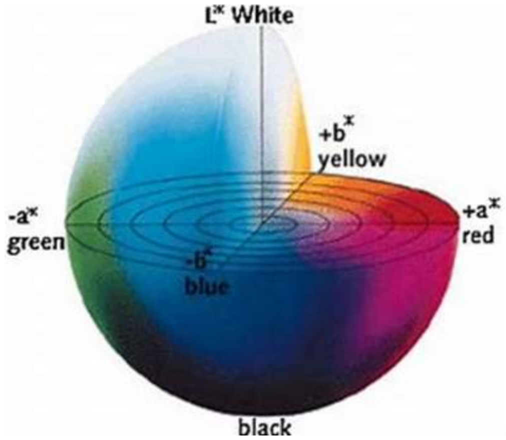


Figure 25: 3-D CIELAB colour space [203,205]

The PO substrate itself (while undergoing a significant change in molecular weight) does not develop significant colour during melt processing. A typical colour development is expected to be in the order of approx. 2-5 YI units. Higher values are contributed by coloured reaction products of the initial protective chemical. *High colour of the PO substrate is therefore an indication of a high degree of chemical reactions involving the protective agents and the potential of formation of LMW fragments which originate from the protective chemical.*

In industrial practice, discolouration of the PO substrate can be a prohibitive feature (e.g., food and drinking water packaging); though this is not always the case (e.g., highly pigmented drinking water pipes). Additive originating discolouration can in many cases be extracted from the PO substrate.

YI measurements were carried out using a Greytag Macbeth Spectro Eye [206]. For productivity reasons, YI is measured on PO granules rather than on moulded plaques, although the latter yield more precise results. Accordingly, measurements undertaken in this study were obtained from PO granules. Accepted industry standard operating procedures were followed according to ASTM D1925 and ISO E 313. The accuracy of the method is ± 0.25 [dimensionless unit].

2.5 Extraction and analysis of PO

2.5.1 Extraction Test (Migration of leachates from PO into extractive medium)

PO granules (10.0 g, after extrusion pass 5) were immersed in deionised water (100 ml). The mixture was stirred at the specified temperature for 72 hours (**Figure 26**). A “blank” with deionised water only was performed in parallel. Pre-trials established, that after 72 hours most extractable fragments had nearly quantitatively been extracted [207,208]. Equally, the method proved not sensitive to a variation of the time interval between sample preparation and extraction test [209,210]. The temperature for the water extraction was varied between 20 and 60 °C in order to cover the use of PO in typical water applications (packaging (e.g. bottles & cups); as well as sanitary water pipes).

Figure 26: Experimental set-up of migration test [208, 218] undertaken at MMU

This extraction procedure represents a simple and generic way to extract fragments from a high number of PO samples. It is not an internationally agreed upon and standardised extraction test as e.g., used by the pipe manufacturing industry to evaluate and certify the performance quality of PO pipes.

Although a very simple test, the reproducibility of the test depended strongly on the conditioning of the glassware to avoid cross-contamination. The glassware was washed with water, acetone (organic solvent) and later-on left in an oven overnight at 300°C. Details of the extraction conditions and analytical procedures are given in **Table 17**.

Table 17: Extraction conditions and principal analytical procedures

Code	Extractive Medium	Extraction	Adsorption	Desorption
E-1	Water (pure Evian)	Granules (pass 5) **72 h @ ~20°C** (RT) 10 g polymer/100 ml H_20	SBSE (“Twister®”) Stir Bar Sorptive Extraction	TD-GC-MS Thermal Desorption focused on a cryotrap prior to GC
E-3	Water (pure Evian)	Granules (pass 5) **72 h @ 40°C** (RT) 10 g polymer/100 ml H_20	SBSE (“Twister®”) Stir Bar Sorptive Extraction	TD-GC-MS Thermal Desorption focused on a cryotrap prior to GC
E-4	Water (pure Evian)	Granules (pass 5) **72 h @ 60°C** (RT) 10 g polymer/100 ml H_20	SBSE (“Twister®”) Stir Bar Sorptive Extraction	TD-GC-MS Thermal Desorption focused on a cryotrap prior to GC
E-2	Ethanol Methylated Spirit 74 OP >94% Ethanol 3-6% Methanol 1% Water	Soxhlet extraction **4 hours @ 200°C** 5 g polymer/35 ml C_2H_5OH	Concentration (N_2) Oily residue reconstituted in ethanol, filtered & injected into GA	TD-GC-MS Thermal Desorption focused on a cryotrap prior to GC

Extraction tests were carried out by the author at MMU and industrial laboratories (names withheld for reasons of confidentiality.

During the extraction procedure, fragments were absorbed and concentrated on a turning stir bar (“Twister®”; **Figure 27**). The sorbent (surface) phase of the stir bar was polydimethylsiloxane PDMS, which is recommended for non-specific sorption of polar chemical structures with a log $K_{ow} > 4$ [211]; with K_{ow} representing the partition coefficient between solubility of the fragment in *n*-octanol versus its solubility in water. This procedure is referred to as stir bar sorptive extraction (SBSE) and was used for extraction procedures **E-1**, **E-3** and **E-4**.

SBSE allows a solvent-free extraction of low molecular weight organic material from water [212-216]. It avoids contamination from organic solvents, concentration procedures, as well as excessive contamination from laboratory equipment. SBSE is reported to be 4 orders of magnitude more sensitive than the method solid-phase micro extraction (SPME) used in prior experiments [211,219-222].

After extraction, the fragments were desorbed from the "Twister®" using a thermal desorption system TD and a cryotrap prior to injection into a gas chromatography instrument [211].

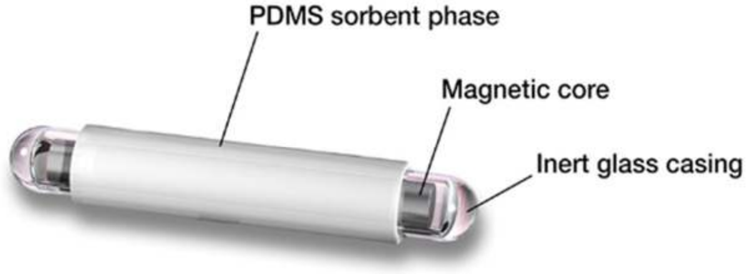


Figure 27: Illustration of a "Twister®" [217]

2.5.2 Gas chromatography mass spectrometry (GC-MS)

Gas chromatography (GC) is an analytical method, where samples, which can be vaporised without decomposition, can be separated, and analysed [223]. The principle is based on the separation of gaseous organic components due to the varying interaction of those molecules with a stationary liquid phase and the mobile gaseous phase. While the target compounds flow with the gas used as mobile phase through a narrow metal tube (column), they interact, based on their physical and chemical properties, to a varying degree with the stationary, solid phase. As consequence, the different target compounds take different times to pass through the column, hence differ in retention time. The equipment used in this study was as listed below [228, 229].

- Gas chromatograph: Agilent 7890A
- Thermal desorption: Gerstel TDS3 equipped with autosampler TDSA2 and LN2 cryotrap
- GC column: Standard apolar DB-5 type

A gas chromatograph is often coupled with a mass spectrometer (MS) [224] and hence referred to as GC-MS. The principle of MS is the ionization of organic compounds followed by rearrangements of chemical structures based on the mass-to-charge ratio (hence ultimately based on their mass).

GCMS analysis was performed in full-scan mode using an AGILENT Quadrupole 5975C Triple-Axis instrument [229].

During the ionization process, samples can fragment. Nevertheless, the fragmentation is mostly unique to the original structure and hence the parent compound can be identified [225-227]. The high sensitivity of SBSE allowed the MS equipment to be operated in full scan mode. Peaks detected were identified using data base library mass spectra NIST17 and by manual interpretation of the fragmentation pattern based on the known additive composition of the various PO samples.

Calibration curves of target fragments (so-called **ARVIN fragments 1 to 10**) were performed with 5 points of calibration and "spiked" into deionised water in the range 0.5 to 10 ppb. For target fragments ARVIN 1, ARVIIN 5 and ARVIN 10, solutions with the corresponding limit-of-detection LD and/or limit-of-quantification LQ were injected. Due to the unavailability of ARVIN 8, the structurally similar ARVIN 9 was used as calibration standard (**Table 18**).

Table 18: Calibration standards

Fragment # [1]	**ARVIN** [2]	**Chemical Name**	**CAS #**	**LD [ppb]**	**LQ [ppb]**
21a	1	4-ethyl phenol	123-07-9	**4.0**	**20.0**
63	2	4-tert-butyl phenol	98-54-4	**0.1**	**0.5**
135	3	2,5-Cyclohexadiene-1,4-dione, 2,6-bis (1,1-dimetylethyl)-	719-22-2	**0.1**	**0.5**
125	4	2,4-di-tert-butyl phenol	96-76-4	**0.1**	**0.5**
142	5	3,5-di-tert-butyl-4-hydroxystyrene	52858-87-4	**20.0**	**100.0**
143	6	3,5-di-tert-butyl-4-hydroxybenzaldehyde	1620-98-0	**0.1**	**0.5**
148	7	3,5-di-tert-butyl-4-hydroxyacetophenone	14035-33-7	**0.1**	**0.5**
156	8	7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione	82304-66-3	**---**	**---**
163	9	3-(3,5-di-tert-butyl-4-hydroxyphenyl) methyl propanoate	6386-38-5	**0.1**	**0.5**
	10	3-(3,5-di-tert-butyl-4-hydroxyphenyl) propanoic acid	20170-32-5	**>10000**	**---**

[1] Fragment # according to chapter 8.3

[2] ARVIN fragment nomenclature according to chapters 4 and 8.3

For non-target fragments (all fragments other than ARVIN 1 to 10; mainly oxidised-aromatic fragments) the closest calibration standard out of **Table 18** was chosen manually and on a case -by-case basis according to the closet retention time, structural similarity, and log K_{ow} [230]. *The quantification of none-target fragments must therefore be interpretated as "ARVIN fragment equivalent".* It is based on the assumption that SBSE extraction recovery and efficiency, as well as MS response, is similar to the calibration standard. The corresponding quantified results need to be considered with caution and as semi-quantitative. *For critical cases the results must be confirmed via an authentic calibration standard.*

The calibration solutions were analysed (at least) in duplicate (SBSE extraction + TD-GC-MS analysis). The samples were analysed directly after the creation of the calibration curves. The calculation was based on the total ion chromatogram TIC. As an example, a typical chromatogram of non-stabilised PP is shown in **Figure 28** and compared with the chromatogram of a very well stabilised version of PP (**Figure 29**). The experimental error is evaluated at ± 1-2 ppb for target structures.

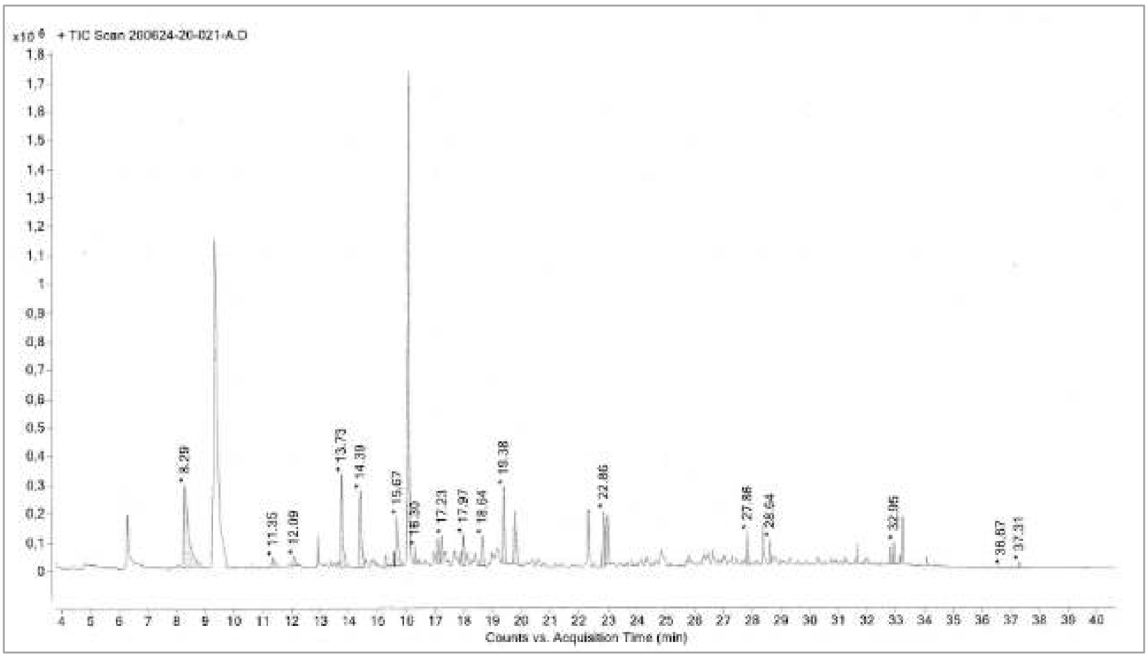


Figure 28: GC-MS chromatogram of non-stabilised PP [230]

Formulation: 750 ppm MS-1

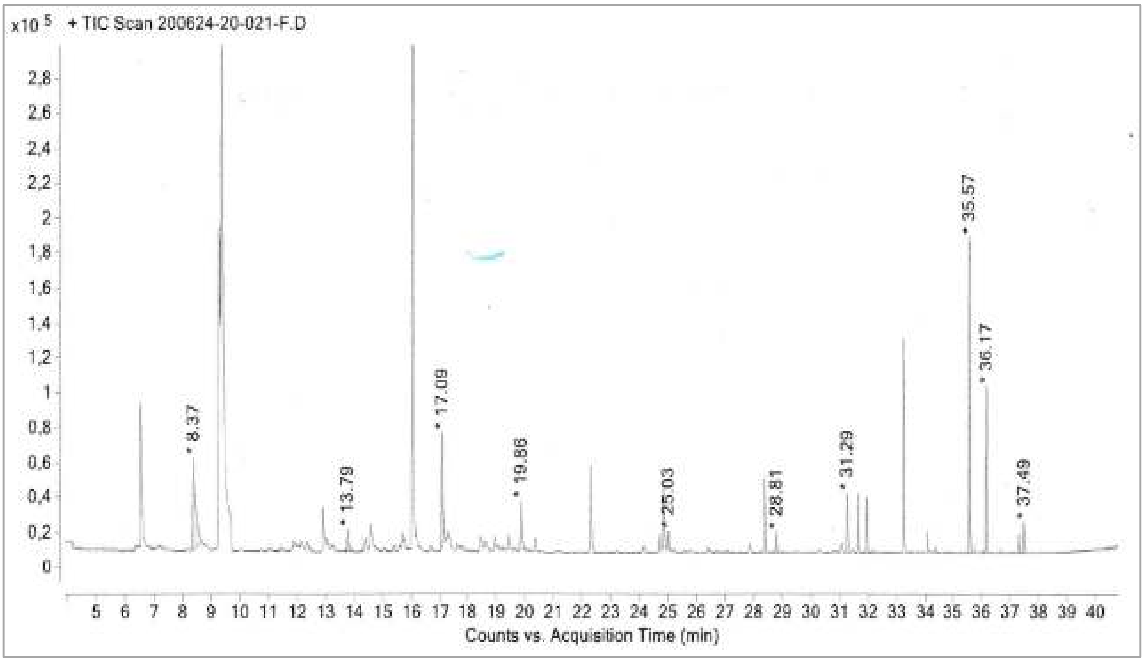
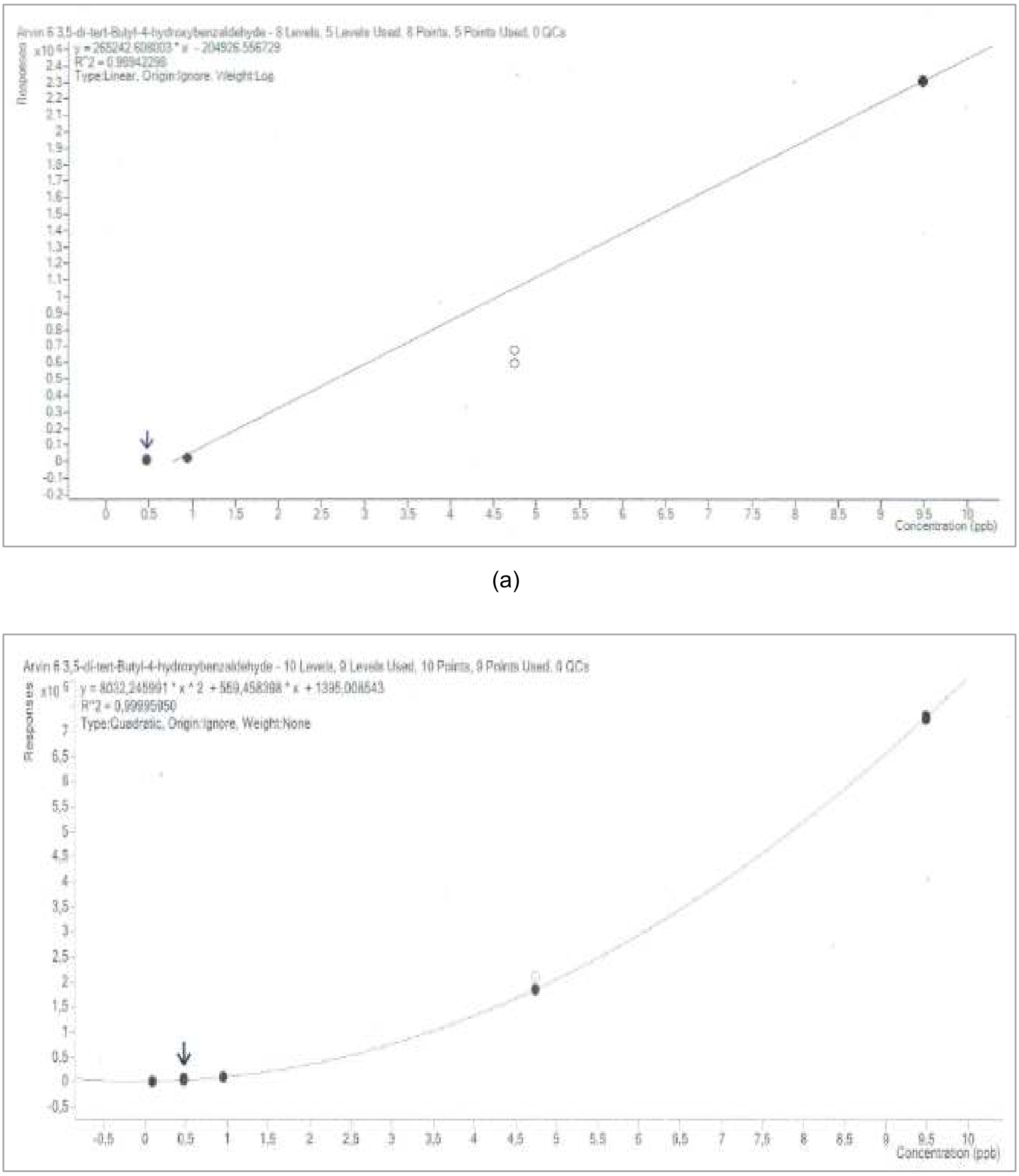


Figure 29: GC-MS chromatogram of stabilised PP [230]

Formulation: 750 ppm MS-1 + 5000 ppm AO-1 + 250 ppm AO-6 + 500 ppm P-5

Contaminants from the analytic procedure were mainly silane and siloxane compounds, which are known to bleed out of the PDM phase of the “Twister®” [211]. Contaminants detected in the “blank procedure” with deionised water were discarded. Occasionally contaminations (in the 1 to 2 ppb level) which could be directly correlated to a parallel project in the lab during sample preparation were also discarded. An example calibration curve is given in **Figure 30** for ARVIN 6 (fragment F# 143 – see results section).



(a)

(b)

Figure 30: Calibration curve of ARVIN 6 (fragment 143 obtained July 2020 (a) [230] and in June 2020 (b) [231]

2.6 Assessment of Toxicity of Extract-able Fragments

An assessment of the toxicity of extracted organics identified by GC-MS is made in several steps. In Step 1, selected of the extracted chemicals are clustered into intentionally added substances **(IAS)** and non-intentionally added substances **(NIAS)** and labelling according to the literature [310,311] is considered. For both groups, the components were searched on the positive list of the (draft) of the European Drinking Water Directive 2184/2020 [233] (Step 2) and on the positive list of regulation10/2011 of the European commission [313] (Step 3); although the latter is intended for food and not water contact. For those fragments not listed, a classification into CRAMER classes I, II and III is attempted and the corresponding threshold of toxicological concern (**TTC)** derived [234] (Step 4). A worst case possible daily intake scenario for water bottles and sanitary pipes is subsequently considered (Step 5).

3 Results and Discussion

3.1 Extraction Temperature

In this chapter the impact of temperature on the extraction of organic compounds, which have been subjected to the same melt-processing conditions (thermal history), is investigated. A temperature-range from 20°C (~ room temperature RT) to 60°C was selected. According to **Figure 19**, this covers the usage of PO for drinking water containers (0 to ~30°C) as well as the usage for sanitary (drinking) water pipes.

PP samples (lot PP-A; **Table 9**) were melt-processed according to conditions C-1 followed by M-1 (**Table 16**). In the first case, the formulation only contains 750 ppm of the modifier MS-1 (calcium stearate) to neutralise acidity originating from Z/N catalyst residues (**Table 1**). The second formulation also contains [750 ppm AO-1 + 750 ppm P-1] as protective chemicals. This type and concentration of protective chemicals package is considered as a typical stabilisation system for PP extrusion grades in the industry with a medium performance level for melt-processing and durability [17, 160, 161].

Figure 31 displays selected properties of the two formulations after melt-processing. In the absence of protective chemicals, a very high MFI (over 40 [g/10 min]) is obtained which indicates a severe oxidative degradation of the PP with a significant reduction of molecular weight. The dominating reaction pathways are reaction R 1.10 and R 1.20 (see **Scheme 1** and **Table 2**).

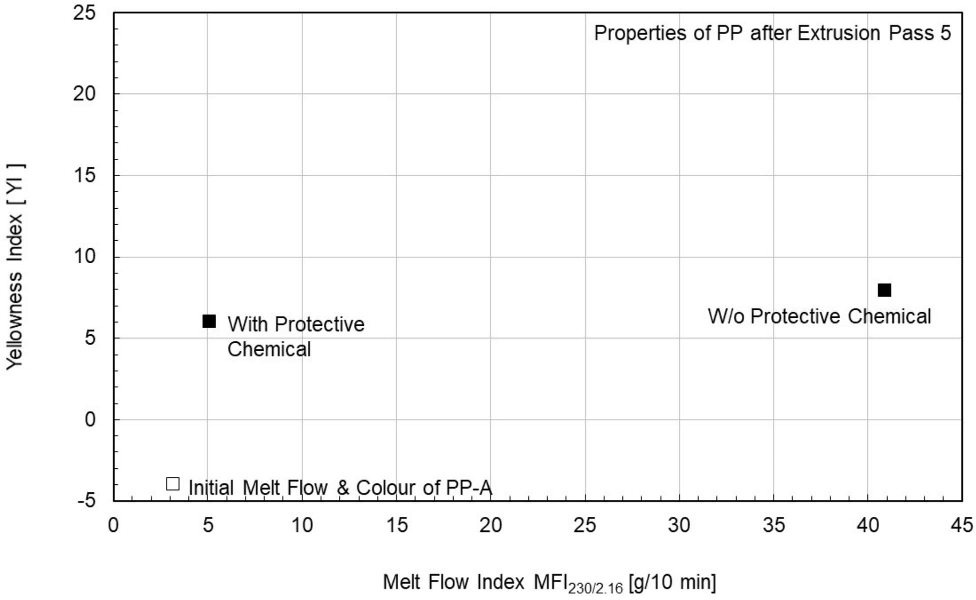
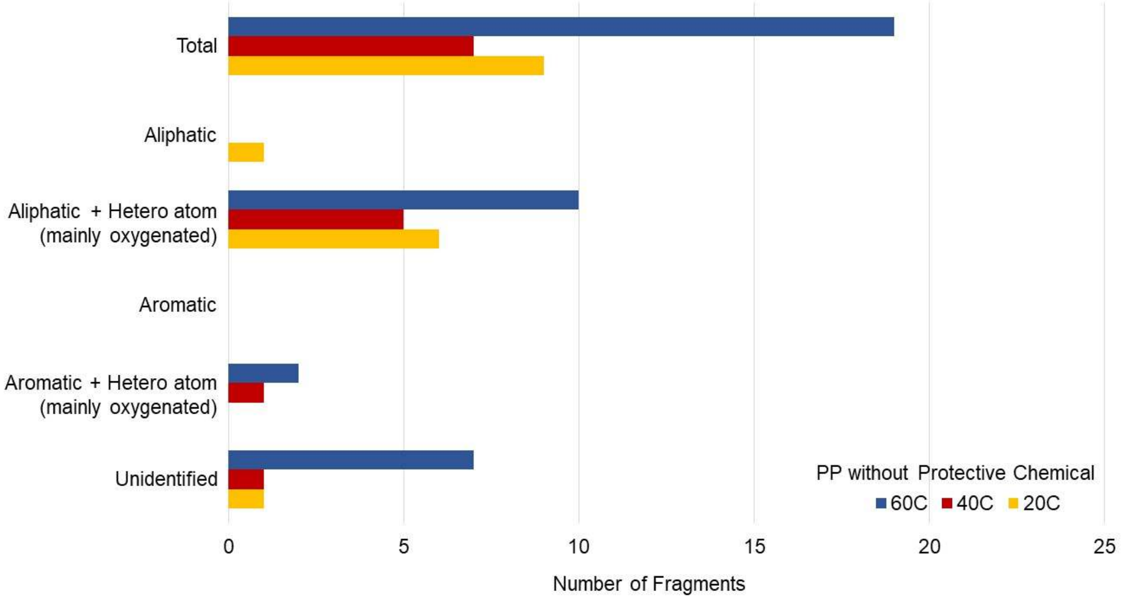


Figure 31: Properties of melt-processed PP in the presence and absence of protective chemicals

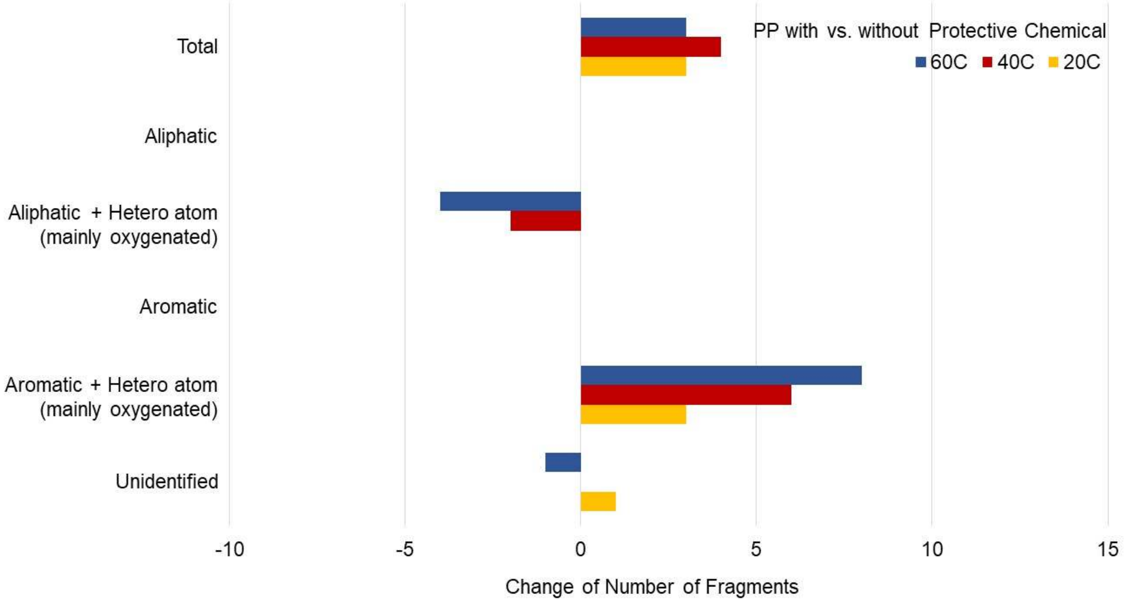
Extrusion Condition:	C-1, M-1
Extraction Condition:	E-1, E-3 & E-4
Formulation:	PP-A + 750 ppm MS-1 PP-A + 750 ppm MS-1 + 750 ppm AO-1 + 750 ppm P-1

The very high MFI correlates with very low MW [235], which results in poor mechanical properties [5], such that the formulation is considered unsuitable for service use. In contrast, the formulation with the protective chemicals package (Phenol AO-1 and Phosphite P-1) results in a much lower MFI, indicating a significant reduction in oxidative degradation. There is also significant increase in colour (by ~10 units) revealing the formation of chromophores of unknown nature both in the presence and absence of the protective chemicals.

Water extraction of PP without protective chemicals reveals the presence of 22 organic extract-able compounds [237,238], which will be termed for the rest of the report as (extract-able) fragments. The total number of fragments is similar at 20 and 40°C but increases by a factor of ~2.5 at 60°C (**Figure 32a**). The total concentration of all extract-able fragments doubles between 20 and 40°C from an initial concentration of ~7 ppb. At 60°C the concentration is a factor of 8.3 higher than that at 20°C (**Figure 33a**). A sub-classification of the type of fragments according to **Table 8** confirms the overall increase in number and concentration of fragments with increasing temperature; especially at 60°C.

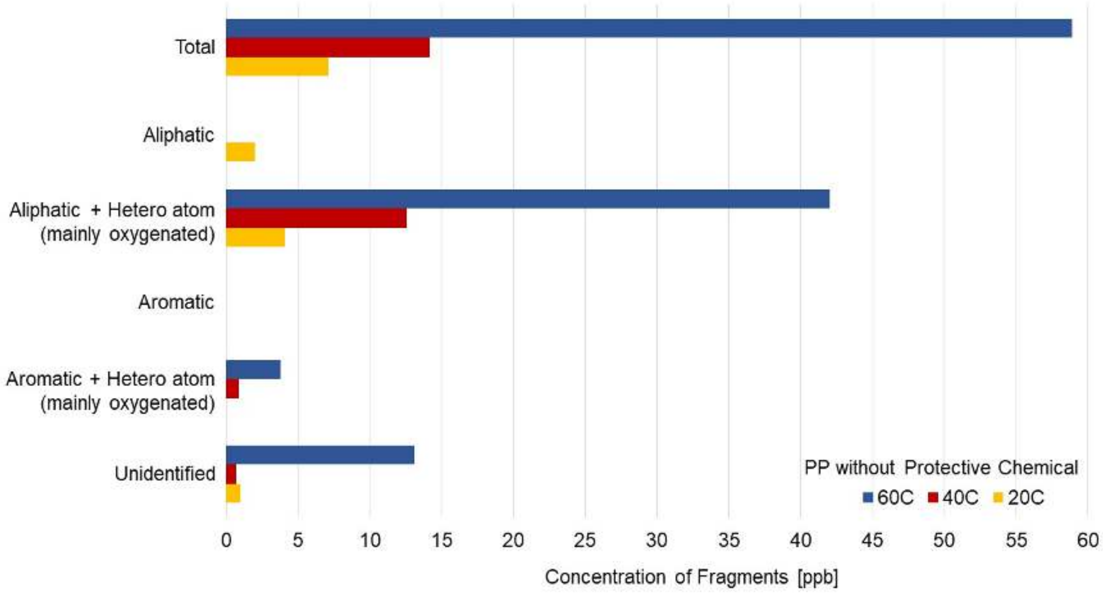


(a)

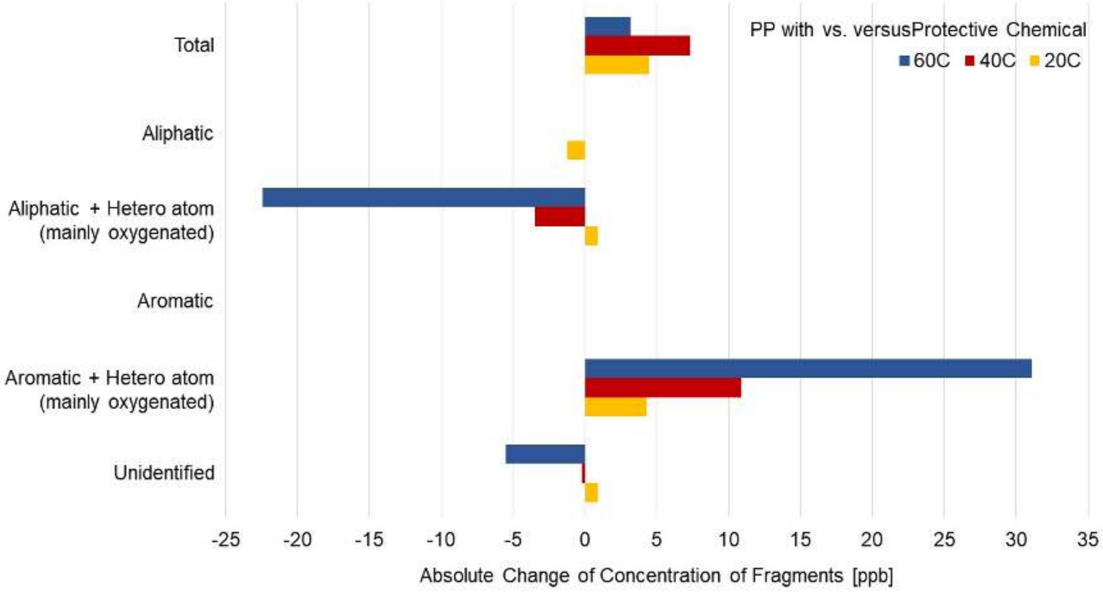


(b)

Figure 32: Number of extract-able fragments from PP without protective chemical (a) and absolute change of the number of fragments due to the presence of protective chemicals (b)



(a)



(b)

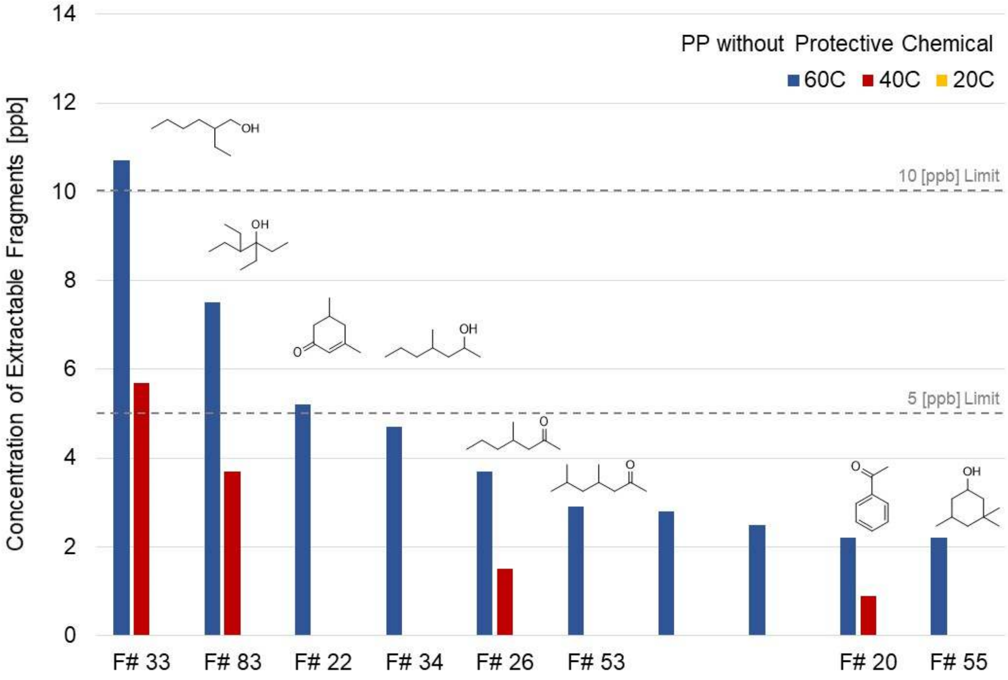
Figure 33: Concentration (ppb) of extract-able fragments from PP without protective chemical (a) and absolute change of the concentration (ppb) of fragments due to the presence of protective chemicals (b)

Oxidised-aliphatic fragments dominate together with unidentified fragments. Although not matched to a specific chemical structure, more than 50% of the unidentified fragments are confirmed to be oxidised. It is therefore postulated that these unidentified species are also oxidised-aliphatic fragments. It is noteworthy that only acetophenone (Fragment F# 20; see **Appendix 7.3**) is detected as an oxidised aromatic fragment. This fragment is postulated to be an oxidation product of typical aromatic solvents (e.g., toluene, styrene, ethylbenzene) potentially used in non-industrial procedures to isolate and/or purify this specific group of PP samples. Only in one case (F# 41) a Hindered Phenol HP derivate is detected. The origin of this fragment remains unexplained.

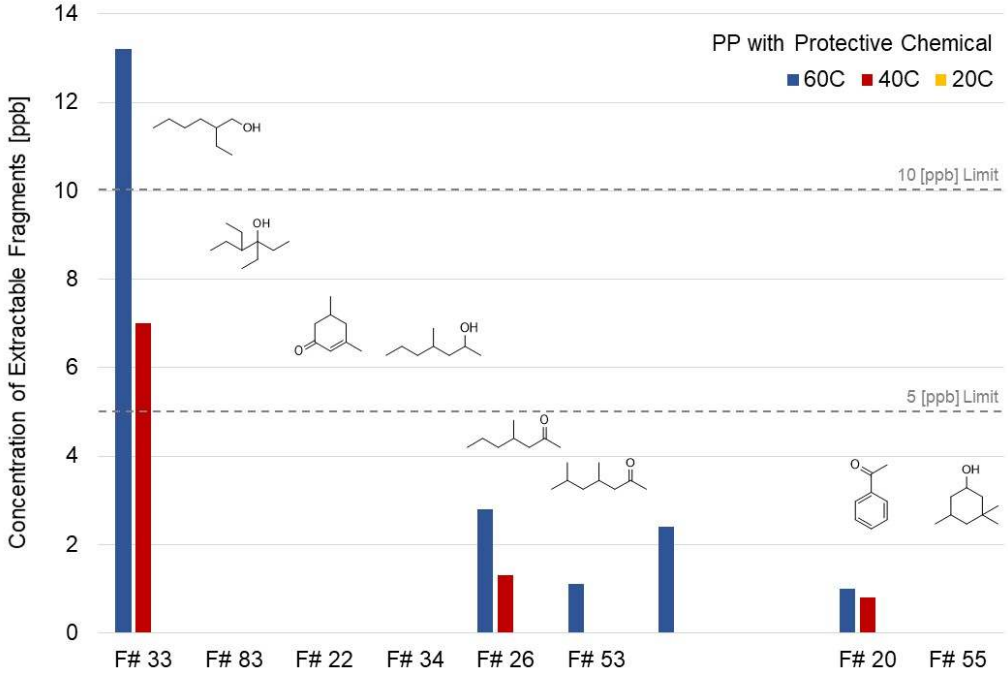
Addition of protective chemicals to PP results in an approximately constant increase in the total number of fragments and a small but constant increase in the total concentration of fragments; independent of the extraction temperature (**Figure 32** and **Figure 33 b**). A more detailed examination revels a decrease in number and a strong decrease in the concentration of oxidised-aliphatic fragments. This effect is more pronounced with increased extraction temperature. At 40 and 60°C, the decrease in the number of fragments is ~ 40%, while the concentration of fragments decreases by ~ 28% at 40°C and ~ 53% at 60°C. No significant impact of the protective chemicals on oxidised fragments is observed at 20°C due to the overall low concentration.

In contrast, a significant temperature dependant increase in number and concentration of oxidised aromatic fragments is observed in the presence of protective chemicals. Oxidised-aromatic fragments, which are already present in low concentration at 20°C increase in number by a factor of ~ 2.7 and in concentration by a factor of ~7.2 at 60°C. This is roughly the same temperature dependence as observed for the total fragments.

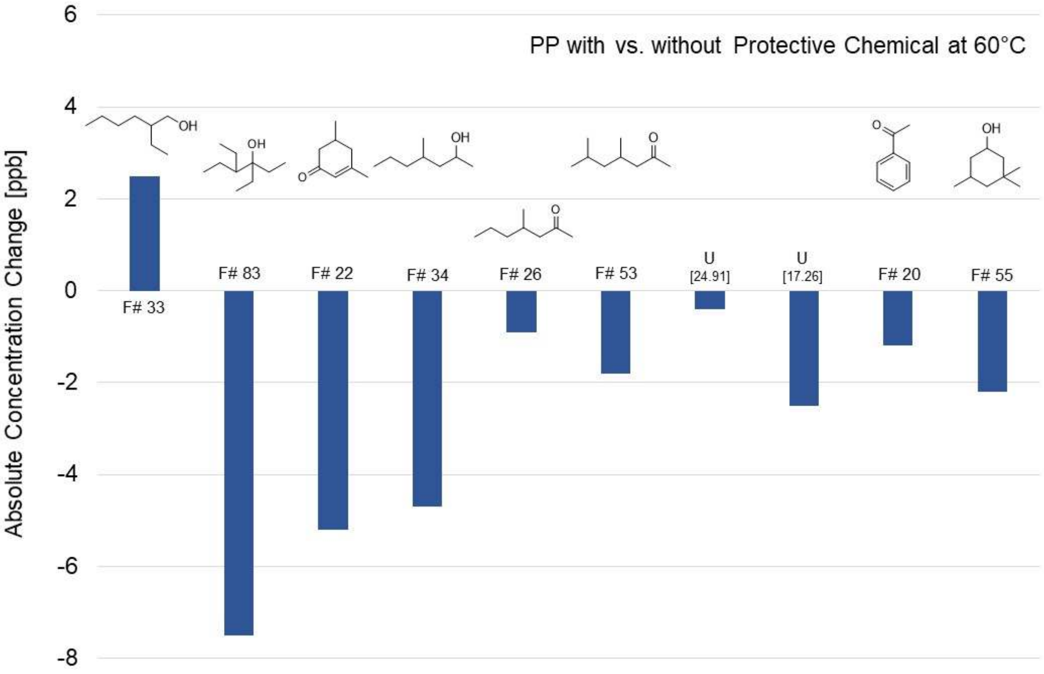
Figure 34a details key fragments 1-10 extracted from PP without protective chemicals ranked by decreasing concentration.


14
12
10
8
6
4
2
0
Concentration of Extractable Fragments [ppb]
PP without Protective Chemical
■ 60C ■ 40C ■ 20C
10 [ppb] Limit
5 [ppb] Limit
OH
OH
O
OH
O
O
O
OH
F# 33
F# 83
F# 22
F# 34
F# 26
F# 53
F# 20
F# 55

(a)

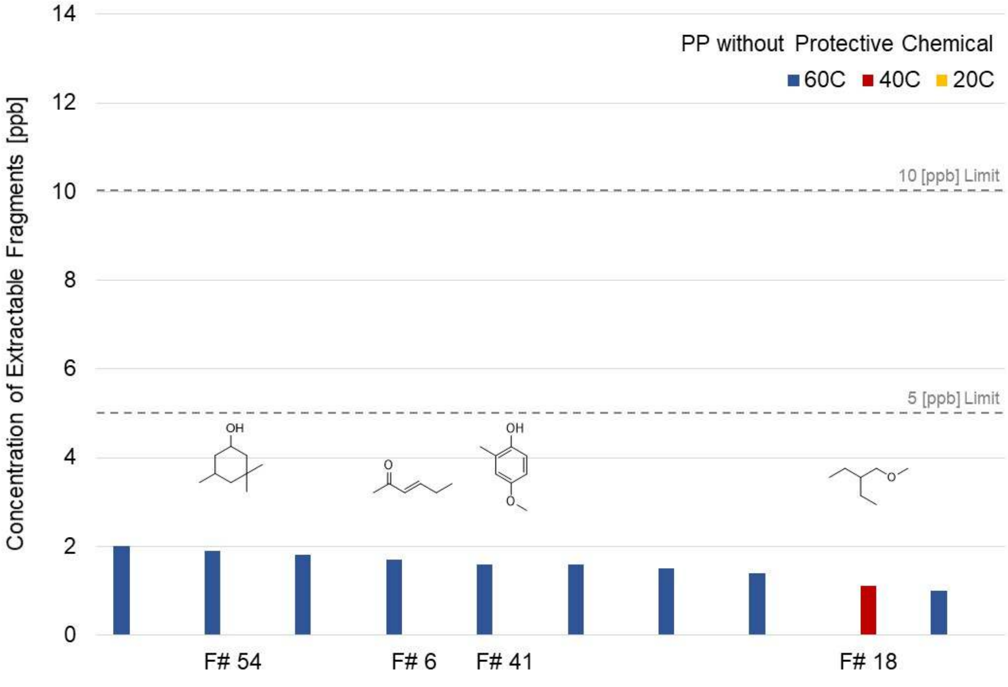

14
12
10
8
6
4
2
0
Concentration of Extractable Fragments [ppb]
PP with Protective Chemical
■ 60C ■ 40C ■ 20C
10 [ppb] Limit
5 [ppb] Limit
OH
OH
O
OH
O
O
O
OH
F# 33
F# 83
F# 22
F# 34
F# 26
F# 53
F# 20
F# 55

(b)

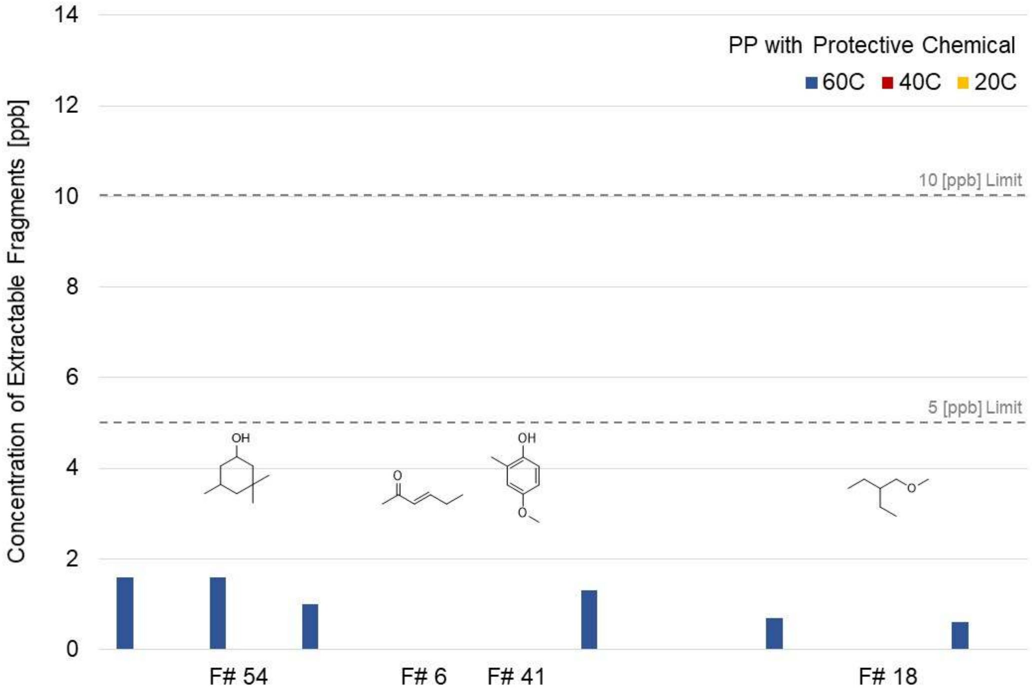


(c)

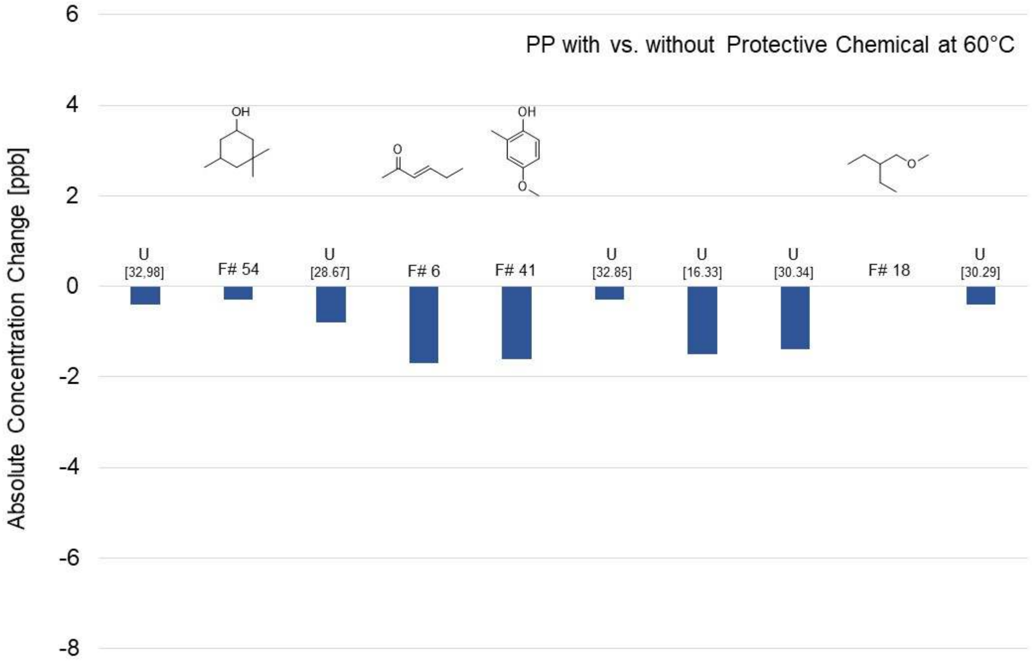
Figure 34: 10 identified extract-able fragments without (a) and with (b) protective chemicals including the difference (c) between the two formulations



(a)



(b)



(c)

Figure 35: 11-20 identified extract-able fragments without (a) and with (b) protective chemicals including the difference (c) between the two formulations

All identified fragments (except F# 20) fall within the class of oxidised aliphatic fragments. Dominant species are alcohols and ketones within a MW range of 120 to 158 g mol^{-1}. None of the fragments is detectable at 20°C while most are only detectable at 60°C. In comparison (**Figure 34b**) 50% of the fragments are no longer extractable in the presence of protective chemicals. Fragments were still extracted but at a lower concentration; with one major exception being fragment F# 33 (2-ethyl-1-hexanol) which increases in concentration. **Figure 34c** illustrates the absolute decrease in concentration of the top 10 fragments. A similar trend is observed in **Figure 35** with key fragments 11-20. A more detailed description and analysis of the identified oxidised aliphatic fragments is undertaken in Section 3.2.

The reduction in the formation of extractable alcohols and ketones is associated with the slower rate of degradation reactions R 1.10, R 1.11, R 1.12 as well as R 1.13 (among others) which moderated by alternative reaction pathways R 3.1, R 3.2 & R 5.2 due to the addition of protective chemicals. Under the selected experimental conditions, it can be concluded that *at elevated extraction temperature, the presence of protective chemicals results in a decrease of extractable oxidised-aliphatic fragments of up to 50%. These oxidised-aliphatic fragments are considered to originate from the PP substrate***.**

In contrast, 15 additional fragments are detected where protective chemicals are present (**Figure 36**). Two further oxidised-aliphatic fragments (F# 7 and F# 109) at 60°C appear to be minor modifications of the fragments identified in **Figure 35** and are therefore considered to originate from the polymer substrate. A third oxidised-aliphatic fragment, F# 173, seems to be a type of “dimer” formed via an unknown reaction pathway from other oxidised-aliphatic fragments like F# 108 or F# 109 (although in the specific examples the MW would be too low). Nine further fragments, belonging to the sub-class of oxidised-aromatic fragments, are detected. With a range of 206 to 292 g mol^{-1}, the MW of these fragments is higher compared with oxidised-aliphatic fragments. Eight resemble the functional group of the Hindered Phenol AO-1 while one of them resembles the aromatic ligand of Phosphite P-1.

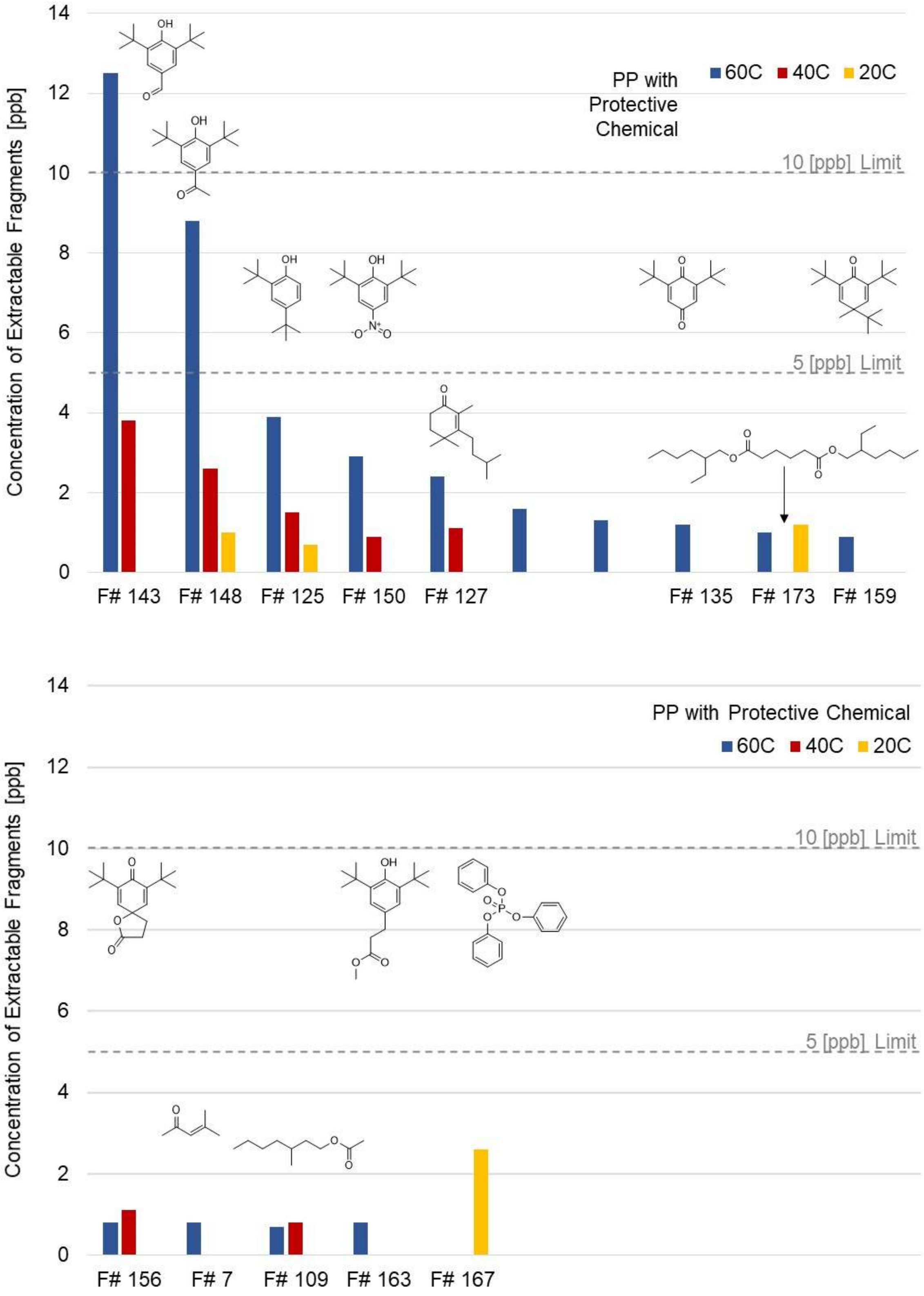
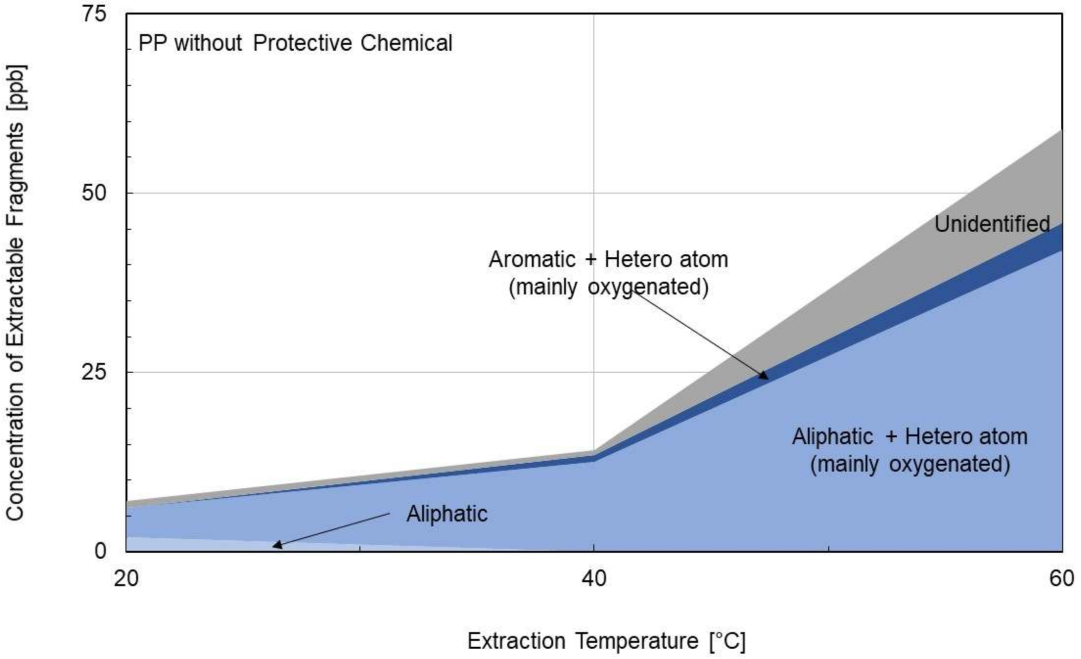


Figure 36: Additional fragments extracted from PP in the presence of protective chemicals

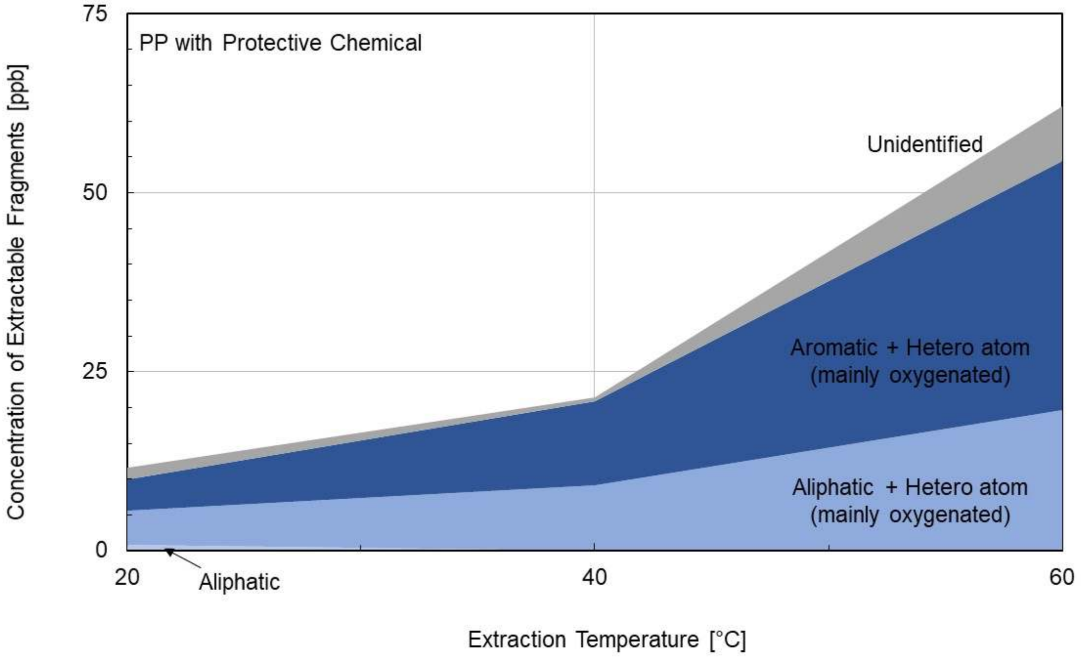
Two fragments are already detected at 20°C. The number increases with increasing temperature by a factor of ~ 4.5 while the concentration increases within this temperature range by a factor of ~ 20.1. One single observation relates to a potential phosphorus containing transformation product of P-1(F# 167). Two further oxidised but unidentified fragments are detected at 60°C. These fragments can neither be clearly attributed to the substrate nor to the protective chemicals. *The specific protective chemicals AO-1 and P-1 cause all the oxidised-aromatic fragments* (with exception of F# 20 as mentioned above)**.** *These fragments are therefore considered as protective chemicals originating fragments.*

Overall, across the investigated temperature range, a similar concentration of organic fragments is extracted from PP independent of the presence or absence of protective chemicals. However, the nature of the fragments changes significantly. Without protective chemicals, most of the fragments are oxidised aliphatic fragments (**Figure 37a**). The concentration increases significantly above 40 °C and constitutes ~ 71% of all quantified fragments at 60°C. In the presence of protective chemicals (**Figure 37b**) only ~31% of the fragments are oxidised aliphatic species, while nearly double this are of an oxidised-aromatic nature at 60 °C.

From **Figure 37** it can be concluded that above 40°C the *actual* service life temperature for the use of a PO article (specifically sanitary or drinking water pipe) is very important, not just from the point of view of extractable fragments. The ‘appropriate’ service life temperature and as direct consequence extraction temperature as discussed is the literature is therefore subject to controversy [156-159]. A constant water temperature as low as 49°C is recommended to avoid scalding at the faucet [157].



(a)



(b)

Figure 37: Increase in concentration of organic fragments (ppb) with extraction temperature (°C) in the absence (a) and presence (b) of protective chemicals

While this appears possible for fossil energy-based water heaters, the temperature is not sufficient to avoid contamination of electrical water heaters with e.g., Legionella [157] or Salmonella [239]. In consequence, water temperatures (in electrical heaters) of more than 65°Care recommended [155]. Newest generation of electrical water heaters seem to be programmable with a temperature profile, where the water is stored at 50°C with occasional but regular time intervals with increased temperature to control pathogens [240]. The length of the heating period varies with the selected temperature. For example, the minimum time to reach a reduction level of 6.5D (reduction of 99.99997% of pathogens) for Salmonella ranges from 314 minutes @ 52°C, over 91 minutes @ 55°C, 11.5 minutes @ 60°C to 88 seconds @ 65°C and 11 seconds @ 70°C [241]. The direct consequence of this is that the selected water temperature profile does affect the type, number, and concentration of extractable fragments.

To attempt to correct extraction data from 60°C to higher and lower temperatures, the following equations were used

$$C_{T1} = [1.155 * T_{T60} - 34.4] \qquad \text{Equation 1}$$

$$C_{T1} = [0.0195 * (T_{T60})^2 – 0.795 * T_{T60} + 12.4] \qquad \text{Equation 2}$$

T1 = Extraction temperature [°C]

For temperatures below the reference temperature of 60°C, a linear regression (Equation 1) of the data for oxidised aromatic fragments in the presence of protective chemicals was used (**Figure 38**). Above the reference temperature, a second-degree polynomial was selected. This regression fits well with other regressions obtained from the individual oxygenated aromatic fragments F# 125 & F# 148, which are both detected at all investigated temperatures. Although only a rough calculation and only valid for extraction periods of 72 hours, it is postulated (within the scope of this report) that *an increase of the extraction temperature from 60 to 70°C (by 10°C) will double the concentration of fragments, while a decrease of the extraction temperature from 60 to 45°C (by 15°C) will half the concentration of fragments*. This statement is valid for organic fragments which are identified and quantifiable at 60°C.

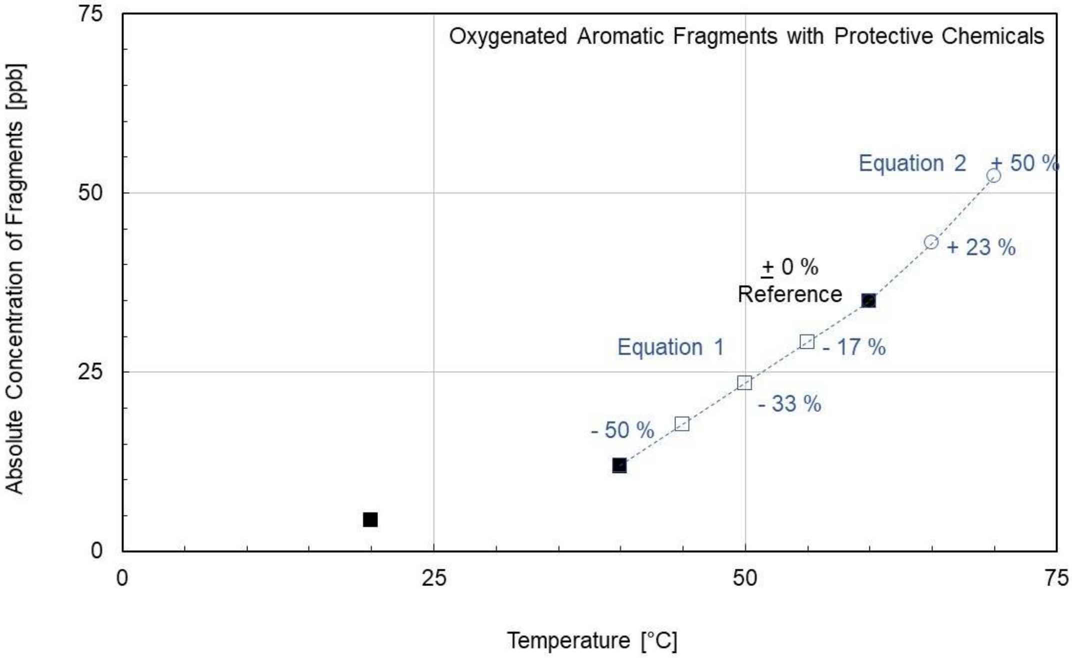


Figure 38: Relative change of the concentration of fragments (ppb) with temperature (°C) (general correlation based on Equation 1 and Equation 2)

It can be concluded from this chapter, that melt-processed PP results in extract-able fragments which are mainly of oxidised aliphatic nature. These fragments start to migrate around 40°C and increase at 60°C significantly in number and even more in concentration. These oxidised-aliphatic fragments are considered as PP substrate originating and are specific to the chemical identity of PP. Addition of protective chemicals results in a significant decrease of oxidised-aliphatic fragments, the effects being predominating at higher temperature. A more detailed discussion of all fragments detected is undertaken in the next section.

Protective chemicals introduce many oxidised-aromatic fragments. Although some are present already at 20°C, most are detected only at 60°C. Whether these fragments are specific in general to the class of protective chemicals of Hindered Phenol and/or Phosphite or only to the specific representative of Hindered Phenols, AO-1, and/or Phosphite, P-1, will be discussed later.

It is noteworthy that no organic fragment was identified which can be directly related to the modifier MS-1.

3.2 Polypropylene Quality

In this section the impact of the quality of different PP batches on the extraction of organic compounds is evaluated.

Three different lots of PP (PP-A, PP-B and PP-C; **Table 9**) were melt-processed according to conditions C-1 followed by M-1 (see **Table 16**). All batches contained 750 ppm of the modifier MS-1, but no protective chemical at all. The three lots of PP are of the same grade and subsequently should be rather similar in catalyst residues, MW and MWD. However, the initial MFI indicates differences (**Figure 39**; open symbols).

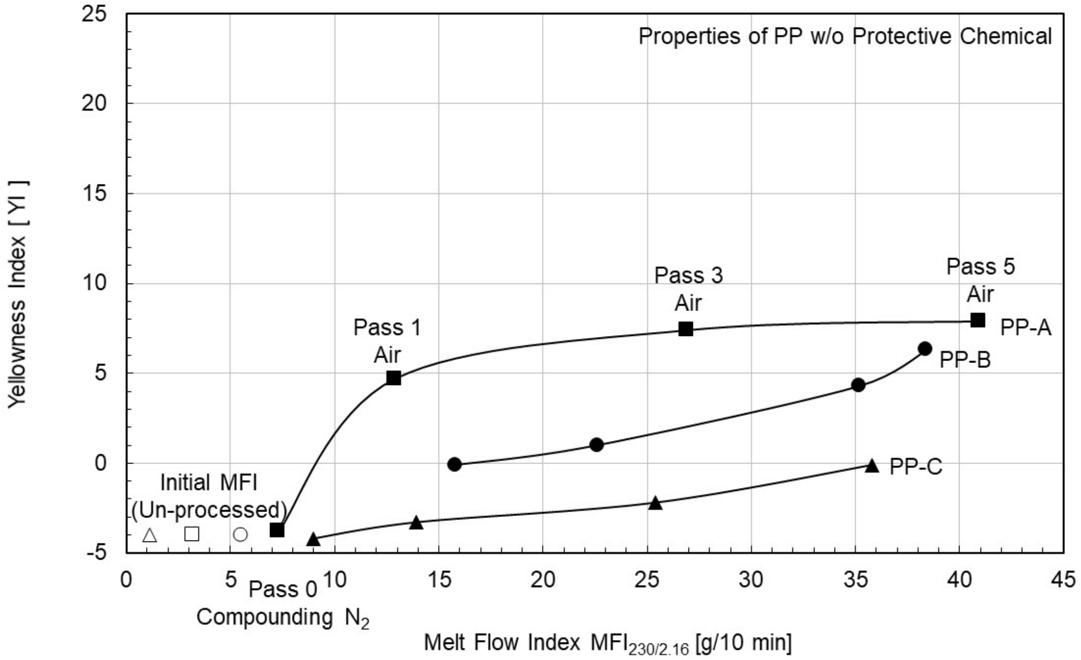
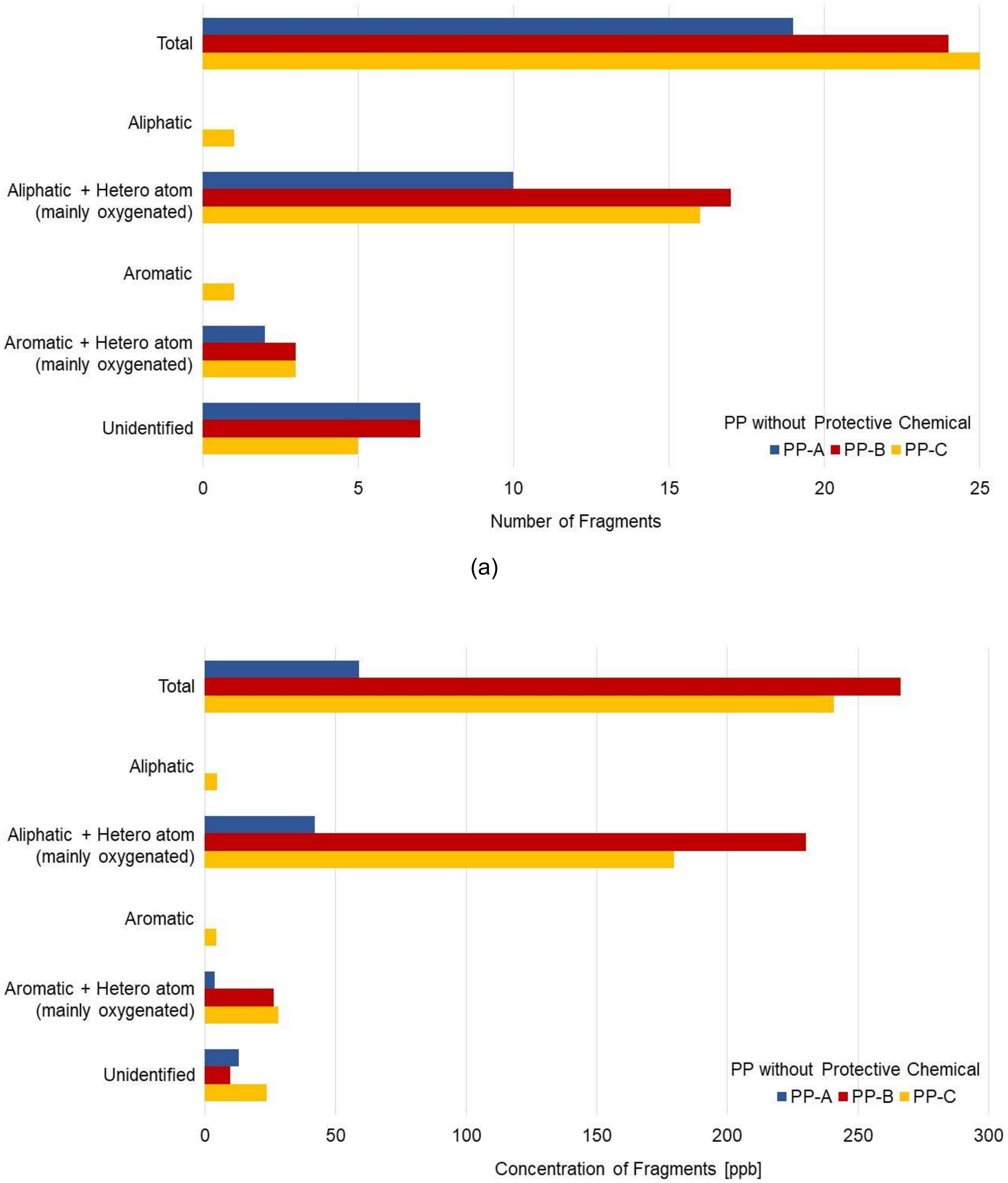


Figure 39: Properties of melt-processed PP in the absence of protective chemicals

Extrusion Condition:	C-1, M-1
Extraction Condition:	E-4
Formulation:	PP + 750 ppm MS-1

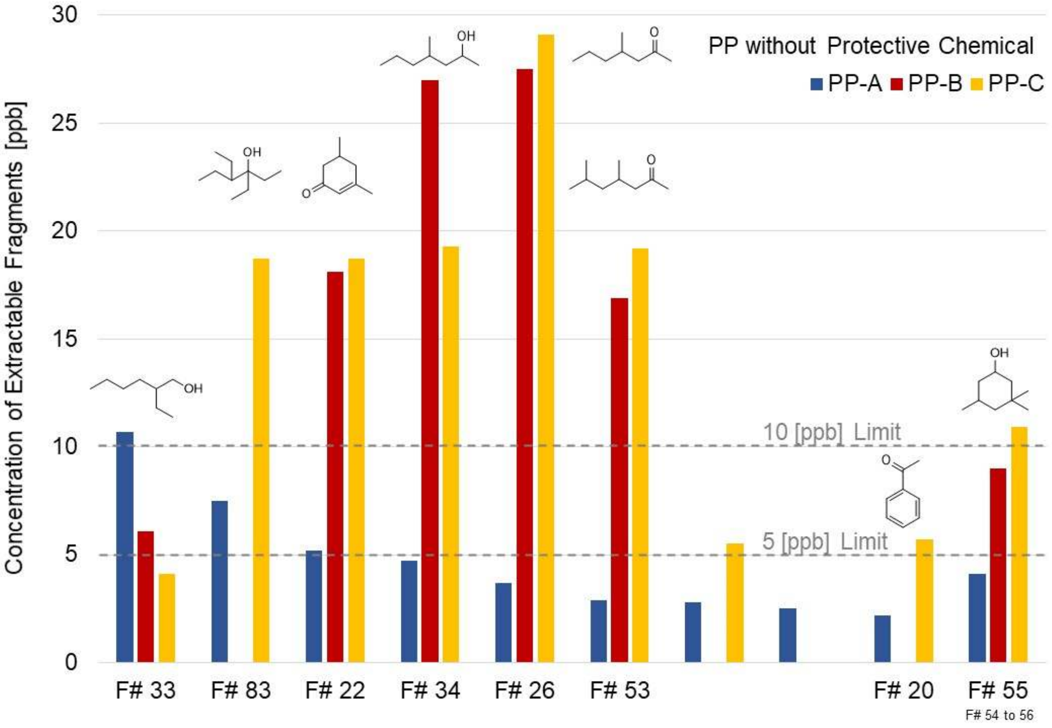
Sample lots, PP-B and PP-C show a similar and almost linear behaviour. Nevertheless, the data is shifted roughly by the difference in initial MFI. In both cases, as MFI increases significantly, colour increase by (only) five (5) YI units. In contrast, PP-A shows a significant increase in colour during extrusion pass 1, while MFI increases as in the case of PP-B and PP-C. This sharp colour increase could be explained by an unusually high concentration of oxygen in the polymer melt [242] and higher probability for reaction R 1.4 (and other reactions which could lead to chromophores). All three lots of PP result in a very high MFI after extrusion pass 5, which is similar considering the experimental error of lab-scale multi pass extrusion. All three PP lots are, from a mechanical point of view, do not meet accepted specifications, so are not suitable for any technical or packaging related application.

Water extraction at 60°C results in 19 extract-able fragments for PP-A, respectively 24 (PP-B [243,244]) and 26 (PP-C [245,246]) fragments. The total concentration of fragments varies significantly. PP-A results in 58.9 ppb; while PP-B and PP-C result in higher but similar levels of 266.2 ppb and 240.7 ppb. The dominant class of extract-able fragments are of an oxidised-aliphatic nature by both number and concentration (**Figure 40**), but several structures could not be identified. Comparing type and concentration of fragments reveals significant differences between PP-A on one side and PP-B together with PP-C on the other side. **Figure 41** compares PP-A in the same format as **Figure 34a** and **Figure 35a**. Thirty key extract-able fragments in decreasing order of concentration are depicted in **Figure 42.** Nearly all fragments identified in PP-A are present at ~4 times higher concentration in PP-B and/or PP-C.

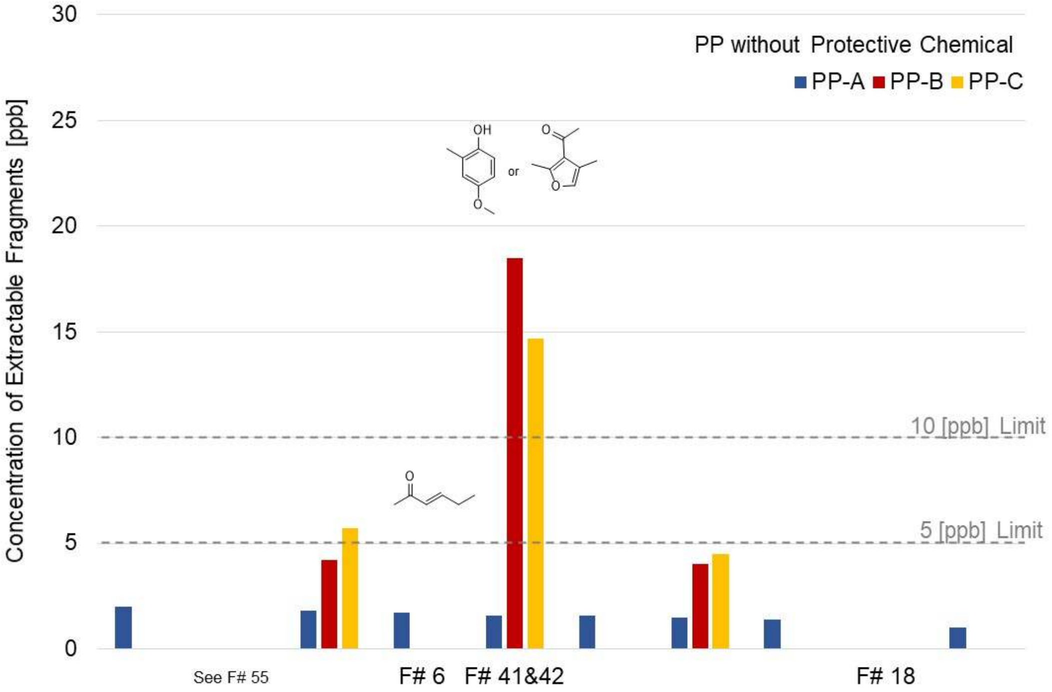


(b)

Figure 40: Number (a) and concentration, ppb, (b) of extract-able fragments from PP without protective chemical

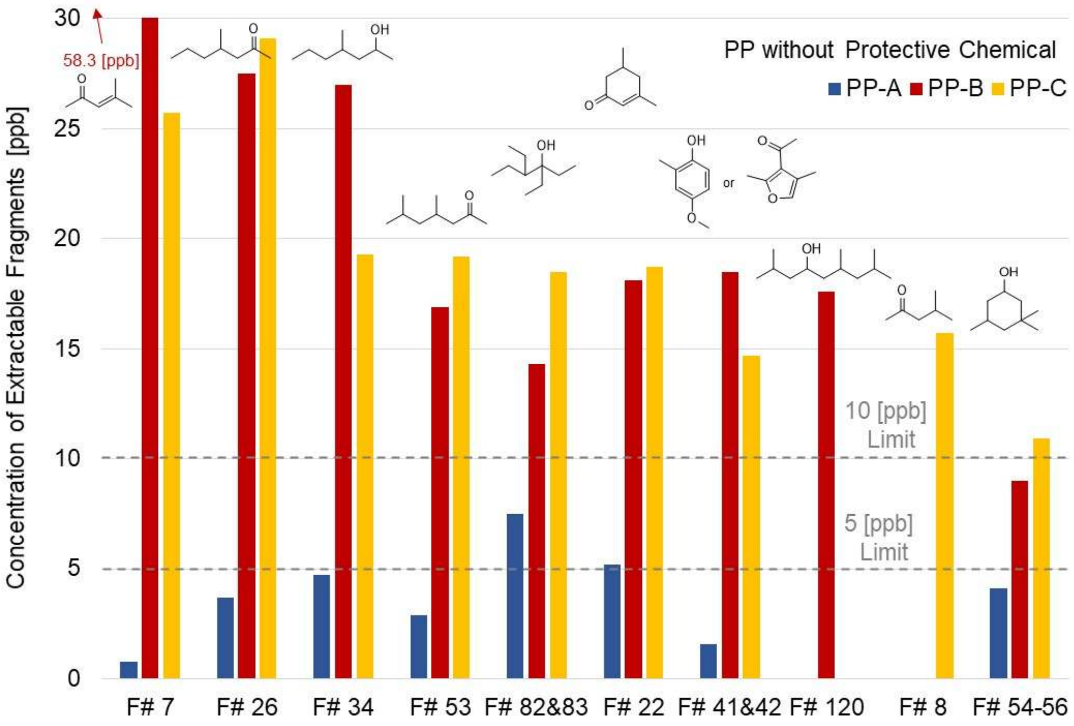


(a)

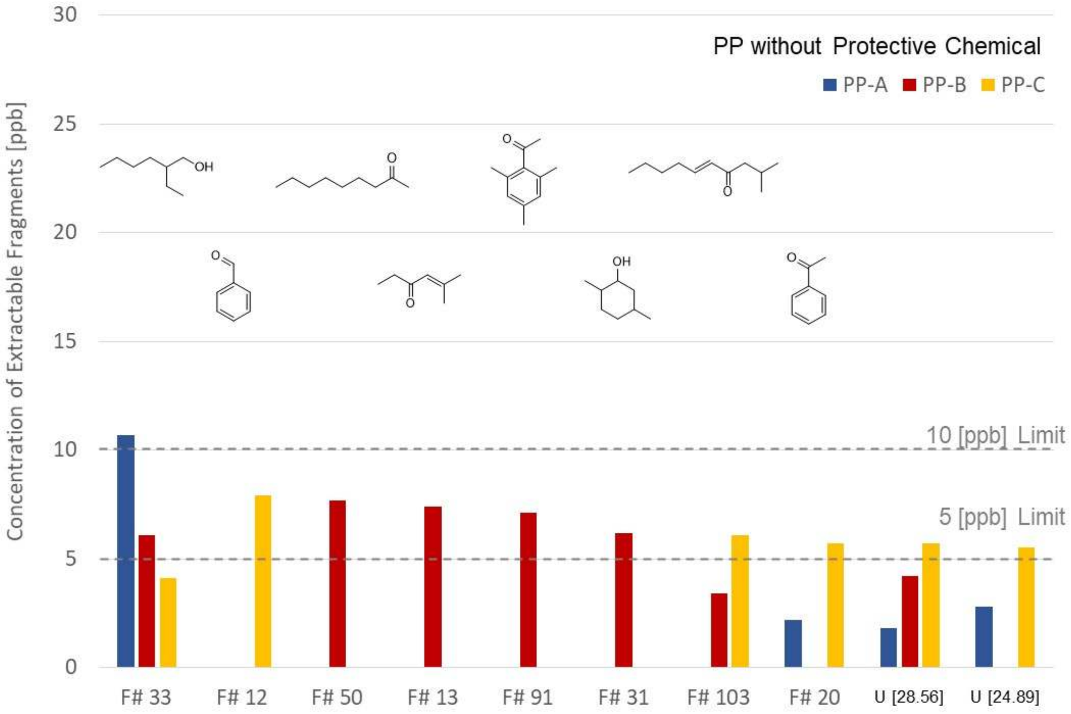


(b)

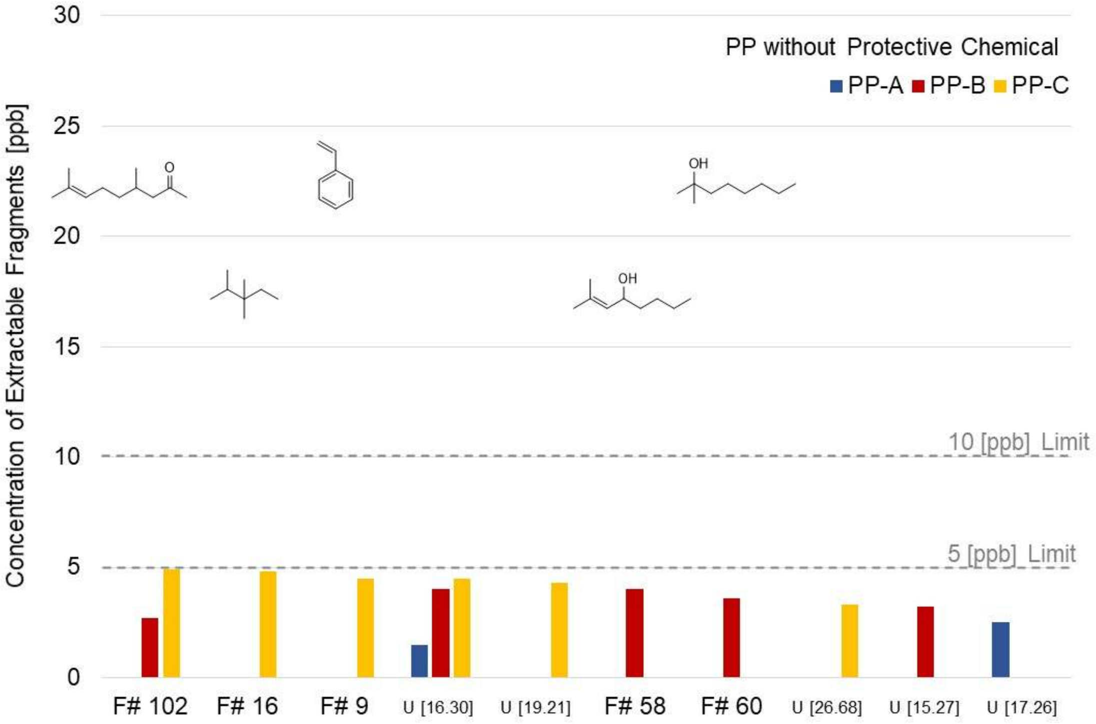
Figure 41: Key 1-10 (a) and 11-20 (b) identified extract-able fragments of PP-A w/o protective chemical in comparison with PP-B and PP-C (same layout as **Figure 34** and **Figure 35**)


Concentration of Extractable Fragments [ppb]
0
5
10
15
20
25
30
58.3 [ppb]
PP without Protective Chemical
PP-A
PP-B
PP-C
10 [ppb] Limit
5 [ppb] Limit
or
F# 7
F# 26
F# 34
F# 53
F# 82&83
F# 22
F# 41&42
F# 120
F# 8
F# 54-56

(a)


Concentration of Extractable Fragments [ppb]
0
5
10
15
20
25
30
PP without Protective Chemical
PP-A
PP-B
PP-C
10 [ppb] Limit
5 [ppb] Limit
F# 33
F# 12
F# 50
F# 13
F# 91
F# 31
F# 103
F# 20
U [28.56]
U [24.89]

(b)



(c)

Figure 42: Concentrations (ppb) of key 1-10 (a), 11-20 (b and 21-30 (c) identified extract-able fragments of PP lots

In contrast, about half of the top 30 fragments are not detected at all in PP-A. More detailed analysis of the oxidised-aliphatic fragments reveals an even larger discrepancy between PP-A and the other lots by a factor of ~5-6. Only alcohols and ketones, but no aldehydes or ethers are detected (**Figure 43**). It is noteworthy, that the relative proportion of alcohols and ketones (relative to the total concentration of oxidised-aliphatic fragments) is the inverse for PP-A. While approximately two thirds (2/3) of the fragments of PP-A are alcohols, PP-B and PP-C result in approximately two thirds (2/3) ketones.

More specifically, for PP-B and PP-C, the sub-class of ketones in the 2-position (2-ketones) constitutes by concentration ~55-60 % of all oxidised-aliphatic extract-able fragments and ~85-90 % of all ketones quantified. In contrast the MWD of aliphatic oxidised fragments is comparable in all three cases (**Figure 44**). Most of the fragments are within a MW range of 100 to 175 g mol^{-1}.

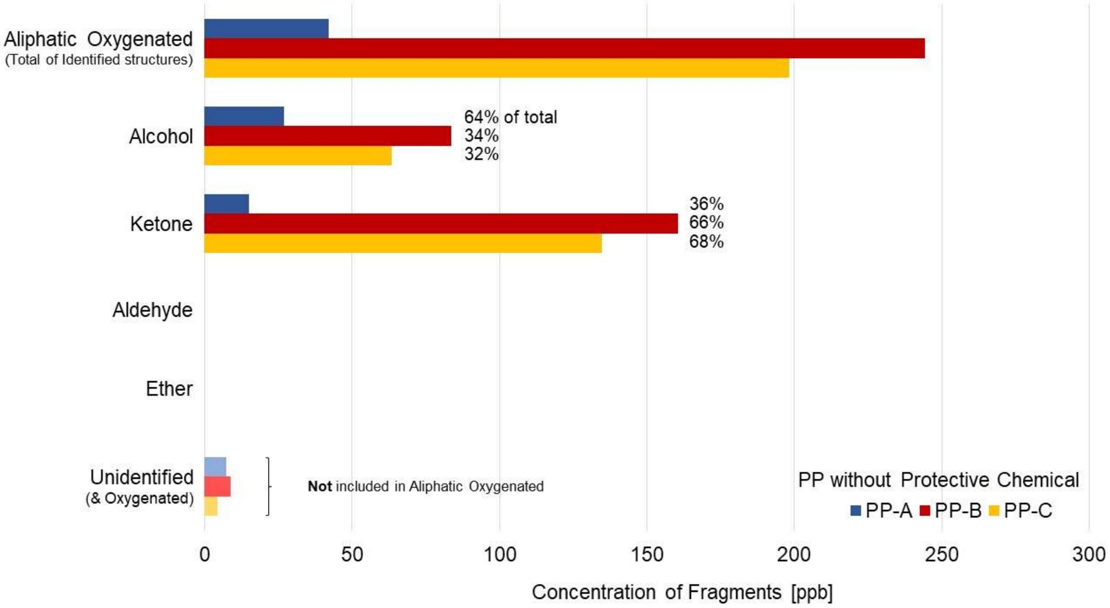


Figure 43: Sub-classification of aliphatic oxygenated fragments into alcohols, ketones, aldehydes, and ethers for various PP lots

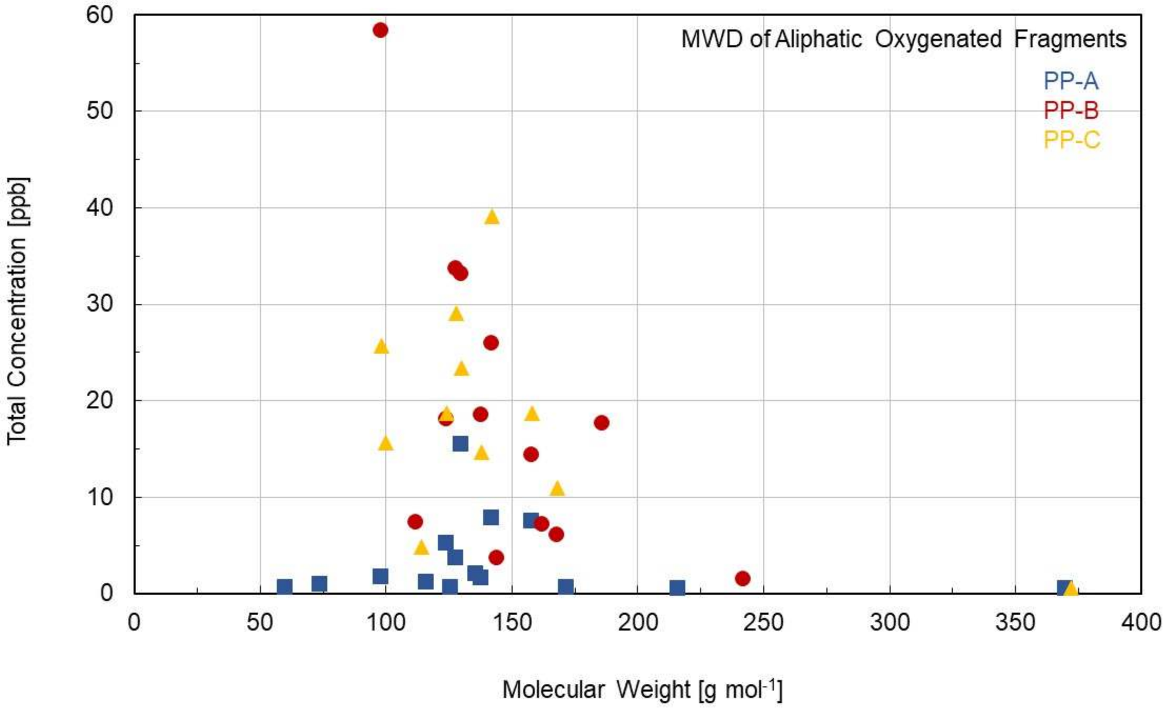
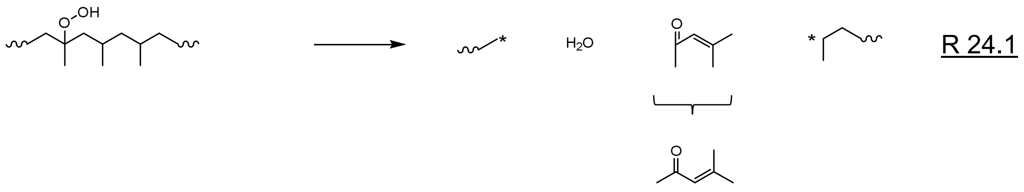


Figure 44: MWD of aliphatic oxygenated fragments from different lots of PP

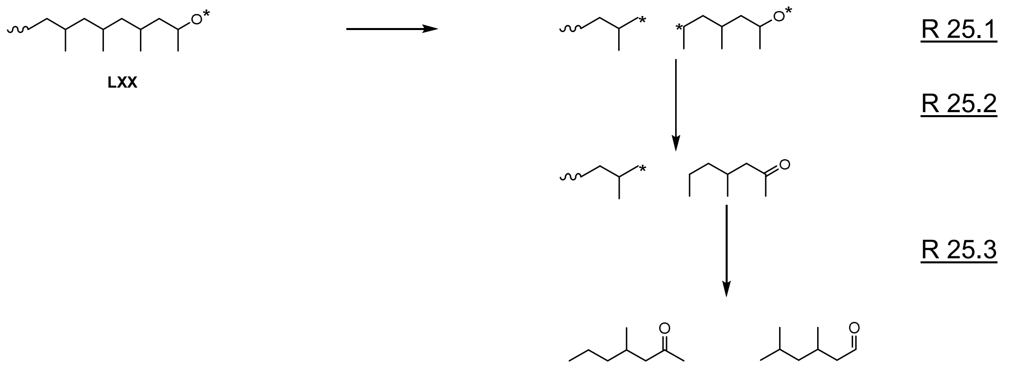
The high concentration of 2-ketones indicates the dominance of reaction R 2.4, which itself is fed by the decomposition of peroxides (principal reaction R 1.6). The formation of oxidised-aliphatic fragments, detected in the highest concentrations, e.g., 4-methyl-3-penten-2-one (F#7; **Scheme 24**) 4-methyl-2-heptanone (F# 26; **Scheme 25**), 4-methyl-2-heptanol (F# 34; **Scheme 26**) and 4,6-di-methyl-2-heptanone (F # 53; **Scheme 27**) has already been postulated earlier [129, 130].



LXIX

3-Penten-2-one, 4-methyl-
Fragment F# 7
$\log K_{OW}$ ~1.94 (aldehyde equivalence scale)

Scheme 24: Formation of 4-methyl-3-penten-2-one (F# 7) during melt-processing of PP without protective chemical

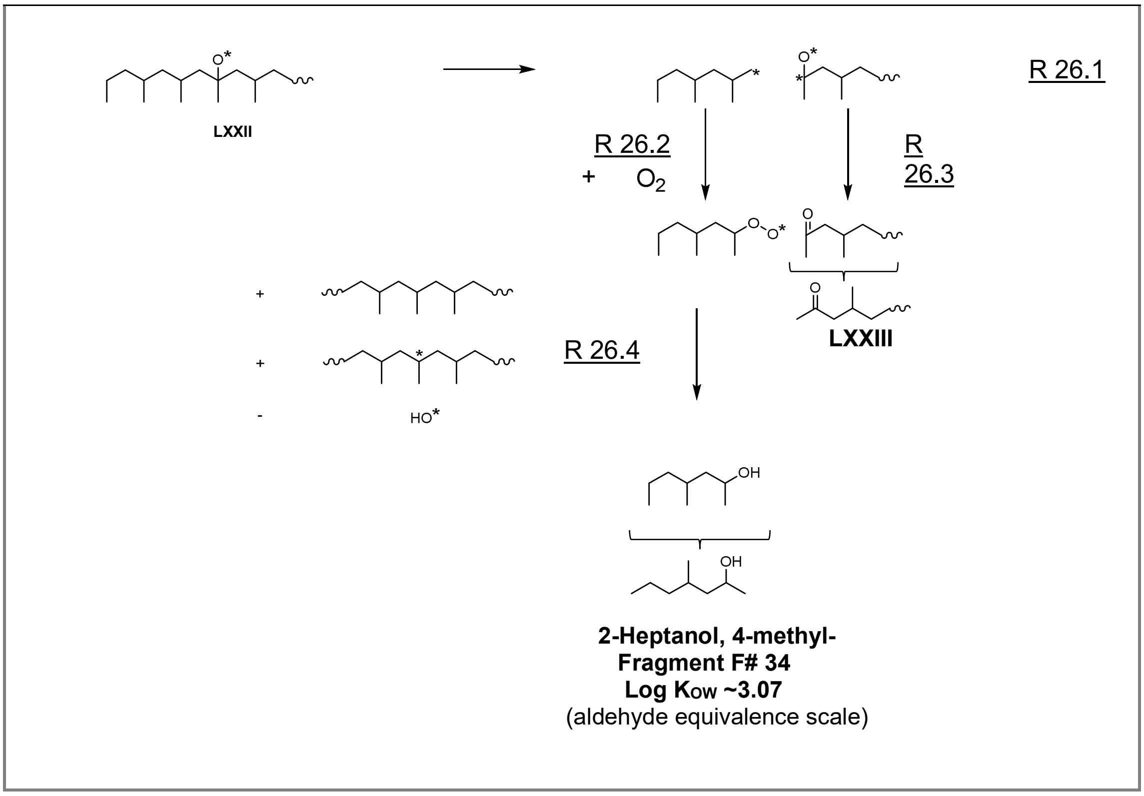


LXX

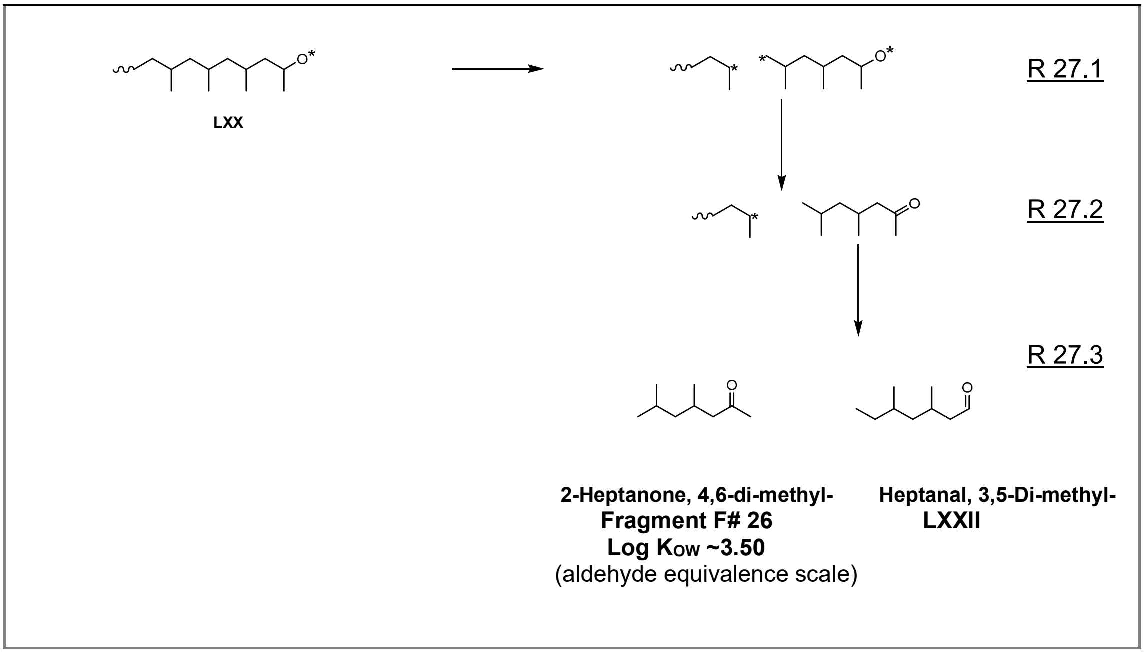
2-Heptanone, 4-methyl-
Fragment F# 26
$\log K_{OW}$ ~3.00
(aldehyde equivalence scale)

Hexanal, 3,5-Di-methyl-
LXXI

Scheme 25: Formation of 4-methyl-2-heptanone (F# 26) during melt-processing of PP without protective chemical

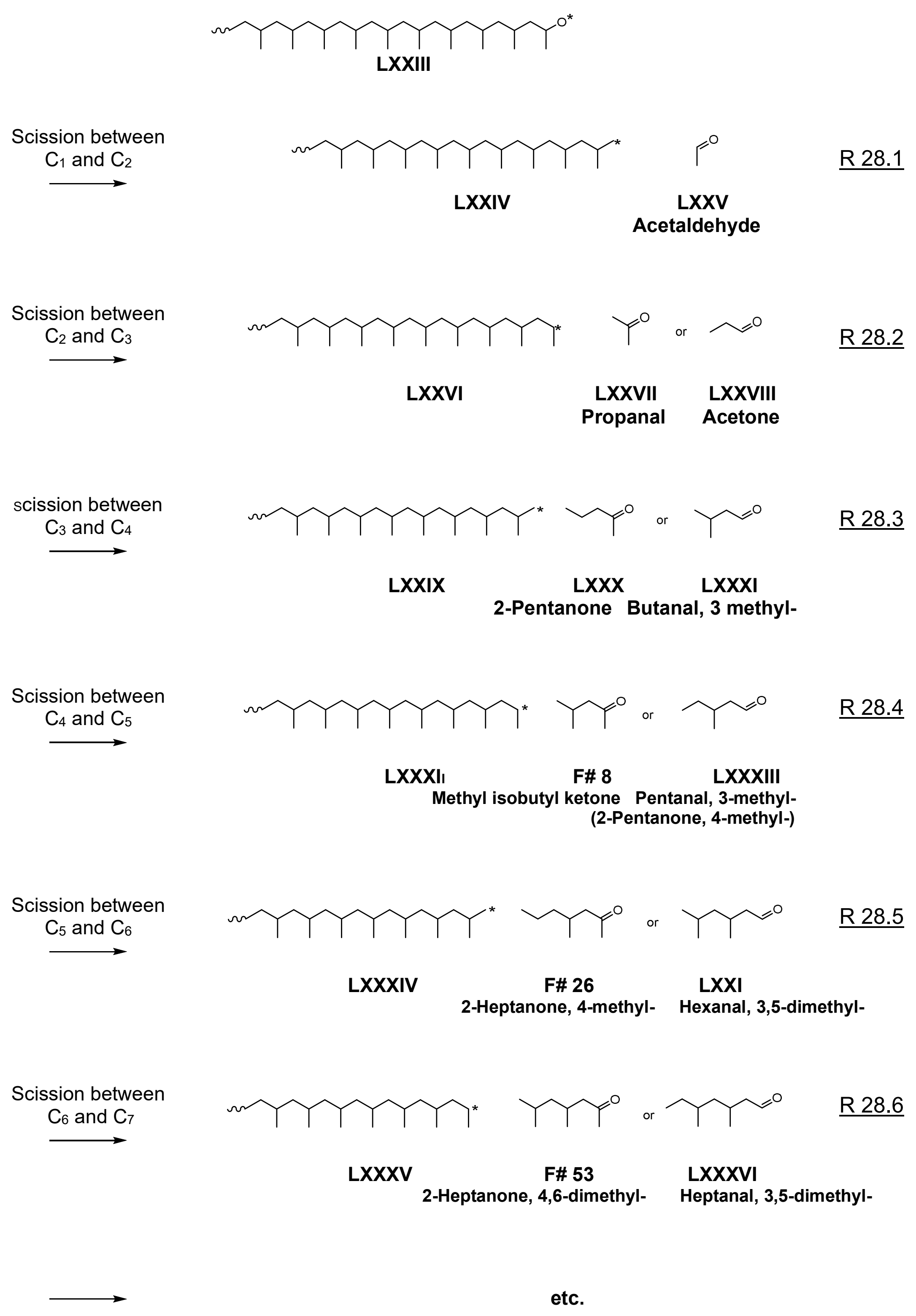


Scheme 26: Formation of 4-methyl-2-heptanol (F# 34) during melt-processing of PP without protective chemical



Scheme 27: Formation of 4,6-di-methyl-2-heptanone (F # 53) during melt-processing of PP without protective chemical

A generalised reaction scheme at melt processing temperature for PP is given in **Scheme 28** [130]. Here it can be seen that 2-ketones are produced over a wide range of MW depending on the location of the scission of the backbone of PP relative to the alkoxy radical position. 2-ketones below ~60 g mol^{-1} are very volatile and evaporate from PP during melt-processing operations [129, 130]. These fragments are not detected during the subsequent water-extraction experiment. As MW of 2-ketones increases from ~60 g mol^{-1} to the range of 100 to 150 g mol^{-1}, it is assumed that fragments are still volatile enough to be partially lost, so only a proportion of the fragments initially formed can be detected during water-extraction. Quantification of these fragments during water-extraction is expected to depend to a high degree on the specific melt-processing conditions such as temperature, surface and dimension of the extruded PP strand, and pressure. Quantified values therefore are expected to scatter significantly. Oxidised-aliphatic fragments above 60 g mol^{-1} to about 175 to 200 g mol^{-1} are water-extractable and constitute a major part of the detected concentration. Above ~200 g mol^{-1}, the log K_{OW} calculated according to **Figure 8** is higher than ~5.5 and the mono-oxidised molecules formed are in general not water soluble. The approximate value of log K_{OW} is calculated based on actual log K_{OW} data of the linear aldehyde series. A change of solvent from water to water/ethanol mixtures would move the limit (right side of the blue bar in **Figure 45**) towards higher MW [247]. A non-polar solvent (e.g., iso-octane) would completely shift the extract-able MW range towards (significantly) higher MW [247,248]. **Figure 45** illustrates the MW range of oxidised-aliphatic fragments which are water extractable. It should be noted that the indicated borders (dotted lines) are not to be considered as sharp borders but rather as "transition ranges".



Scheme 28: General reaction scheme for formation of 2-ketones during melt-processing of PP w/o protective chemical [130]

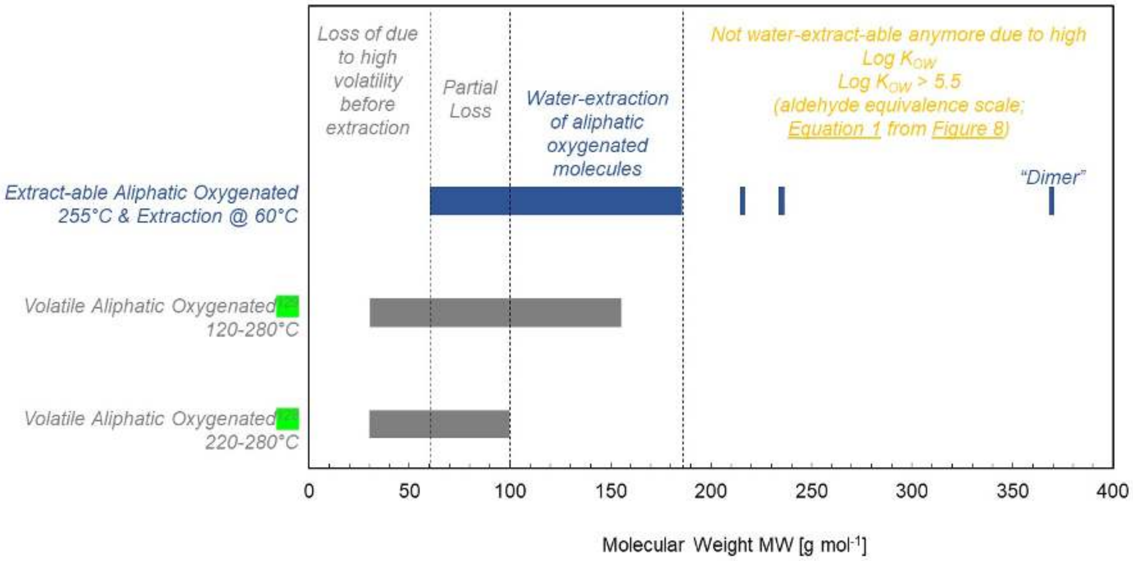


Figure 45: Impact of MW on volatility and water extractability of aliphatic oxygenated fragments of PP

The three lots of the same PP extrusion grade (with a nominal MFI of 3.2) already differ significantly in MFI and consequently in initial MW. MW ranges from ~310 000 g mol^{-1} (PP-B), > ~380 000 g mol^{-1} (PP-A), to ~500 000 g mol^{-1} (PP-C) [249]. However, this ranking cannot explain the observed differences in the fragment type and concentration. The strong increase in colour of PP-A after compounding and during extrusion pass 1 (see **Figure 39**) points to the formation of chromophores initiated by an excess of oxygen (air) in the melt. A higher concentration of oxygen could favour the formation of hydroperoxides and subsequently bimolecular reactions of hydroperoxides (R 1.12) or bimolecular reactions of peroxy radicals (R 1.13, R 1.14 and particularly R 1.16). All reactions mentioned will modify the ratio aldehyde/ketone-to-alcohol towards a higher percentage of alcohol. Another explanation, supported by the significantly lower concentration of total extract-able fragments, could be a prolonged storage time of the PP after compounding and a subsequent volatilization of LMW fragments. Lab work on PP-A took place mid 2018 with handling procedures potentially not yet as sophisticated as two years later during the work on PP-B and PP-C. In 2018, the time interval between compounding and multi-pass extrusion as well as between extrusion and extraction was neither documented nor controlled. It should also be stated that the three PP lots are of experimental nature. PP is not available commercially without protective chemicals.

Separation from the reaction medium, catalyst deactivation and work-up of experimental PP grades are not standardized and might be responsible for significant variations.

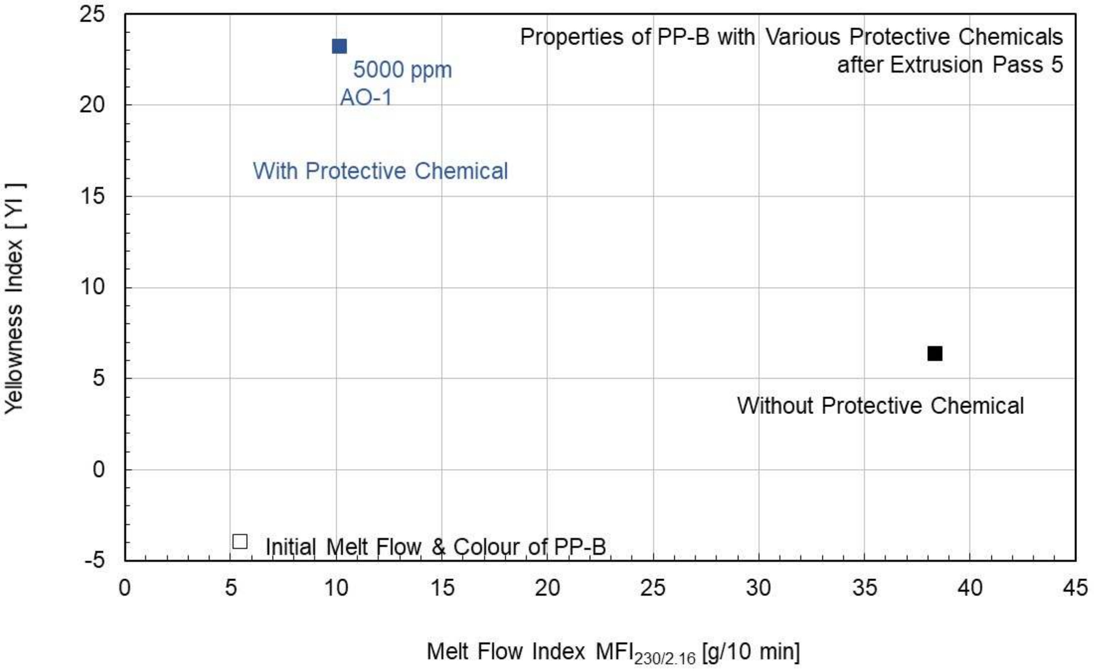
3.3 Protective Chemicals during Melt-Processing

3.3.1 Impact of the Class of Protective Chemical

In this section the impact of various types of protective chemicals (and their mixtures) on the extraction of organic compounds is investigated. The nature of the protective chemicals is chosen to have a significant impact onto the rate of oxidation of PP during melt processing (so-called “processing stabilizers”). The impact of the selected protective chemicals on service life (LTTS) is not considered here.

PP-B and PP-C containing 750 ppm of MS-1 were processed without protective chemicals as indicated in **Figure 39**. An additional formulation based on PP-B also contains 5000 ppm of the Hindered Phenol AO-1. An additional formulation based on PP-C also contains 750 ppm of the Phosphite P-1. Addition of P-1 or alternatively AO-1 results in a significant decrease in MFI. The lower MFI indicates a significant reduction in oxidative degradation of PP, resulting from the partial inhibition of reactions R 1.10 and R 1.20. Although AO-1 is added at a factor of 6.7 times higher concentration than P-1, similar MFI are obtained. It is important to note that there is significant colour development of the formulation containing AO-1.

The number and concentration of extract-able fragments from PP-B and PP-C, under extraction conditions E-4, is discussed in **Figure 40**. **Figure 47** compares the number and concentration of fragments in the presence of protective chemicals versus the absence of protective chemicals (in **Figure 40**). The two classes of protective chemicals, Hindered Phenol HP and Phosphite P, result in significant differences in the fragments detected. The addition of P-1 results in a significant decrease in the total number and total concentration of fragments. The relative reduction of the concentration is ~70%. This reduction is mainly due to a reduction



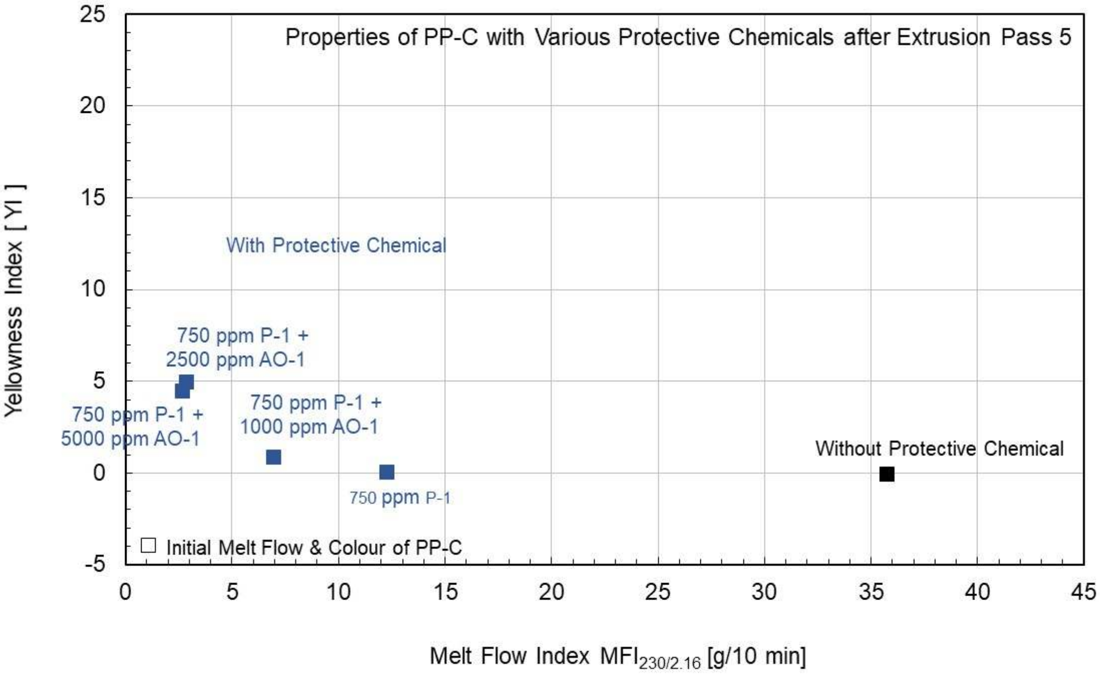
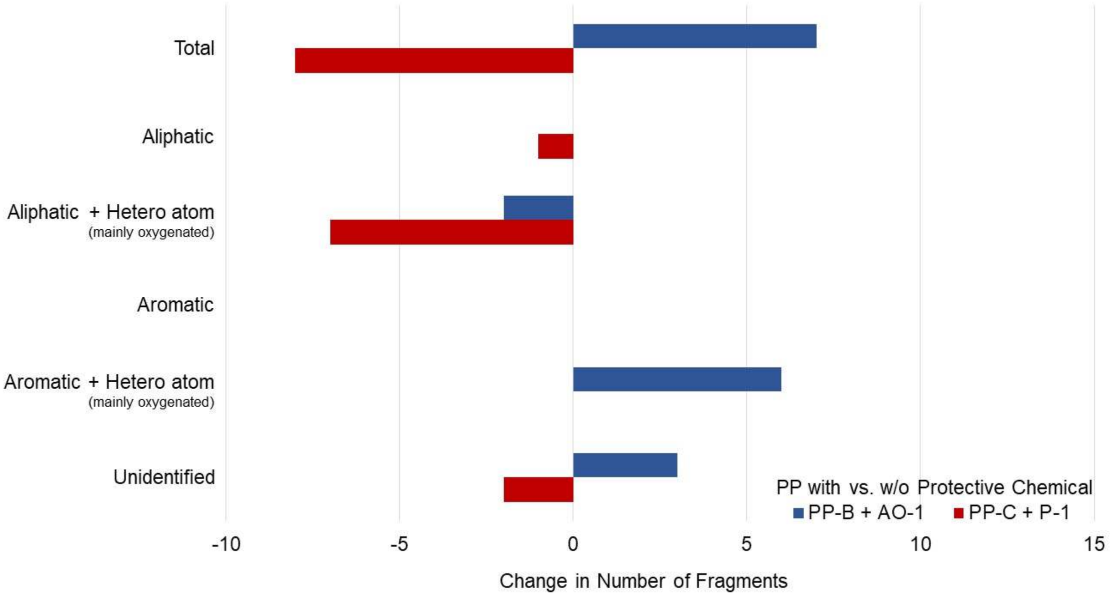
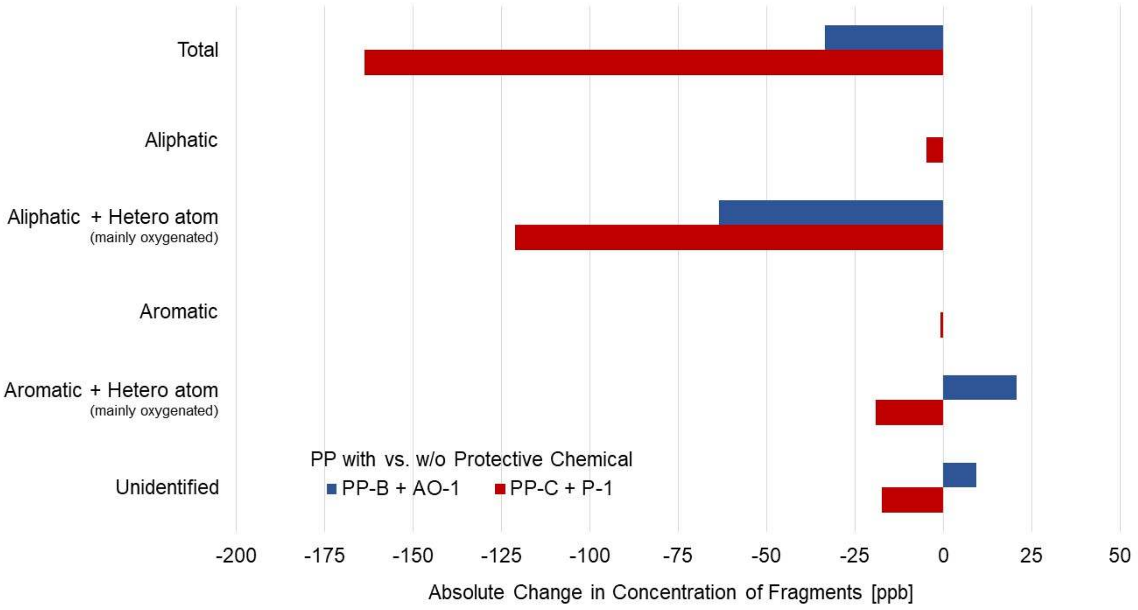


Figure 46: Properties of melt-processed PP in the absence and presence of different classes of protective chemicals
5000 ppm AO-1 (top chart) and 750 ppm P-1 (bottom chart)

Extrusion Condition: C-1, M-1
Extraction Condition: E-4
Formulation: PP + 750 ppm MS-1


Total
Aliphatic
Aliphatic + Hetero atom
(mainly oxygenated)
Aromatic
Aromatic + Hetero atom
(mainly oxygenated)
Unidentified
PP with vs. w/o Protective Chemical
■ PP-B + AO-1
■ PP-C + P-1
-10
-5
0
5
10
15
Change in Number of Fragments

(a)


Total
Aliphatic
Aliphatic + Hetero atom
(mainly oxygenated)
Aromatic
Aromatic + Hetero atom
(mainly oxygenated)
Unidentified
PP with vs. w/o Protective Chemical
■ PP-B + AO-1
■ PP-C + P-1
-200
-175
-150
-125
-100
-75
-50
-25
0
25
50
Absolute Change in Concentration of Fragments [ppb]

(b)

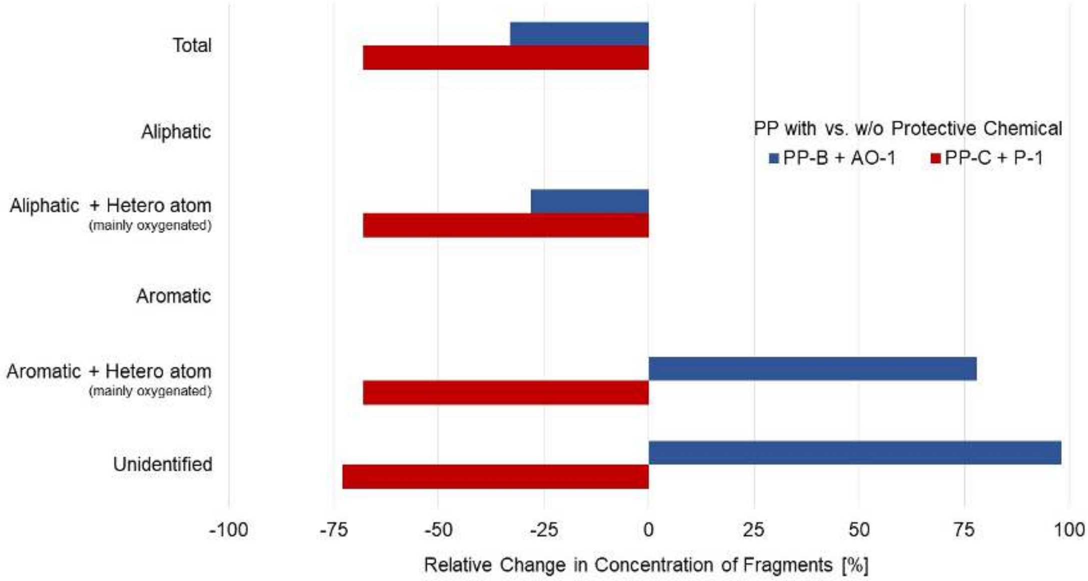
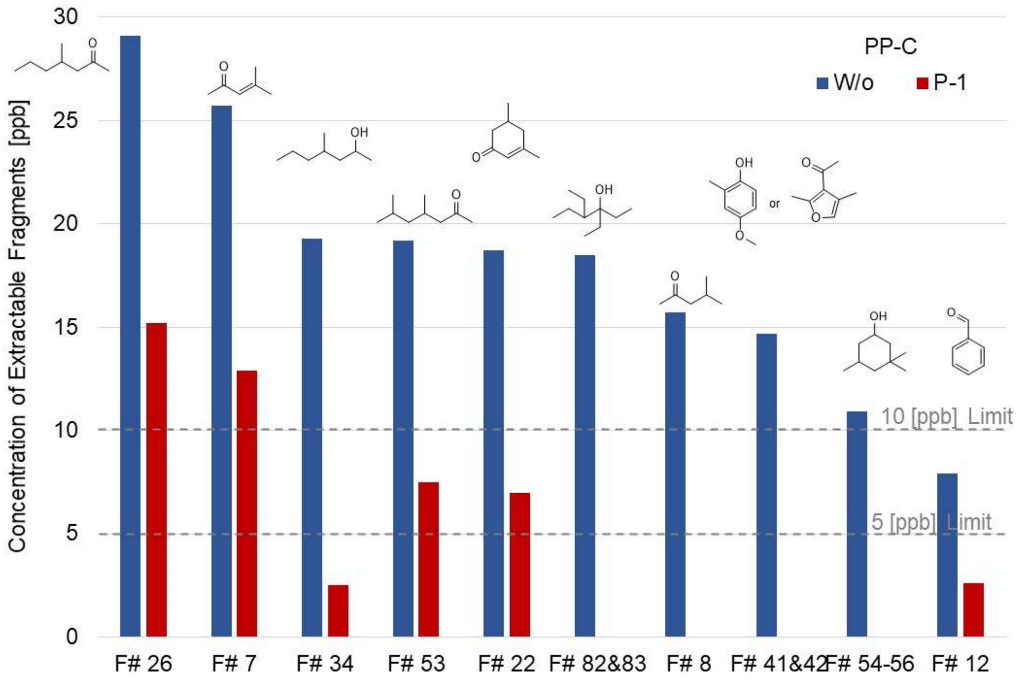
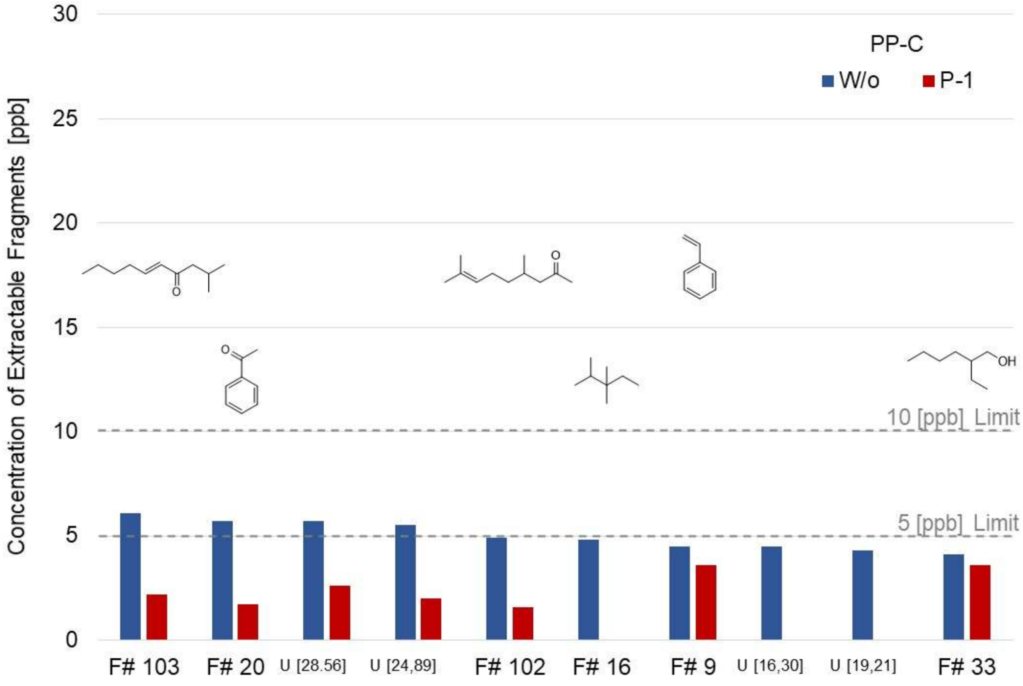


Figure 47: Change of fragments of PP with protective chemicals versus without protective chemicals
Absolute change in number (a)
Absolute change in concentration, ppb (b)
Relative change in concentration, ppb (c)

of oxidised-aliphatic fragments and to a minor extent due to unidentified fragments (of which some seem to be of oxidised nature). In contrast, addition of a 6.7 times higher concentration of AO-1 results in a higher number of fragments and decreases the total concentration to a lesser degree. The relative change is only ~30%.; though AO-1 still decreases oxidised-aliphatic fragments. However, oxidised-aromatic and unidentified fragments increase. This increase could potentially be related to the high concentration of AO-1 and is examined in detail later. In contrast, the pronounced effect of P-1 on reduction of (oxidised-aliphatic) fragments is explained by alternative reaction R 16.2, which decreases the probability of reaction R 16.1 (respectively R 1.6, R 1.9 and R 1.12) and, which subsequently does not feed into, for example, reactions R 24.1 to R 28.6. A closer analysis of the fragments detected in PP-C indicates a global reduction of all fragments. Out of the 23 fragments listed, 10 are no longer detected in the presence of P-1 (**Figure 48**). Where quantifiable, the reduction is > 50% except for 2 fragments (**Figure 49**).


PP-C
W/o
P-1
Concentration of Extractable Fragments [ppb]
30
25
20
15
10
5
0
10 [ppb] Limit
5 [ppb] Limit
O
OH
or
F# 26
F# 7
F# 34
F# 53
F# 22
F# 82&83
F# 8
F# 41&42
F# 54-56
F# 12


PP-C
W/o
P-1
Concentration of Extractable Fragments [ppb]
30
25
20
15
10
5
0
10 [ppb] Limit
5 [ppb] Limit
O
OH
F# 103
F# 20
U [28.56]
U [24,89]
F# 102
F# 16
F# 9
U [16,30]
U [19,21]
F# 33

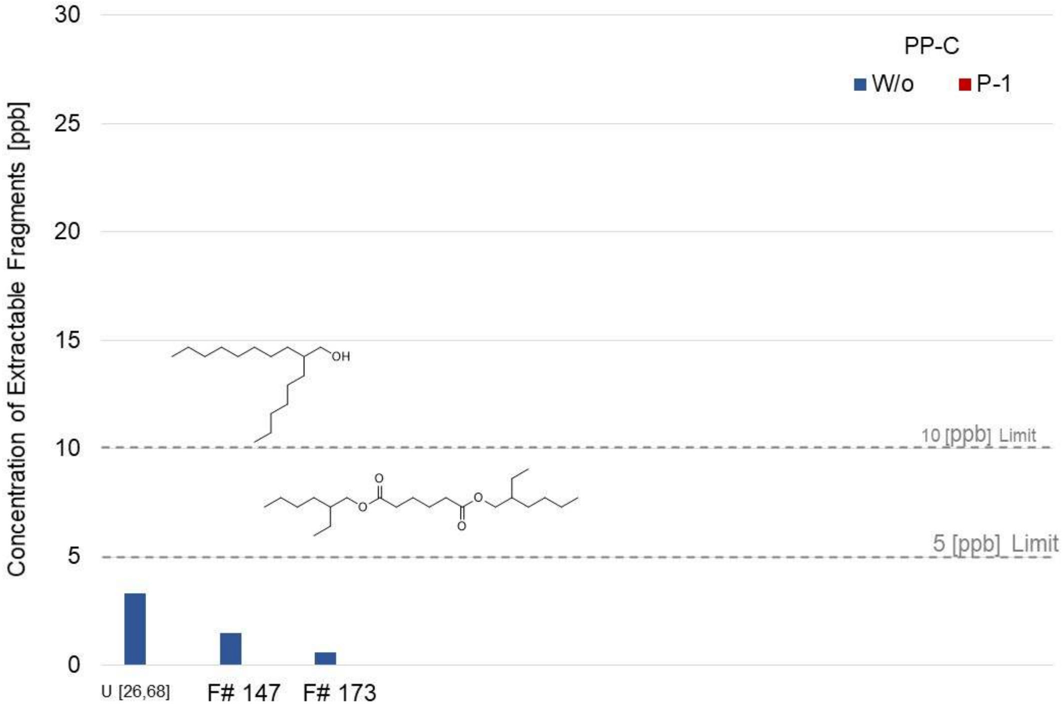
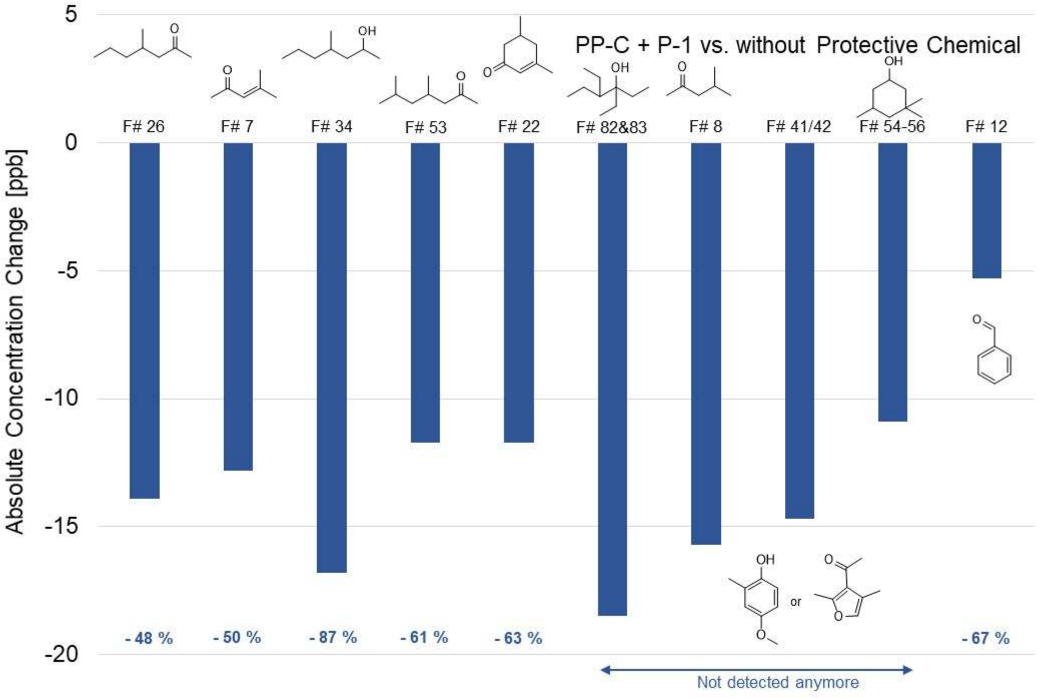


Figure 48: Concentration of fragments (ppb) detected in PP-C without (w/o) protective chemical and in the presence of P-1



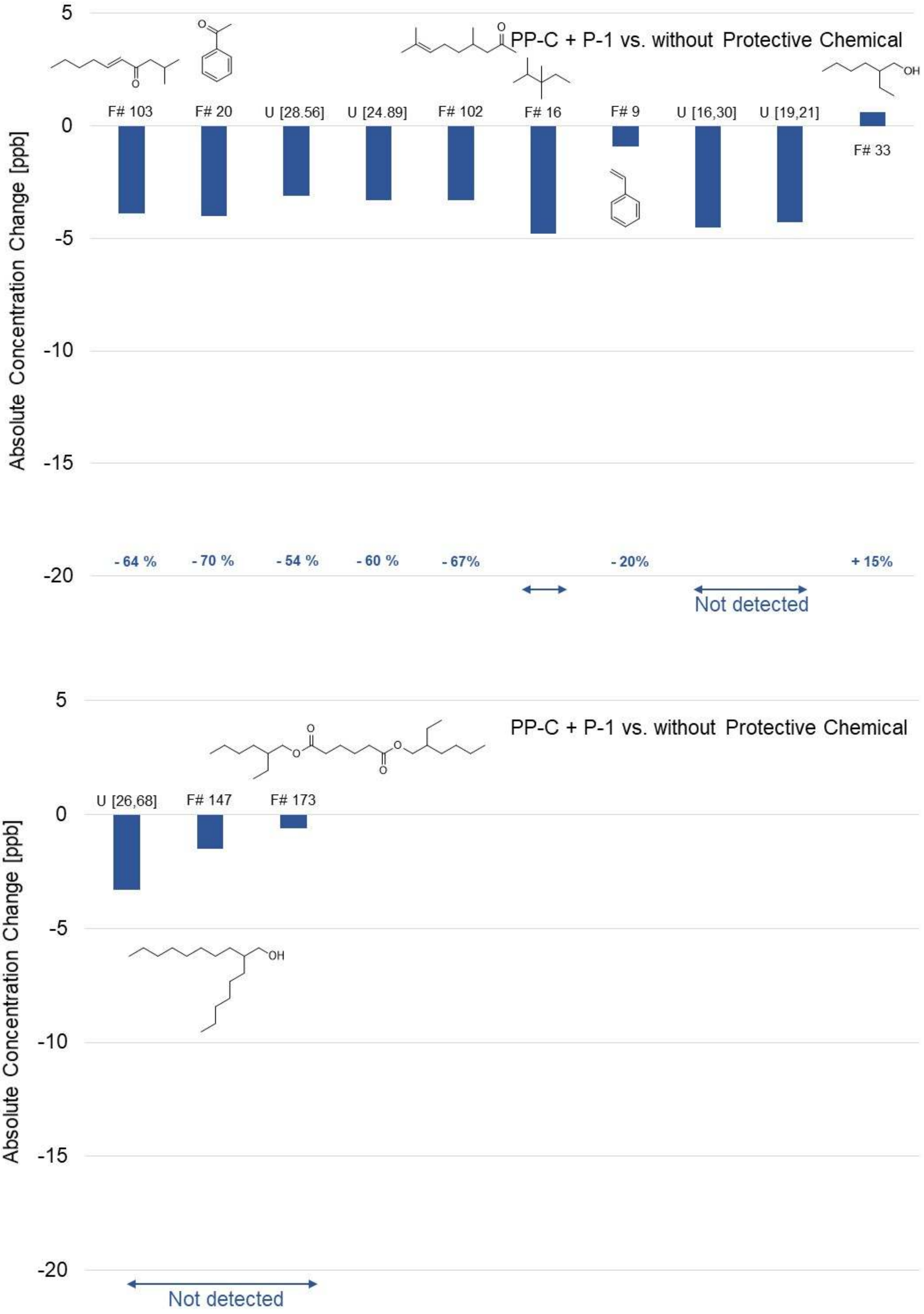


Figure 49: Reduction of fragments as absolute change in concentration (ppb) for PP-C in the presence of P-1

One of these fragments (F# 9, styrene) originates most likely from the (non-industrial) isolation of the PP batch at the end of the synthesis and is therefore not further discussed. The reason for the small increase of fragment F# 33 is not understood.

Addition of P-1 to PP-C results in three additional fragments (**Figure 50**). The unidentified fragment with a retention time of 18.64 minutes could potentially be related to fragment F# 54-56. Fragment F# 77 belongs to the class of oxidised-aliphatic (cyclic) fragments. Its cyclic (not aromatic) nature indicates that its origin is from the PP substrate. *Fragment F# 125 (2,4-di-tert-butyl phenol) is believed to be an intermediate from the synthesis of the phosphite P-1 and/or a hydrolysis product according to* ***Scheme 18***. F# 125 is the only fragment which can be clearly associated with the protective chemical P-1.

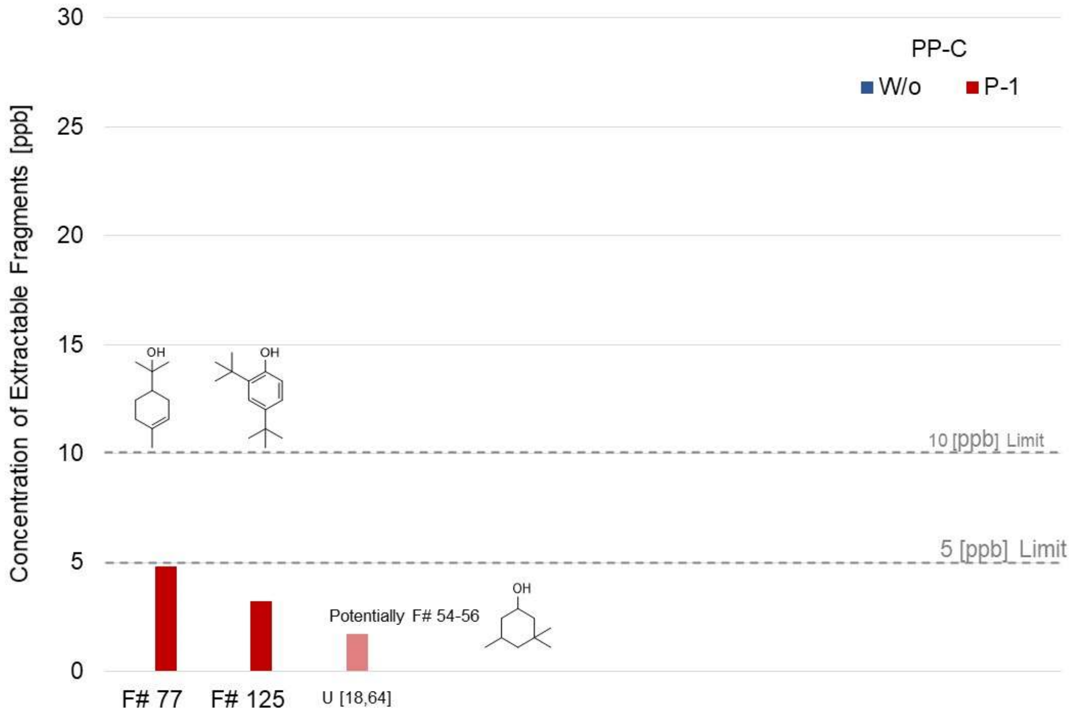
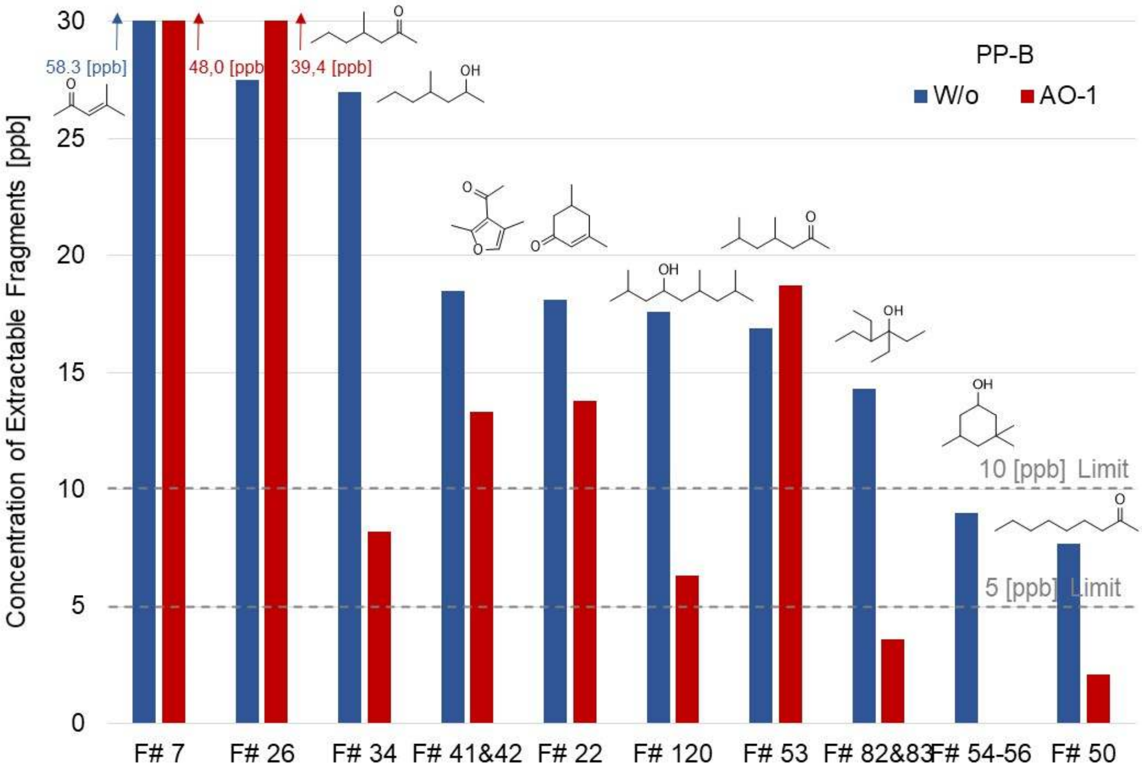
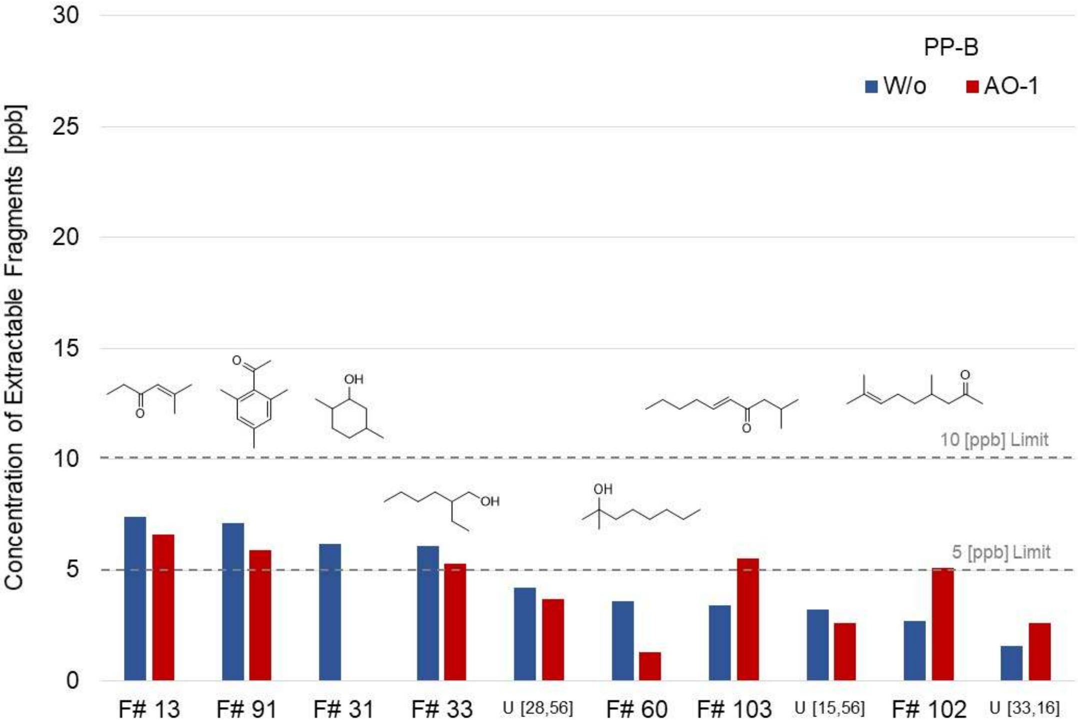


Figure 50: Additional fragments detected in PP-B in the presence of Phosphite P-1

A closer analysis of the fragments detected in PP-B in the presence of the Hindered Phenol AO-1 yields a different result than P-1 (**Figure 51**). The overall reduction of fragments, initially detected in PP-B, is of lower magnitude (**Figure 52**). Alcohols seem to be reduced to a higher degree than ketones; several ketones even increase in concentration. This is confirmed by a direct comparison of the relative reduction of further sub-classes of oxidised-aliphatic fragments (**Figure 53**).





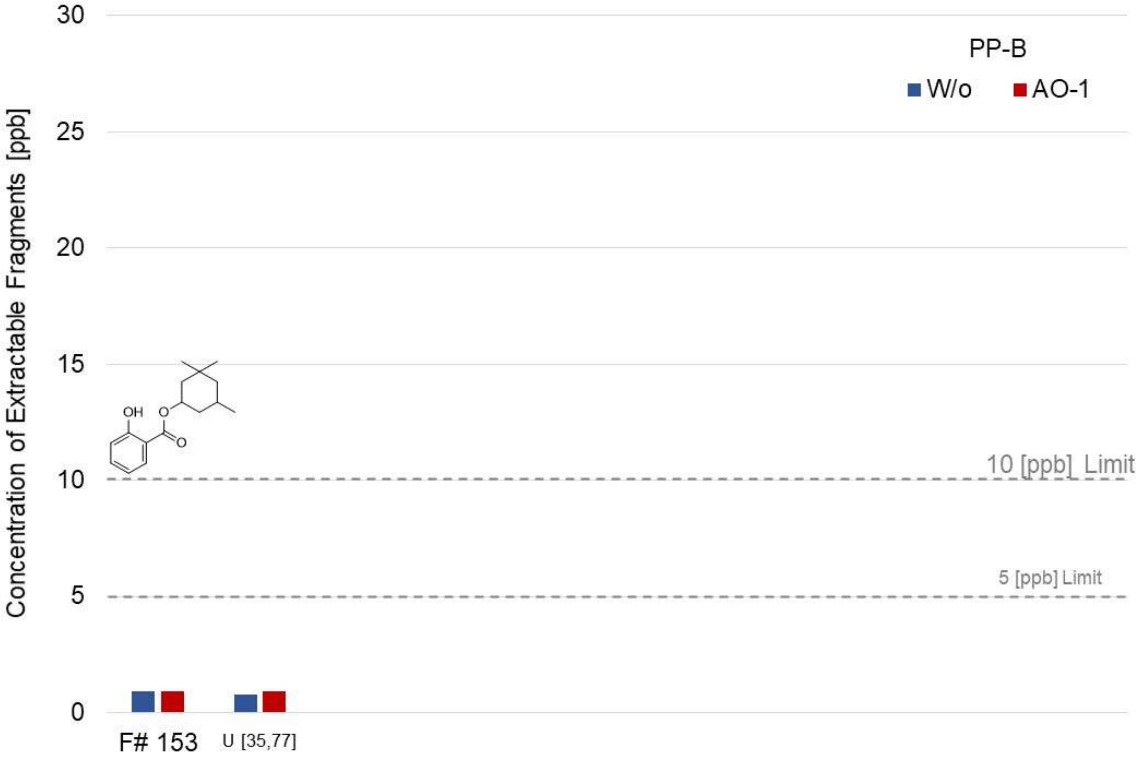
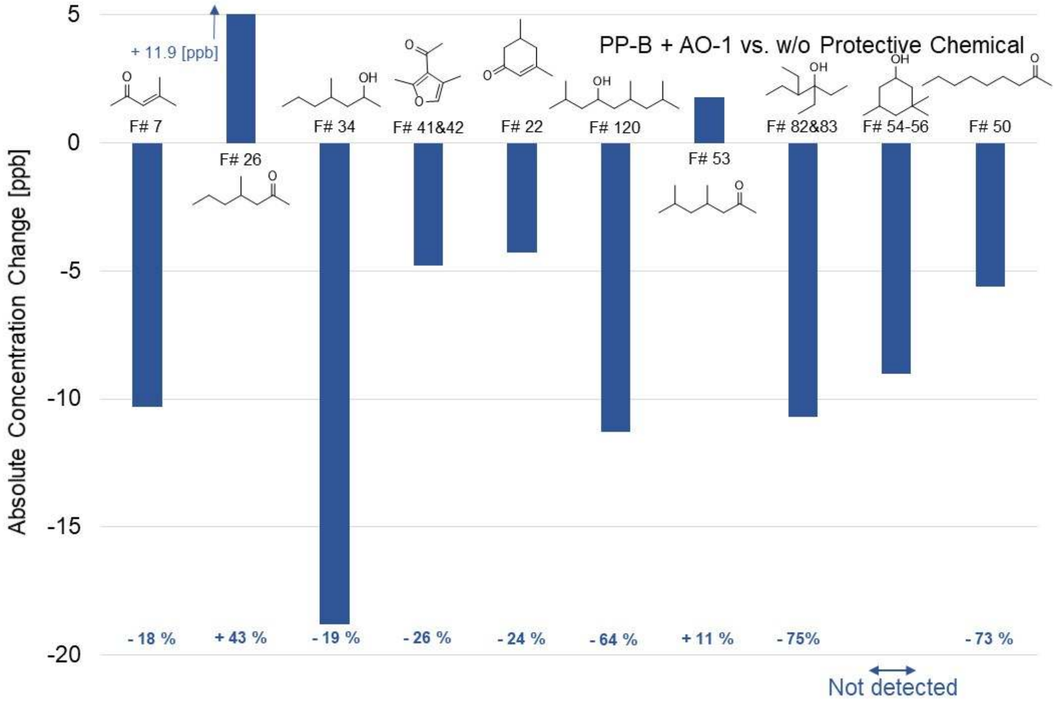


Figure 51: Concentration of fragments (ppb) detected in PP-B without (w/o) protective chemical and in the presence of Hindered Phenol AO-1


PP-B + AO-1 vs. w/o Protective Chemical
Absolute Concentration Change [ppb]
5
0
-5
-10
-15
-20
+ 11.9 [ppb]
F# 7
F# 26
F# 34
F# 41&42
F# 22
F# 120
F# 53
F# 82&83
F# 54-56
F# 50
- 18 %
+ 43 %
- 19 %
- 26 %
- 24 %
- 64 %
+ 11 %
- 75%
- 73 %
Not detected

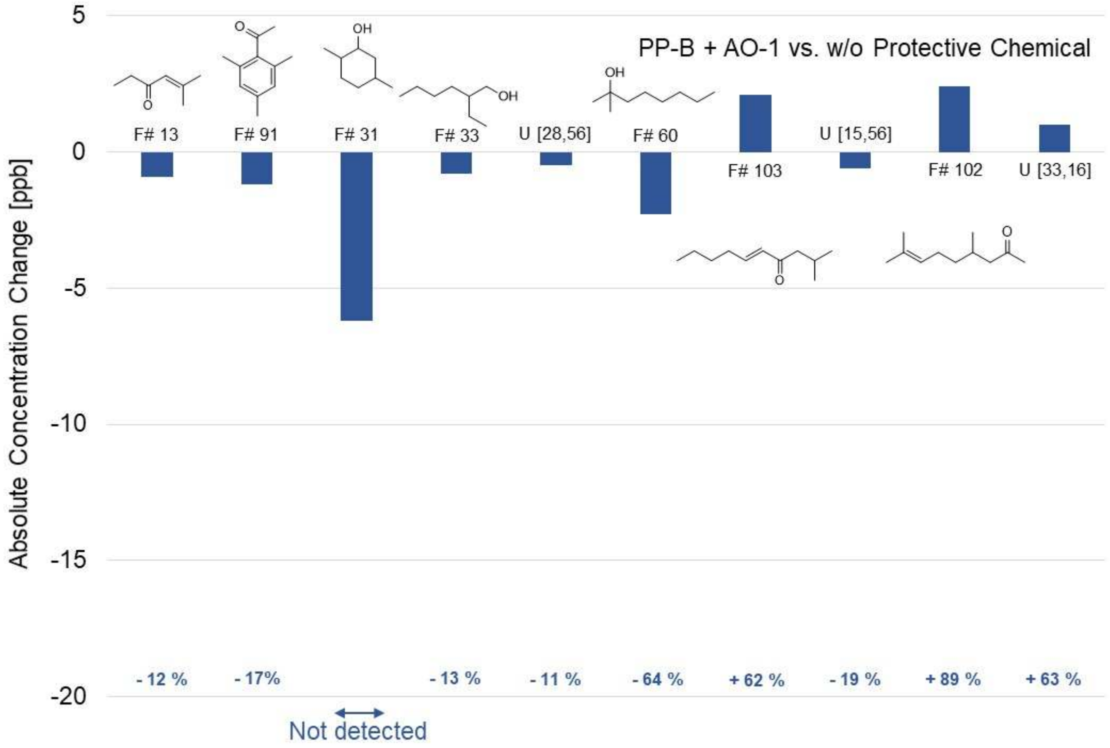

PP-B + AO-1 vs. w/o Protective Chemical
Absolute Concentration Change [ppb]
5
0
-5
-10
-15
-20
F# 13
F# 91
F# 31
F# 33
U [28,56]
F# 60
F# 103
U [15,56]
F# 102
U [33,16]
- 12 %
- 17%
- 13 %
- 11 %
- 64 %
+ 62 %
- 19 %
+ 89 %
+ 63 %
Not detected

Figure 52: Reduction in absolute concentration of fragments (ppb) for PP-B in the presence of AO-1

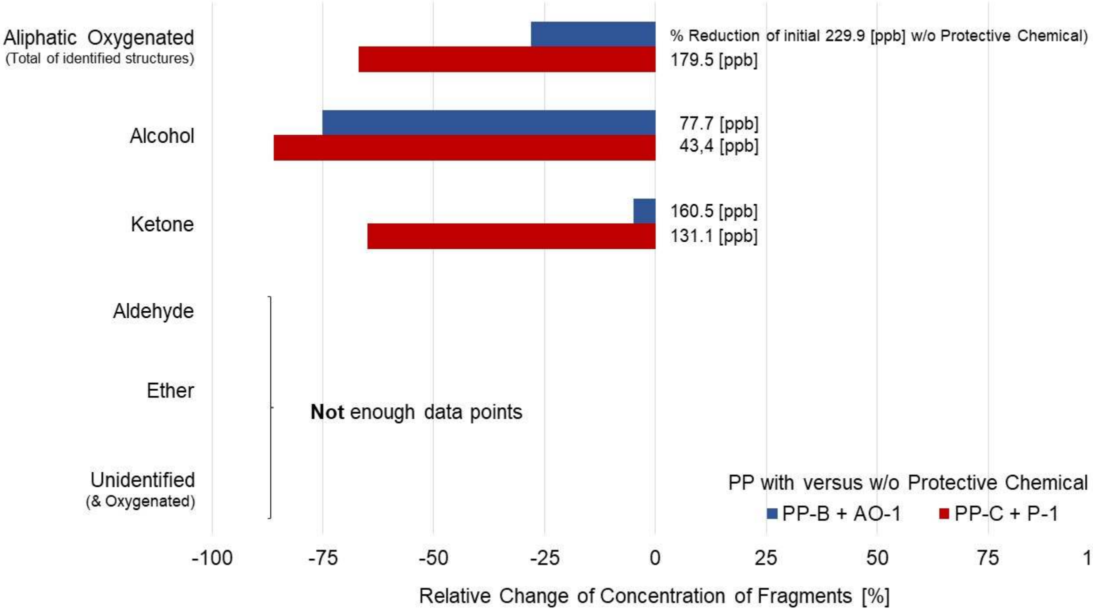


Figure 53: Relative change in concentration (ppb) of various oxidised-aliphatic fragments in the presence of Phosphite P-1 or alternatively Hindered Phenol AO-1

While both classes of protective chemicals reduce aliphatic alcohols by ~75 %, only the Phosphite P-1 reduces aliphatic ketones to any significant degree. 70 % of the ketones are 2-ketones. This is in line with earlier reports[129,130] that the formation of 2-ketones proceeds via hydroperoxides. Addition of a protective chemical which acts according to a peroxide decomposing mechanism (such as Phosphite P-1) offers an alternative reaction pathway to R 1.6 and R 1.9. Therefore, less secondary alkoxy radicals feed into reaction **Scheme 25**, **Scheme 27** and generically **Scheme 28**. The reduction of fragment F# 7 can be explained by a decrease of reaction R 24.1 due to a decomposition of macromolecular hydroperoxide LXIX via reaction R 16.2. It is proposed that this observation can be generalised to all classes of protective chemicals which act according to a peroxide decomposition mechanism. The reduction of aliphatic alcohol fragments by Hindered Phenol AO-1 can be explained by the alternative reaction R 6.1 instead of R 26.4.

Addition of AO-1 to PP-B results in nine additional fragments (**Figure 54**). The very high concentration of AO-1 of 5000 ppm (6.7 times higher than P-1) is important to remember. Apart from four unidentified fragments, one aliphatic alcohol (F# 35) is detected. F# 35 is structurally like fragments F# 33 & F# 34, which are detected already in PP-B without protective chemicals. Fragment F# 35 is therefore considered as a substrate-originating fragment.

The other five fragments seem to originate from AO-1. Fragment F# 148 can be formed via reaction R 11.2; while fragment F# 143 can be formed via a similar reaction R 10.2, but to a lesser extent. In both cases, fragment F# 135 is co-generated via reactions R 10.3 and R 11.3. In contrast, fragment F#156 is formed via a different mechanism according to the sequence of reactions R 13.1 followed by R 13.2 and R 15.1. Fragment F# 156 is specific to Hindered Phenols HP synthesized via the intermediate “Metilox” (**Figures 12** and **13**). Fragment F# 163 (also referred to as AO-39) is the intermediate “Metilox” which is considered an unreacted raw material.

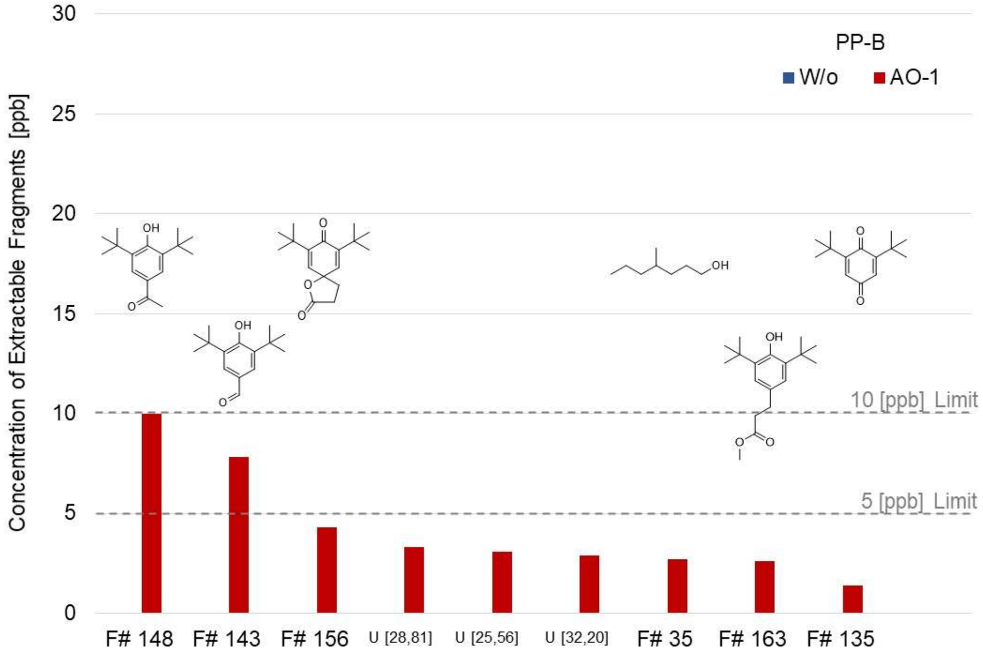


Figure 54: Additional fragments detected in PP-C in the presence of Hindered Phenol AO-1

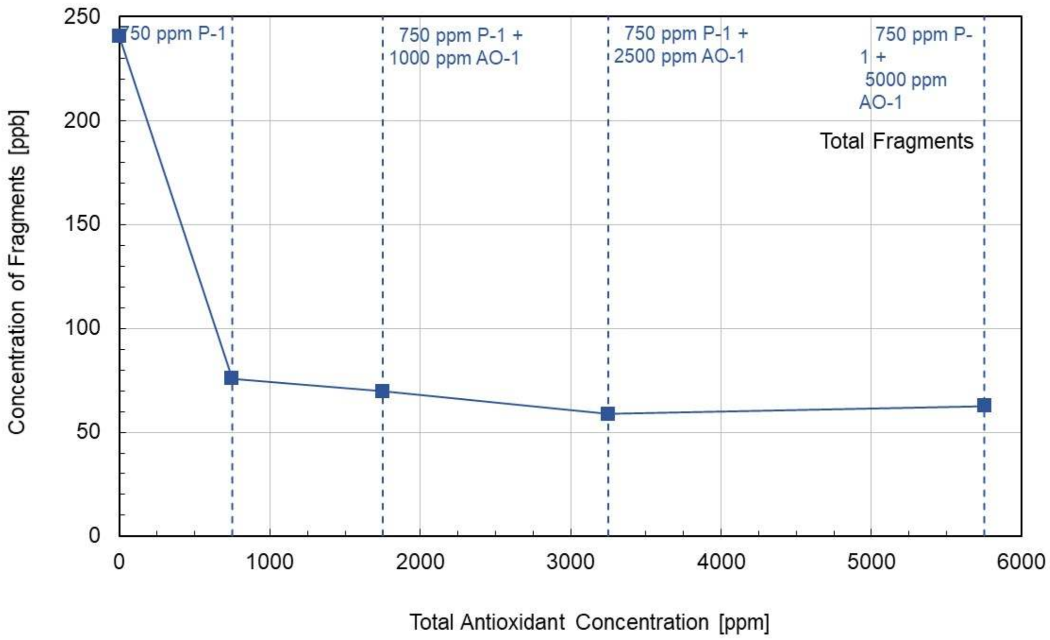
AO-1, which is added at 5000 ppm relative to only 750 ppm of P-1, results in five protective chemical originating fragments (versus 1 for P-1) and a total concentration of these fragments of 26.1 ppb (versus 3.2 ppb for P-1). This observation is further investigated in the following section.

3.3.2 Synergistic Effect of Hindered Phenol with Phosphite

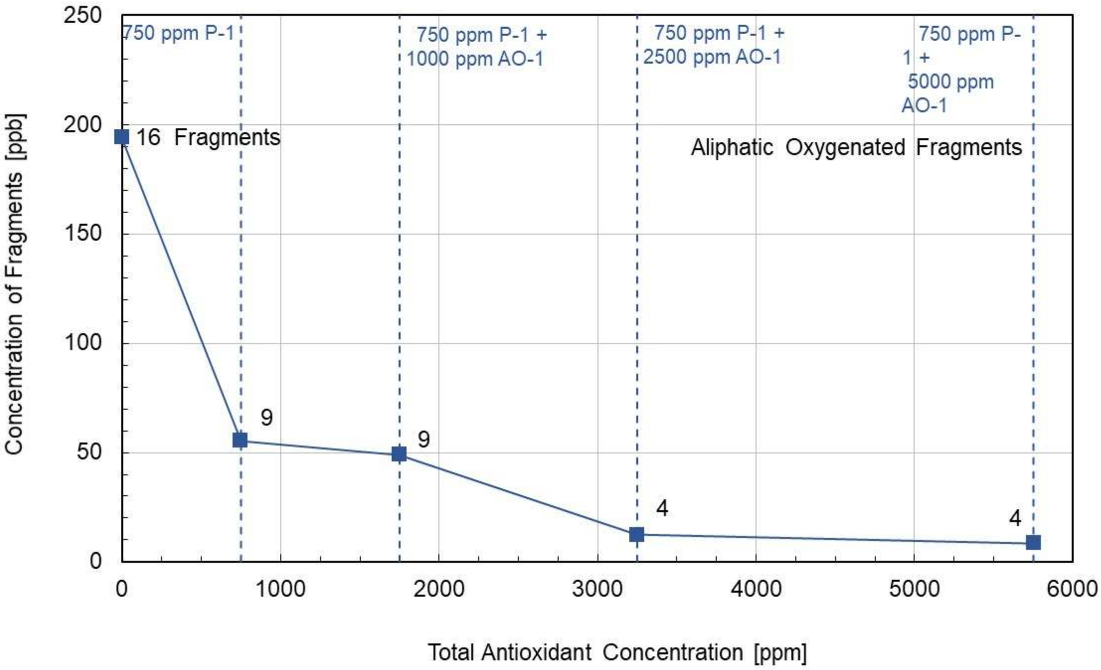
In this chapter the addition and subsequent increase in the concentration of AO-1 to PP-C (which already contains 750 ppm of P-1 and 750 ppm MS-1) is investigated. Here, the concentration of AO-1 was increased from 0 to 5000 ppm. Melt-processing and extraction conditions were the same as in Section 3.3.1.

The addition of AO-1 results in a continuous decrease in MFI (**Figure 46**). At high concentrations of AO-1 the protection of PP-C obtained is considered very good, though the observed increase in colour of ~5 YI units should be noted. This is an indication of an increased amount of transformation products of AO-1 formed.

Addition of 750 ppm P-1 to PP-C causes a significant reduction in the concentration of fragments (as discussed in Section 3.3.1). After an initial reduction of ~69%, a further reduction of only ~5% is achieved by the addition of 1000 ppm AO-1; resulting in a total reduction compared with the non-stabilized PP-C of ~75%. To a first approximation, addition of more than 2500 ppm AO-1 to 750 ppm P-1 (and hence in total 3250 ppm of protective chemical) results neither in a further reduction of MFI (**Figure 46**), nor in a further decrease of the concentration of fragments (**Figure 55a**). No aliphatic fragments except F# 16 (in PP-C without protective chemical) are observed. Aromatic fragments are associated with F# 9 (styrene), most likely from the substrate purification. As the concentration remains relatively constant around 3-5 ppb, this observation is not discussed further. Oxidised-aliphatic fragments decrease over the whole range of addition of AO-1. At 5000 ppm AO-1 and 750 ppm P-1, the change in the number of fragments is ~75% and in concentration ~96% (**Figure 55b**). 2-Ketones show the same tendency; in general representing ~70-80% of the oxidised-aliphatic fragments (**Figure 3.25c**). Up to an AO-1 concentration of 1000 ppm (in addition to 750 ppm P-1), the decrease of total fragments correlates well with the decrease in oxidised-aliphatic (2-ketone based) fragments. Above this concentration, the decrease of oxidised-aliphatic fragments continues while the concentration of total fragments remains stable.



(a)



(b)

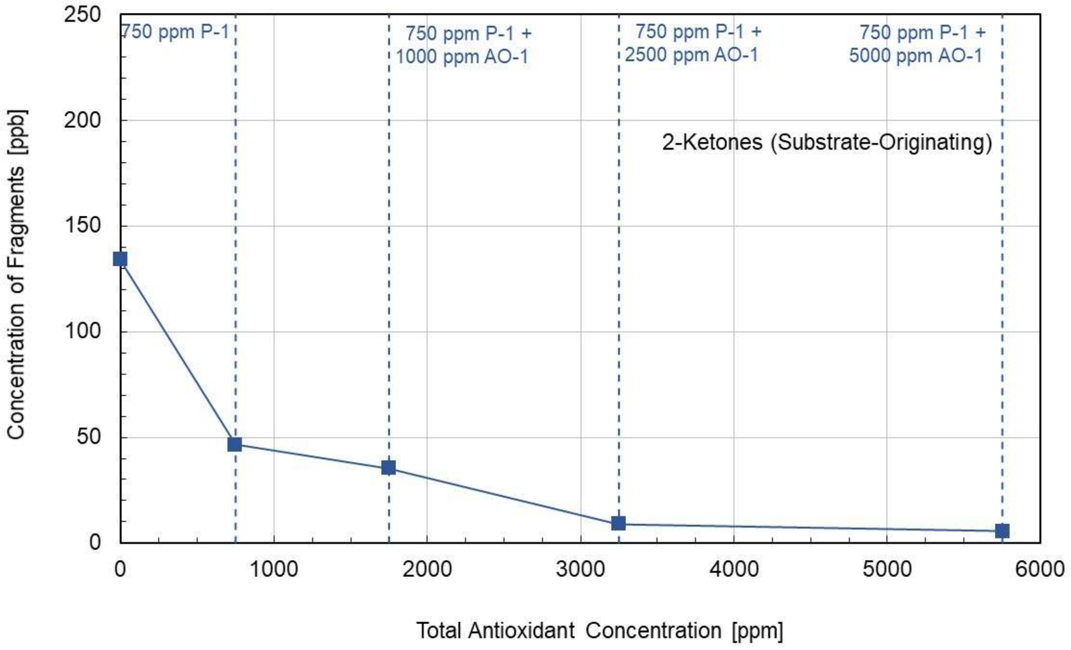


Figure 55: Concentration of fragments (ppb) as function of concentration & composition of protective chemicals
Total fragments (a)
Aliphatic-oxygenated fragments (b)
2-Ketones (c)

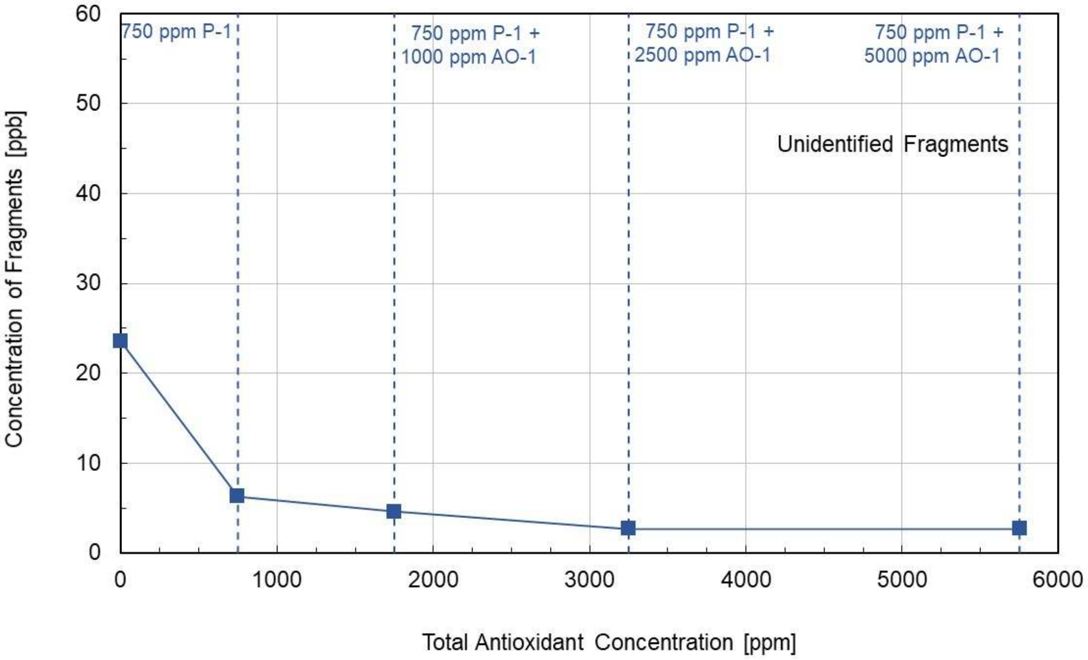


Figure 56: Concentration of unidentified fragments as function of concentration & composition of protective chemicals in PP-C

Unidentified fragments (**Figure 56**; note the different scale) follow the same trend as oxidised-aliphatic fragments, so are suspected to be of an oxidised-aliphatic nature. The observations in **Figure 55** and **Figure 56** indicate the formation of fragments of a different nature (at least) above a concentration of AO-1 of 1000 ppm.

One specific oxidised-aliphatic fragment F# 51 (Nonanal) is present from the point at which AO-1 is added and increases with its concentration (**Figure 57**). The mechanism of its formation is not yet understood.

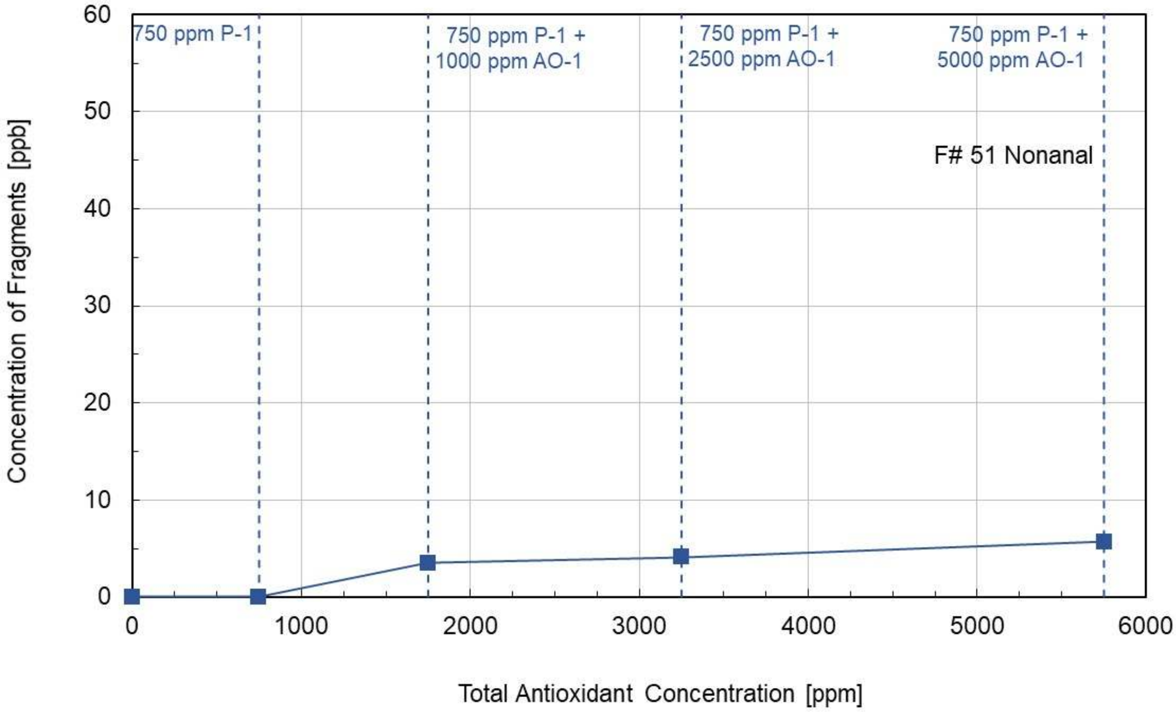
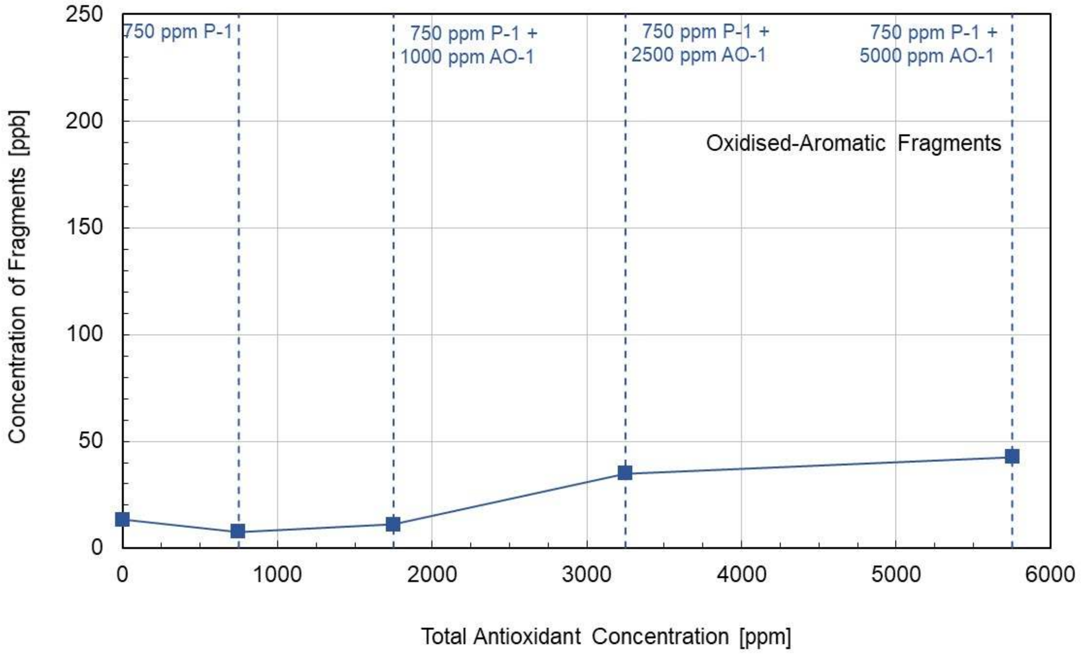


Figure 57: Concentration of F# 51 Nonanal as function of concentration & composition of protective chemicals

Oxidised-aromatic fragments apparently increase above 1000 ppm of AO-1 (**Figure 58a**). Corrected for oxidised-styrene derivatives (F# 12 Benzaldehyde & F# 20 Acetophenone) an overall increase is observed, the slope of which decreases above 2500 ppm AO-1 (**Figure 58b**). Separation of fragment F# 125, which remains constant throughout the entire experiment if P-1 is present, confirms the increase of all other oxidised aromatic fragments as a function of the concentration of AO-1 (**Figure 58c**), note the different scale). It appears that F# 125 is formed at a constant rate via reactions R 18.1 to R 18.3 independent of the degree of synergistic effect between the Phosphite P-1 and the Hindered Phenol AO-1. It appears to depend only on the initial concentration of P-1 and potentially its hydrolysis state. All other oxidised-aromatic fragments originate from AO-1 and are identified in **Figure 54**.

An overlay of oxidised-aliphatic and oxidised-aromatic fragments, the latter excluding oxidised-styrene derivatives, indicates major changes in the concentration of the two fragment categories between additions of 1000 and 2500 ppm AO-1. Within this concentration range, a cross-over is observed at ~ 2000 ppm AO-1

(**Figure 59a**); at this concentration AO-1 fragments, originating from protective chemicals, dominate. The different scale of the lower chart in **Figure 59b** highlights the major contribution of fragments F# 143 and F# 148, which represent ~ 90% of the fragments originating from protective chemicals. Together with the minor fragment F# 135, all three are detected the moment AO-1 is added to the formulation. In contrast, fragments F# 156 and F# 163 are not detected at concentrations of AO-1 of 1000 ppm, only at elevated concentrations. **Figure 60** confirms significant changes in the range between 1000 and 2500 ppm AO-1 (each time in addition to 750 ppm P-1). MW increases and MFI decreases until 2500 ppm AO-1 (i.e., a total concentration of 3250 ppm). MW is derived from the literature (graphical) [249v]. At higher concentration of AO-1 only marginal changes in MW and MFI still occur. Oxidised-aliphatic fragments remain constant in number but still decrease by ~ 4 ppb. Oxidised-aromatic fragments remain constant in number and increase by ~ 6 ppb.



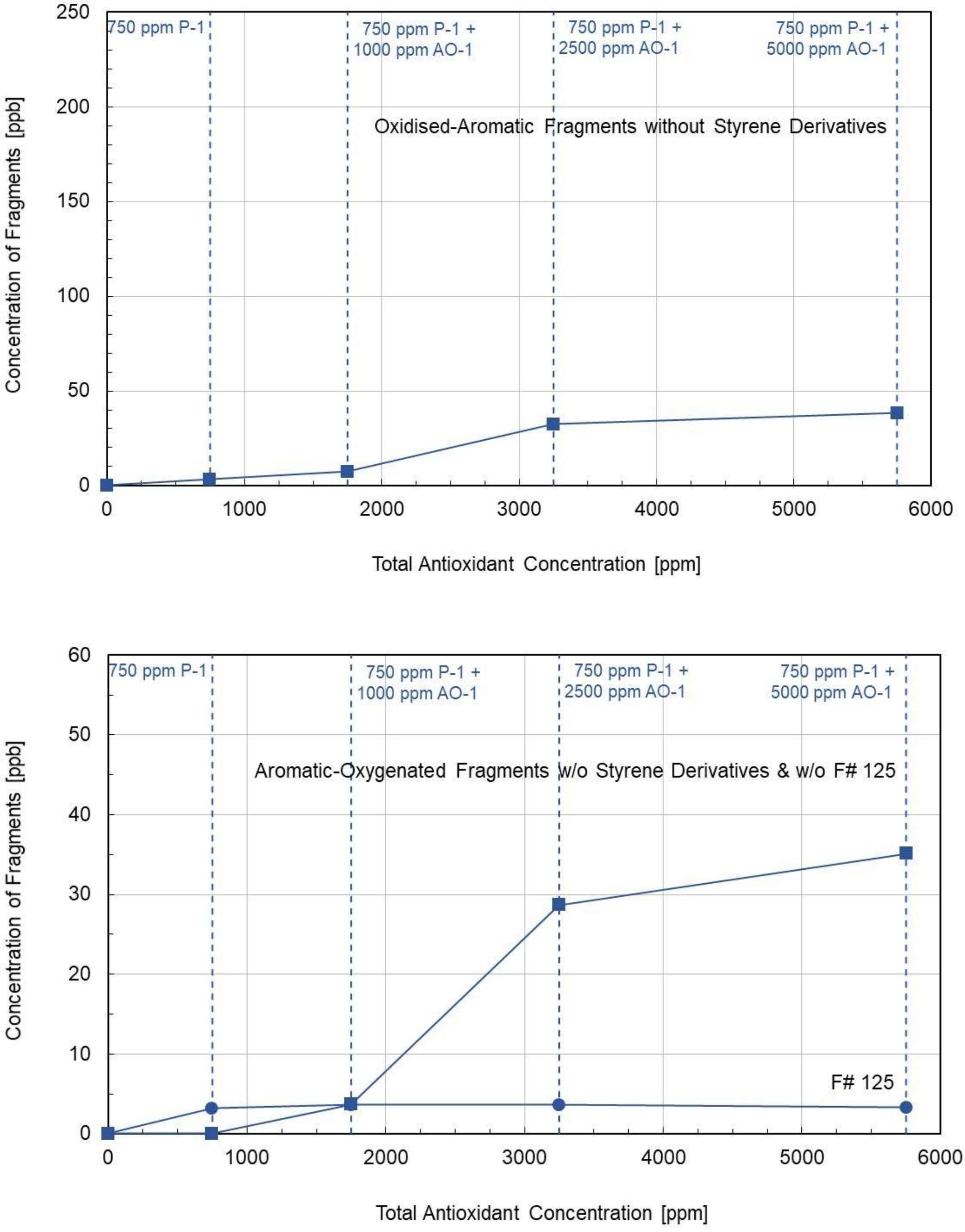
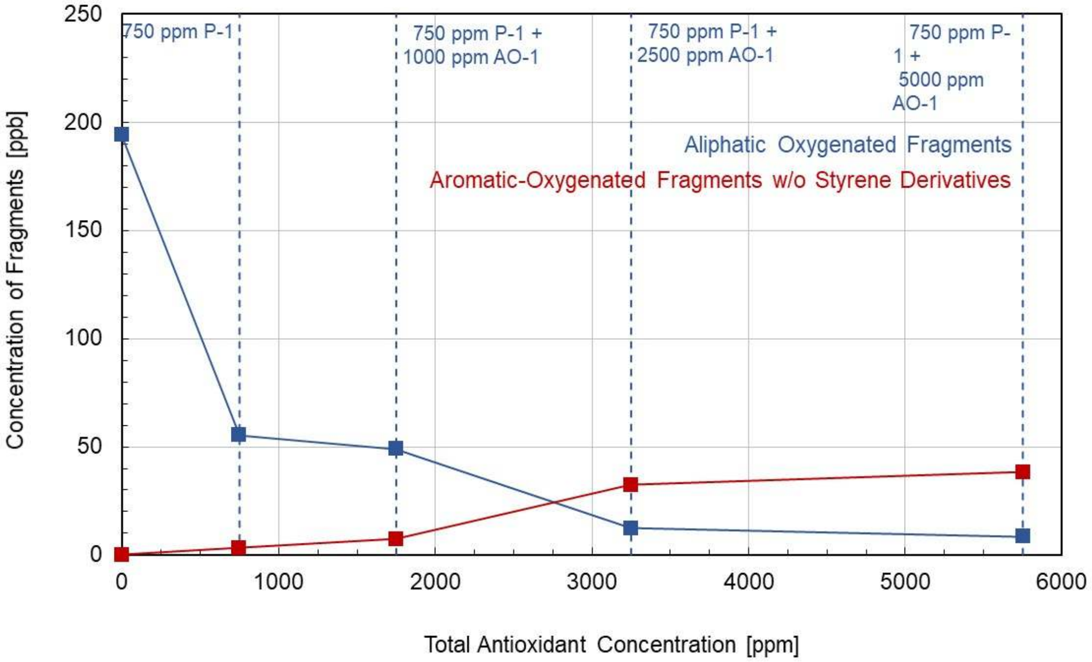
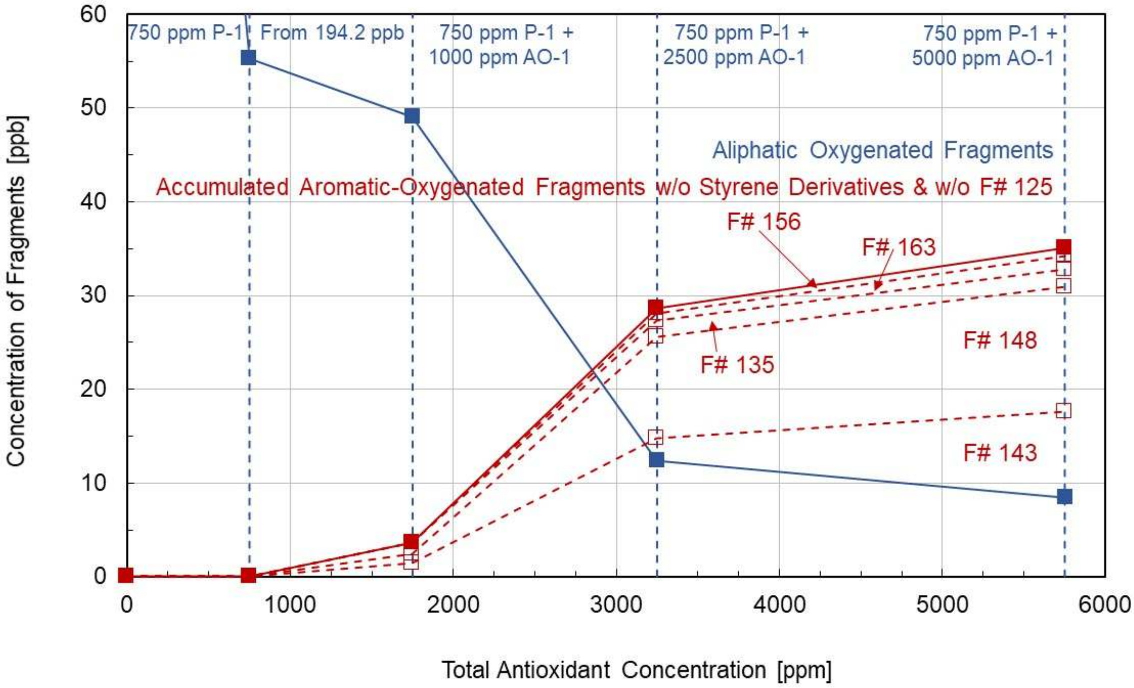


Figure 59: Concentration of aromatic oxygenated fragments as function of concentration & composition of protective chemicals (a) and corrected for oxygenated styrene derivatives (b) and further corrected for F# 125 (c)



(a)



(b)

Figure 59: Concentration of aliphatic oxygenated and aromatic oxygenated fragments as function of concentration & composition of protective chemicals

It can be concluded that there is *an inversely proportional relationship between oxidised-aliphatic fragments and oxidised-aromatic fragments F# 135, F# 143, F# 148 & F156* (but not F# 163 and F# 125). However, above 2500 ppm AO-1, a further doubling of the concentration to 5000 ppm results only in a limited decrease of MFI (**Figure 61a**) and a respective increase in MW of ~ 2-3% (**Figure 61b**). Nevertheless, oxidised-aliphatic fragments still decrease at the expense of a further increase (~ 20%) in AO-1 originating oxidised-aromatic fragments.

Independent of this observation, the part of the molecules of AO-1 which react during melt-conversion are potentially no longer available for its function as thermal stabiliser.

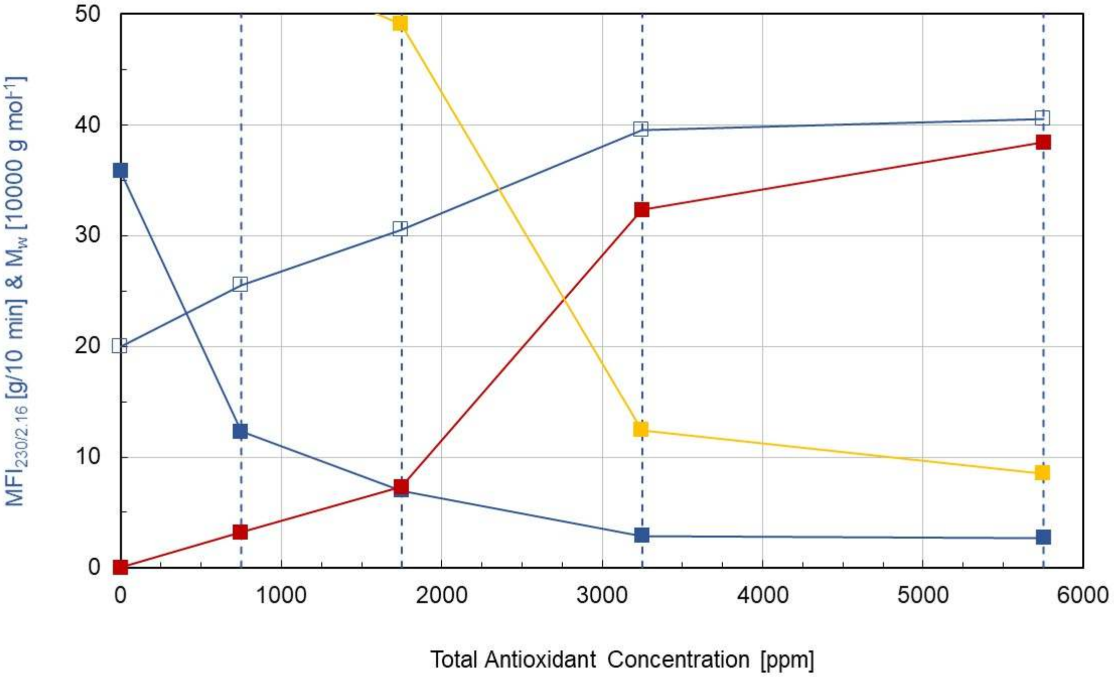
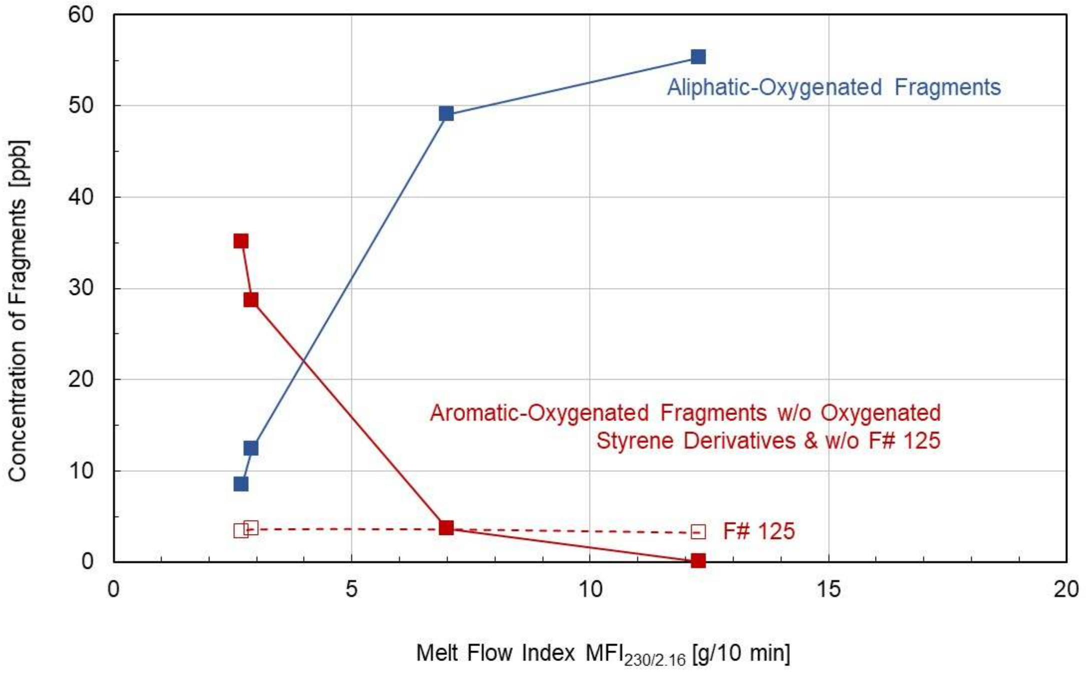
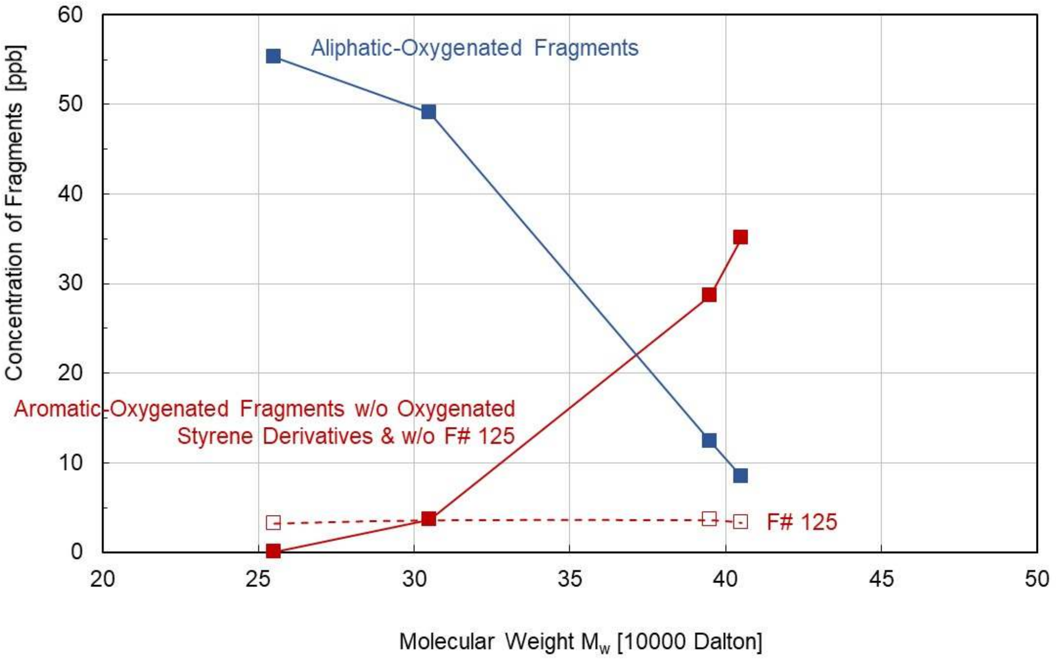


Figure 60: MFI, MW, concentration of aromatic oxygenated and aliphatic oxygenated fragments as function of concentration & composition of protective chemicals

From this section it can be concluded that for the synergistic mixture of protective chemicals [P-1 + AO-1] investigated, there is an inverse proportionality between oxidised-aliphatic (originating from the PP substrate) and oxidised-aromatic fragments (originating mainly from the Hindered Phenol AO-1). The fragments concerned (fragments F# 135, F# 143, F# 148 & F# 156), are designated as primary or secondary transformation products from AO-1. Fragment # 163 is an unreacted impurity from the synthesis of AO-1 and increases with the concentration of AO-1. Fragment F# 125 is the hydrolysis product of the Phosphite P-1 and is postulated to increase only with the concentration of P-1 and is indicative of the degree of hydrolysis of P-1. One specific, PP originating, oxidised-aliphatic fragment F# 51, the aldehyde Nonanal, is only detected in the presence of AO-1. It increases with the concentration of AO-1 (while all other oxidised-aliphatic fragments decrease).



(a)



(b)

Figure 61: Change of fragment concentration (ppb) as a function of MFI and MW

3.3.3 Alternative Synergistic Effect

In Section 3.3.2, the classic approach of the combination of one Phosphite with one Hindered Phenol was discussed. In this approach the hinderance of the Hindered Phenol is "high", meaning as in the case of AO-1 a 2,6-di-*tert*-butyl hinderance. Here it was noted that the sub-class of Hindered Phenol functions as a protective chemical in the entire temperature range from -50 to + 300°C. However, the specific hinderance around the phenolic group determines its contribution at high temperature (melt-processing) versus moderate temperature (service life) [250,251].

In this section the influence of a second Hindered Phenol which can work synergistically with a Phosphite during melt processing, while the initial Hindered Phenol (AO-1) functions exclusively as a long-term thermal stabilizer, is investigated. The intention here is to separate the protective activity during melt-processing from the protective activity during long term service life. This is achieved by use of

Hindered Phenols with different bond dissociation energy of the phenolic OH group (**Table 3** and **Table 4**) [252]. The formulation of PP-B (containing 750 ppm MS-1 as antacid) and PP-B containing the same antacid and 5000 ppm AO-1 were further developed. Starting with 5000 ppm AO-1 alone, in successive steps a more and more dedicated "processing stabilization package" was introduced. First, P-1 was added at a concentration of 1000 ppm. A similar formulation has already been discussed in Section 3.3.1 (PP-C + 750 ppm MS-1 5000 ppm AO-1 + 750 ppm P-1). In this case, the protection during melt conversion is based on the synergistic effect of [AO-1+P-1], as reported numerous times [254,255], and in contrast to the use of AO-1 alone. In a further formulation, 250 ppm of AO-6 was introduced. In this formulation the protective effect during melt-processing is expected to be the contribution of synergism between the phenol and phosphite [AO-6 + P-1]. The reason for this is the lower bond dissociation energy of AO-6 versus AO-1 and consequently the higher rate constant for reaction R 3.1 *c.f.* R 6.1 (**Table 19** [252,253]). In the final formulation, P-1 is replaced by P-5, which is a more efficient protective chemical during melt-processing, due to a higher phosphorus content (higher molar activity) and the presence of 2 phosphorus centres [178]. **Table 20** summarises the different formulations.

Table 19: Structure, hinderance and bond dissociation energy of AO-1 vs. AO-6

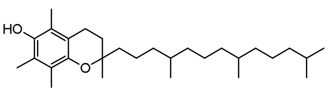
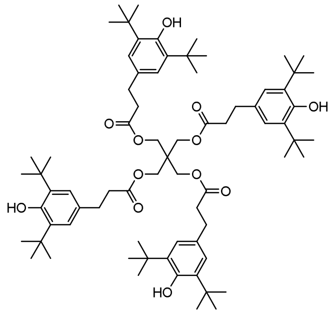
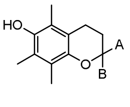
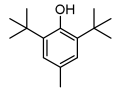
Property	***AO-6***	***AO-1***
Chemical Structure		
Functional Group		 ***AO-28***
Rate Constant k $[M^{-1} s^{-1}]_{AIBN}$ initiated autooxidation of styrene (F# 9) at 30°C [252,253] Reaction similar to R 3.1	320	1.4

Table 20: Formulations and major contribution to prohibition of oxidation (All formulations containing 750 ppm MS-1 and based on PP-B)

Formulation	***Major Contribution Protective Chemical***	
	Melt-Processing	***LTTS***
No protective chemical		
5000 ppm AO-1	AO-1	Remaining AO-1
5000 ppm AO-1 + 1000 ppm P-1	[P-1 + AO-1]	Remaining AO-1
5000 ppm AO-1 + [1000 ppm P-1 + 250 ppm AO-6]	[P-1 + AO-6] synergism	AO-1
5000 ppm AO-1 + [1000 ppm P-5 + 250 ppm AO-6]	[P-5 + AO-6] synergism	AO-1

All formulations are prepared and melt-processed according to conditions C-1 and M-1 (**Table 16**) and extracted according to method E-4 at 60°C (**Table 17**). Melt-processing of these six formulations resulted in a surprising observation (**Figure 62**). The combination of 5000 ppm AO-1 with 1000 ppm P-1 results in a good protective effect (as already seen in **Figure 46b** with a similar formulation). Addition of AO-6 and substitution of P-1 with P-5 does not result in an improved protection during melt-processing. It is concluded that a high concentration of AO-1 with a minimum concentration of P-1 results already in a very good protective effect. Addition of (under melt-processing conditions) more active protective chemicals does not result in a lower MFI and hence higher MW. Nevertheless, a lower colour is observed which could indicate a lower concentration of transformation products arising from the Hindered Phenol.

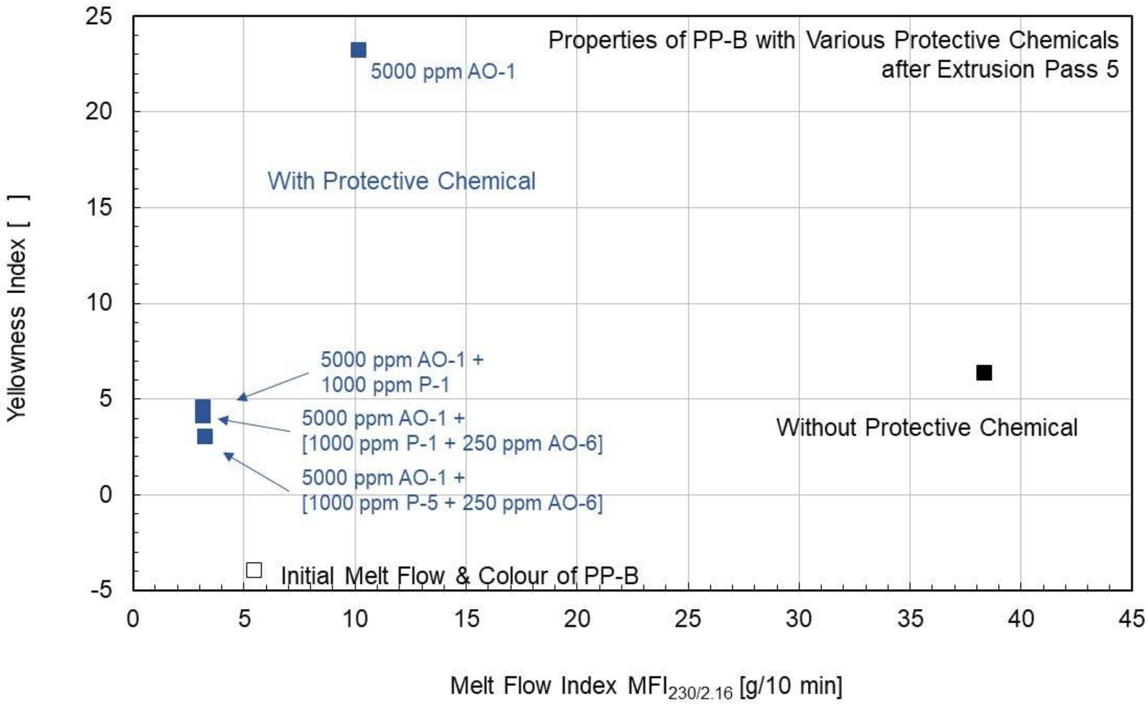
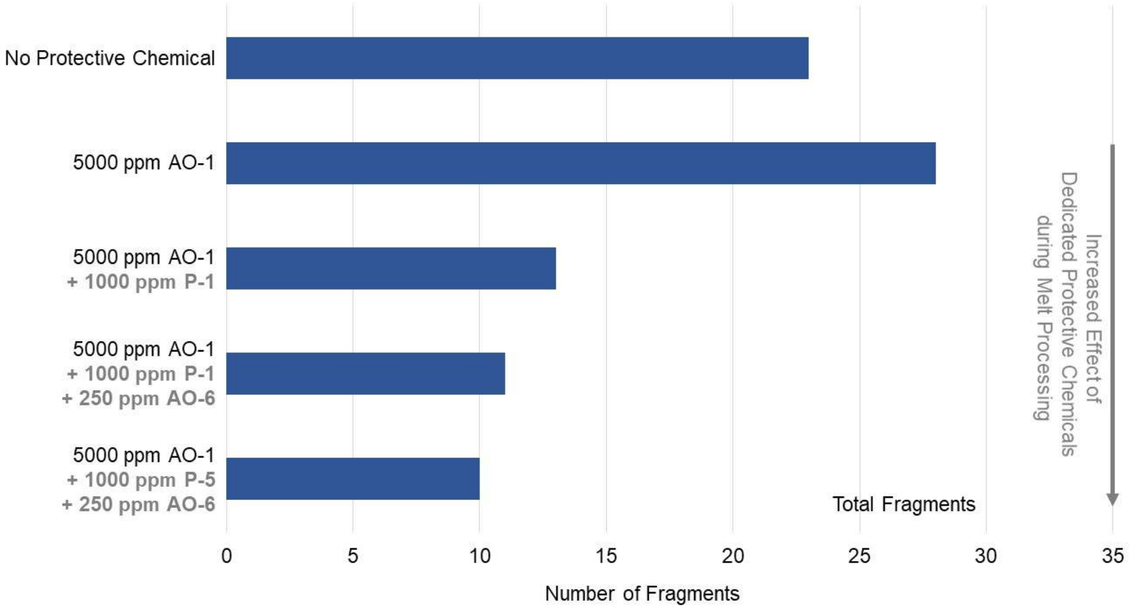


Figure 62: Properties of melt-processed PP in the absence and presence of different classes of protective chemicals

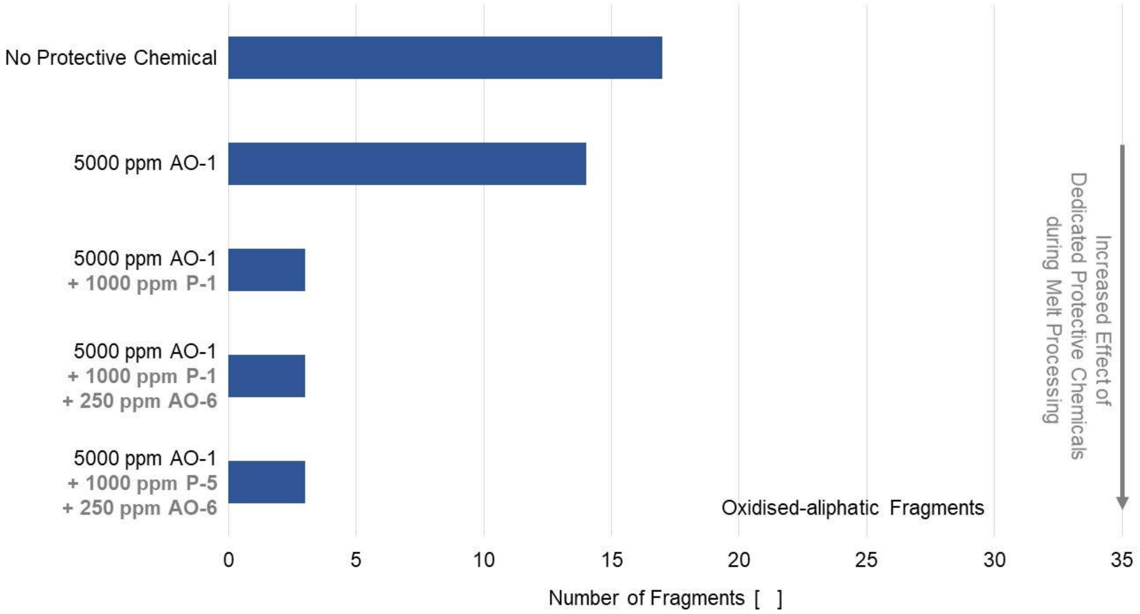
Extrusion Condition:	C-1, M-1
Extraction Condition:	E-4
Formulation:	PP + 750 ppm MS-1

Although the three formulations shown in **Figure 62** yield a similar MW protection during melt-processing, they differ in number (**Figure 62a**) and concentration (**Figure 63b**) of total fragments detected. Moving from 5000 ppm AO-1 alone to [5000 ppm AO-1 + 1000 ppm P-5 + 250 ppm AO-6] increases the effect of a dedicated mixture of protective chemicals for melt-processing only. Along this direction, the number and concentration of total fragments decreases. The number of fragments (relative to the formulation without protective chemical) decreases by more than half, while the concentration of total fragments decreases by ~90%. It is noted that the addition of AO-1 alone increases the number of different fragments by ~20%.

No aliphatic or aromatic fragments are detected. A further detailed analysis of the fragments focuses therefore on oxidised-aliphatic, oxidised-aromatic, and unidentified fragments. **Figure 64** confirms that the vast majority of the fragments formed in PP-B without protective chemical are of an oxidised-aliphatic nature. *Formulations containing Phosphite (either P-1 or P-5) reduced oxidised-aliphatic fragments by ~80% in number and by ~95% in concentration*.



(a)



(b)

Figure 63: Number (a) and concentration (lower chart) of total fragments depending on mixture of protective chemicals

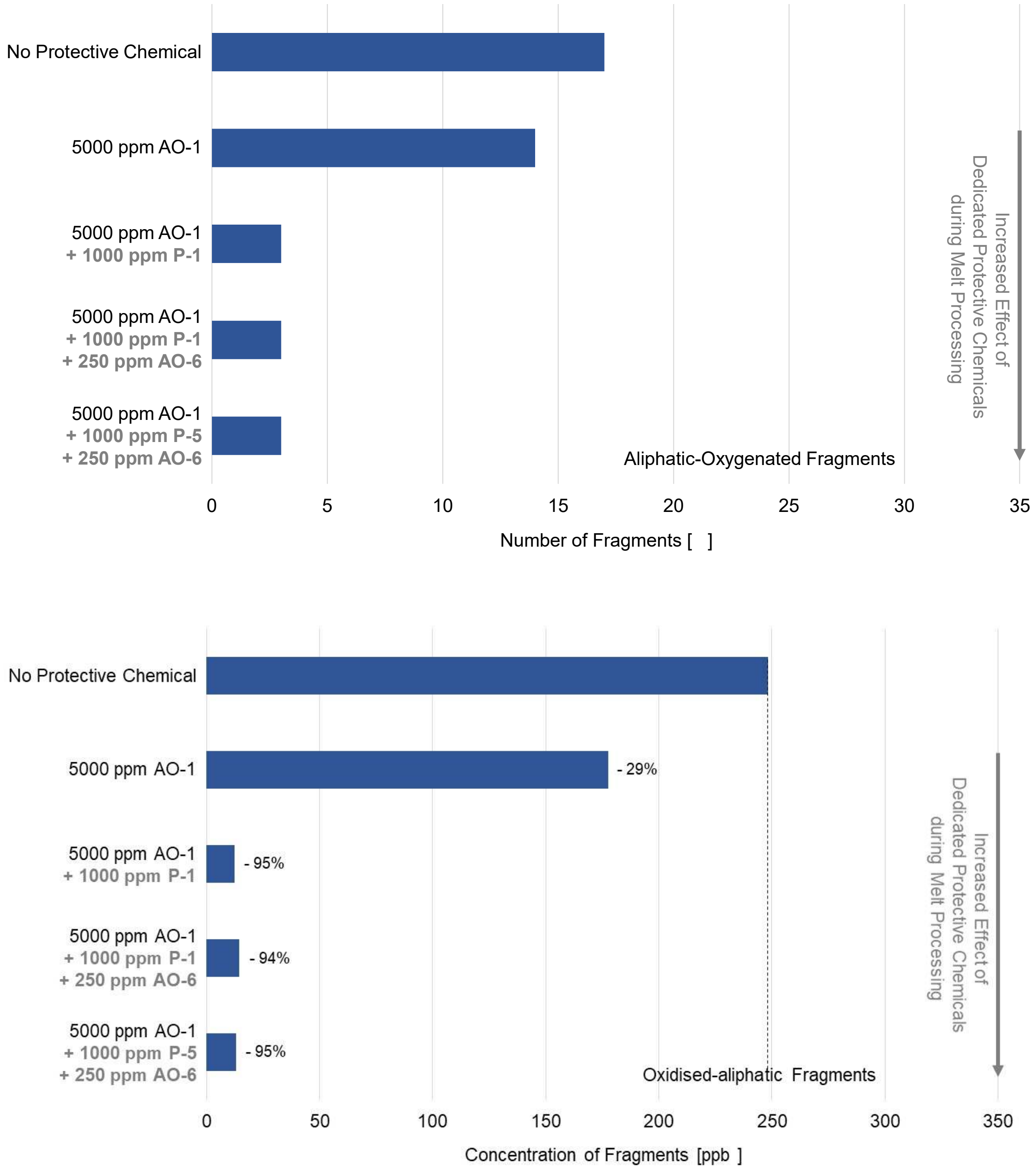


Figure 64: Number and concentration (ppb) of oxidised-aliphatic fragments depending on mixture of protective chemicals

An identical observation is made for the specific sub-category 2-ketones (aliphatic) (**Figure 65**). The only difference is (as observed earlier in Section 3.3.1) that AO-1 alone is not able to suppress the formation of ketones in an efficient manner. The three formulations containing Phosphite can be neither distinguished by MFI and MW, nor by the efficiency in reduction of oxidised-aliphatic fragments. The formulations differ though in oxidised-aromatic fragments. PP-B without protective chemicals contains two oxidised-aromatic fragments which AO-1 alone cannot completely suppress. In contrast, the Phosphite containing formulations are able to successfully supress these two fragments (**Figure 67**). The fragments are identified in **Figure 66**. As fragments F# 91 and F# 153 are already detected in PP-B without protective chemicals, they are believed to originate from the polymer substrate.

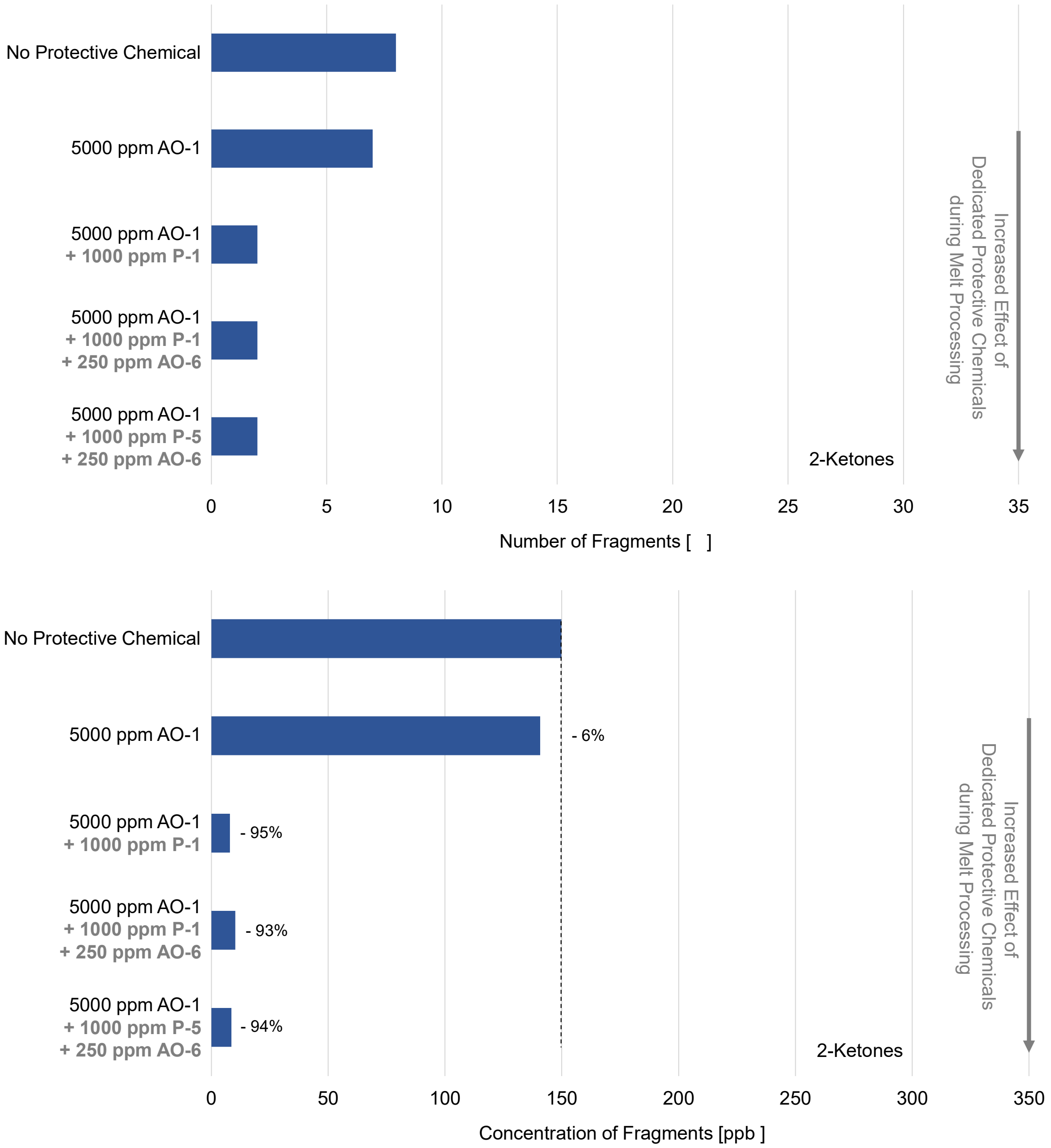
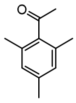
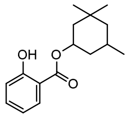


Figure 65: Number (upper chart) and concentration, ppb (lower chart) of 2-ketones depending on mixture of protective chemicals

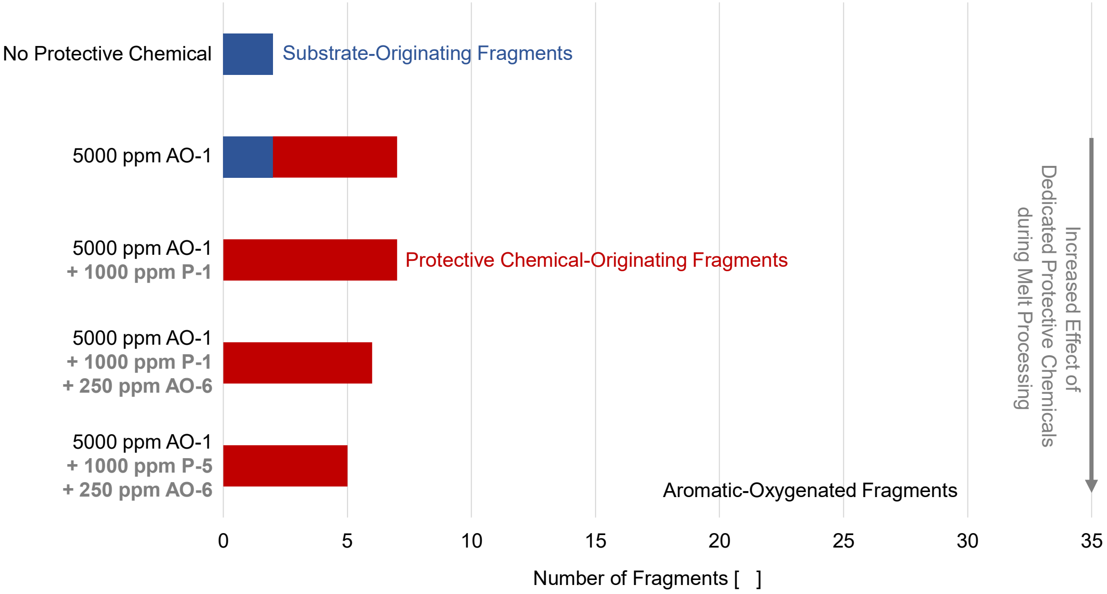


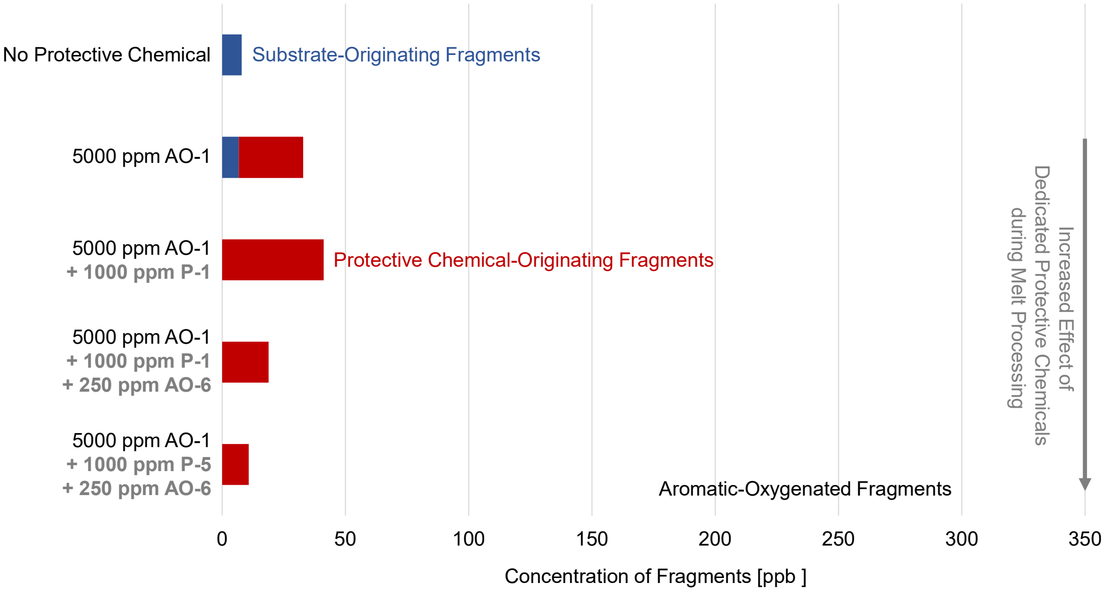
F# 91



F# 153

Figure 66: Substrate-originating aromatic-oxygenated fragments





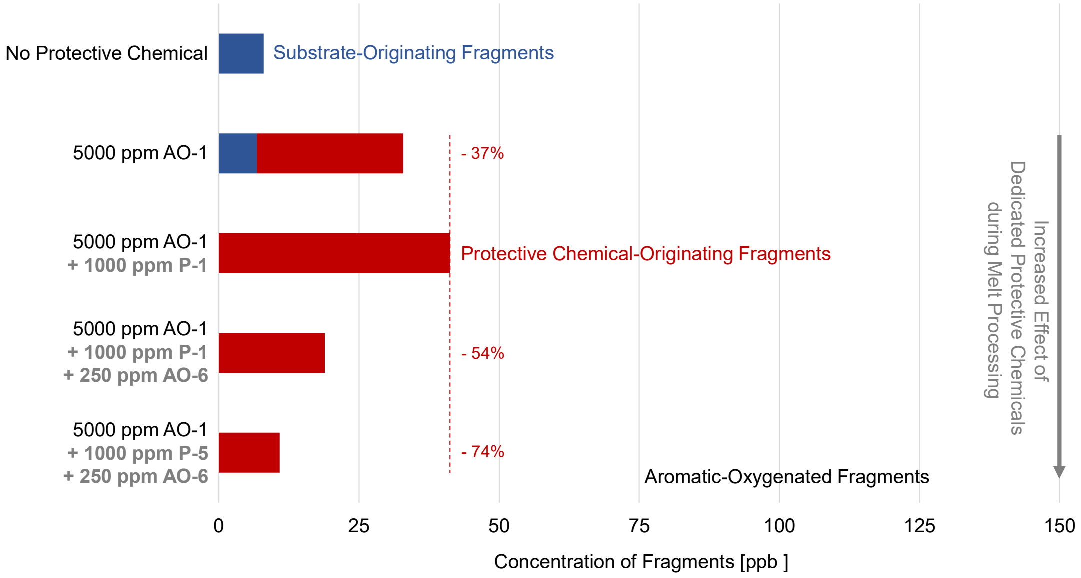


Figure 67: Number (upper chart) and concentration, ppb (middle & lower chart) in different scale) of aromatic-oxygenated fragments depending on mixture of protective chemicals

The formulation containing [5000 ppmAO-1 + 1000 ppm P-1] results in the highest number and concentration of oxidised-aromatic fragments; even higher than the formulation with AO-1 alone. The reasons for this are complex. In this formulation f fragment F# 142 was analysed for only time in the entire investigation. With a LD of 20 ppb and a LQ of 100 ppb, it can only be stated that in the formulation [5000 ppm AO-1 + 1000 ppm P-1] the fragment is present at a concentration between 20 and 100 ppm. For practical reasons when displaying results graphically, it is counted as being present at a 20 ppm only. By the nature of its formation, it appears plausible that F# 142 is also present in other formulations; but below 20 ppb and hence not detected. For some figures, F# 142 is excluded to allow better comparability of the results.

Introduction of 250 ppm AO-6 and subsequent substitution of P-1 by P-5 results in a decrease of ~28% by number and ~74% by concentration of oxidised-aromatic fragments. The nature of the Hindered Phenol-originating fragments (**Figure 68**) is the same for all formulations containing protective chemicals (except for F# 142 as discussed previously). Apart from four fragments (F# 135, F# 143, F# 148 & F# 163), three unidentified fragments originate from AO-1.

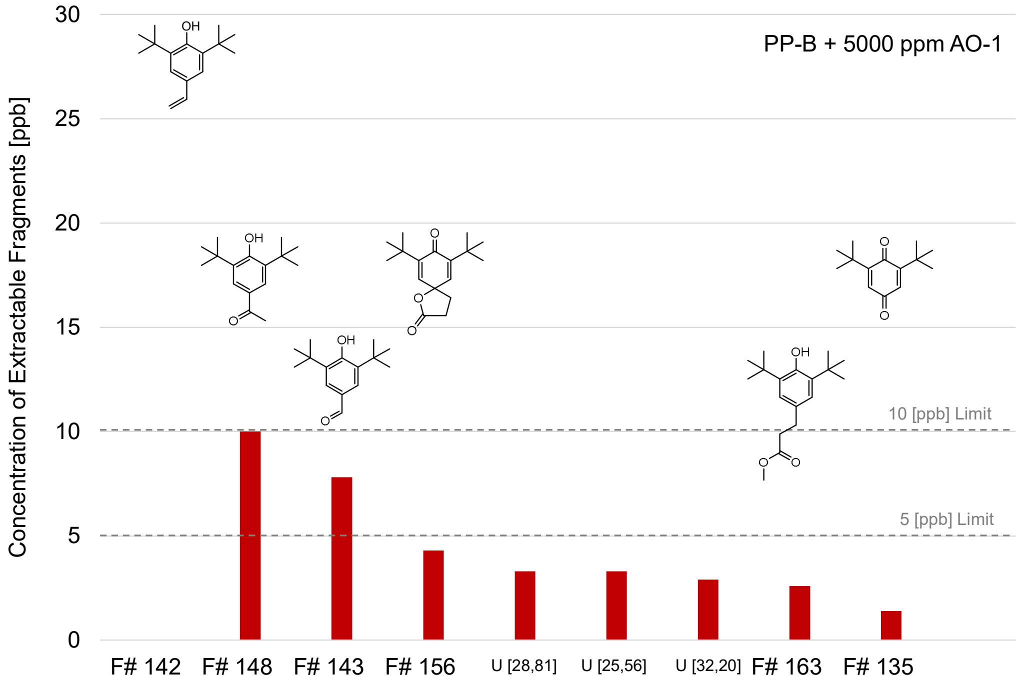
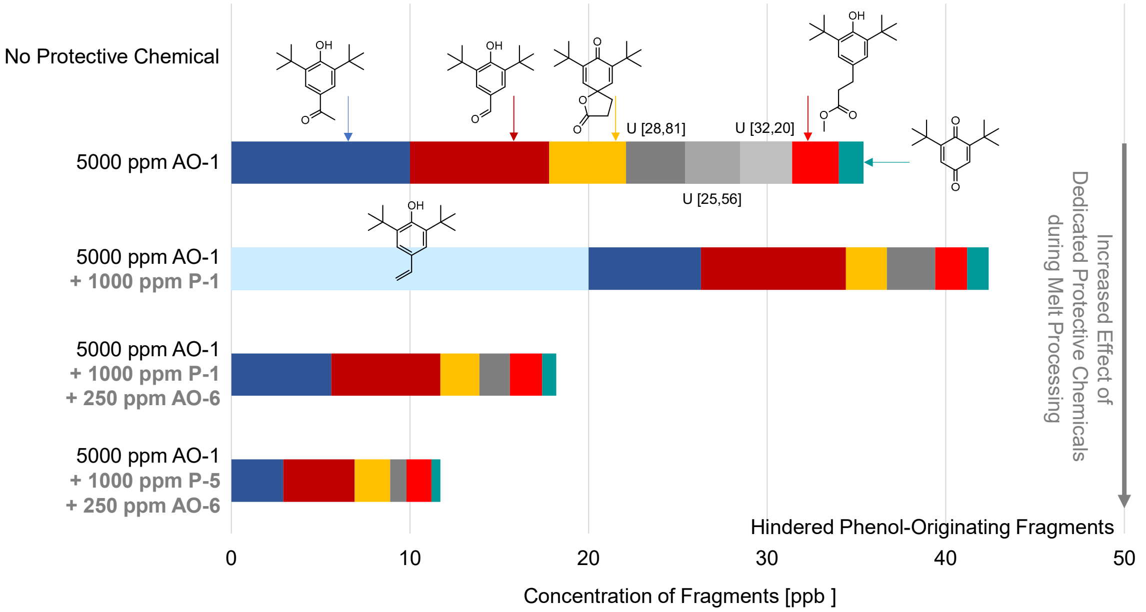
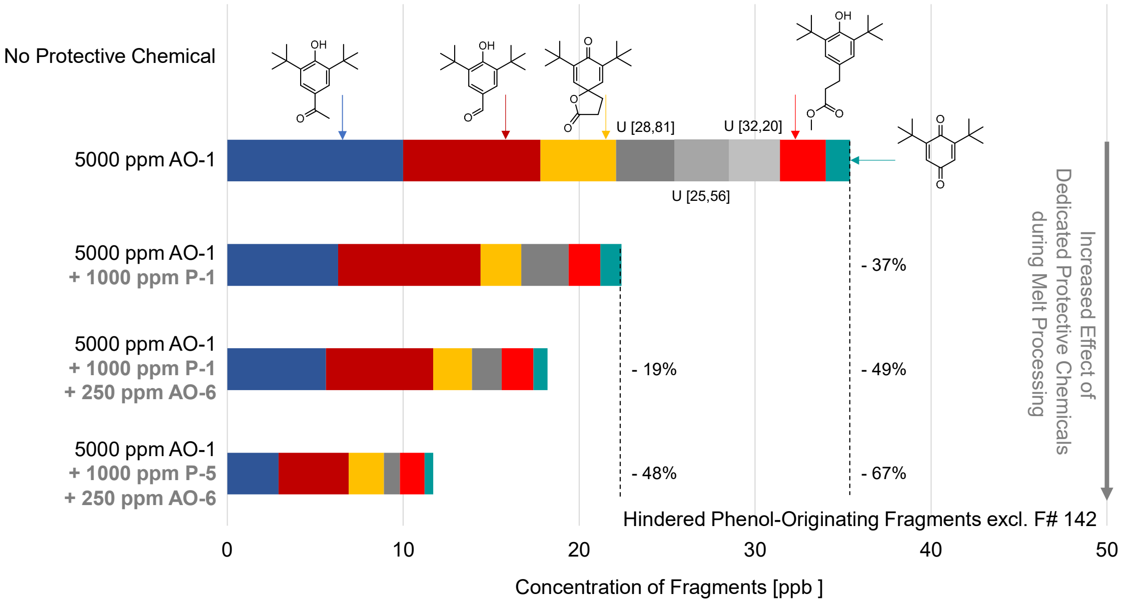


Figure 68: Concentration (ppb) of Hindered Phenol AO-1 originating fragments



(a)



(b)

Figure 69: Concentration of (ppb) Hindered Phenol AO-1 originating fragments depending on mixture of protective chemicals (excl. F# 142, (b))

There is a proportional decrease in fragments originating from AO-1 during melt-processing, as the dedicated mixture of protective chemicals increases. This effect is more obvious after exclusion of F# 142 (**Figure 69b**). Fragments originating from AO-1 cannot be reduced by number but are reduced in concentration. The reduction is ~ 67% relative to 5000 ppm AO-1 alone and ~ 48% relative to [AO-1 + P-1]. In formulations containing P-1 minor concentrations of the fragment F# 125 are detected (**Figure 70**). No fragments can be associated directly with AO-6 or P-5. The production of unidentified fragments mirrors oxidised-aromatic fragments; however, there is a higher contribution of fragments originating from the polymer substrate. Addition of AO-1 increases both number and concentration of unidentified fragments. The mixture of protective chemicals [P-5 + AO-6] reduces the concentration of unidentified fragments by ~83% (**Figure 71**). The mixture [P-5 + AO-6] causes a near complete suppression of unidentified fragments (independent of the origin).

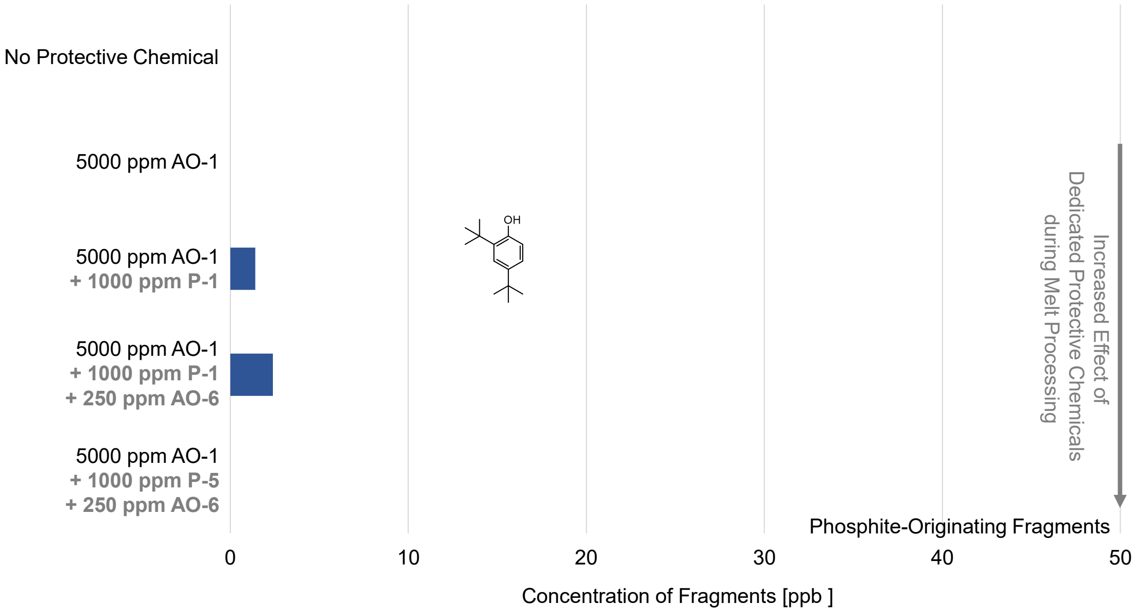


Table 70: Fragments originating from Phosphite P-1 dependent on mixture of protective chemicals

It can be concluded that this tailored mixture of protective chemicals for PP *specifically during melt-processing* results neither in lower MFI nor higher MW, nor lower oxidised-aliphatic (substrate-originating) fragments. Comparing **Figure 61** with **Figure 72a** reveals similar behaviour for the system [AO-1 + P-1]. However, increase in the AO-1 concentration in **Figure 61** results in a decrease of oxidised-aliphatic fragments and an increase in oxidised-aromatic fragments. All but one of these fragments (F# 125) originate from AO-1. In contrast, introduction of a dedicated mixture of protective chemicals, specifically for protection during melt-processing results in *a decrease of oxidised-aliphatic fragments and a decrease of oxidised-aromatic fragments* (**Figure 72c**). It is postulated that the introduction of AO-6 establishes a synergistic effect with P-1 during melt-processing; while the kinetically slower (higher hindered) AO-1 contributes less to reaction R 3.1, rather to further transformation reactions (in the presence of AO-6). Consequently, less (extractable) transformation products are formed.

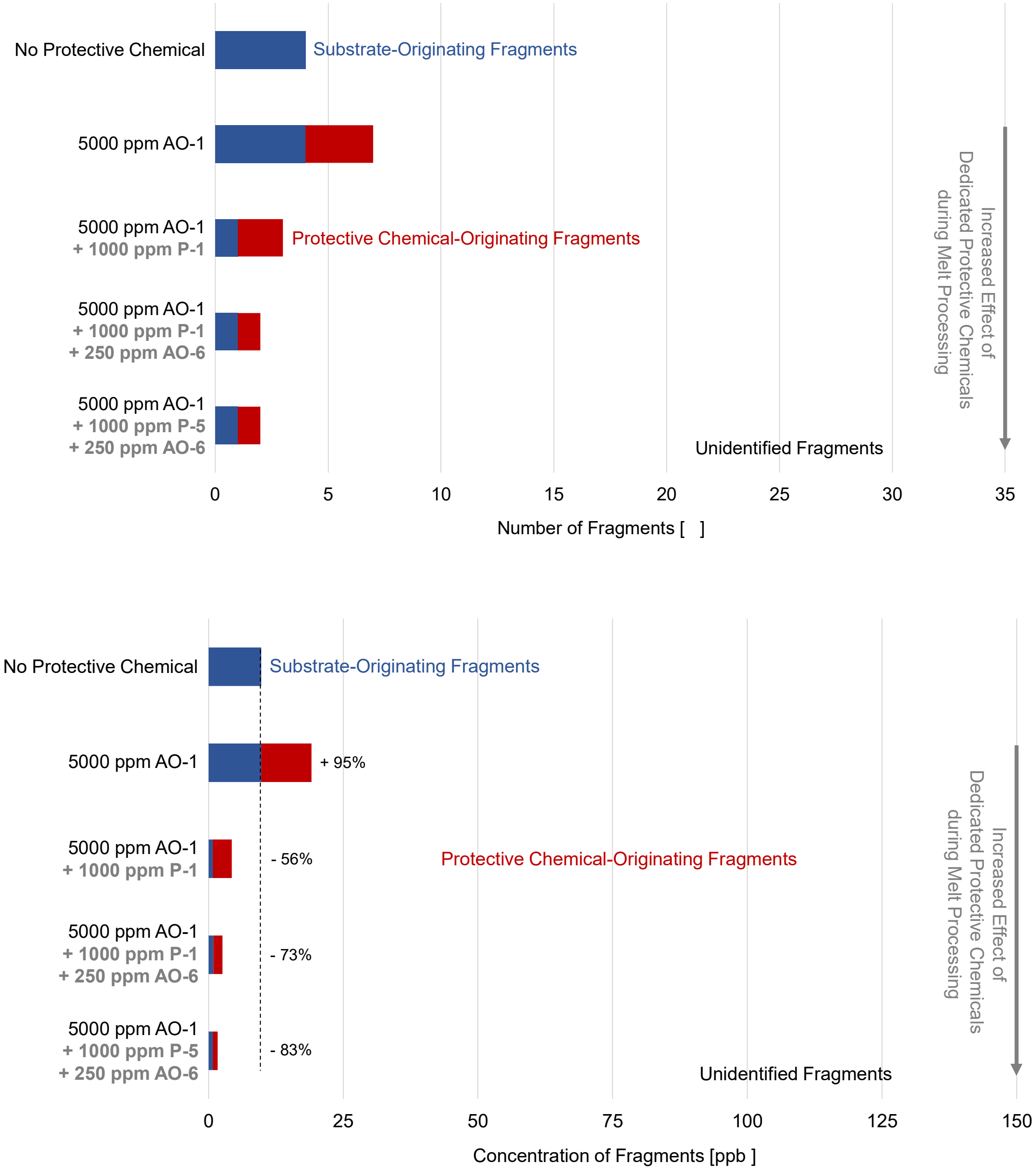
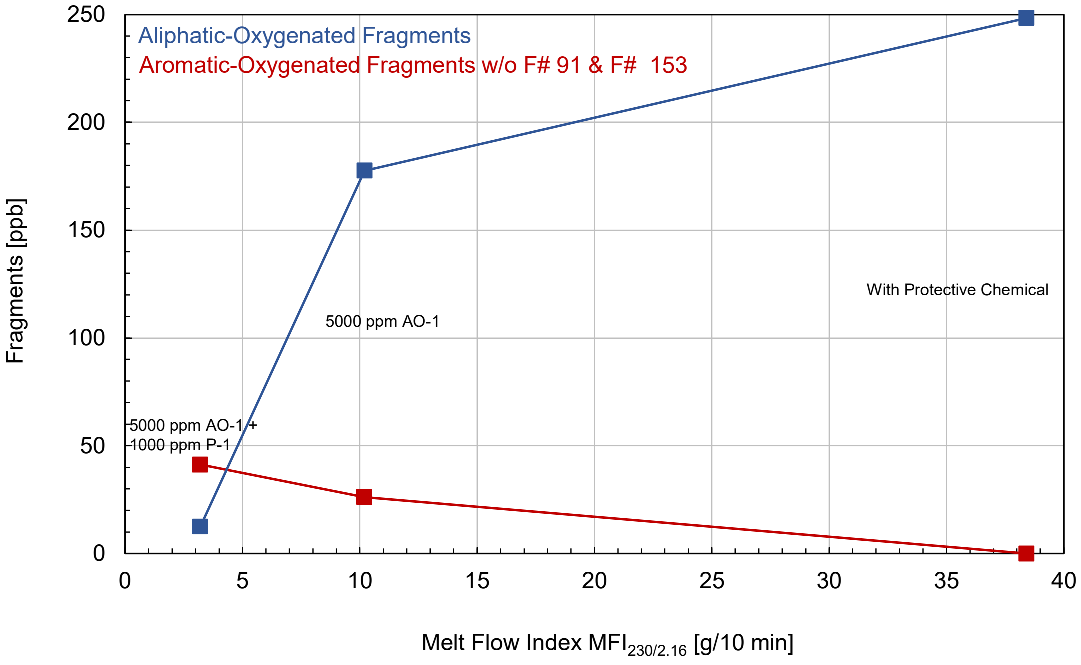
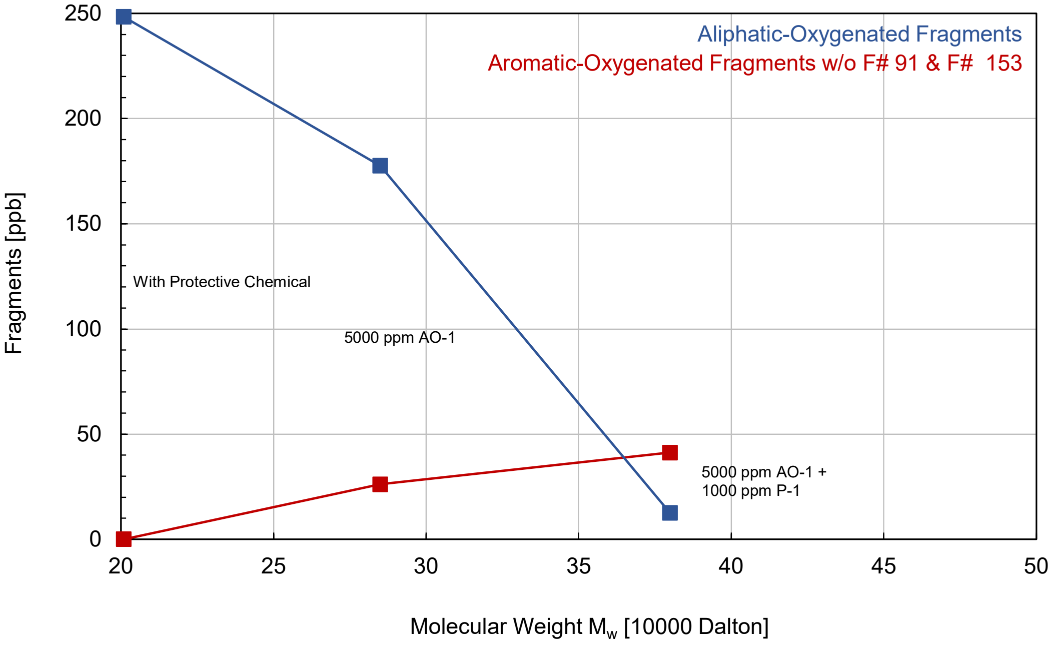


Figure 71: Number (upper chart) and concentration (middle and lower chart) in different scale) of unidentified fragments depending on mixture of protective chemicals


Aliphatic-Oxygenated Fragments
Aromatic-Oxygenated Fragments w/o F# 91 & F# 153
Fragments [ppb]
250
200
150
100
50
0
0
5
10
15
20
25
30
35
40
Melt Flow Index MFI230/2.16 [g/10 min]
5000 ppm AO-1 +
1000 ppm P-1
5000 ppm AO-1
With Protective Chemical


Aliphatic-Oxygenated Fragments
Aromatic-Oxygenated Fragments w/o F# 91 & F# 153
Fragments [ppb]
250
200
150
100
50
0
20
25
30
35
40
45
50
Molecular Weight Mw [10000 Dalton]
With Protective Chemical
5000 ppm AO-1
5000 ppm AO-1 +
1000 ppm P-1

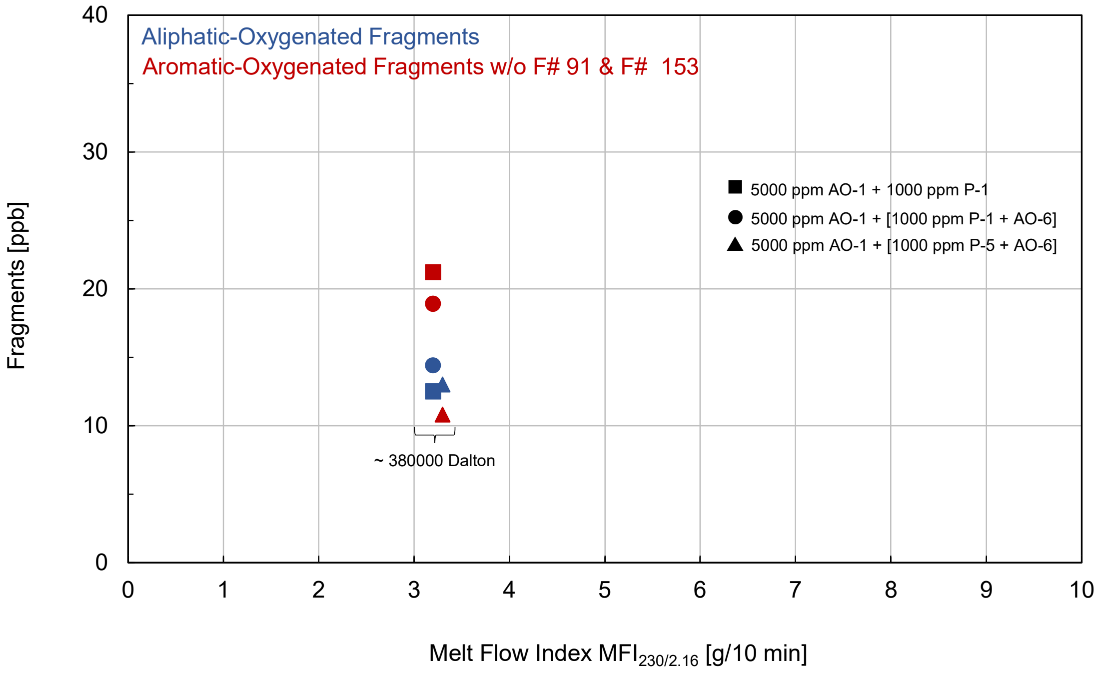
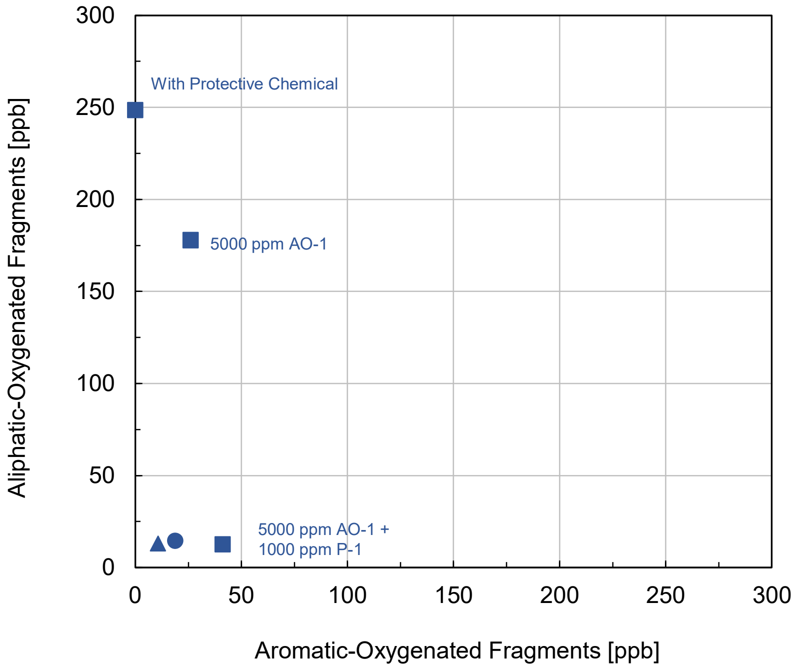
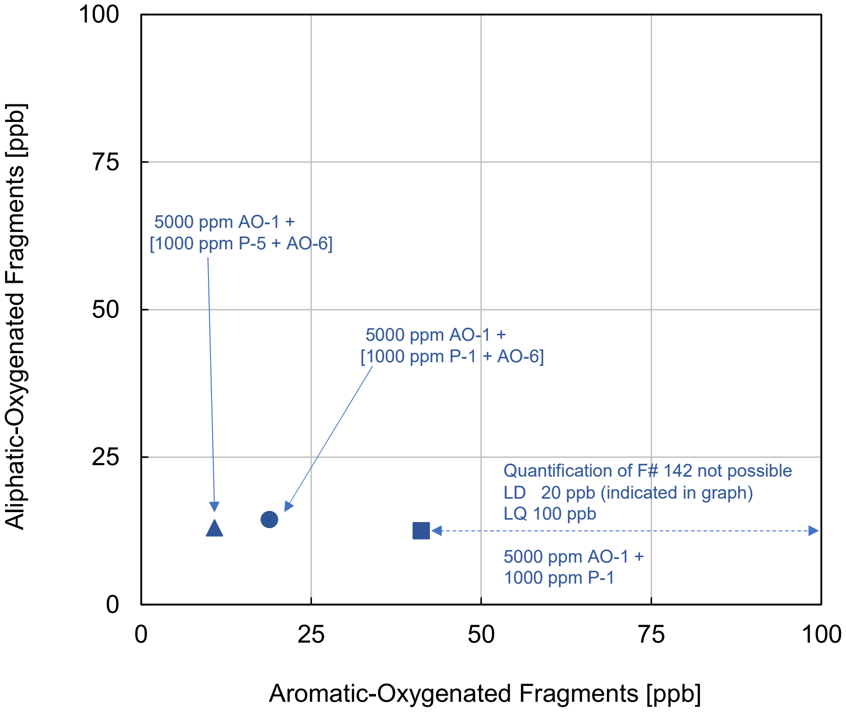


Figure 72: Fragments detected as a function of MFI and MW [249]

The effect described is even more pronounced when P-1 is substituted with P-5. **Figure 73** positions the various formulations in a grid; oxidised-aliphatic and PP substrate-originating fragments versus oxidised-aromatic and protective chemical-originating fragments. PP without protective chemicals results in a very high concentration of substrate-originating fragments. This concentration can be decreased by the addition of a mixture [AO-1 + P-1]; but only at the expense of the generation of more fragments originating from protective-chemicals. The formulations 'as mapped' shift from the top left corner diagonal downward to the right. It is noteworthy that while the composition changes, a factor ~4.5 less fragments are detected (**Figure 73a**).



(a)



(b)

Figure 73: Oxidised-aromatic (and protective chemical-originating) fragments versus oxidised-aliphatic-oxygenated (and PP substrate-originating) fragments

Figure 73b expands the three points clustered in the bottom left-hand corner of chart **Figure 73a**. The addition of AO-6 and later-on the substitution of P-1 with P-5 leads to a shift of the x-axis data points to lower values. At the same concentration of polymer substrate originating fragments, there is a reduction in protective chemical originating fragments by a factor of ~4 (note in the case of F# 142 this is a factor of ~2 if F# 142 is not considered). As already seen in Figure 3-32, the total concentration of fragments for the best performing package (of [P-5 + AO-6] + AO-1) is ~90%; i.e., a factor of ~10x less *c.f.* PP not containing protective chemicals.

In these experiments, AO-6 is the representative example of kinetically fast CB-D and P-5 the representative of effective PD Phosphites. As such, it is considered that the observed effect is not limited to this specific Hindered Phenol and/or Phosphite. Chapter 3.3.2 and 3.3.3 confirm the dominant role of Phosphite as PD to control the number and in particular the concentration of extractable fragments.

3.3.4 Limits of the Use of Phosphite

Although the Phosphites examined so far are effective PD their performance is limited by susceptibility to hydrolysis (**Scheme 18**). Therefore, an examination of the influence of hydrolysis on performance and fragmentation is considered in this section.

To assess the effects of hydrolysis the formulation containing [5000 ppm AO-1 + 1000 ppm P-1] was repeated, but the Phosphite P-1 was hydrolysed prior to incorporation into PP-B. P-1 was subjected to a saturated salt solution of potassium chloride KCl in a desiccator at 60°C for 5 days [256]. At the end of the exposure period, a significant change in the appearance and consistency of P-1 was observed. The crystalline off-white powder was transformed into a yellowish viscous liquid with corrosive character. This change is attributed to a high degree of hydrolysis. Irrespective of this the exact degree of hydrolysis manifested by the concentration of transformation products (according to R 18.1 to R 18.3) is quantified.

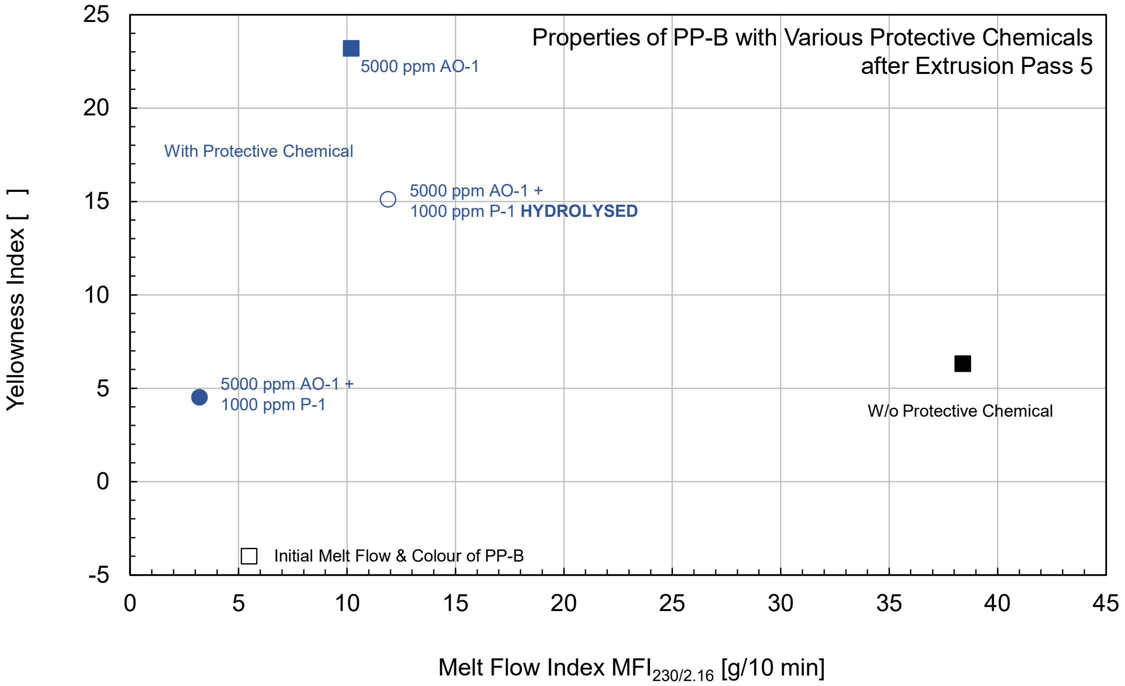
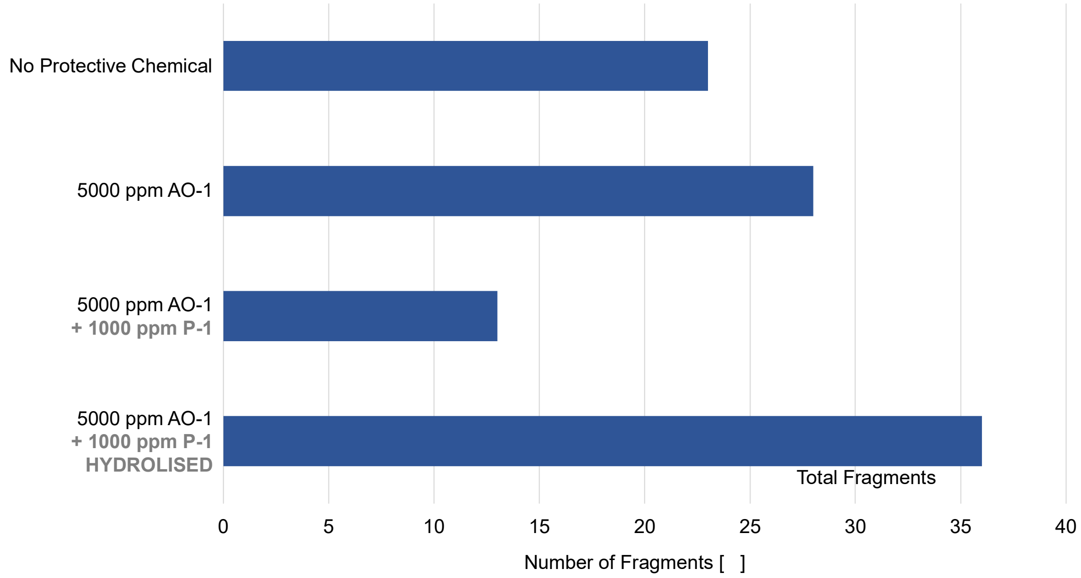


Figure 74: Properties of melt-processed PP in the presence of hydrolysed phosphite

Extrusion Condition:	C-1, M-1
Extraction Condition:	E-4
Formulation:	PP + 750 ppm MS-1

Hydrolysis of P-1 seems to destroy the synergistic effect between AO-A1and P-1 as reflected by changes in MFI. The formulation behaves in a similar manner to 5000 ppm AO-1 alone. The slight improvement in colour can be attributed to phosphorous acid and/or phosphates.



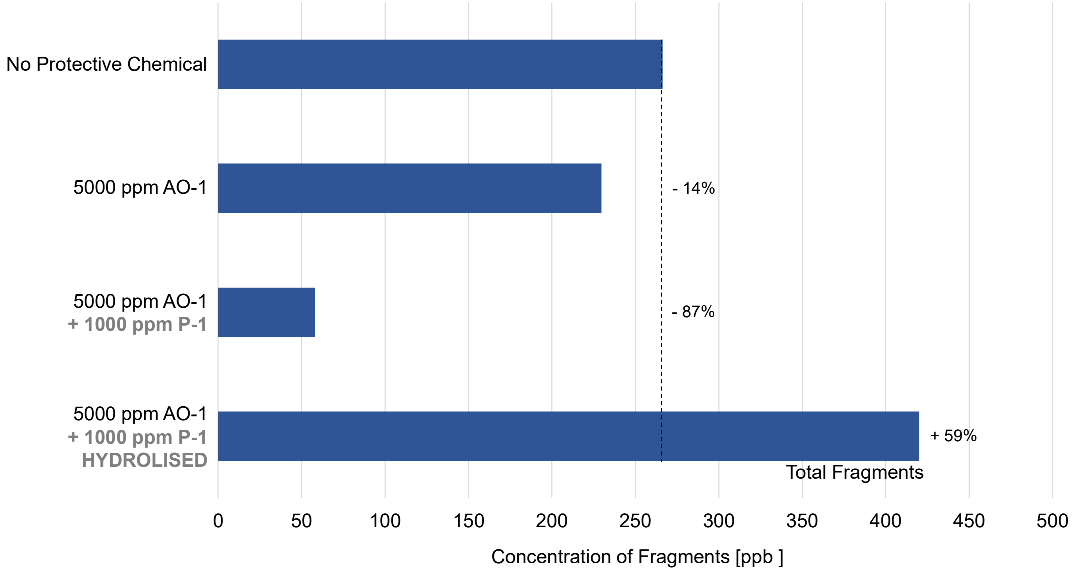
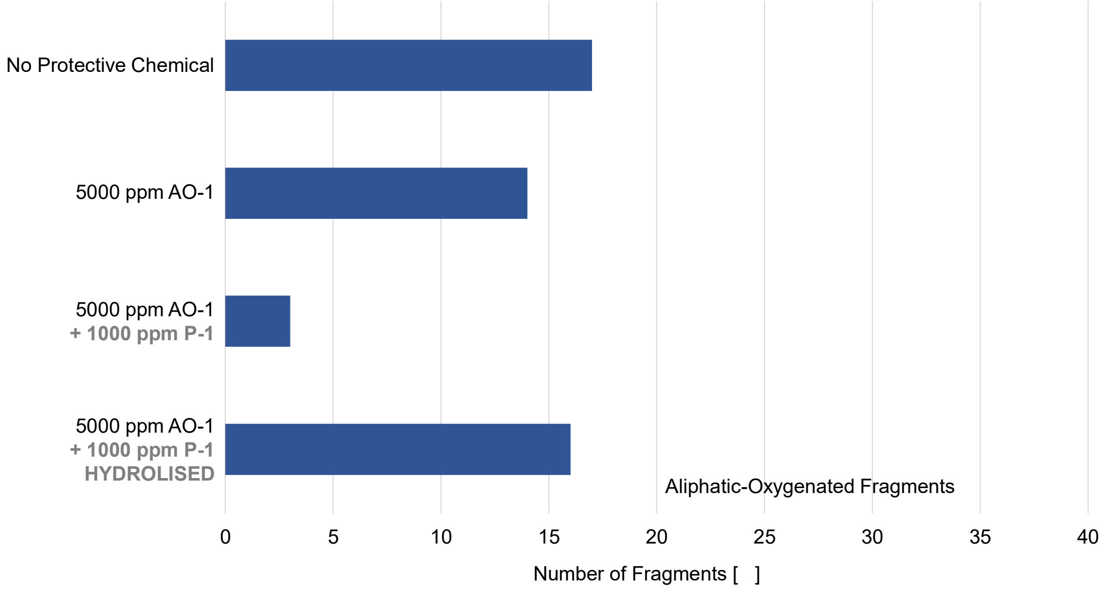


Figure 75: Number (upper chart) and concentration, ppb (lower chart) of total fragments in the presence of hydrolysed phosphite

The presence of hydrolysed P-1 contributes to a significant increase in number and concentration of fragments. Here, this formulation constitutes the by far highest number and concentration of fragments (**Figure 75**). This increase cannot be attributed to oxidised-aliphatic fragments, which remain nearly stable (**Figure 76**); although the concentration of 2-ketones increases markedly (**Figure 77**). It is plausible that the absence of "intact" Phosphite P-1 prevents the non-radical decomposition of the peroxides (R 5.2) that are responsible for the appearance of 2-

ketones. The same is true for oxidised-aromatic fragments, significant differences are observed (**Figure 78**). The highest number and by far the highest concentration of oxidised-aromatic fragments are detected.



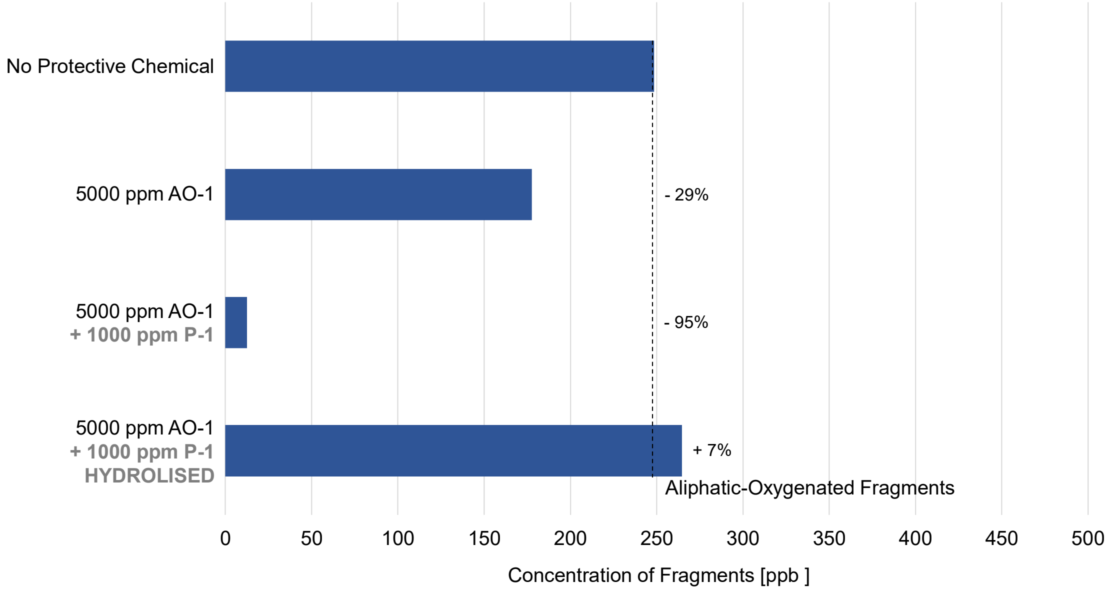
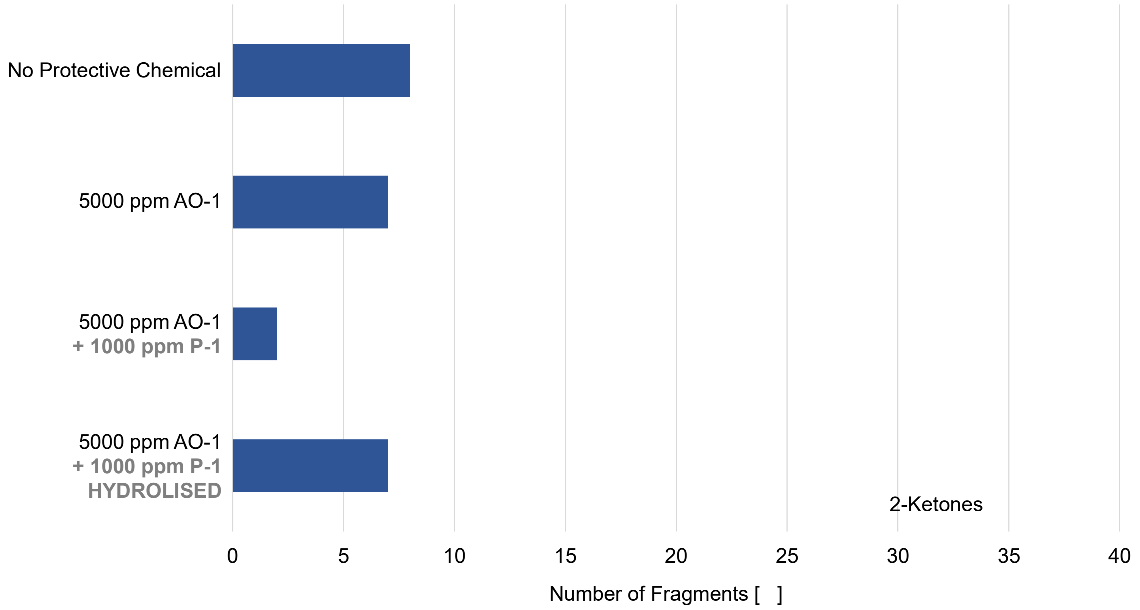


Figure 76: Number (upper chart) and concentration (lower chart) of aliphatic-oxygenated fragments in the presence of hydrolysed phosphite

Hydrolysis of P-1 prevents the suppression of the two oxidised-aromatic and substrate-originating fragments (F# 91 and F# 153; **Figure 66**) which are detected in PP-B without protective chemicals. Even worse, the concentration of these fragment seems to increase. Protective chemical fragments that originate remain stable in number but increase considerably in concentration. This observation is related mainly to the high concentration of fragment F# 125, which is the expected hydrolysis product of P-1 according to **Scheme 18**. **Figure 80** indicates the additional fragments detected in the presence of hydrolysed P-1. Apart from 2 unidentified fragments, an additional ketone (F# 100) is detected. The origin of fragment F# 81 is unclear; but might be a mis-assigned peak and potentially constitute i another ketone. Fragment # 61 (or isomers thereof) can be explained by a partial dealkylation under acidic conditions of fragment F# 125 (or 2,6-di-teriary-butyl phenol, **Structure XIII** in **Scheme 8)** [257,265]. Formation of the latter will be discussed later-on.



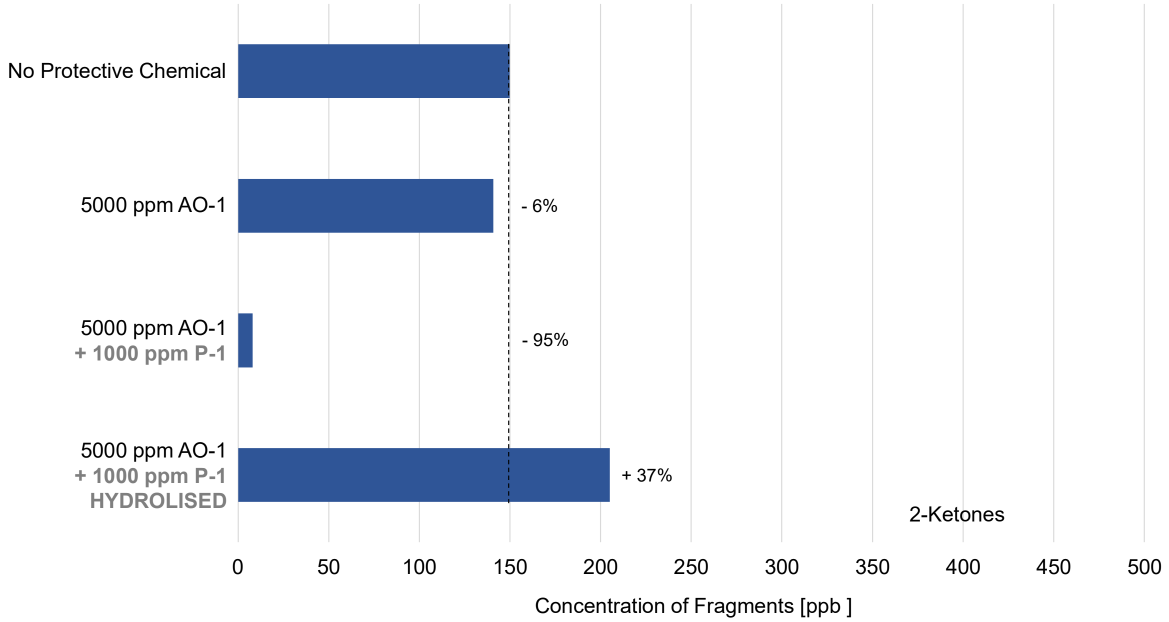


Figure 77: Number (upper chart) and concentration, ppb (lower chart) of 2-ketones in the presence of hydrolysed phosphite

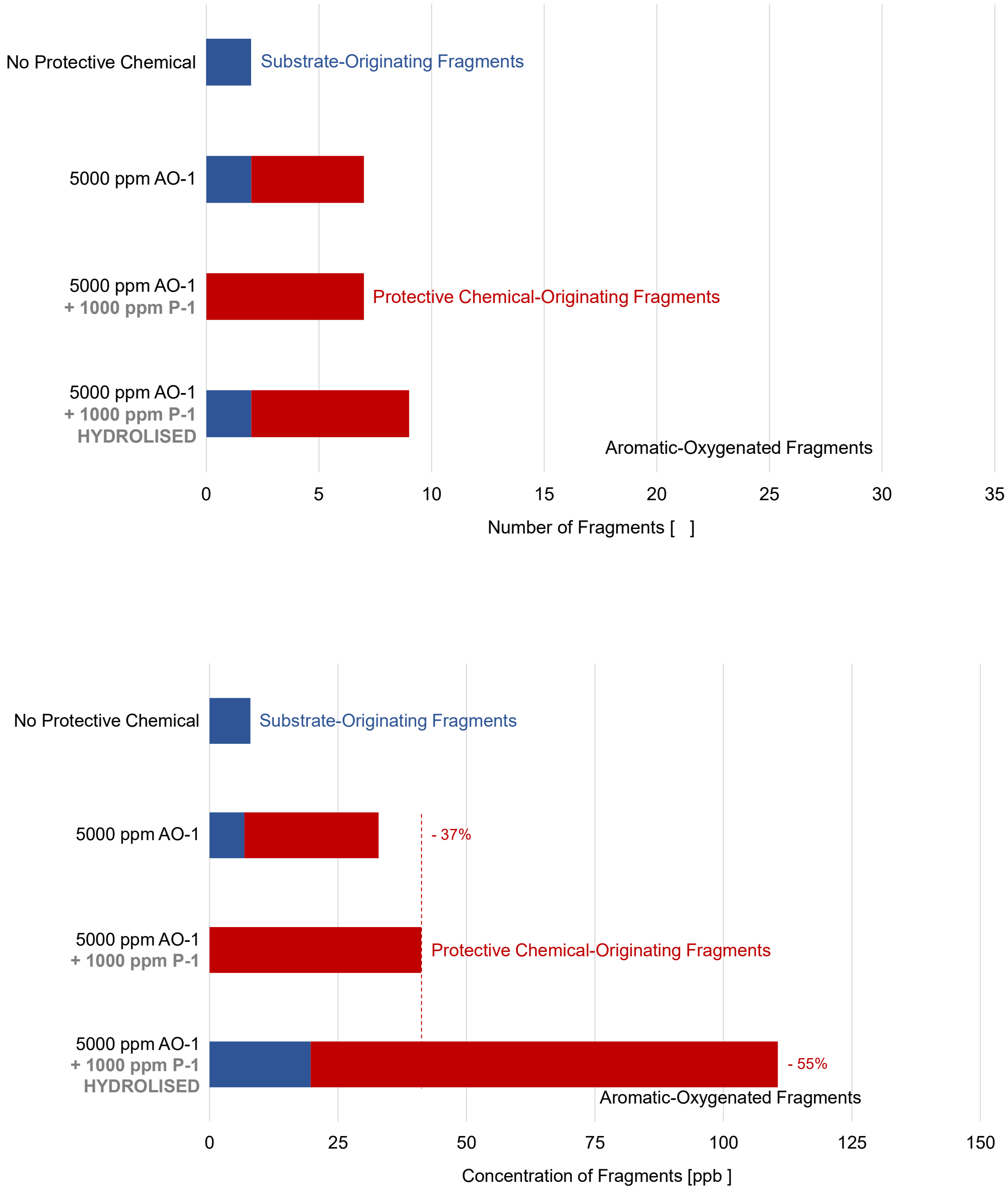


Figure 78: Number (upper chart) and concentration, ppb (lower chart) in different scale) of aromatic-oxygenated fragments in the presence of hydrolysed phosphite

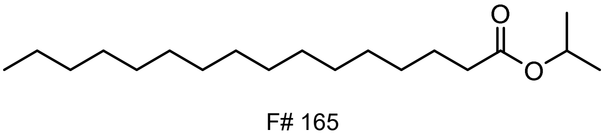


Figure 79: Fragment F# 165 originating from MS-1

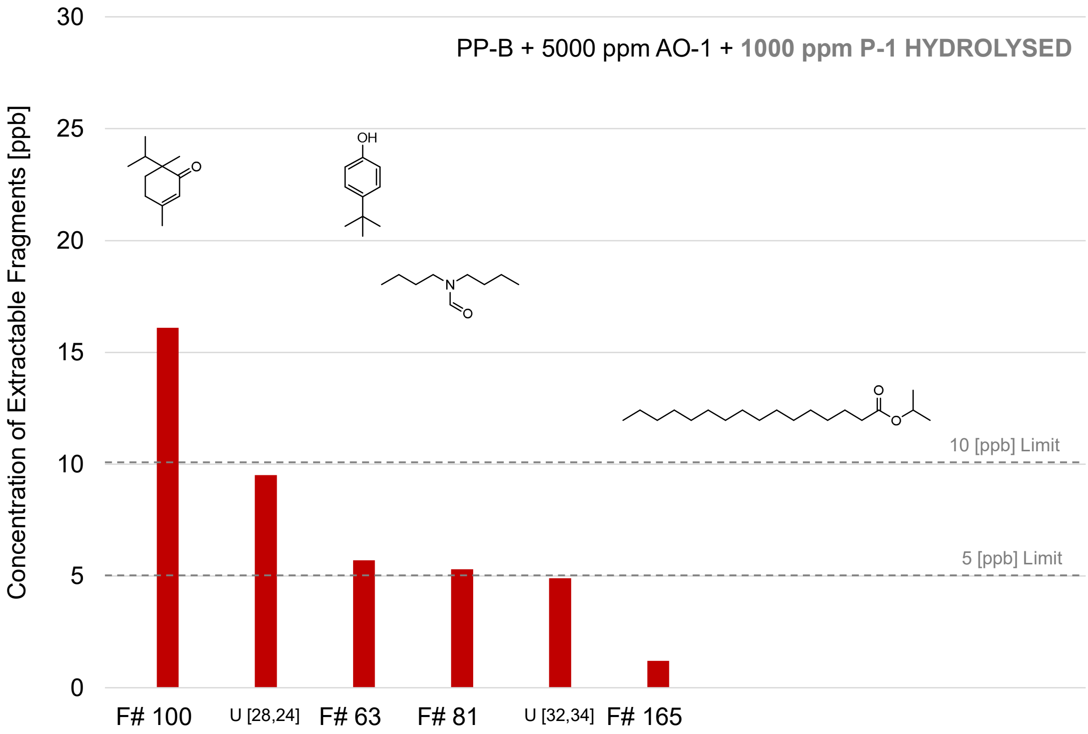
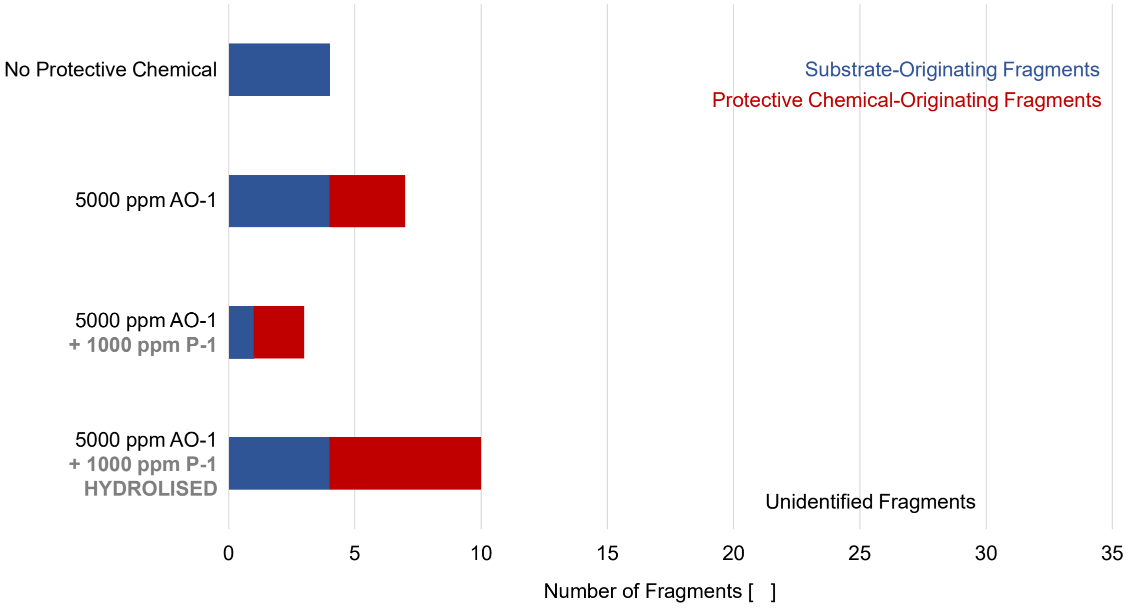


Figure 80: Concentration (ppb) of additional fragments in the presence of hydrolysed P-1

Fragment F# 165 (isopropyl palmitate; **Figure 79**) appears to originate from the antacid MS-1 (calcium stearate). Fragment F# 165 could be explained by reaction of MS-1 with acidic species and the subsequent formation of 1-hexadecanol [259-261]. 1-hexadecanol could further react with a LMW alcohol in a condensation reaction to form fragment F# 165. The LMW alcohol could be formed as an extractable degradation product of PP (like **Scheme 26**). It is rare in this research, that a fragment from a metal soap (utilised as antacid) is detected. The detection of F# 165 is remarkable as its estimated log K_{OW} of 8.16 indicates a very poor solubility in water. One possible explanation could be a (very) high concentration of this chemical at the surface of the PP granule.

Concerning unidentified fragments (**Figure 81**), the hydrolysis of P-1 does not allow the number and concentration of unidentified fragments already present in PP-B without protective chemicals to decrease any further. In contrast, both show a significant increase.

Section 3.3.2 and the first half of Section 3.3.3 suggest for the example of P-1 (and even more so P-5) the use of Phosphite to prevent oxidative degradation in PP by the PD mechanism. This observation seems enhanced in the presence of a hindered Phenol as CB-D (AO-1 and to a greater extent AO-6) due to a synergistic effect between these protective chemicals. Nevertheless, the observations from **Figures 74 to 81** conclude that onset of hydrolysis in the Phosphite not only results in a loss of the synergistic effect but in a poorer protective effect overall. Hydrolysis of P-1, leads to transformation products that decrease the pH of the matrix and result not only in an increase in the number and concentration of oxidised-aliphatic- (and substrate-originating) fragments, but in an increase in number and concentration of oxidised-aromatic (and protective chemical-originating) fragments.



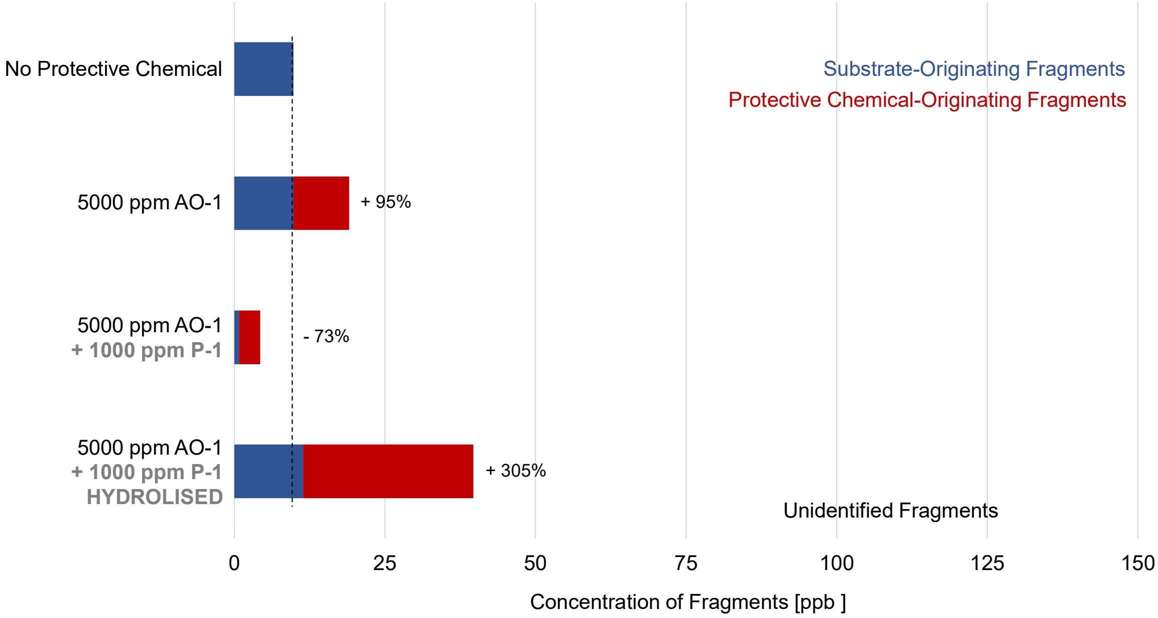
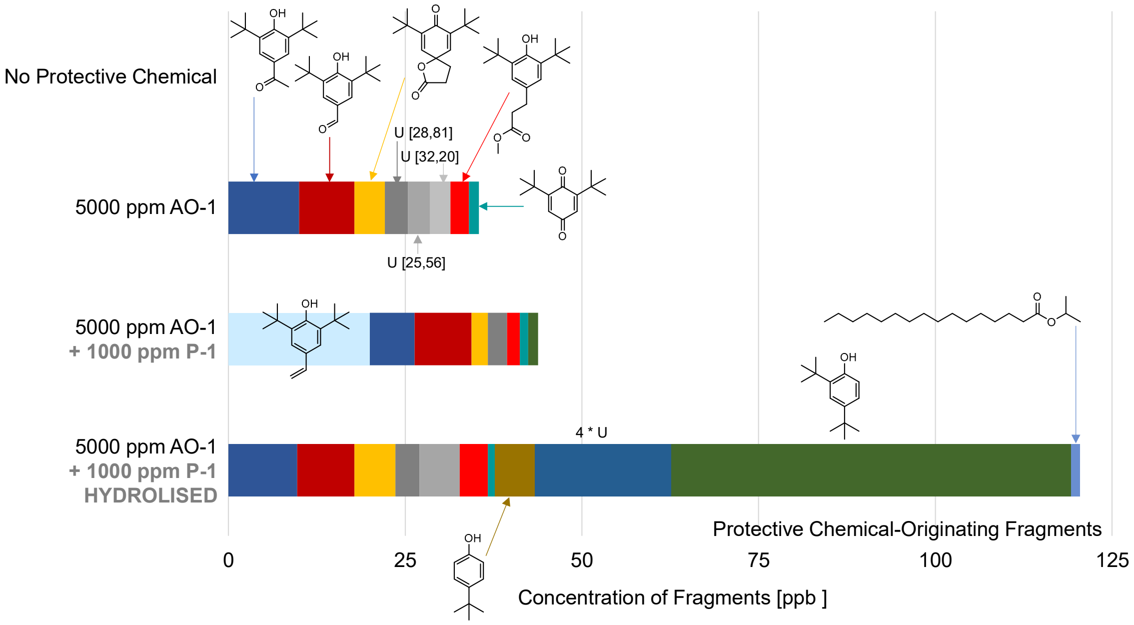
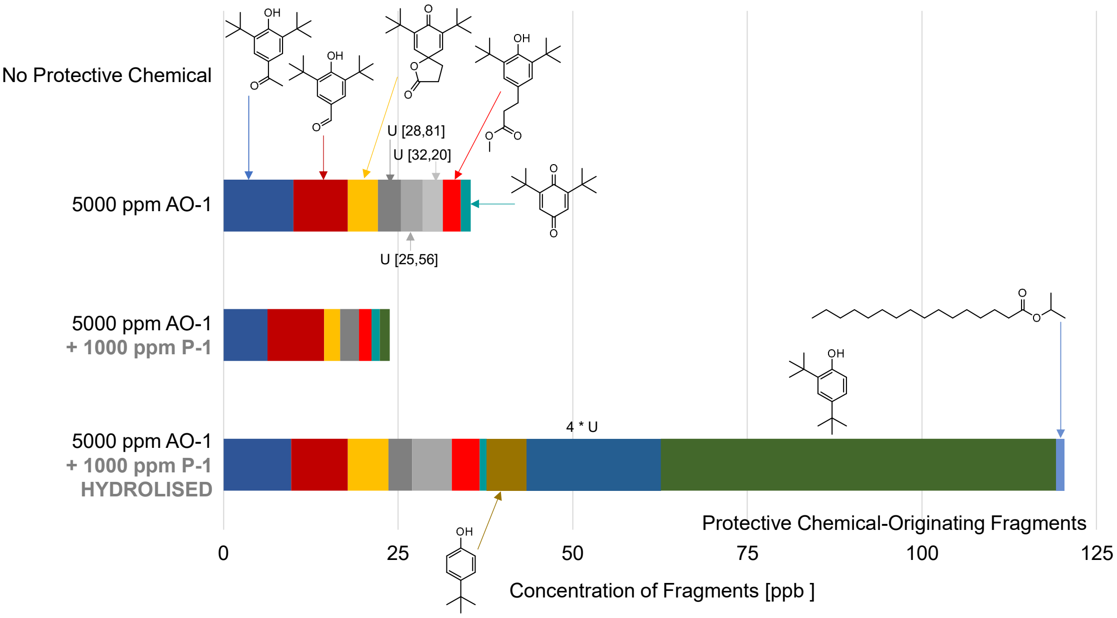


Figure 81: Number (upper) and concentration, ppb (middle & lower chart) in different scale) of unidentified fragments in the presence of hydrolysed phosphite

Figure 82 gives an overview over the situation. To allow comparison, fragment F# 142 is omitted (for previously discussed reasons of limited detectability) (**Figure 82b**). As a first approximation, this shows that hydrolysed P-1 results in the same or slightly increased concentration of fragments already detected in the formulation containing only AO-1. However, this is only true for fragments F# 135, F# 143 & F# 148. *Fragments F# 135, F# 143 & F# 148 seem to be unaffected by the hydrolysis of P-1*. In contrast, fragments which can be formed via a mechanism involving hydrolysis are increased in concentration, as is the case for AO-1 alone (F# 156 and F# 163). Two additional fragments appear, which may be formed directly or indirectly due from the hydrolysis (F# 63 and F# 165). The concentration of fragment F# 125 is increases markedly as it constitutes one of the direct transformation products of P-1 via hydrolysis.



(a)



(b)

Figure 82: Protective chemical & modifier originating fragments in the presence of hydrolysed phosphite (excl. F# 142 in the lower chart)
(4*U composed of unidentified fragments with retention time 28.24, 32.34, 32.53 & 33.41 min)

It is proposed that the onset of hydrolysis of P-1 (and potentially any other component in the PP substrate or any manipulation of the PP substrate inducing hydrolysis) will accelerate the formation of many other fragments which can be formed directly or indirectly (e.g., due to lower pH) via a hydrolysis mechanism.

This risk of hydrolysis and its effect on extractable fragments leads to two conclusions. First where Phosphite PD are used, hydrolysis has to be prohibited. Secondly, alternative protective chemicals, which are strong PD but not susceptible to hydrolysis (these may or may not be phosphites) require investigation (see Section 3.3.5).

3.3.5 Alternative Protective Chemicals

Hydrolysis antagonises the ability of P-1 to suppress oxidised fragments. In general, the efficacy of Phosphites during melt-processing is inversely proportional to their hydrolytic stability [262]. In this section various Phosphite structures are compared, along with other classes of protective chemicals in order to mitigate the effects of hydrolysis.

Sample preparation was carried out under conditions C-1 and M-1. Extraction was carried out under conditions E-1 corresponding at an extraction temperature of only 20°C. Conclusions from Section 3.1 indicate that most oxidised-aliphatic fragments are not extracted at this temperature; so, no detailed discuss of fragments arising from the polymer substrate is undertaken. In contrast, oxidised-aromatic fragments are extracted; though it is recognised that some oxidised-aromatic fragments might not be detected at this temperature. The formulations are based on PP-A containing 750 ppm MS-1 as antacid and protective chemicals added as single component at a concentration of 1000 ppm.

3.3.5.1 Sub-class of protective chemicals of Phosphite

Figure 83 indicates the efficacy of various Phosphites as protective chemical during melt-processing. Except P-1, all other Phosphites show good processing performance. The overall discolouration of the samples is rather low and equal or better to PP-A without protective chemicals.

Surprisingly (and in contrast to Section 3.2) the number of total fragment (**Figure 84)** does not correlate with the retention of MFI (**Figure 83**). P-9 results in a higher number of total fragments. Apart from the expected ketones, an increased number of saturated and unsaturated aldehydes is detected [263]. Even the number of fragments for P-3 seem high in comparison with Section 3.2 (reduction by only ~25%). The other Phosphites reduce the number of fragments by ~50-70%.

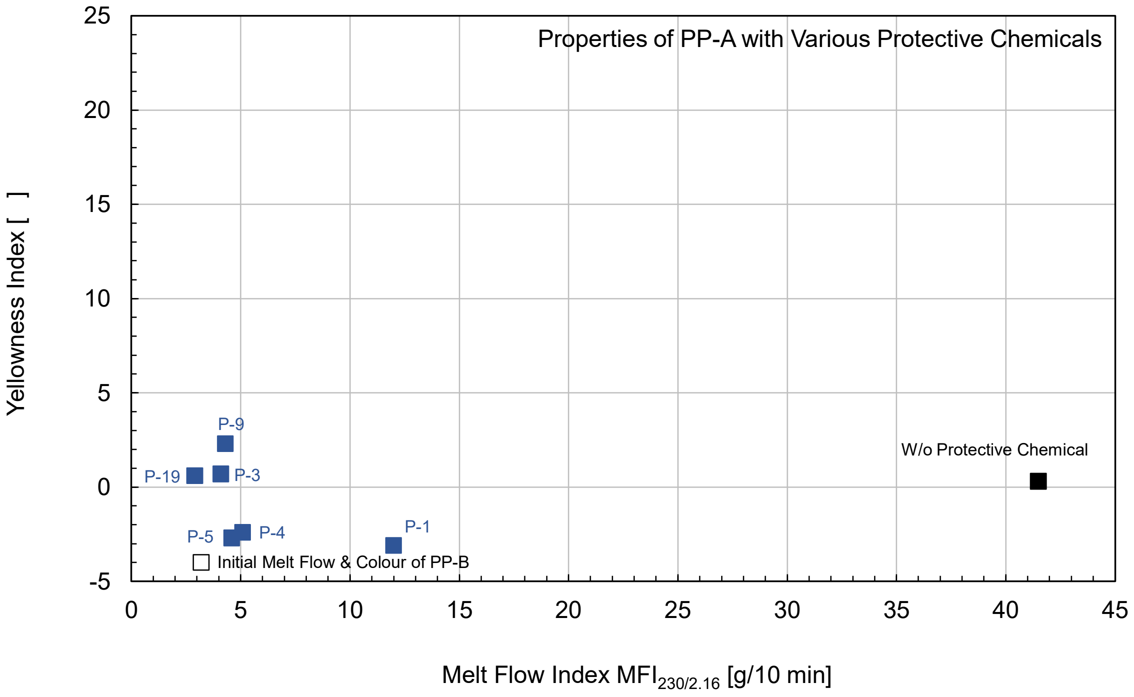


Figure 83: Properties (YI versus MFI) of melt-processed PP in the presence of various phosphites

Extrusion Condition:	C-1, M-1
Extraction Condition:	E-1
Formulation:	PP + 750 ppm MS-1

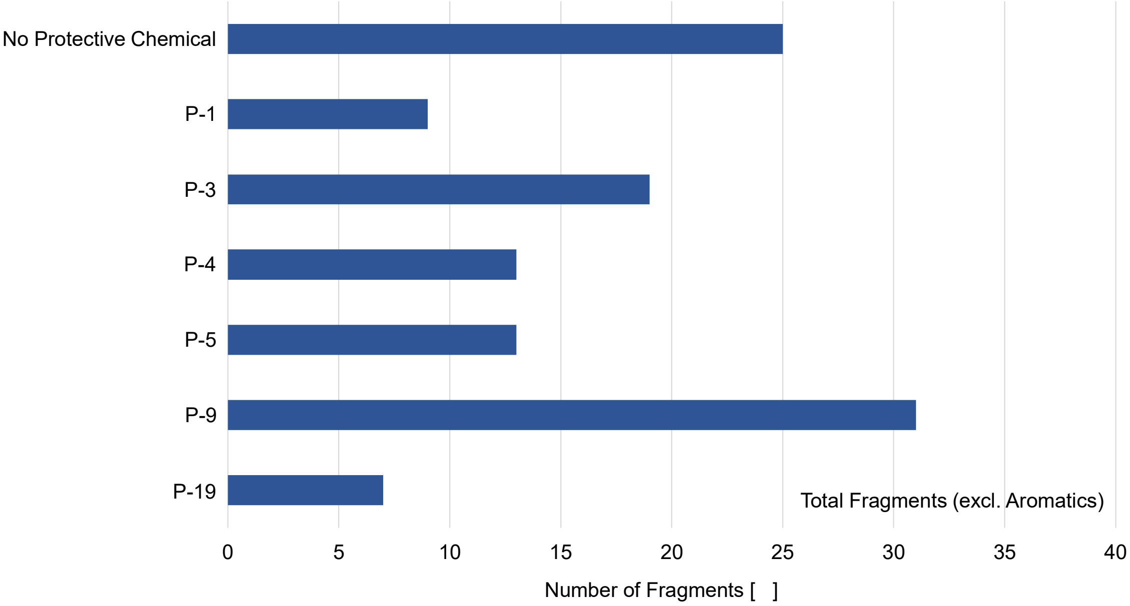
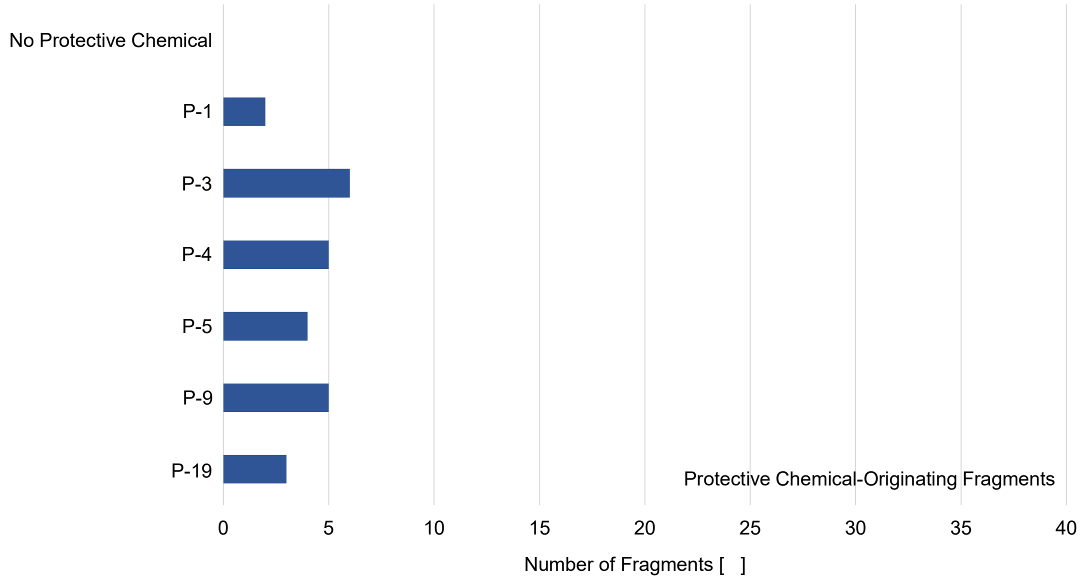
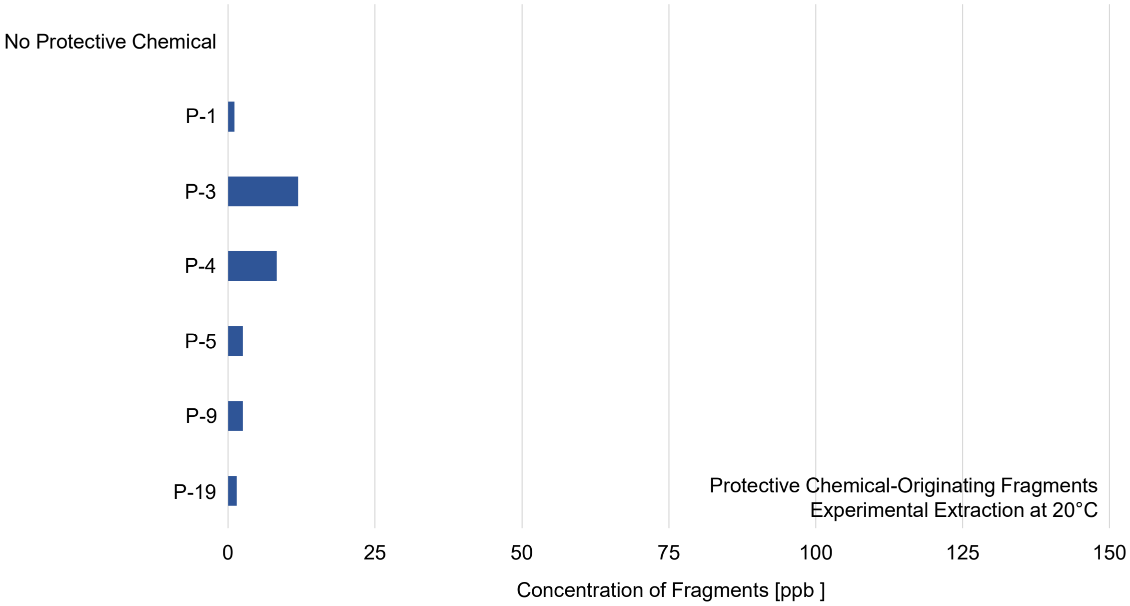


Figure 84: Number of total fragments in the presence of various phosphites

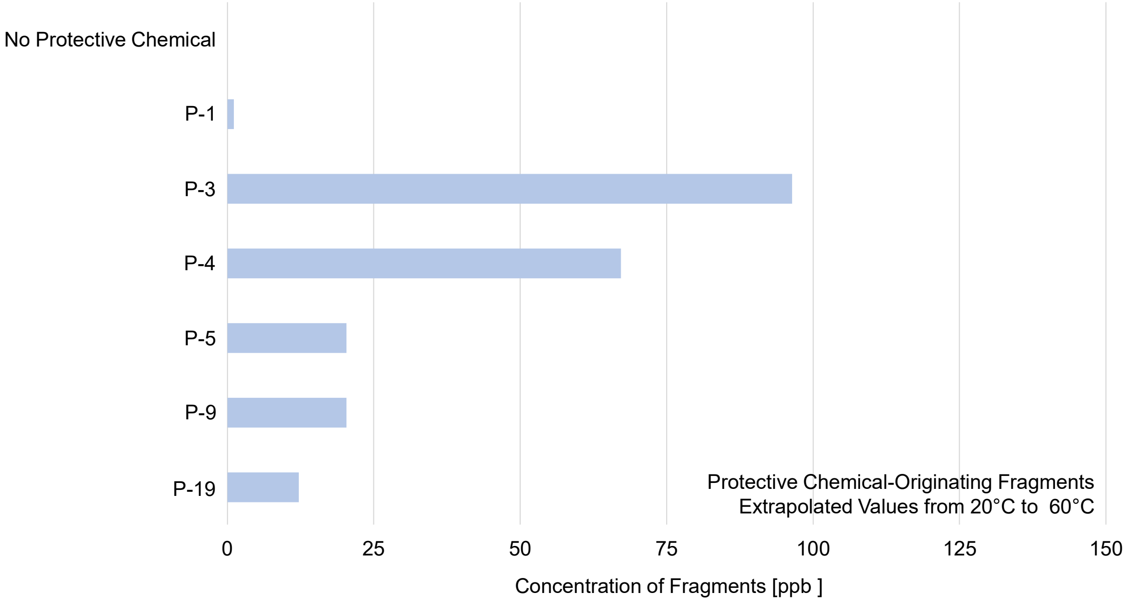
No further investigation of oxidised-aliphatic fragments is undertaken. The number and concentration of Phosphite-originating fragments remains low but doesn't correlate with efficacy as protective chemical (**Figure 85**). At 20°C most Phosphites contribute less than or equal to five fragments to the overall extraction. Quantification of the Phosphite-originating fragments indicates at 20°C higher concentrations for P-3 and P-4. Extrapolation of these values according to **Figure 38** (respectively **Equations 1, and 2**) results in relatively high concentrations of fragments for P-3 and P-4 (**Figure 85b**). Nevertheless, these seem to be in line with the hydrolytic stability of the various Phosphites (**Figure 86**).



(a)



(b)



(c)

Figure 85: Number and concentration (ppb) of fragments originating from various phosphites ((c) extrapolated from 20°C to 60°C)

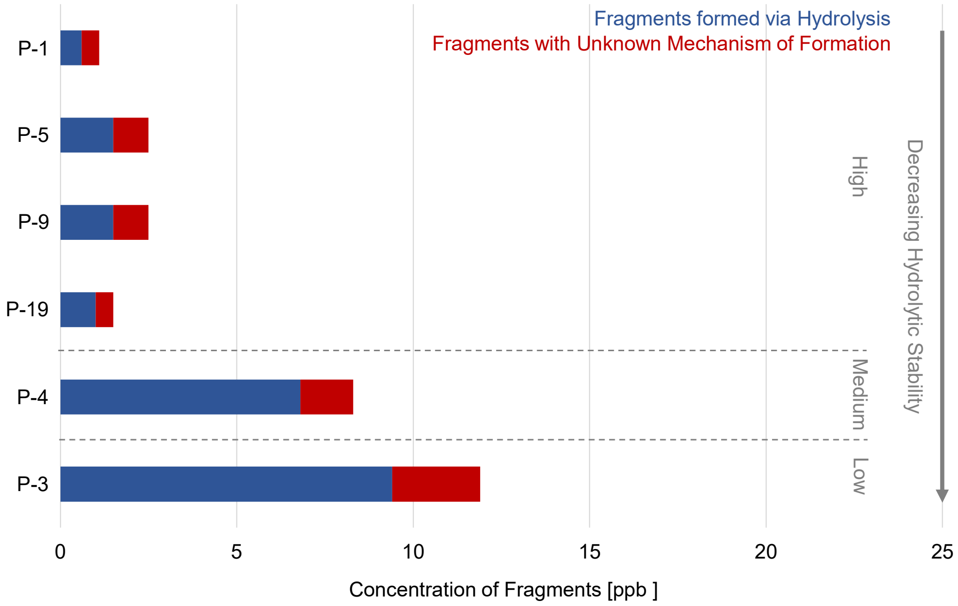
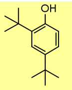
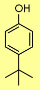
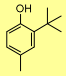
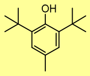
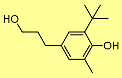
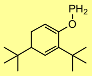
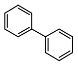


Figure 86: Concentration of fragments of various phosphites vs. hydrolytic stability

Figure 86 regroups the data in **Figure 85b** on a different scale and with a different ranking of the Phosphites. The Phosphites are now aligned in descending order of hydrolytic stability (as generally accepted in the plastics industry) [264]. P-3 is regarded as a hydrolytically sensitive chemical where special precautions in handling and storage are necessary. P-4 is considered less sensitive to hydrolysis but handling and in-polymer hydrolysis is still an issue. The other four Phosphites are considered to have a low sensitivity to hydrolysis, although differences between the different molecules exist. The Phosphite-originating fragments are separated into fragments which are known to be formed via hydrolysis (blue part of the bar in **Figure 86** and items highlighted in yellow **Table 21** [263,265]). It is noted that *of the identified fragments, most are transformation products due to hydrolysis, rather than the protective PD mechanism*. In addition, when the concentration of F# 125 in P-3 (at 60 ^{o}C) is extrapolated it is very similar to the experimentally detected concentration of F# 125 in artificially hydrolysed P-1 (see Section 3.3.4). It seems reasonable that P-3 has hydrolysed to a significant degree during melt-processing and the water extraction procedure. The number of unidentified fragments seems in general to increase with increasing sensitivity to hydrolysis (at least for the Phosphites which are very sensitive to hydrolysis). However, a mechanistic explanation for this is not possible here due to the unknown nature of the fragments. Three of the unknown fragments are detected in several of the Phosphite formulations.

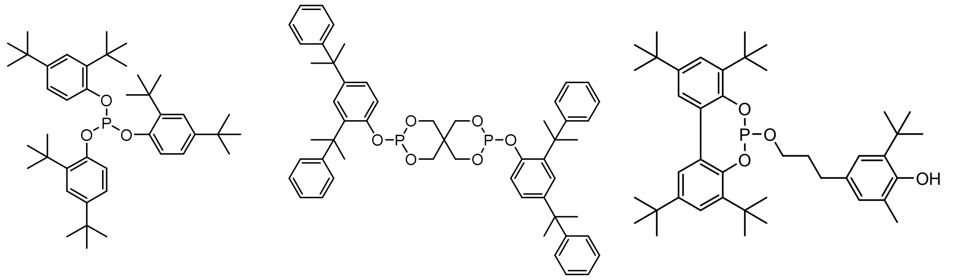
Table 21: Phosphite-originating fragments

Fragment	*P-1*	*P-3*	*P-4*	*P-5*	*P-9*	*P-19*
 F# 125	**0.6** [ppb] 4.9	**9.4** 76.1	**6.3** 51.0		**0.5** 4.1 Dealkylation ?	
 F# 63			**0.5** 4.1			
 F# 93					**0.5** 4.1	
 F# 136					**0.5** 4.1	
 U [36.15] / F# 138 ?						**0.5** 4.1
 U [36.02] / F# 145						**0.5** 4.1
Suspected Cumyl-phenol Derivatives U [14.67] & U [32.02]				**0.6 + 0.9** 4.9 + 7.3		
 F# 76			**0.5** 4.1			
U [15.75]		**0.5** 4.1	**0.5** 4.1	**0.5** 4.1		**0.5** 4.1
U [21.16]		**0.5** 4.1				
U [29.68]					**0.5** 4.1	
U [30.92]		**0.5** 4.1				
U [31.24]		**0.5** 4.1	**0.5** 4.1		**0.5** 4.1	
U [31.81]	**0.5** 4.1	**0.5** 4.1		**0.5** 4.1		

Yellow highlighted fragments formed due to hydrolysis
Concentrations as experimentally quantified at 20°C extraction temperature
Black values are extrapolated from 20°C to 60° C according to **Figure 3.8**

It can be concluded from this section, that although the findings from Section 3.3.1 point to the use of an efficient PD for the Phosphites examined; molecules which are more effective than P-1 *cannot* be suggested, because of high sensitivity to hydrolysis. The actual degree of hydrolysis after melt-processing and water extraction would be difficult to predict and could vary significantly as Phosphite hydrolysis is an auto-accelerating reaction mechanism. Because of this, P3 and P-4 should be excluded. Although P-9 seems hydrolytically stable, a high number of oxidised-aliphatic fragments are generated. In particular, the presence of aldehydes points to the presence of a (highly) Hindered Phenol. Aldehyde (instead of ketone) formation was already observed with AO-1 (Section 3.3.1). This suggests the presence of high concentrations of fragments F# 136.

Overall, the lowest number and (in case of fragments that originate from protective chemicals) concentration of fragments is observed with P-1, P-19 and potentially P-5. All three Phosphites are hydrolytically relatively stable and seem suitable for use in PO articles with low amounts of water-extractable fragments. Nevertheless, there are differences between these Phosphites. To maintain MFI (**Figure 83**), P-5 is more efficient as PD than P-1. The oxidation of the first P-centre of the Phosphite P-5 to yield a mono-phosphite-mono-phosphate intermediate state is reported to be significantly faster than the corresponding kinetics for the mono-phosphite P-1 [266]. The P-19 structure is beneficial because of the synergistic effect of (reduced) Hindered Phenol through a CB-D mechanism, along with the PD capability of a Phosphite (**Figure 87**).



4.8% P — P-1

7.3% P — P-5

4.7% P
1.5 Molar Activity [mol OH/kg Additive]
P-19

Figure 87: Chemical structure of P-1, P-5, and P-19

Another difference exists related to the regulatory and indirect food contact status of the Phosphites. The indirect food contact approval for P-1 (as well as P-3) covers only the initial molecule. In contrast, the indirect food contact approval of P-5 and P-19 (as well as P-9) includes the initial phosphite and (selected) expected transformation products, including hydrolysis products [184,185].

Considering this, an examination of alternative PD protective chemicals, which are effective during melt-processing, is warranted.

3.3.5.2 Other chemistry classes

Most protective chemicals in this section are either natural molecules, modified natural molecules and/or direct food additives (with the exception of AO-36 and HYA-1). Beyond their high activity during melt-processing, it is expected that these natural molecules undergo transformations, even under high temperature (and shear), that yield non-hazardous transformation products, in a similar way to natural metabolic processes. All the molecules examined here function according as CB-D; with several being considered as carbon-centred rather than oxygen-centred radical scavengers. HYA-1 is reported to have PD functionality as well.

AO-6 is a natural antioxidant. It is used as a direct food (contact) additive under the code E 306 (respectively E 307 to 309). AO-6 by itself or derivatives like Vitamin E acetate are reported as an excellent processing antioxidants [267]. AO-58 (Vitamin C palmitate) is a fat-soluble (lipophile) version of vitamin C [268]. It is a synthetic modification of the natural vitamin C, but eventually could break down (via hydrolysis) into the vitamin and palmitic acid. It is well-known as a direct food additive E 304. AO-53 (TBHQ *Tert*-butyl-*p*-hydroquinone) is a synthetic antioxidant and direct food additive (E 319). It is used for example in unsaturated vegetable oils. It is reported to be synergistic with E 310 (propyl gallate) [269,270] as well as E 320 (AO-59) and E 321 (AO-28). AO-60 (gallic acid) was tested, as the corresponding esters (propyl gallate (E 310) and octyl gallate) were not available. The latter two are reported as good antioxidants for food [271,272]. Further esters of AO-60 are reported, such as: dodecyl gallate [273] (lipophile and analogue of AO-2 and AO-6); epicatechin gallate; or epigallocatechin gallate.

The last two protective chemicals are purely synthetic and mainly used in plastic applications of polymers. AO-36 is a “capped” bisphenol, with the acryloyl-modified phenolic group being able to scavenge carbon-centred radicals as well as oxygen-centred radicals. It is reported to be very active during melt-processing in the absence of oxygen (compounding step under nitrogen blanket); particularly for the preservation of the MFI of high molecular weight PE pipe grades [275,276]. HYA-1 is a processing stabilizer of the hydroxylamine class, hence comprising a different active functional group against oxidation when compared to phenols and phosphites. The activity of hydroxylamine is based on the intermediate nitrone state [120,212,276].

The formulations are melt-processed and compounded as outlined in the beginning of Section 3.3.5. The extraction temperature is 20°C. Overall the protective effect with respect to MFI is good, but less pronounced that the best tested Phosphites. AO-60 performs exceptionally, followed by AO-6 and AO-36. AO-58 results in a similar MFI to that afforded by P-1. AO-53 and HYA-1 perform in between the afore-mentioned clusters (**Figure 88**).

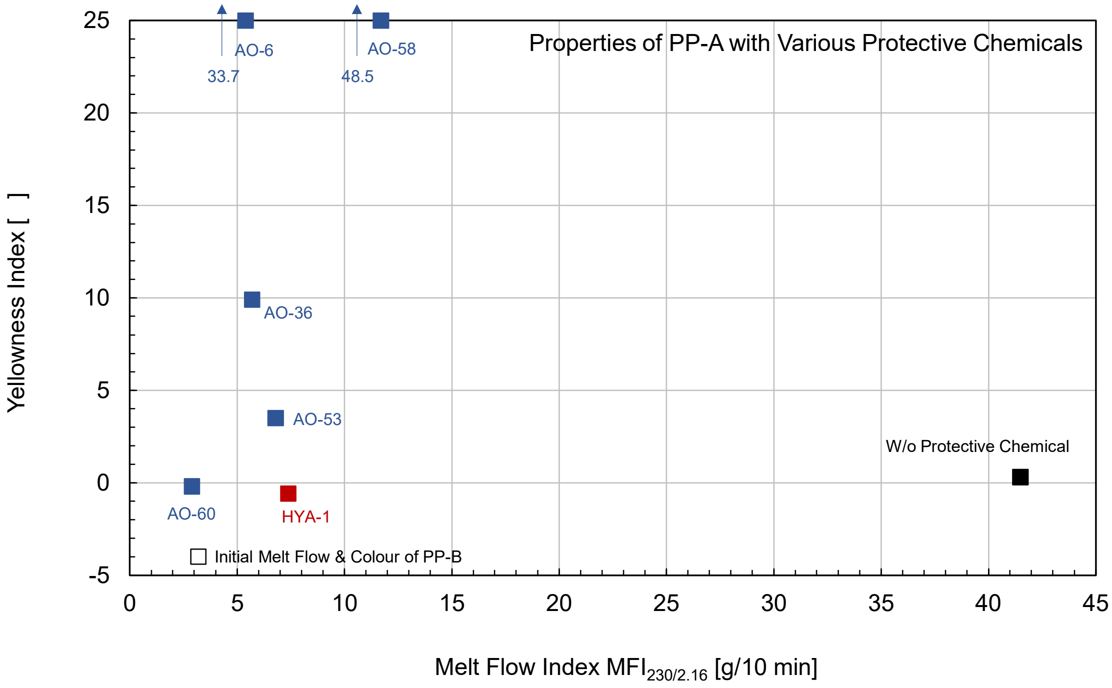


Figure 88: Properties of melt-processed PP in the presence of various classes of protective chemicals

Extrusion Condition:	C-1, M-1
Extraction Condition:	E-1
Formulation:	PP + 750 ppm MS-1

Most remarkable, and in strong contrast to the class of Phosphites, is the moderate to high colour. Colour formation during melt-conversion, as in the case of AO-6, AO-36 and to a minor degree AO-53, could indicate the formation of oxidised-aromatic transformation products. AO-58 starts and remains at a very high colour level without any further increase during melt-processing. The colour of AO-60 decreases during melt-processing. This behaviour is not yet understood.

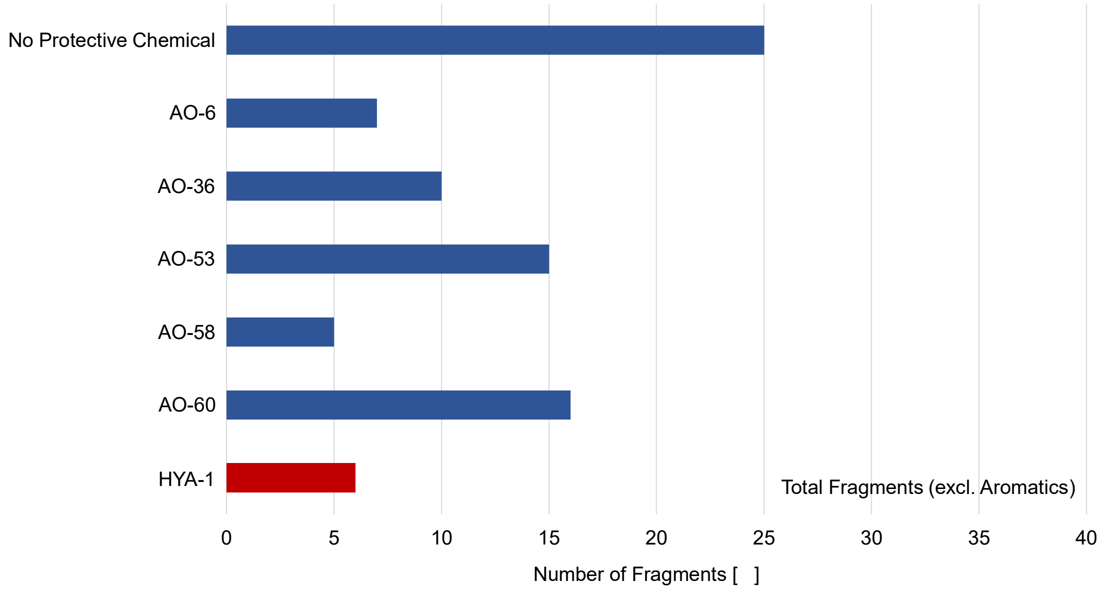


Figure 89: Number of total fragments in the presence of various classes of protective chemicals

All protective chemicals decrease the total number of fragments. AO-53 and AO-60 by ~20 % and the other by ~50 to 70%. Overall, the level appears slightly lower than for the class of Phosphites (**Figure 89**). The number and concentration of protective chemical-originating fragments is low; on average lower than for the class of Phosphites (**Figure 90**). *AO-58 and HYA-1 do not show any contribution to the formation of fragments originating from protective chemicals*. In contrast, AO-53 results in an elevated concentration of fragments. The parent protective chemical by itself is extracted and mainly the corresponding *p*-benzoquinone (F# 95). This seems plausible by the low Log P_{OW} (2.26 - 2.94 *est.*) of the protective chemical (see Figure 8 for comparison). **Table 22** gives an overview of all fragments associated directly with the protective chemicals evaluated here. In contrast to the class of Phosphites, no common fragments are found; but all fragments identified belong (of course) to the class of (more or less) Hindered Phenols.

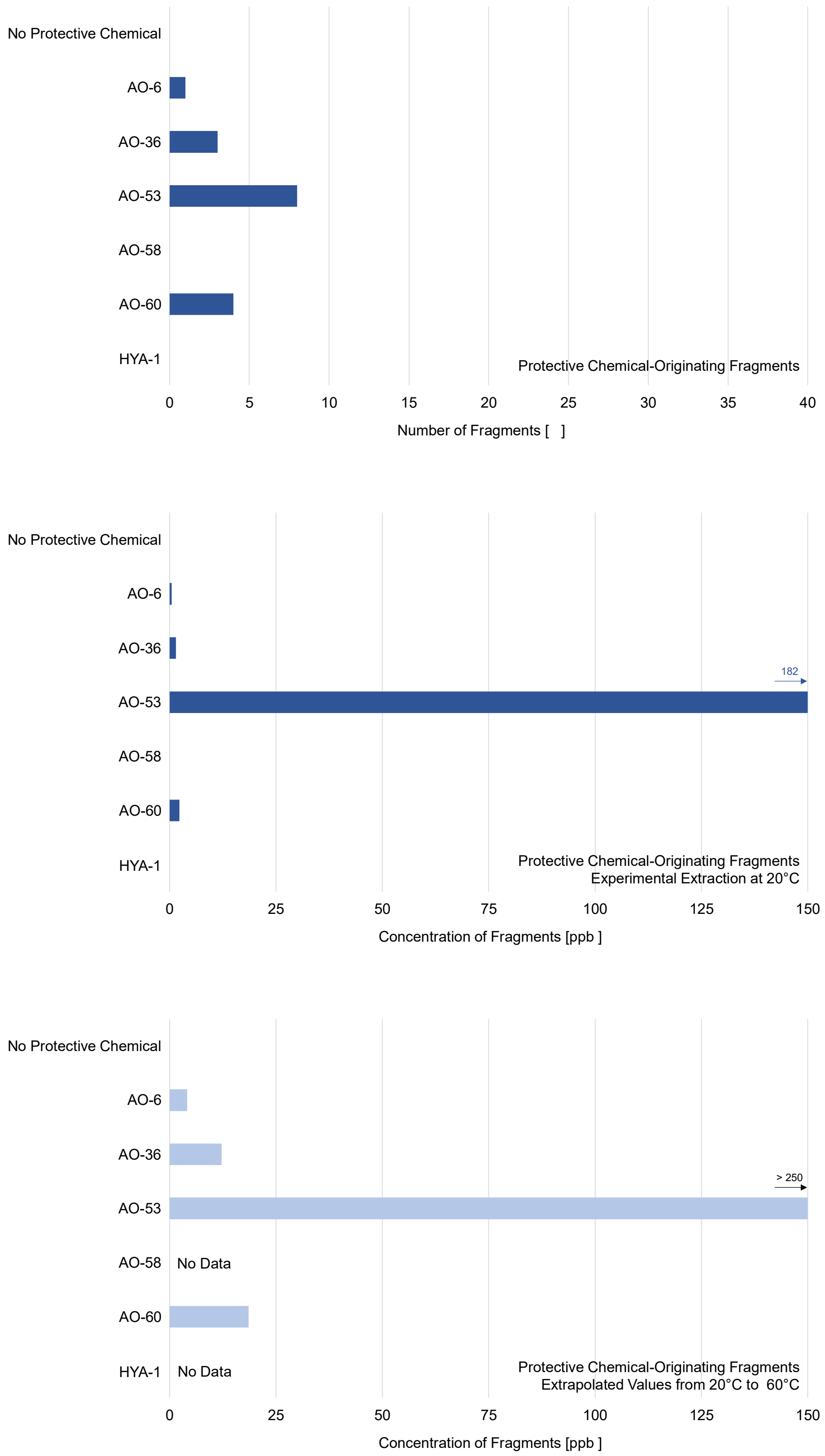
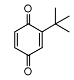
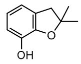
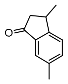
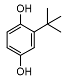
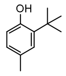
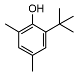
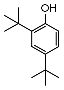
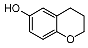
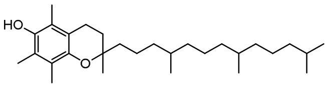


Figure 90: Number and concentration (ppb) of fragments originating from various classes of protective chemicals (Lower chart extrapolated from 20°C to 60°C)

Table 22: Fragments originating from various protective chemicals (also see **Table 21**)

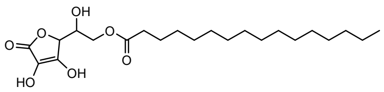
Fragment	***AO-6*** *E 307-309*	***AO-36***	***AO-53*** *E 319*	***AO-58*** *E 304*	***AO-60*** *(E310-312)*	***HYA-1***
 F# 95			**163.7** > 250			
 F# 88			**6.8** 55.1 **0.5** Isomer 1 4.1 **0.9** Isomer 2 7.3			
 F# 85			**2.9** 23.5			
 **AO-53**			**2.1** 17.0			
 F# 93		**0.5** 4.1				
 F# 110		**0.5** 4.1				
 F# 125		**0.5** 4.1 Mis-assigned peak				
 U 25.09] / F# 65	**0.5** 4.1					
Dehydrogenated Tert.-butyl-benzoquinone			**2.3** U [26.62] 18.6 **0.5** U [29.08] 4.1			
U [13.23]					**0.8** 6.5	
U [21.16]					**0.5** 4.1	
U [26.08]			**1.8** 14.6			
U [27.53]			**0.5** 4.1			
U [30.92]					**0.5** 4.1	
U [31.81]					**0.5** 4.1	

To re-iterate, no fragment could be directly associated with the protective chemicals AO-58 and HYA-1. Only one unidentified fragment, around the limit of detection LD, is detected for AO-6. *Therefore, the protective chemicals listed in **Figure 91** are potentially suitable for use in PO articles with low water-extractable fragments*. Nevertheless, some differences exist between the (low) Hindered Phenols and the class of Hydroxylamine. HYA-1 does not contribute to colour formation during melt-processing; in contrast to AO-6 and AO-58. The use of the latter two would therefore be limited to (highly) pigmented PO applications, or at least to applications which are not colour sensitive. *The lack of PD mechanism of AO-6 and AO-58 might result in higher concentrations of ketones that originate from the polymer substrate* (see **Section 3.3.3**). It seems noteworthy, that AO-6 and AO-58 are reported as synergistic mixtures in life science applications [42]**.** *Attention is drawn to the fact that all three protective chemicals are of lipophilic character, with the corresponding Log P_{OW} above 6 or above 12. By structure (**Figure 91**), all three protective chemicals are expected to fragment partially into non- water-soluble, lipophilic compounds.*



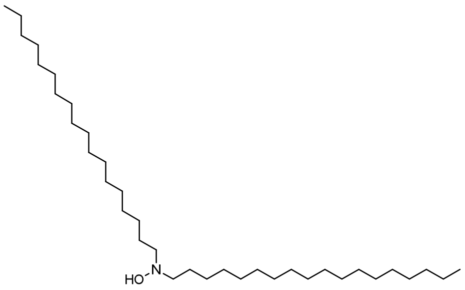
Log P_{OW} = 12.2

AO-6



Log P_{OW} = 6.0

AO-58



Log P_{OW} = 13.2

HYA-1

Figure 91: Chemical structure of AO-6, AO-58 and HYA-1

3.4 Protective Chemicals during Service Life

Most of the chemicals investigated in chapter 3.3.5 do not have, or have only a very small, protective effect during the use of a fabricated PO product. The maximum durability achievable with these chemicals is in the range of several days or weeks [277,278]. For longer durability (several months to several decades) additional chemicals must be added. Here at low to moderate temperatures the ability of oxygen to migrate into the surface layers of a thick-section polymer (e.g., pipe) or through a polymer (e.g., packaging) should be taken into account. From a theoretical point of view, protective chemicals with effect during service life conditions fall into two categories; those *with* effect during melt-processing (such as (high) Hindered Phenols, **Section 2.5.1** and **Figure 10**) and those *without* effect during melt-processing such as HAS (excluding HOR-HAS; see Section 2.5.3). In industrial practice though an additional category exists (Hindered Phenols with **l***ow* effect during melt-processing). No melt protecting activity should prohibit the formation of oxidative transformation product which originated from the protective chemical. In this section, the impact of protective chemicals that affect the formation of water-extractable fragments during service life condition is investigated.

Sample preparation and extraction conditions were chosen as described in Section 3.3.5. The extraction temperature was 20°C. For the same reasons as discussed in Section 3.3.5, a detailed discussion of fragments originating from the polymer substrate is omitted. The formulations are based on PP-A containing 750 ppm MS-1 as antacid. Protective chemicals are added as single component at a concentration of 1000 ppm.

3.4.1 Protective Chemicals with Effect during Service Life but not Melt-Processing

Many commercial HAS are known, but none of the three HAS selected for this study contain a “N-O-R” functionality (hence being called NOR-HAS or NOR-HALS). Therefore, the three molecules selected should be active during melt-processing to a very minor degree and in consequence few transformation product should be formed. As well as their high molecular weight, potential stabilizer-originating fragments should essentially be limited to impurities and not completely reacted raw material. HAS-5 contains ester bonds in the backbone but no triazine moieties. In contrast, HAS-16 contains triazine moieties. Triazine containing HAS are known to impart a “bitter” taste to drinking water [191]. The characteristic of HAS-16 is the MWD, which does not contain molecules below 1000 g mol^{-1} [191]. HAS-25 contains large cyclo-aliphatic side groups and no triazine moieties. The molecular weight and molecular weight distribution of the three HAS differs significantly.

None of the three HAS gave significant protection during melt-processing (**Figure 92**). This is in accordance with **Figure 10** and the explanation previously given for **Figure 16.** Duration of the melt-processing state (only several minutes), and oxygen deficiency conditions in the processing equipment (**Table 3**), does not allow the formation of the nitroxyl radical as active protective species. The low discolouration of the samples confirms this observation.

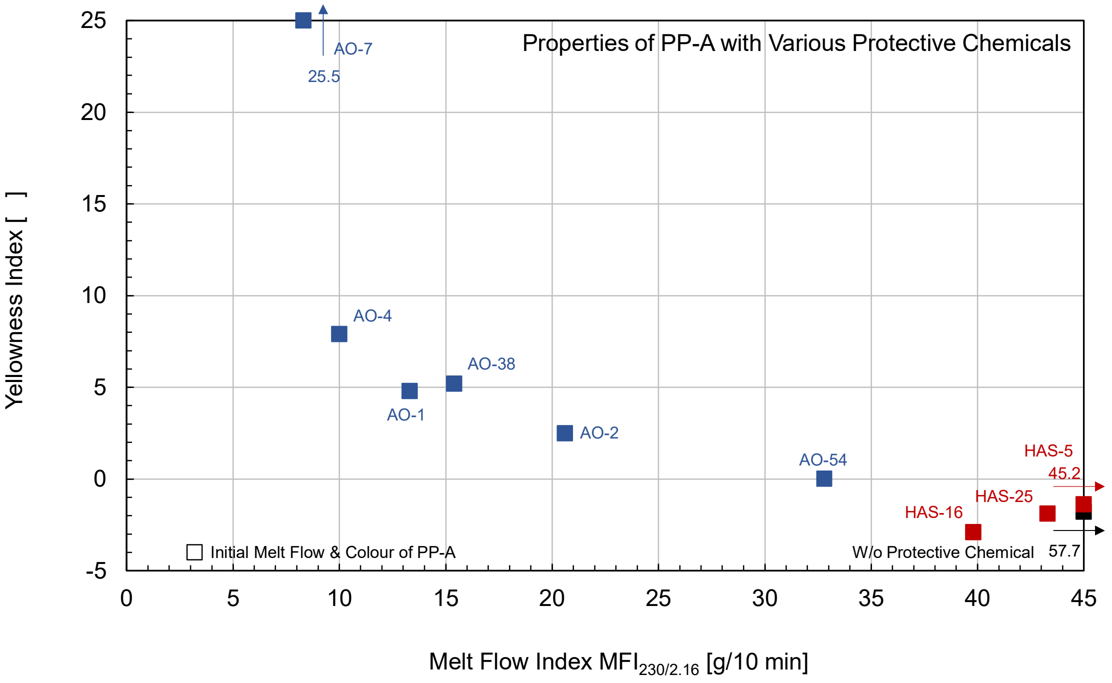


Figure 92: Properties of melt-processed PP in the presence of various classes of protective chemicals with effect during service life

Extrusion Condition: C-1, M-1
Extraction Condition: E-1
Formulation: PP + 750 ppm MS-1

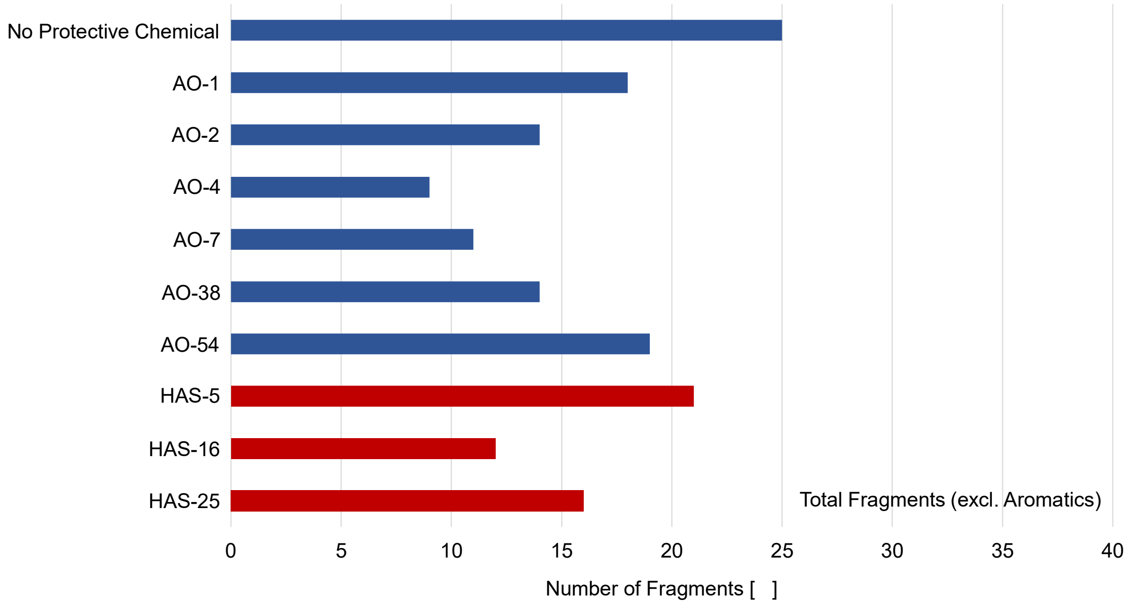


Figure 93: Number of total fragments in the presence of Hindered Phenols and HAS

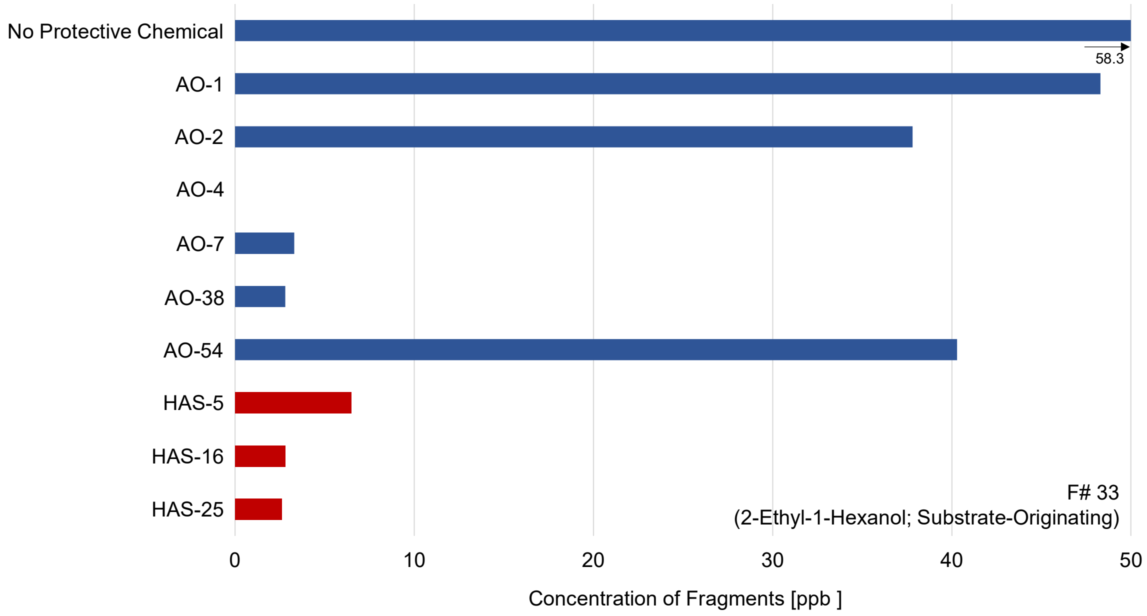


Figure 94: Concentration of fragment F# 33 in the presence of different Hindered Phenol or HAS

Despite the limited effect on MFI, the HAS clearly decrease the number of total fragments [265,279]. The effect is within the range of Hindered Phenols, or slightly inferior (**Figure 93**). According to Section 3.1, many oxidised-aliphatic fragments are not extracted at 20°C. However, for one specific fragment F# 33 an interesting observation is made. F# 33 is found in high concentration in PP-A without protective chemicals. In the presence of HAS, this concentration is decreased by ~90 %. Only low Hindered Phenols (such as AO-7 and AO-38) reach a similar level of reduction. This data confirms earlier conclusions and suggests (Section 3.3.1) that not only AO-1, but high Hindered Phenols (e.g., 2,6-di-teriary-butyl) in general are not able to prevent the formation of alcohols during melt-processing. This observation can at this point not be investigated further due the lack of data on oxidised-aliphatic fragments at this extraction temperature. Nevertheless, it is plausible from **Figure 95** that HAS modifies the formation of (LMW) alcohols (**Scheme 26**).

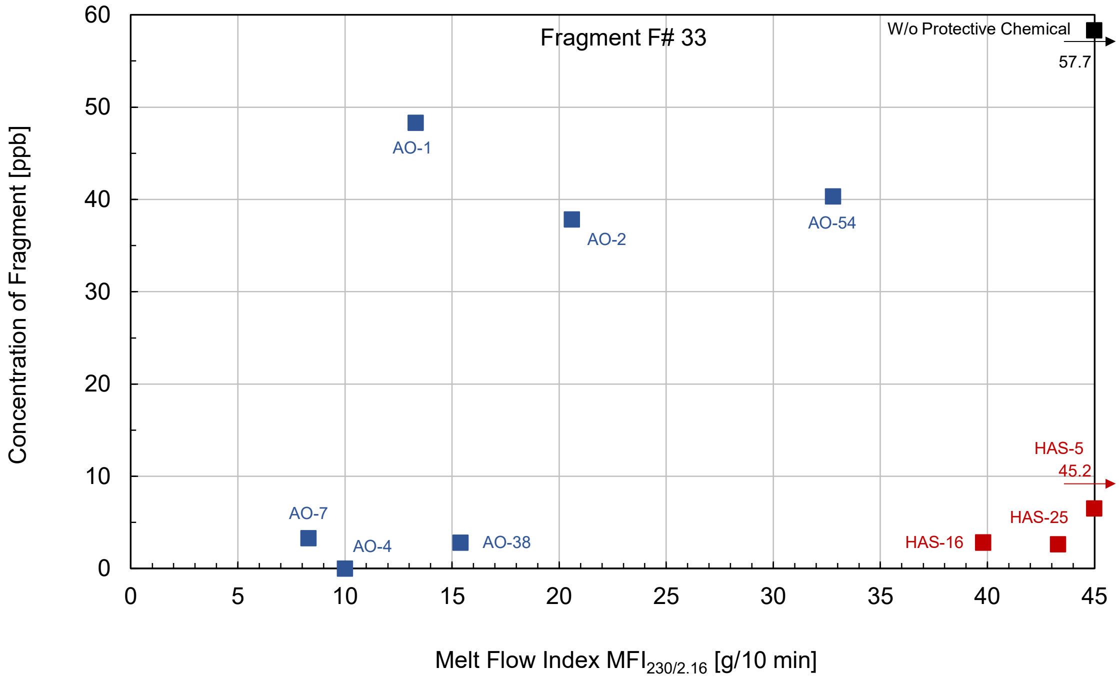
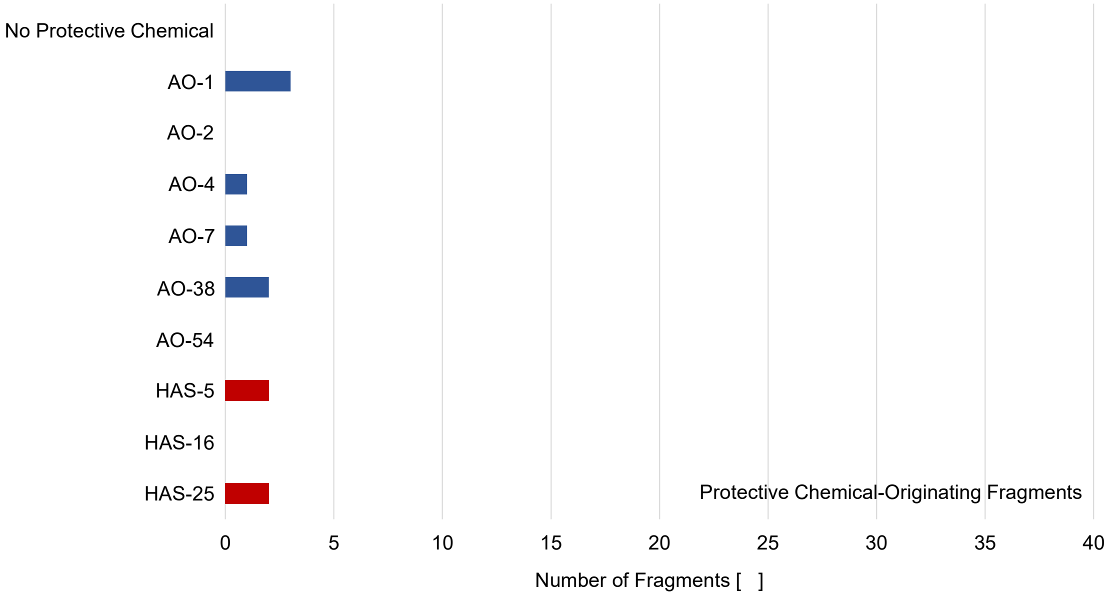
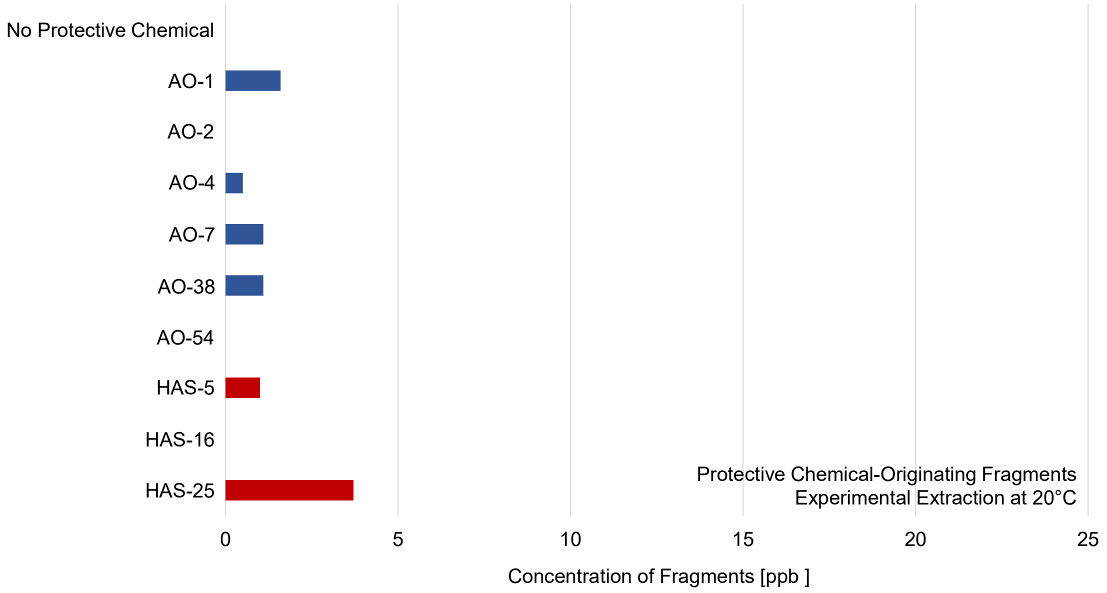


Figure 95: Concentration (ppb) of fragment F# 33 versus MFI

For one of the HAS no fragments are seen, while the remaining HAS contributed two fragments (**Figure 96**). The concentrations of the fragments are low at 20°C and still low for fragments that originate from HAS-5, once extrapolated to 60°C. **Table 23** identifies the detected fragments. The fragments can be related partially to HAS-5 and HAS-25, but neither seems to be a transformation product due to their activity as protective chemical. No fragment is detected which can be associated directly with the functional group of HAS (2,2,6,6-tetramethyl-piperidine or the corresponding nitroxyl radical). Fragment F# 112 is known as raw material for HAS-25 [191]. It is noteworthy, that no unidentified fragments are detected. Overall, the number and concentration of fragments seems lower than for protective chemicals that are effective during melt-processing (**Figure 96** compared with **Figure 85** and **Figure 90**). While HAS-16 does not result at all in fragments originating from protective chemicals, preference is given to HAS-5 (and potentially HAS-25) due to the absence of triazine moieties and the corresponding impact on the taste of drinking water (**Figure 97**).





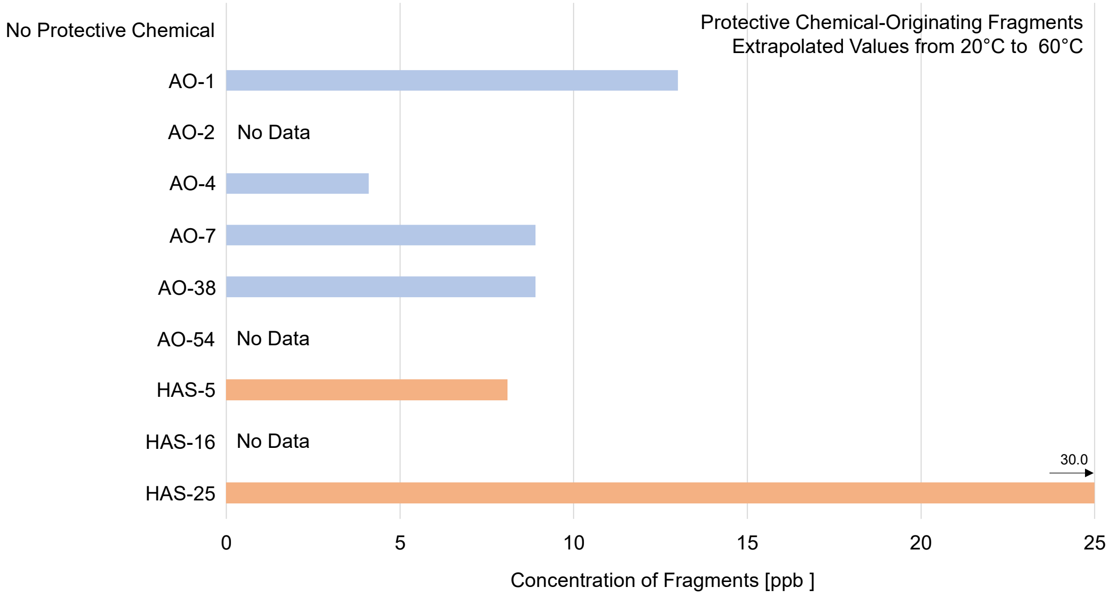
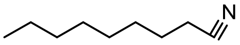
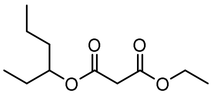
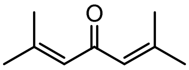
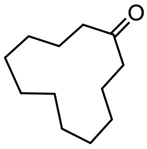
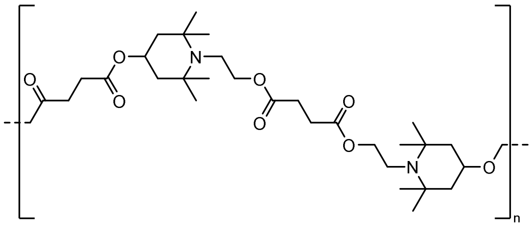


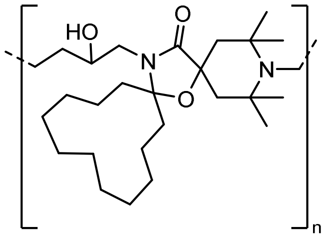
Figure 96: Number and concentration (ppb) of fragments originating from various classes of protective chemicals with effect during service life (Lower chart extrapolated from 20°C to 60°C)

Table 23: Fragments originating from various protective chemicals (also see **Table 21**)

Fragment	***HAS-5***	***HAS-16***	***HAS-25***
 F# 46	**0.5** 4.1		
 F# 131	**0.5** 4.1		
 F# 40			**0.5** 4.1
 F# 112			**3.2** 25.9



HAS-5



HAS-25

Figure 97: Chemical structure of HAS-5 and HAS-25

3.4.2 Protective Chemicals with Effect during Service Life and Melt-Processing

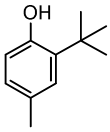
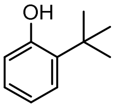
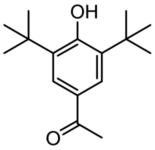
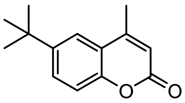
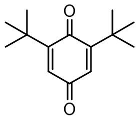
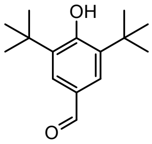
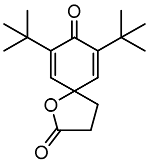
Comparison of fragments of oxidised-aliphatic species arising from formulations containing HAS and Hindered Phenol is difficult, as Hindered Phenols have a protective effect (of varying degree) during melt-processing. The investigation is therefore focussed on fragments originating from the protective chemical of the class of Hindered Phenol.

As stated previously, AO-1 is considered the “workhorse” of the PP (and to a certain degree as well the HDPE) industry. AO-2 is manufactured by a similar synthetic route to AO-1. Therefore, it should result in the same water-extractable fragments. However, the lower “conformational and steric strain” of this linear molecule versus the structure of AO-1 (which consists of 4 hindered phenols substituted on a pentaerythritol group via ester bonds) means less fragmentation is expected. Additionally, the lower molar activity of AO-2 should also result in fewer fragments. For AO-2, hydrolysis reaction of the ester bond, can form stearic acid, which is not soluble in water, but in hot ethanol [280]. AO-4 is manufactured by a different synthetic route. It should be noted that AO-4 contains only carbon-carbon and carbon-hydrogen bonds (apart from the three phenolic groups) and hence constitutes an intrinsically more stable molecule than AO-1 and (to a certain degree) AO-2. From a kinetic point of view, AO-1, AO-2 and AO-4 should have equivalent hydrogen donor capability (phenolic hydrogen); though obviously their molar activity is different. AO-7 is also hindered phenol but is exclusively based on carbon-carbon and carbon-hydrogen bonds and hence intrinsically more stable than the ester bond containing AO-1. It is not a defined molecule but an oligomer with a molecular weight distribution. Some of the phenolic groups are highly hindered (like AO-1); but some phenolic groups have a reduced hinderance, with one ortho-position not being substituted. Thus, some phenolic hydrogens are more labile than those of AO-1; therefore, a higher activity during melt-processing would be expected. AO-38 contains relatively weak ester bonds (as does AO-1); but is reported to not fragment under water-extraction conditions [281]. AO-54 is structurally like AO-2 but based on an alkylated hydroxybenzoic acid ester. The carboxyl functionality in the *para*-position of the phenolic groups (inductive effect) seems to significantly decrease the availability of the phenolic hydrogen and hence renders AO-54 in contrast to AO-2 less reactive under melt-processing conditions.

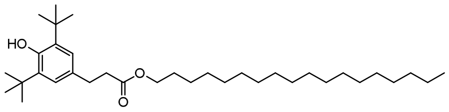
The experimental set-up was the same as in Section 3.4.1. Most of the selected HP have a considerable protective impact during melt-processing. However, AO-2 yields a limited effect while AO-54 approaches the level of the HAS discussed earlier. The colour development is in line with the activity of the protective chemicals (**Figure 92**). The low colour of AO-2 and AO-54, which approaches the level of HAS based formulations, could indicate a lower concentration of oxidative transformation products.

The HP representatives with the lowest effect during melt-processing (AO-2 and AO-54) result in no fragments originating from protective chemicals. Remarkably, AO-4 contributes only one fragment (at its LD) despite its rather good protective effect on MFI. It is noteworthy, that AO-4 shows a better effect as protective chemical but at the same time results in fewer fragments than AO-1. All fragments identified can be associated with the functional group(s) of HP **Table 24**).

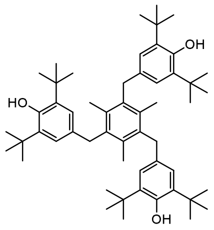
Table 24: Fragments originating from Hindered Phenols with effect on service life (also see **Table 21**)

Fragment	*AO-1*	*AO-2*	*AO-4*	*AO-7*	*AO-38*	*AO-54*
 F# 93				**1.1** 8.9		
 F# 62					**0.6** 4.9	
 F# 148	**0.6** 4.9					
 F# 132					**0.5** 4.1	
 F# 135			**0.5** 4.1			
 F# 143	**0.5** 4.1					
 F# 156	**0.5** 4.1					

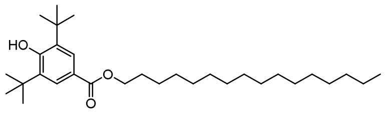
Fragments F# 135 (R 7.4, R 8.4, R 10.3, R 11.3 & R 12.3), F# 143 (R 9.2, R 10.2 & R 12.3), F# 148 (R 9.2 & R 11.2) and F# 156 (R 15.1) are transformation products of Hindered Phenols with established mechanisms of formation. F# 132 also appears to be a transformation product, but with an unclear mechanism of formation. Fragments F# 62 and F# 93 represent the functional groups of the corresponding Hindered Phenols AO-38 and AO-7. The mechanism for the detachment of the functional group is not yet established. Two of the three Hindered Phenols (AO-2 and AO-54), which are most suitable, are of lipophilic nature; including some of the predictable (hydrolysis) transformation products (**Figure 98).** Given that low activity during melt-processing correlates for some Hindered Phenols with low fragmentation, it is noted that AO-3 (not tested in this study) is expected to have a reduced activity during melt-processing [282] (**Figure 99**).



AO-6

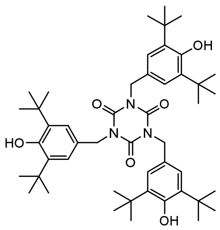


AO-48



AO-54

Figure 98: Chemical structure of AO-2, AO-4 and AO-54



AO-3

Figure 99: Chemical structure of AO-3

As the selected protective chemicals are added to prolong the service life of PO articles, the impact on LTTS was examined. Granules from the compounding operation C-1 were subjected to accelerated heat aging at 130°C. All protective chemicals in Section 3.4 contribute significantly to an increase in LTTS over the 'pure' PP-A (**Figure 100**). Nevertheless, at 130°C the contribution varies by a factor of ~4 with AO-54 resulting in weakest performance and AO-1 by far strongest performance.

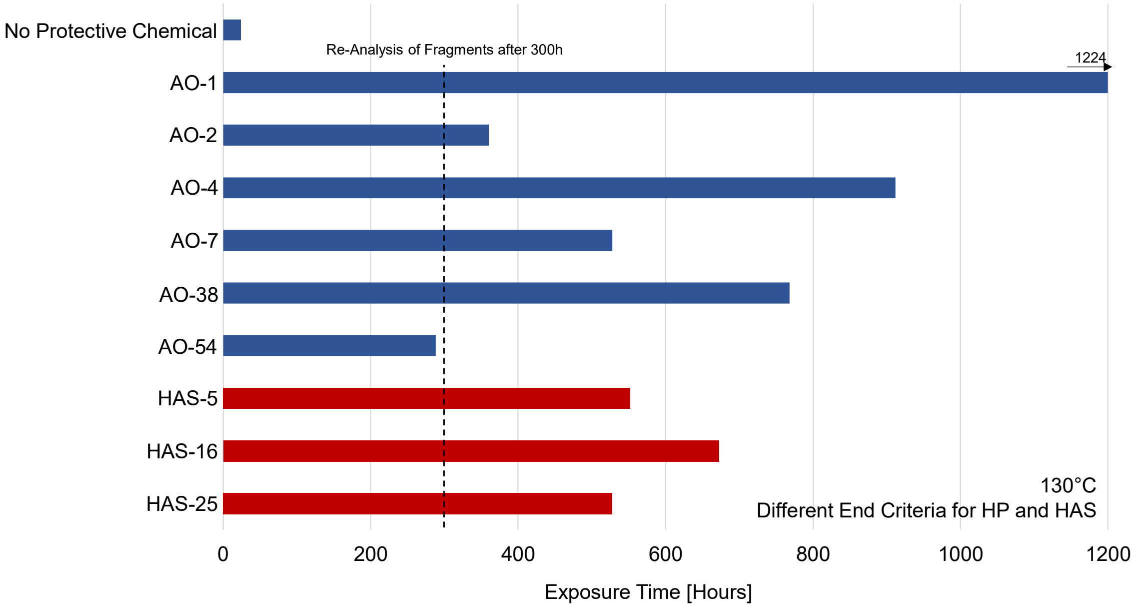


Figure 100: LTTS contribution of various Hindered Phenols respectively HAS

Compounding Condition: C-1
Exposure: Granules from C-1 at 130°C in circulating hot air oven
Formulation: PP + 750 ppm MS-1 + 1000 ppm protective chemical
Failure Criterion: Beginning of disintegration of granules (Hindered Phenol)
Onset of "burning" (HAS)
LTTS procedure L-1

At this point a reminder of the temperature dependency of LTTS data is warranted (refer to **Figure 18**). LTTS data, closer to real service life conditions of 60-80°C (e.g., for PO drinking water pipes, is derived from literature [117,283-285,286,285] for selected protective chemicals (**Figure 101**). At 60°C (and in 120 μm film), all Hindered Phenols contribute significantly to LTTS. The variation between the best (AO-1) and worst (AO-54) is only a factor of ~1.5 to 2. From this data it can be concluded that

AO-2 and AO-54 act as protective chemicals during the service life of PO-based plastic products (this is in addition to AO-1, AO-3 and AO-4, which are used for this purpose by the PO industry).

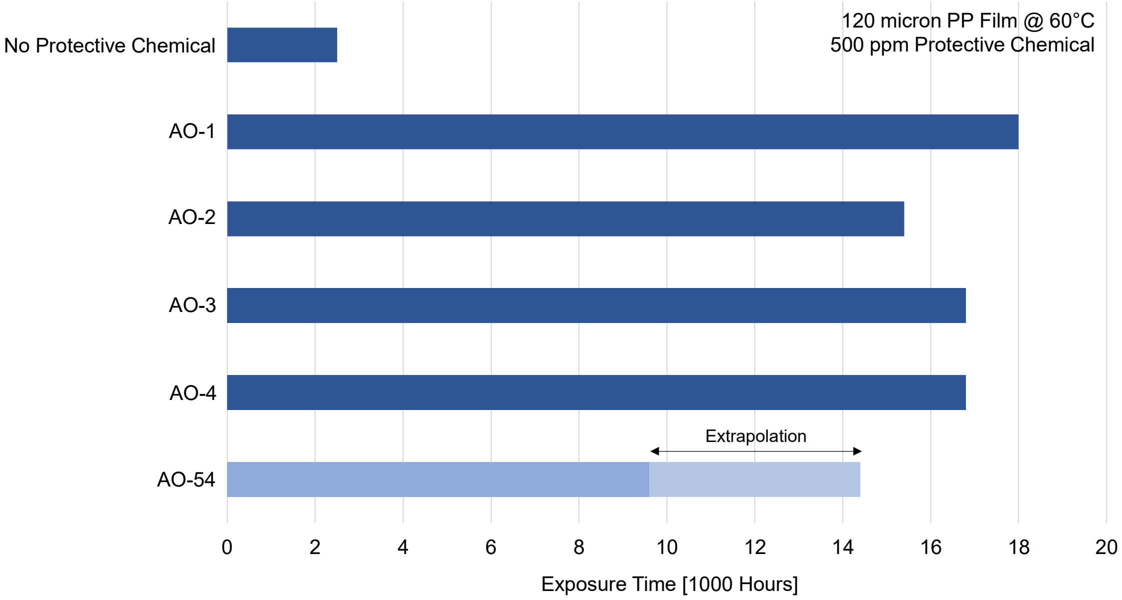


Figure 101: LTTS contribution of various Hindered Phenols at low temperature [117,286,287]

Compounding Condition:	260°C
Exposure:	120 micron film at 60°C in circulating hot air oven
Formulation:	PP + 1000 ppm MS-1 + 500 ppm protective chemical
Failure Criterion:	Visual inspection for signs of decomposition (powder formation)
Extrapolation:	AO-54 extrapolated from other experiments

In parallel to these experiments, some granules of selected formulations (given in **Figure 100**) were taken out of the oven after 300 hours and were subjected to water extraction condition E-4 (at 60°C). Note that the sampling point is intentionally set after 300 hours; just after the failure of the first formulation containing a protective chemical. The findings are discussed in Section 3.5.2 (Thermal treatment of LMW fragments).

Due to the limitation of HAS in PO applications such as pressured pipe (see **Figure 17**), further investigation of fragments is undertaken only for HP. Hindered phenols AO-1, AO-3, AO-4 and AO-38 are examined at 5000 ppm concentration in the presence of 750 ppm P-1 and 750 ppm MS-1. This type of formulation is typical of formulations used in the industry to obtain a service life of several decades for thick section PO (e.g., pipes) at ambient temperature. Additionally, the LMW intermediate for AO-1 (and AO-2) is investigated (see **Figure 12**). Note that AO-39 ("Metilox" is referred to in this section as AO-39) is used as an intermediate and no further purification is carried out. PP-C without protective chemicals has already been discussed in detail Section 3.2. Equally the formulations of PP-C containing P1 (**Section 3.3.1**) as well as PP-C containing P-1 and 5000 ppm AO-1 (**Section 3.3.2**) have already been discussed in detail. The following section focusses therefore on differences between the selected Hindered Phenols (used as protective chemicals to improve service life and LTTS).

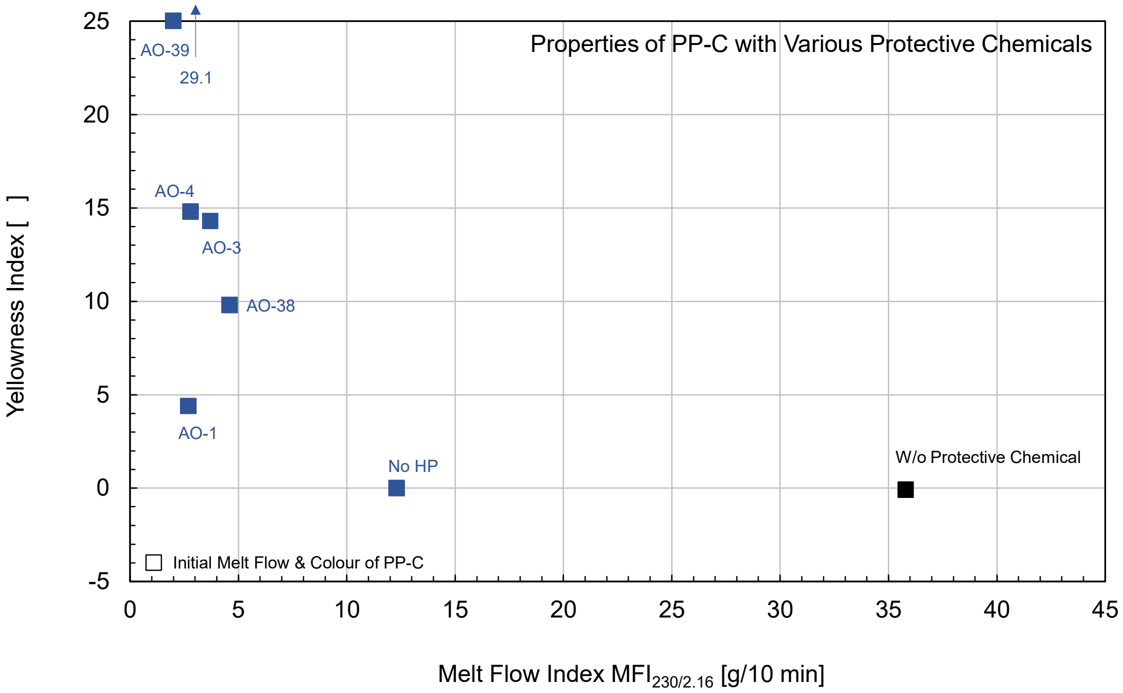
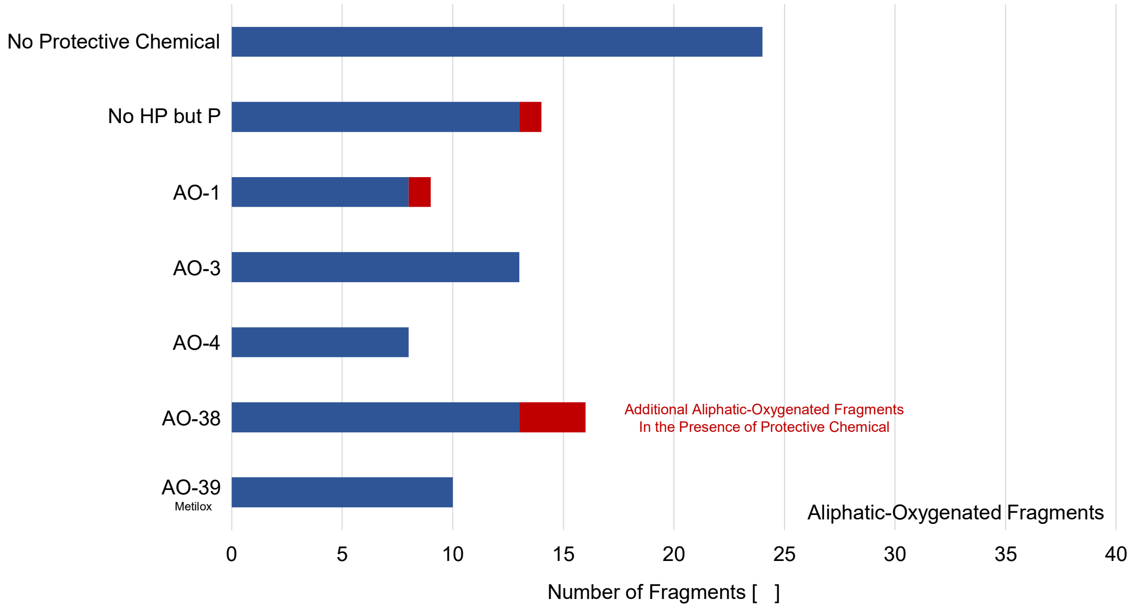


Figure 102: Properties of melt-processed PP in the presence of various Hindered Phenols with effect during service life

Extrusion Condition: C-1, M-1
Extraction Condition: E-1
Formulation: PP + 750 ppm MS-1 + 5000 ppm Hindered Phenol

All formulations containing HP result in a rather low MFI, indicating a sufficient protection of PP during melt-conversion. This is a consequence of the high concentration of Hindered Phenol (5000 ppm), which together with Phosphite P-1, gives a high overall concentration of protective chemicals (5750 ppm) with corresponding synergism between the two antioxidants. AO-1 cannot be differentiated from AO-3, AO-4 and AO-39. Excellent performance is seen by the LMW Hindered Phenol AO-39. The performance of AO-38 is not maintained throughout the experiment, which is in line with previous research [285]. The various Hindered Phenols show a different degree of colour development. The very high colour of development and high initial colour of AO-39 could be due to the 'quality' of the initial molecule.

The investigation of fragments originating from the polymer substrate focusses on oxidised-aliphatic fragments. As established in Section 3.3.1, the presence of the Phosphite P-1 decreases the number and (more significantly) the concentration of fragments. Addition of (high concentrations) of Hindered Phenol results in two different responses. For AO-1, AO-4 and AO-39 similar performance and a further reduction is achieved, while for AO-38 no additional reduction in fragments occurs. AO-3 seems to be intermediate in performance between these antioxidants. AO-1, AO-4 and AO-39 result in a ~90-95% reduction of oxidised-aliphatic fragments versus PP-C without protective chemical and, in a ~65-70% reduction relative to the formulation containing P-1 only (**Figure 103**). It is noteworthy, that out of the 2,6-di-*tert*-butyl substituted Hindered Phenols (AO-1, AO-3 and AO-4) the one which is least effective during melt-processing, results in a higher number and concentration of fragments.



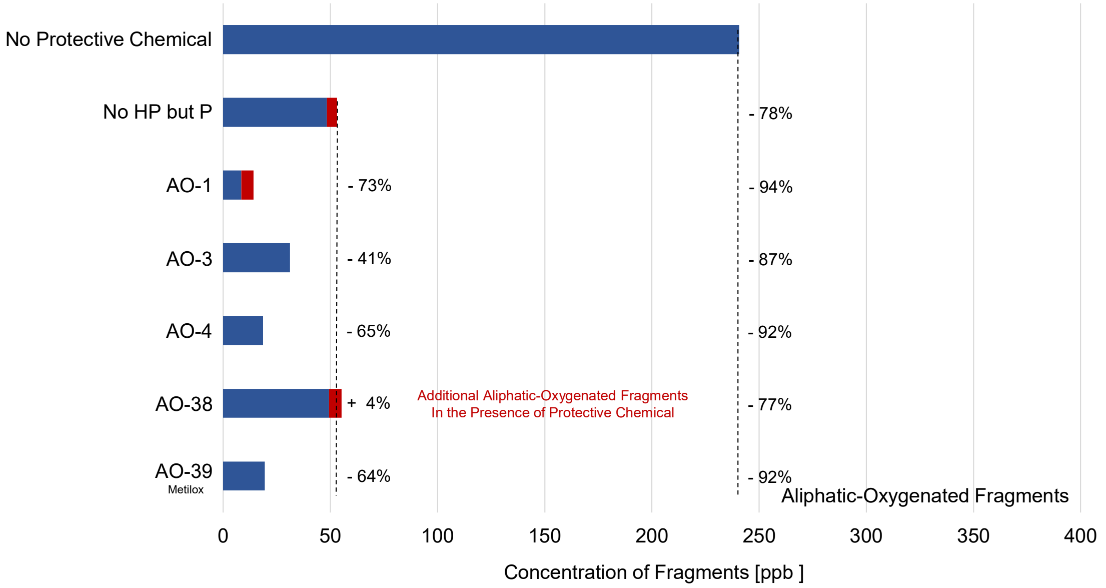
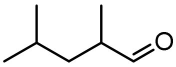
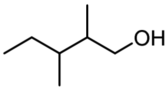
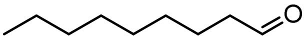
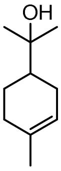


Figure 103: Number and concentration (ppb) of aliphatic-oxygenated fragments in the presence of various Hindered Phenols

Table 25: Additional fragments originating PP substrate in the presence of selective protective chemicals

Fragment	***No HP but P***	***AO-39*** *"Metilox"*	***AO-1***	***AO-3***	***AO-4***	***AO-38***
 F# 15						**1.8**
 F# 19						**1.6**
 F# 51			**5.7**			
 F# 77	**4.1**					**2.4**

Two hindered Phenols, AO-1 and AO-38, contribute to the formation of low concentrations of additional oxidised-aliphatic fragments and fragments originating from the polymer substrate. The fragments are identified in **Table 25**.

Significant differences are observed for fragments originating from protective chemicals. The number of fragments varies by a factor of ~2 if only commercially available protective chemicals are considered and by a factor of ~10 if the intermediate AO-39 is also considered (**Figure 104**). AO-3 results in less fragments than AO-1 and AO-4 in the least number of fragments; three in total. The same trend is seen for the concentration of fragments. The initial AO-39 molecule is water-soluble enough to be extracted at a level of 300 ppb. Nevertheless, its Log P_{OW} is 4.9, a relatively high value. It is assumed therefore that the concentration detected constitutes its solubility limit in stagnant water. Under experimental conditions here, this indicates that (at 60°C and 5000 ppm initial concentration of AO-39), only ~6.5 ppm of AO-39 is extracted by water. The AO-39 water extract also contains

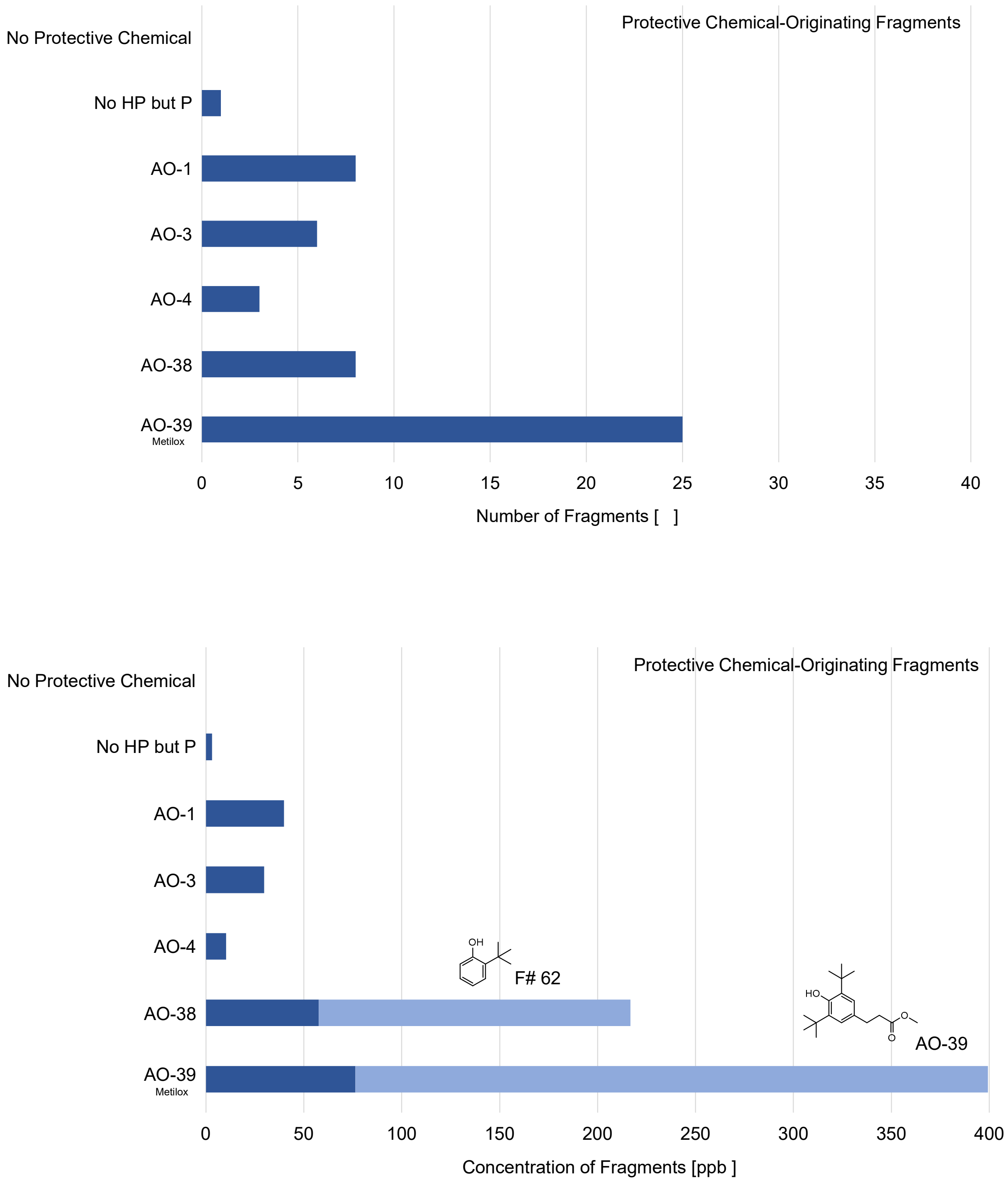


Figure 104: Number and concentration of protective-chemical-originating fragments in the presence of various Hindered Phenols

impurities such as F# 61 (N,N-diethyl aniline). This fragment cannot be associated directly with AO-39. A possible explanation might be a lack of purification operations, as AO-39 is generally used in a captive manner as intermediate. Most strikingly, seven fragments are identified with a longer retention time than AO-39 itself (**Table 26b;** unidentified fragments highlighted in yellow). A longer retention time indicates a lower mobility in the GC column. One possible explanation would be a higher MW of the fragments. The corresponding mechanism of formation is not understood. AO-38 yields an unexpected behaviour. Fragment F# 62 constitutes more than 70% of the quantified fragments. F# 62 is reported as hydrolysis product of AO-38 [285], however the concentration detected and overall speed of hydrolysis appears too high and is not in agreement with earlier work [152,281,288,289]. **Table 26** indicates the individual fragments.

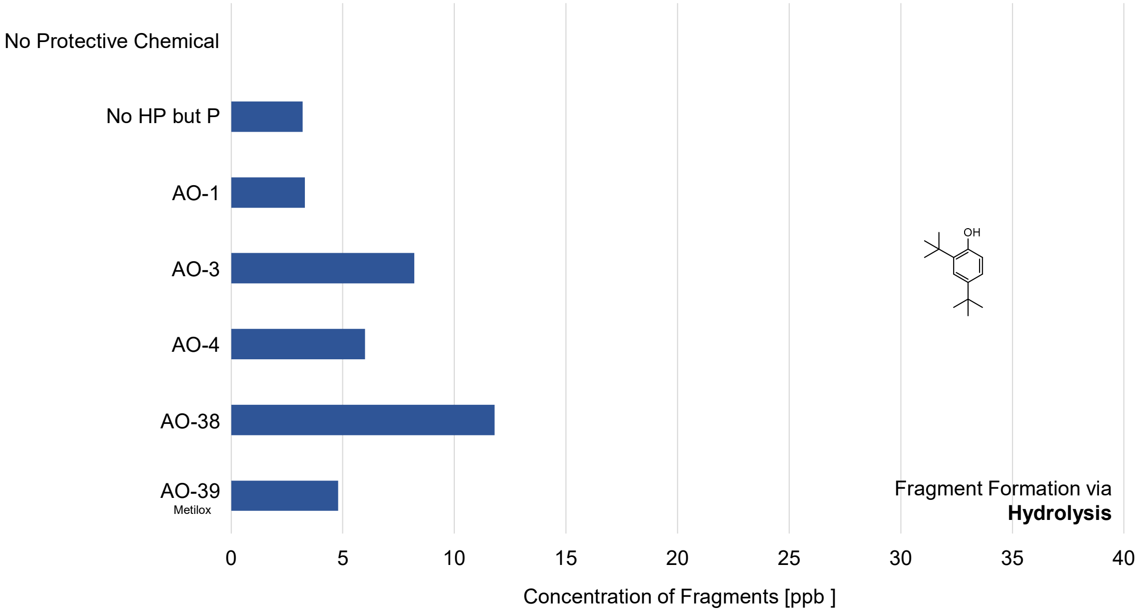


Figure 105: Phosphite P-1 fragments formed via direct hydrolysis

Table 26a: Identified fragments originating from various Hindered Phenols and P-1

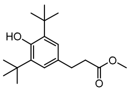
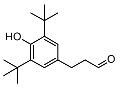
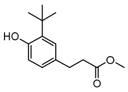
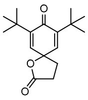
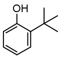
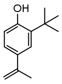
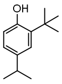
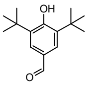
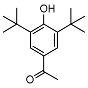
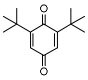
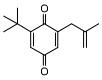
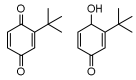
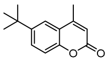
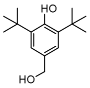
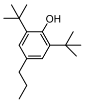
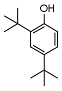
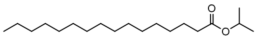
Fragment	*None*	*AO-39* *"Metilox"*	*AO-1*	*AO-3*	*AO-4*	*AO-38*
 F# 163		**323.0**	**1.4**			
 U [30.00] / F# 157 Proposed structure		**2.9**				
 U [36.22] F# 158 Proposed structure		**14.9**				
 F# 156		**0.7**	**0.9**			
 F# 62 or isomer		**6.2**				**159.2**
 U [32.63] Proposed structure		**0.8**				**37.3**
 U [34.72] Proposed structure						**1.8**
 F# 143		**4.7**	**17.6**	**6.3**	**1.0**	**0.6 ?** Miss-assigned peak?
 F# 148		**1.8**	**13.3**			
 F#F# 135		**4.6**	**1.9**	**3.8**	**3.4**	
 U [31.51] Proposed structure				**2.7**		

Table 26b: Identified fragments originating from various Hindered Phenols and P-1

Fragment	***None***	***AO-39*** *"Metilox"*	***AO-1***	***AO-3***	***AO-4***	***AO-38***
 F# 95 or F# 96						**1.3**
 F# 132						**4.3**
 F# 144				**8.0**		
 U [35.45] / F# 149 Proposed structure			**0.5**			
 F# 125	**3.2**	**4.8**	**3.3**	**8.2**	**6.0**	**11.8**
 F# 165		**1.6**		**0.7**		
U [25.25]		**0.9**				
U [25.58]		**6.7**				
U [20.68]		**1.2**				
U [34.16]		**0.5**				
U [34.35]		**0.5**				
U [35.19]						**0.5**
U [36.56]		**2.6**				
U [37.16]			**0.9**			
U [38.33]		**1.1**				
U [38.50]		**0.7**				
U [38.65]		**8.8**				
U [39.61]		**4.2**				
U [39.81]		**1.9**				
U [40.25]		**0.7**				
U [41.66]		**0.5**				

Fragment F# 125 is formed via direct hydrolysis of Phosphite P-1 (**Scheme 18**). The *hydrolysis of phosphite is not only reported in atmospheric moisture but in the polymeric substrate during melt-processing as well* [90,91,99]. It appears though that the reported lower efficacy of AO-3 and AO-38 [282] during melt-processing must (to an extent) be compensated by a higher activity of P-1. This could explain the higher F# 125 concentration in formulations containing AO-3 and AO-38.

Fragment F# 156 appears to be only formed in formulations containing AO-1 or AO-39 (**Figure 106**). This observation can be generalized to all protective chemicals of the class of Hindered Phenols which are synthesized via the intermediate “Metilox” (AO-39). The proposed reaction sequence is:

Disproportionation of cyclohexadienonyl radical to form quinone methide (R 13.1)
⇩
Equilibrium of quinine methide with cinnamate (R 13.2)
⇩
Hydrolysis of cinnamate (similar to R 14.2)
⇩
Formation of F# 156 from cinnamate (R 15.1)

Scheme 29: Formation of fragment F# 156

This transformation is only plausible for Hindered Phenols which are partially hindered in the *para*-position with a propionic acid or propionic acid ester (**Figure 107**). Although the values quantified for F# 156 are generally low, it is reminded that an auto-accelerating hydrolysis reaction is involved. It seems plausible that hydrolysis of other protective chemicals (see chapter 3.3.4) or other additives present increase the rate of hydrolysis in the reaction sequence outlined above. Equally any procedure employed to modify the properties of PO which involve hydrolysis reactions could increase the rate of hydrolysis to form fragment F# 156 (see **Section 2.3**).

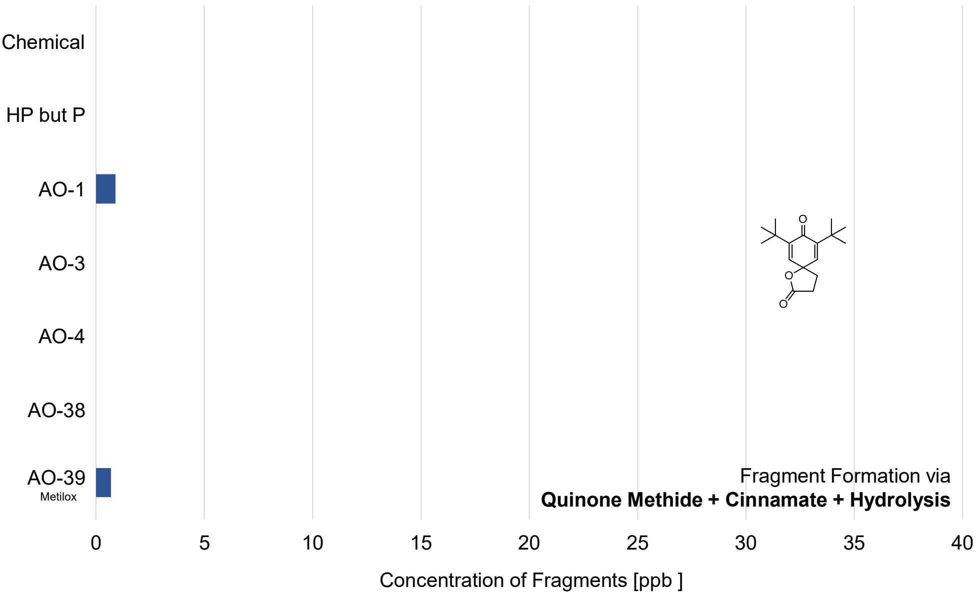


Figure 106: Fragment F# 156 formation via indirect hydrolysis of cinnamate (Structure XXXXV)

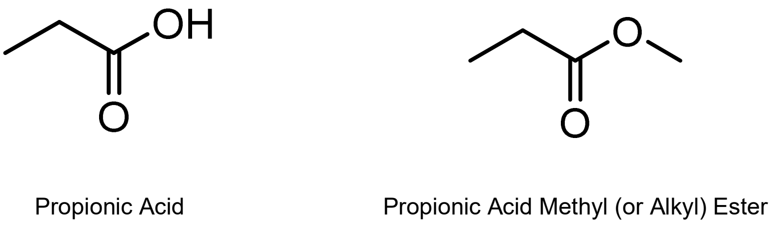
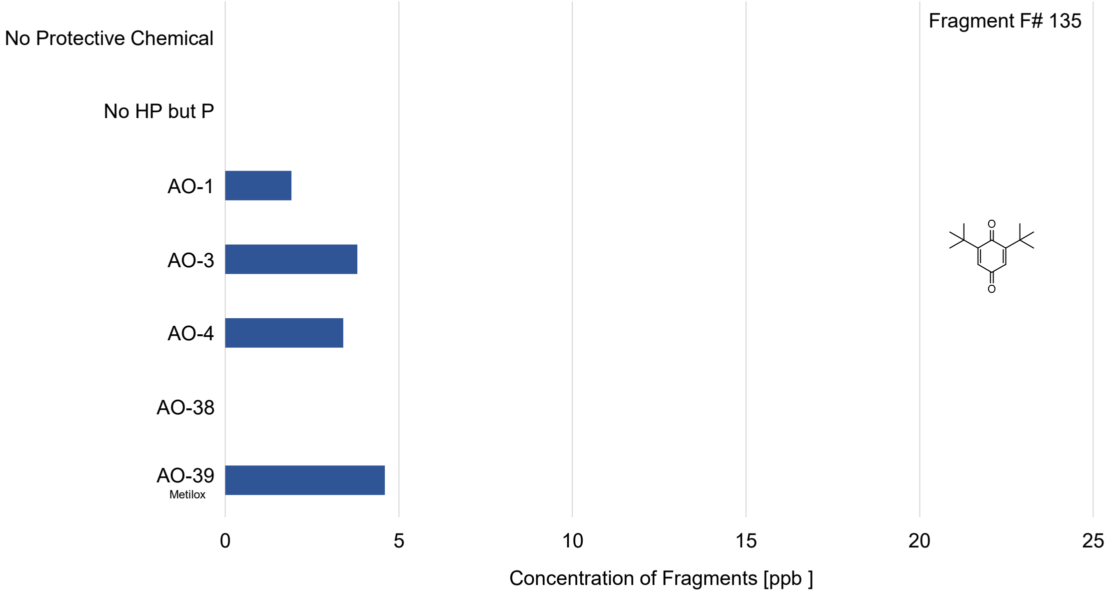
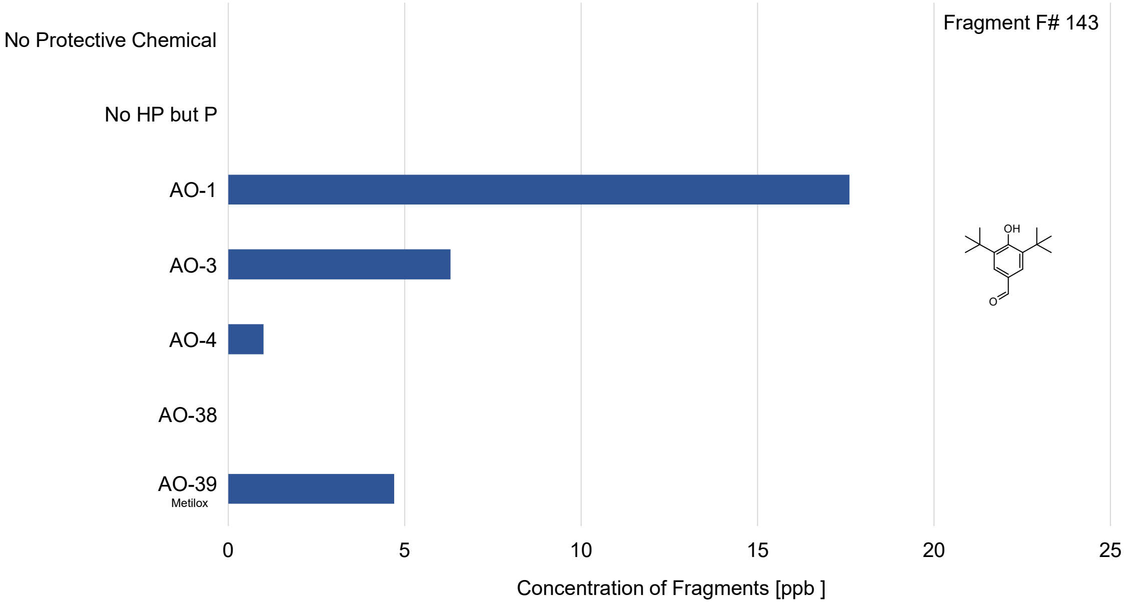


Figure 107: Hinderance of HP in p-position with propionic acid derivatives

For the 2,6-di-*tert*-butyl Hindered Phenols AO-1, AO-3 and AO-4 the relative formation of Fragments F# 135, F# 143 and F# 148 (**Figure 108**) is discussed. Fragment F# 148 is only formed by “Metilox”-based Hindered Phenols. The corresponding aldehyde (F# 143) seems to be formed preferentially by “Metilox”-based Hindered Phenols. By far the lowest tendency of formation is with AO-4. In contrast, formation of F# 135 is the inverse of this; more favoured for AO-3 and AO-4 rather than AO-1. *All three fragments are formed by alternative reaction pathways* *of the thermally unstable structures:* **XXIIX** (**Scheme 9**), **XXXI** (**Scheme 10**) **XXXVI** (**Scheme 11**) **and XXXX** (**Scheme 12**) [71,72].





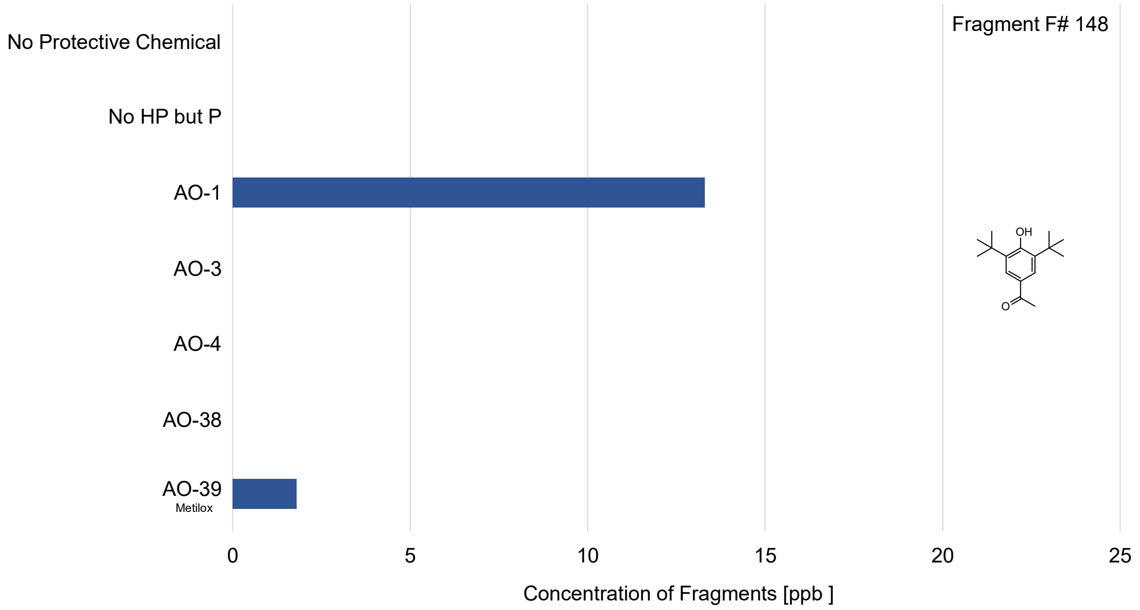
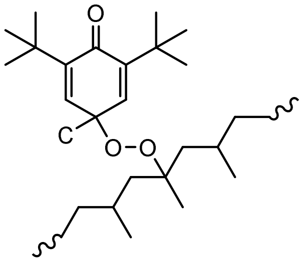


Figure 108: Individual Fragments F# 135, F# 143 and F# 148



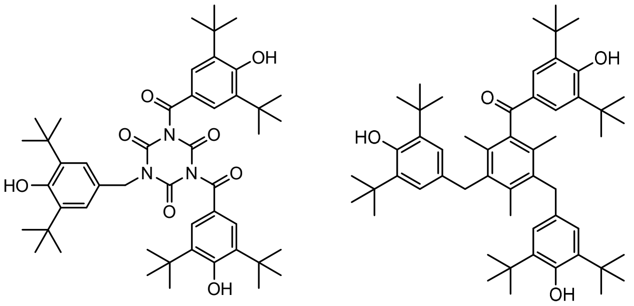
Structure XXIIX
(**Scheme 9**)

Figure 109: Structure XXIIX with generic substituent in para position

Partially Hindered Phenols with a tertiary carbon in β-position and/or a bulky group (such as isocyanurate for AO-3 and mesitylene for AO-4) do not undergo a bond cleavage at the β-carbon, so do not form fragment F# 148. One potential explanation could be the difficult steric access to form an association between the β-carbon and the oxygen of the peroxide group. In contrast, the corresponding HMW ketones that are not cleaved are reported for AO-3 [77] and AO-4 [73,77]. For the same reason, the formation of fragment F# 143 is not favoured but is possible. In this case the scission may occur between the α- and β-carbon. Alternatively, where there are limits to the formation of F# 143 or F# 148 the formation of F# 135 is favoured. This reaction pathway (R 11.3) seems less pronounced for AO-1. **Figure 111** summarises the fragment composition via this reaction pathway. It is noteworthy that AO-39 forms less of the three fragments though the larger quantity (*c.f.* AO-39) of higher MW fragments in **Table 26b** should be noted.

Isocyanurate backbone of AO-3 (N constitutes β-position to phenolic moiety)

Mesitylene backbone of AO-4 (non-substituted C constitutes β-position to phenolic moiety)



“Un-cleaved” para-ketone of AO-3

“Un-cleaved” para-ketone of AO-4

Figure 110: “Un-cleaved” HMW ketones from AO-3 and AO-4 [73,77]

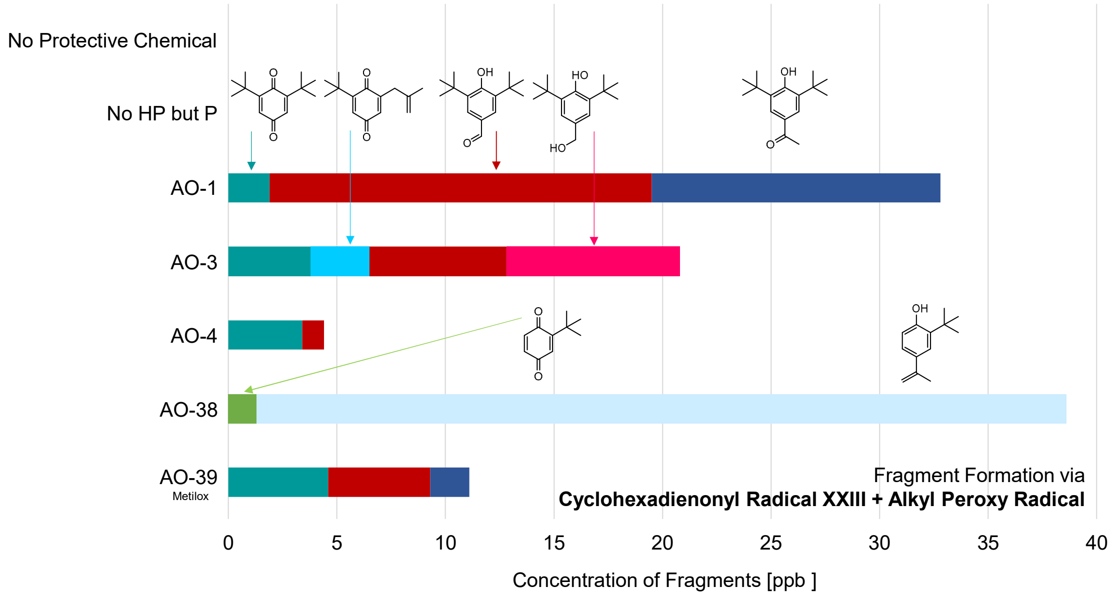


Figure 111: Concentrations (ppb) of fragments formed from various decomposition pathways of structure XXXI (**Scheme 10**) rstructure XXXVI (**Scheme 11**) and structure XXXX (**Scheme 12**)

3.5 General Technologies to Suppress LMW Organic Fragments

Previous sections in this report have investigated how water-extractable organic fragments are formed in stabilised PO, as well as strategies for their suppression. Fragments originating from the PO substrate tend to be mainly oxidised-aliphatic compounds. The correlation between MW and water-extractability (of hydrocarbons) is summarised in **Figure 45** (**Section 3.2**). In contrast, fragments originating from protective chemicals tend to be oxidised-aromatic compounds (as long as the choice of protective chemicals is limited to typical Hindered phenols (e.g., AO-1) and aromatic Phosphites (e.g., P-1)). Several fragments originating from protective chemicals are of higher MW (200 – 300 g mol^{-1}) than the fragments originating from oxidised-aliphatic-compounds (indicated in **Figure 45**).

The purpose of this section in the report is to explore selected strategies for the reduction of (water) extract-able LMW fragments *already generated*. Due to the MW ($\leq C_{20}$-C_{25}) and type of fragments, strategies which are employed for the reduction of volatile organic compounds (VOC), as well as for reduction of odour, could also be used for the reduction of water-extractable organic compounds. Generally, those strategies consist of [290,291]

- Inhibition of formation
- **Devolatilization / washing-off**
- **Physical adsorption**
- Chemical reaction
- Masking
- Offsetting
- Microbial degradation

Today's demands for low emission polyolefins requires a combination of several of the above-mentioned strategies to achieve the required targets [292]. In the following sections two of the strategies will be focussed on; namely, physical adsorption and devolatilization/washing-off.

3.5.1 Scavengers of LMW Organic Compounds

Formulations characterising durable PO applications were prepared according to conditions C-1 and M-1. The selected composition was PP-A + 750 ppm MS-1 + 750 ppm P-1 + 5000 ppm Hindered Phenol. AO-1 and AO-4 were chosen as Hindered Phenols because they resulted in in a significantly different profiles of the fragments formed (**Section 3.4.2**). Two different scavengers of LMW organic compounds were added to the above formulations at 5000 ppm

- Synthetic hydrotalcite (O-3; [295])
- Zeolite (O-4 [296,297])

Both scavengers were used as received (with respect to commercial quality). The scavenger O-3 is generally used in PO applications, whereas the scavenger O-4 is generally used in PVC applications and does not have the appropriate surface treatment for PO (its surface is generally judged too active).

Both formulations containing HP provide sufficient MFI stability during melt-processing. However, the actual MFI value and the colour indicate rather severe processing conditions (**Figure 112**). Addition of O-3 reduces the MFI. This could be explained by the addition of an inorganic material to the PP melt. In contrast, the addition of O-3 to AO-1 reduces MFI, despite the inorganic character of O-4. This could indicate increased chain scission leading to lower MW.

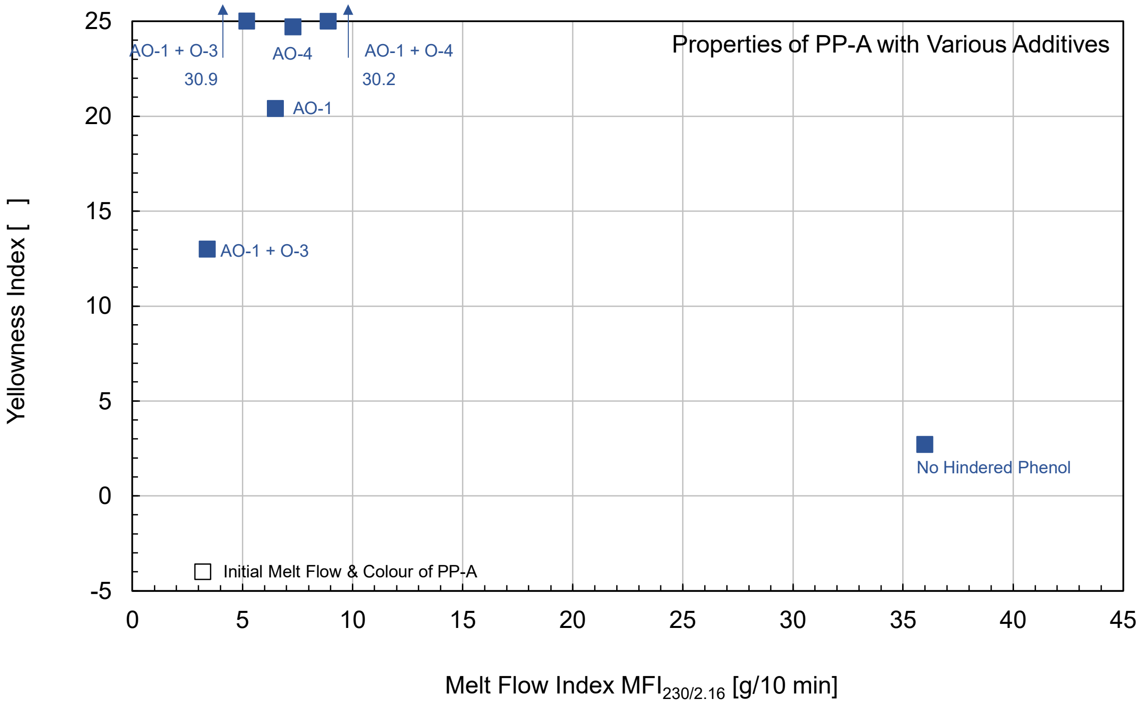
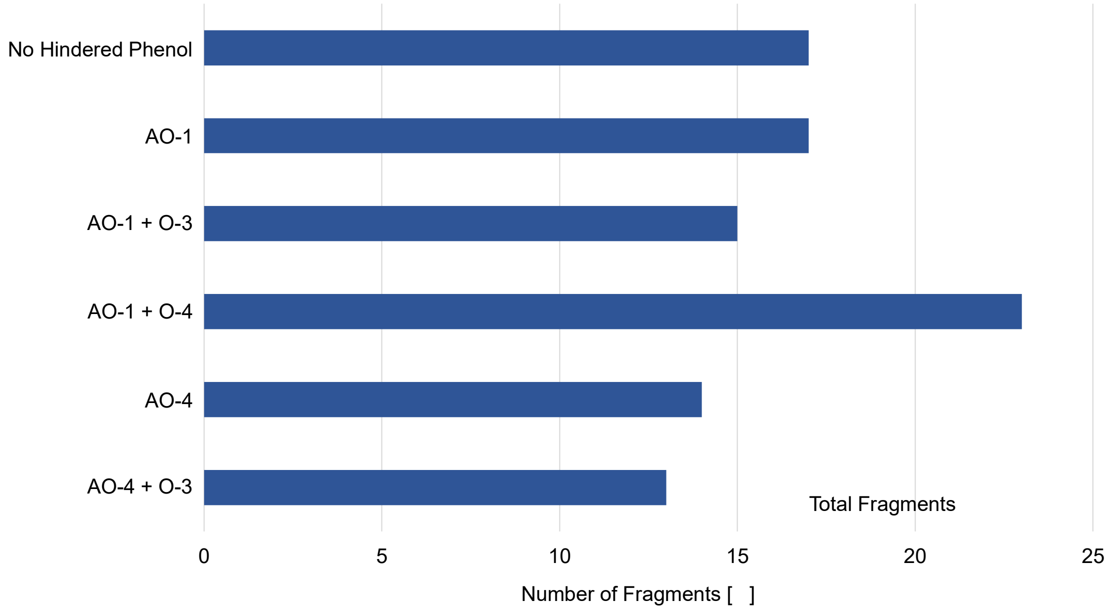


Figure 112: Properties of melt-processed PP in the presence of various classes of protective chemicals as well as scavengers

Extrusion Condition:	C-1, M-1
Extraction Condition:	E-1
Formulation:	PP + 750 ppm MS-1 + 750 ppm P-1 + 5000 ppm Hindered Phenol + 5000 ppm Scavenger



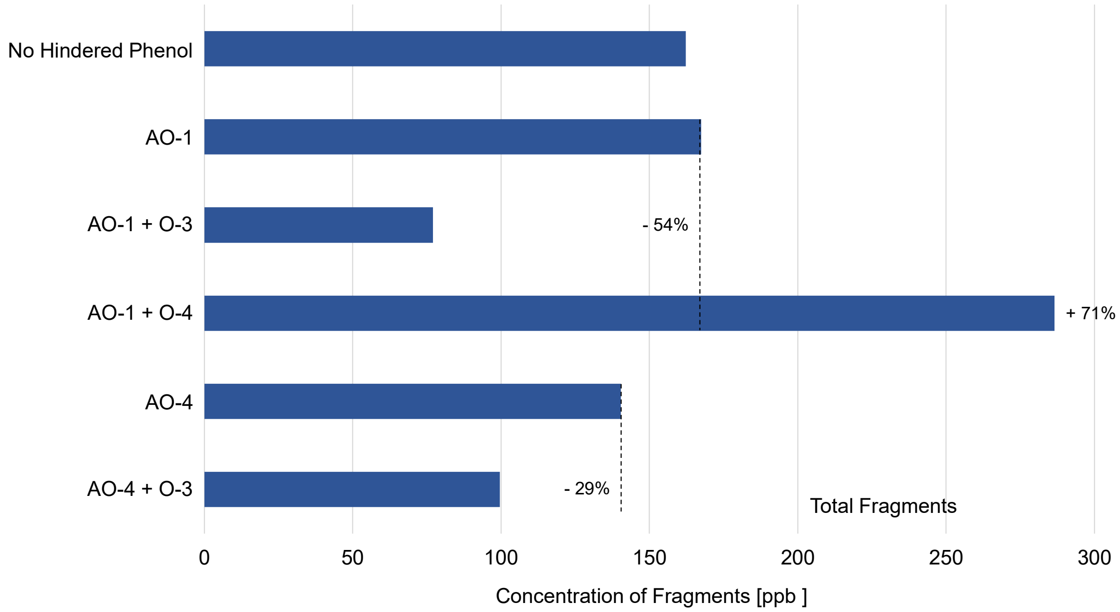
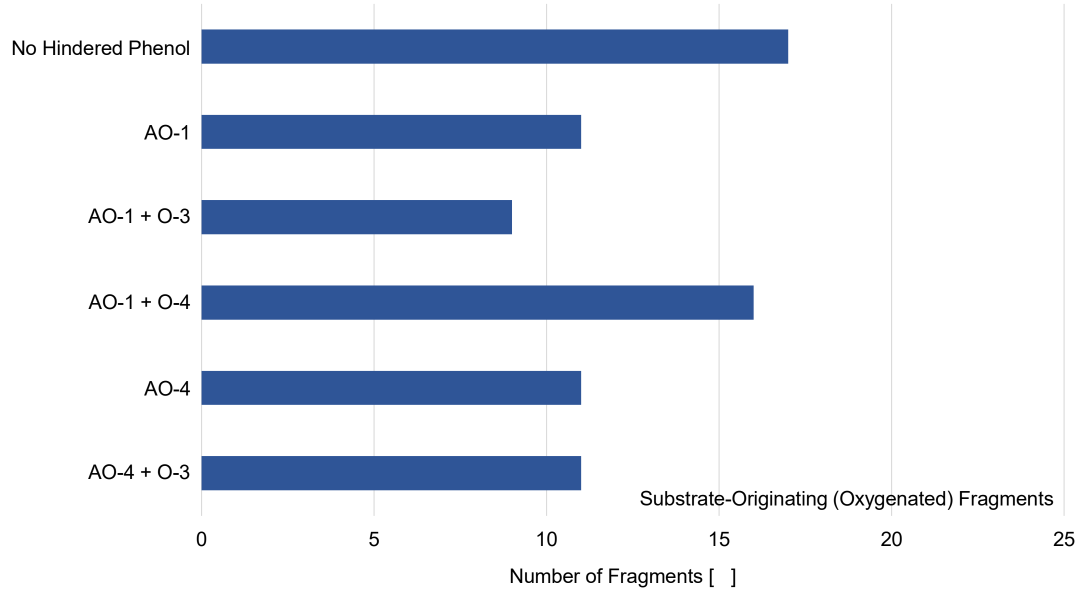


Figure 113: Number (a) and concentration, ppb, (b) of total fragments in the presence of inorganic scavengers

Addition of the scavenger O-3 results in a reduction in the total number and concentration of fragments (**Figure 113**). The reduction is in the range of ~50% (for AO-1) to ~30% (AO-4); with the AO-4 containing formulations at lower level overall. In contrast, addition of O-4 results in a higher number and ~70% higher concentration of fragments. The composition of fragments is dominated by (mainly) oxidised fragments that arise from the polymer substrate (**Figure 114**). The individual fragments are nearly identical to the ones observed in Section 3.2. Two observations are worth noting. Firstly, the very marked reduction (by ~70%) where O-3 is added to AO-1. Secondly, where O-4 is added to AO-1 an increase in the concentration fragments already present, as well as the appearance of four new fragments (**Figure 115**). Although these fragments have not been observed previously, three of the four are of an oxidised-aliphatic nature. *It can be concluded that addition of O-3 reduces fragments originating from the polymer substrate by at least 30%.*



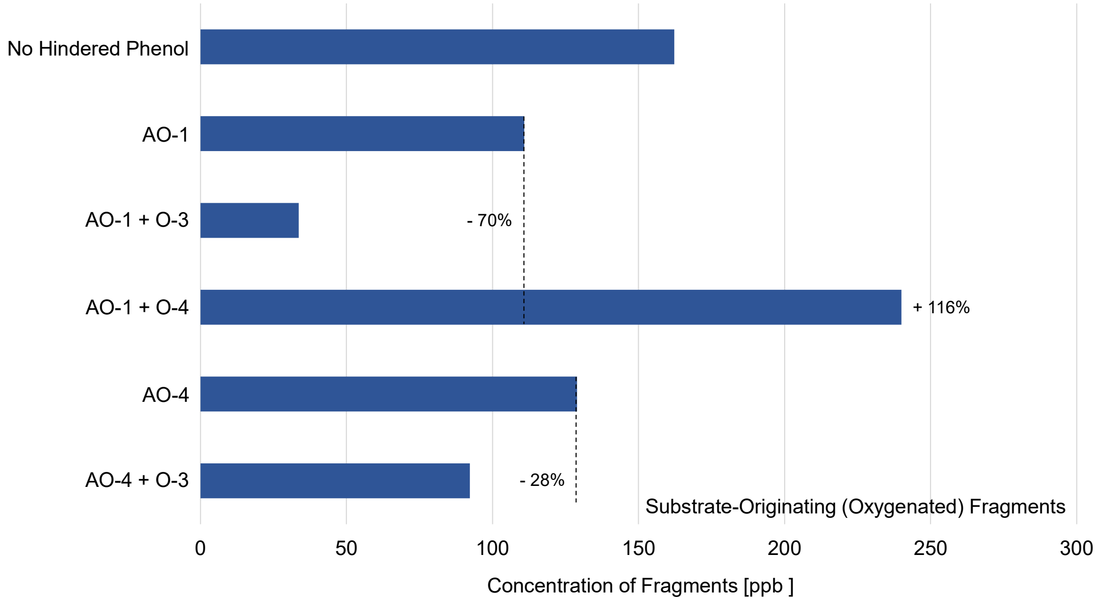


Figure 114: Number and concentration of substrate-originating (mainly oxidised) fragments in the presence of inorganic scavengers

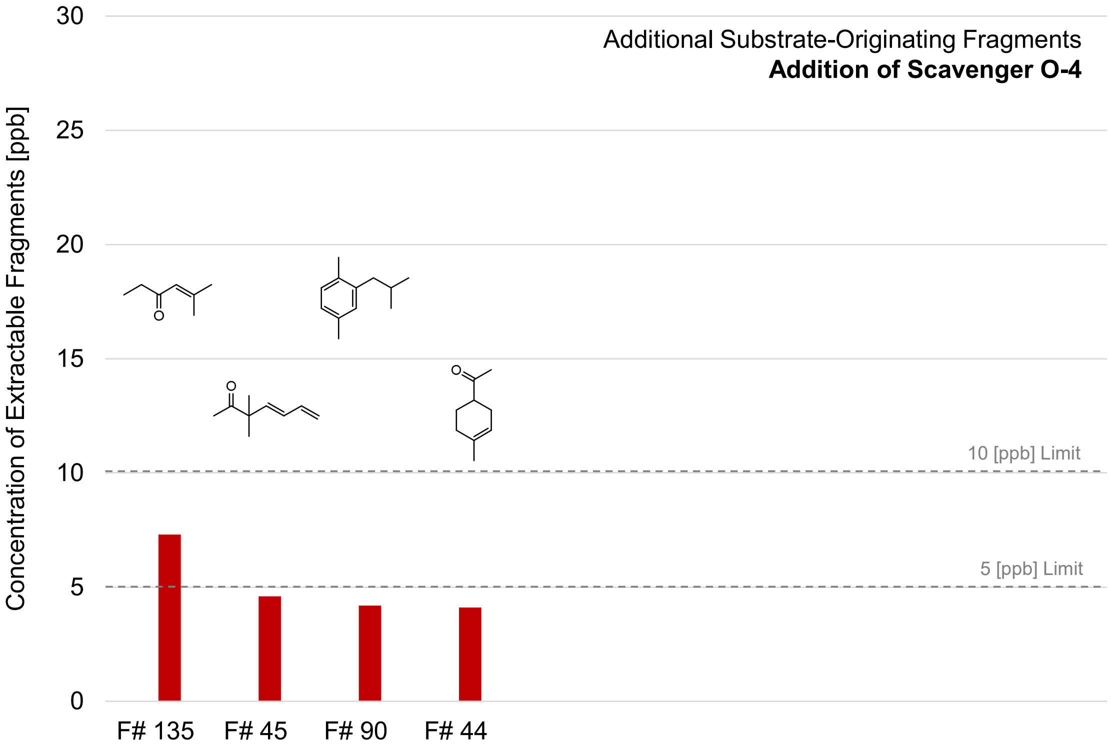


Figure 115: Concentrations (ppb) of additional substrate-originating (and oxidised) fragments in the presence of inorganic scavengers

Fragments originating from protective chemicals do not decrease in number when an inorganic scavenger is added. This statement is true for both, O-3 and O-4 **(Figure 116)**. Both inorganic scavengers are responsible for the appearance of new fragments. In the case of O-3, fragment F# 165 is detected (Figure 3-85). This fragment has already been seen earlier (Section 3.3.5), but only under conditions of hydrolysis of an additive in the formulation. It originates most likely from the antacid MS-1. Addition of O-4 results in the appearance of partially dealkylated HP-type fragments (F# 21a and F# 63). These fragments (or their isomers) originate from the dealkylation of a 2, 4-di-alkyl- and a 2, 6-di-alkyl- Hindered Phenol. The dealkylation takes place at the surface of an inorganic additive (e.g., talc, O-4) due to the composition of the additive itself, or impurities in the additive (e.g. metal ions). It is likely that some part of the composition acts in a catalytic way for the degradation of the antioxidants [298-300].

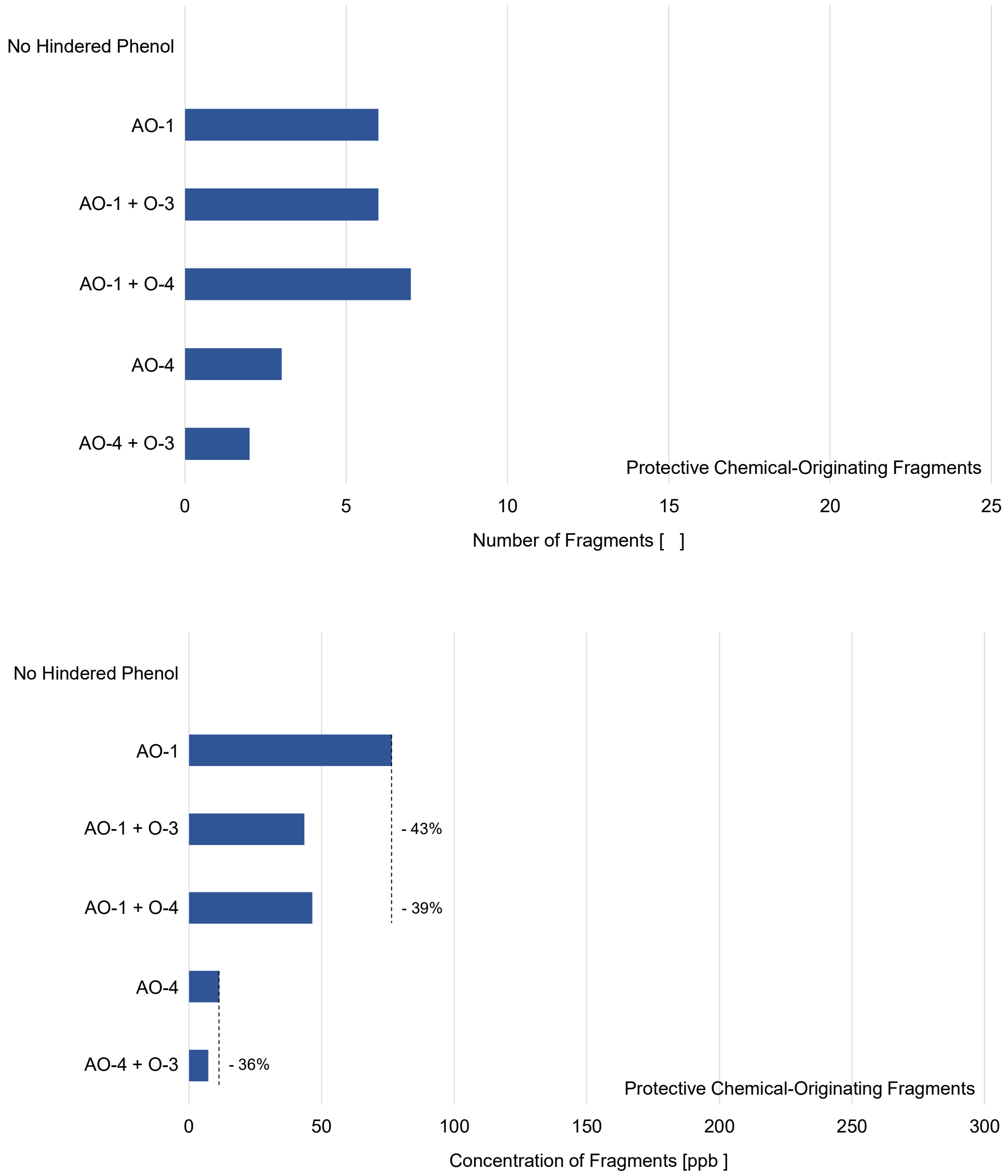
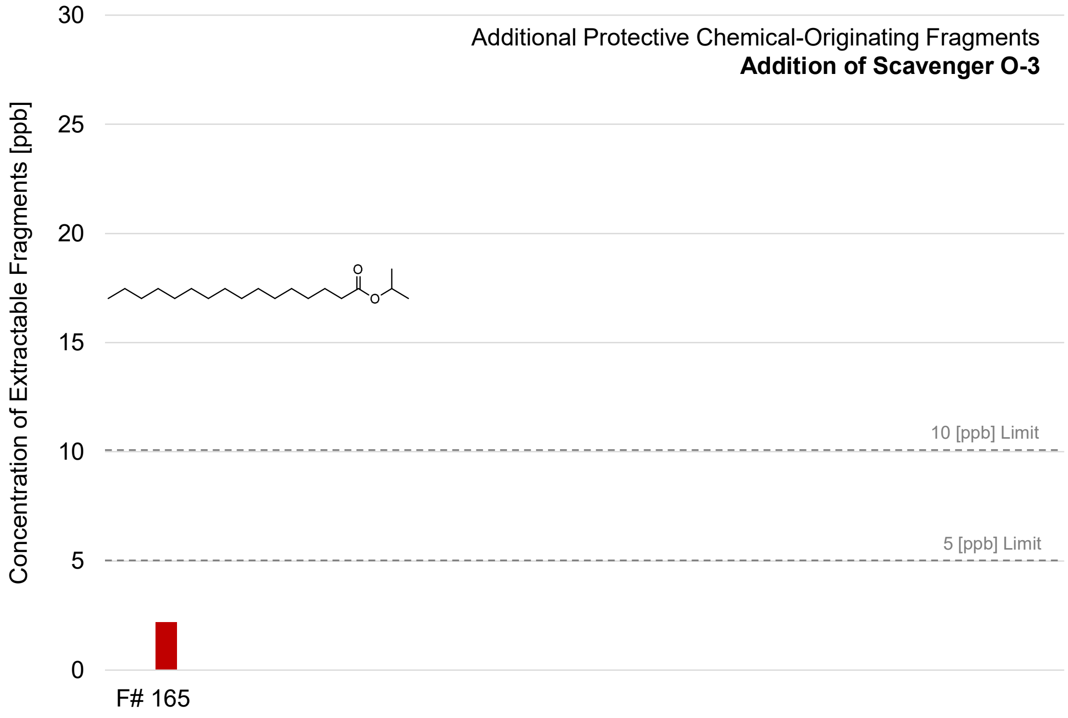


Figure 116: Number (a) and concentration, ppb, (b) of protective chemical-originating fragments in the presence of inorganic scavengers



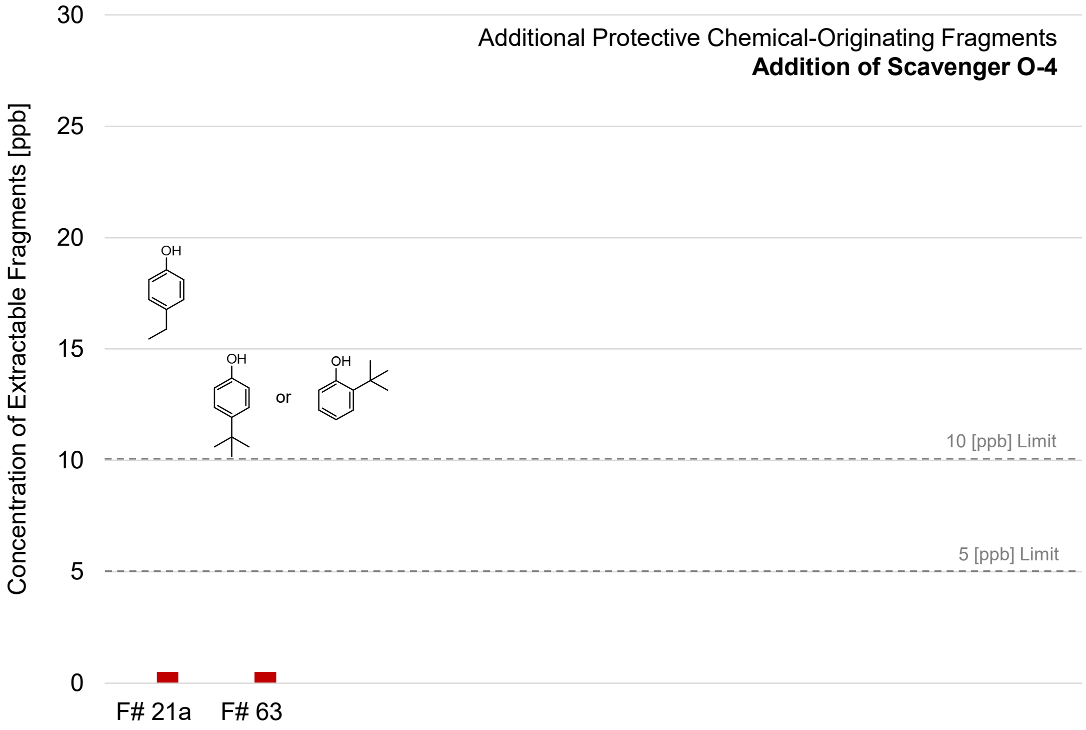


Figure 117: Concentration (ppb) of protective chemical-originating fragments in the presence of inorganic scavengers O-3 (top chart) or O-4 (lower chart)

It should be noted that fragment F# 142 has a LD of 20 ppb and LQ of 100 ppb. As earlier, F# 142 was detected but could not be quantified. Its actual concentration is between 20 and 100 ppb. For practical reasons, in **Figure 118** and **Figure 119**, 20 ppb are indicated. Nevertheless, it is assumed that F# 142 is present in other formulations, but below its LD. F# 156 and F# 163 are present at elevated, though low, concentration in the presence of O-3. The formation of F# 156 involves a hydrolysis reaction. F# 163 is most likely present as unreacted intermediate but, it could be formed via hydrolysis and/or transesterification.

There is also evidence [300] that insufficient metal soap (e.g., MS-1 or acid scavenger in general) leads to a de-alkylation of the tertiary butyl groups of Hindered Phenols due to the activity of the catalyst residues.

Fragment F# 125 from the Phosphite P-1 is increased in the presence of O-3 (**Figure 118**). Together with the appearance of fragment F# 165 and the elevated concentration of F# 156 (which involve hydrolysis reactions for its formation; **Figure 119**), collectively this data suggests an *O-3 induced hydrolysis of selected protective chemicals.*

Figure 119 displays distinct differences in the fragment mix resulting from the Hindered Phenols AO-1 (**Figure 119a**) and AO-4 (**Figure 119b**). In the presence of AO-1, a higher number and significantly higher concentration of fragments is present without addition of inorganic scavengers (blue bars). Fragment F# 142 is detected again in a formulation containing a high concentration of AO-1 (5000 ppm), which is judged (based on MFI and colour data) as “severe” processing.

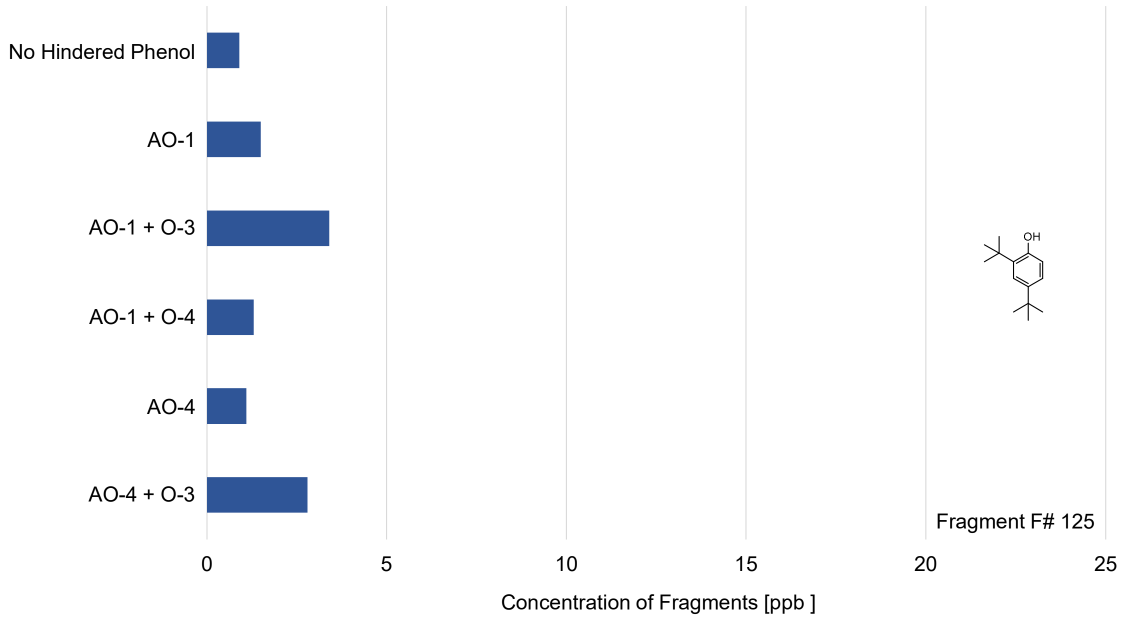
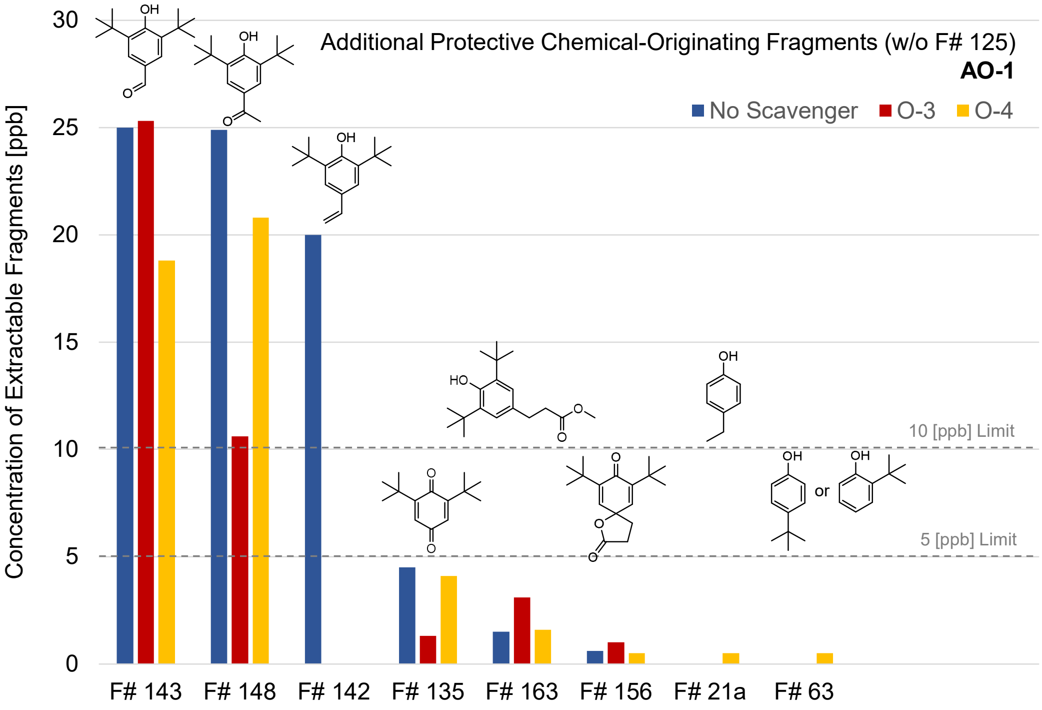


Figure 118: Fragment F# 125 in the presence of inorganic scavengers



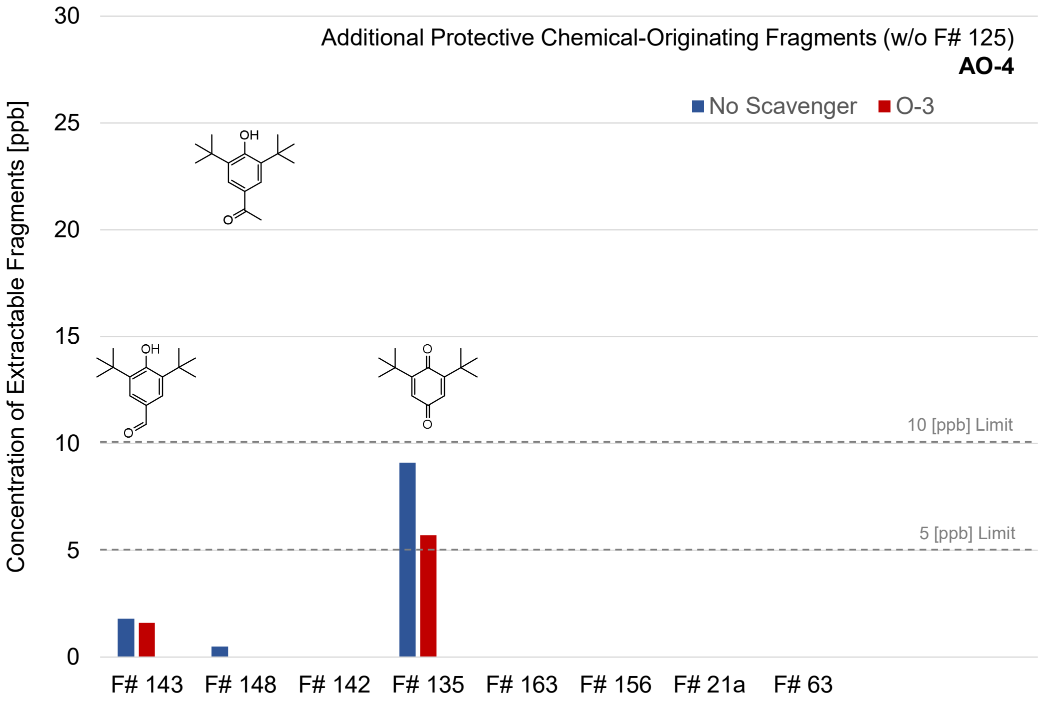
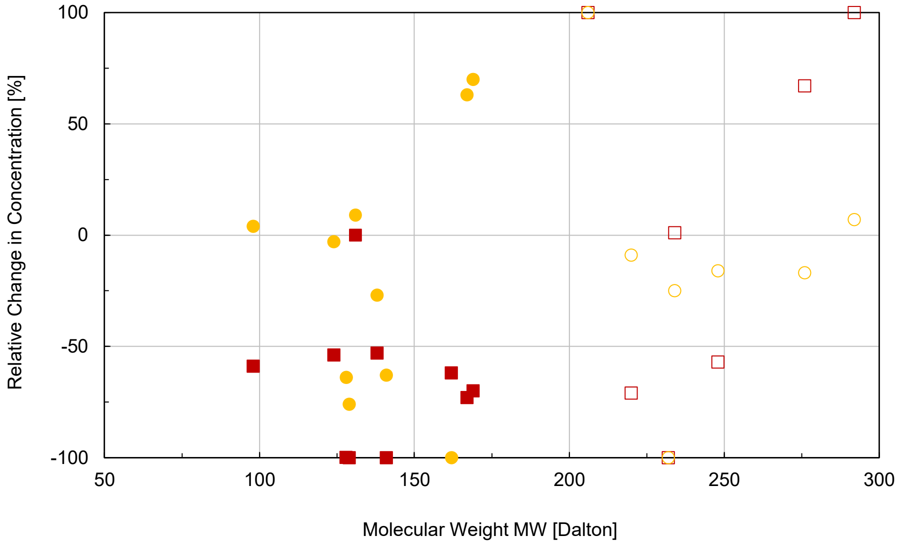


Figure 119: Concentrations (ppb) of fragments from AO-1 and AO-4 in the presence of inorganic scavengers

Again, this points towards an *O-3 induced hydrolysis of selected protective chemicals*. Neither fragments can be formed in AO-4 due to a different synthetic route. *For both Hindered Phenols, the addition of O-3 decreases fragment F# 135 but not fragment F# 143*. The reason for this is not clear. Fragment F# 148 (disfavoured in AO-4) decreases in the presence of O-3. Overall, it can be concluded that the addition of O-3 seems has a specific role in the formation of fragment F# 135. O-4 shows a similar but less pronounced trend. However, it is reminded that two additional fragments (F# 21a and F# 63) are formed.



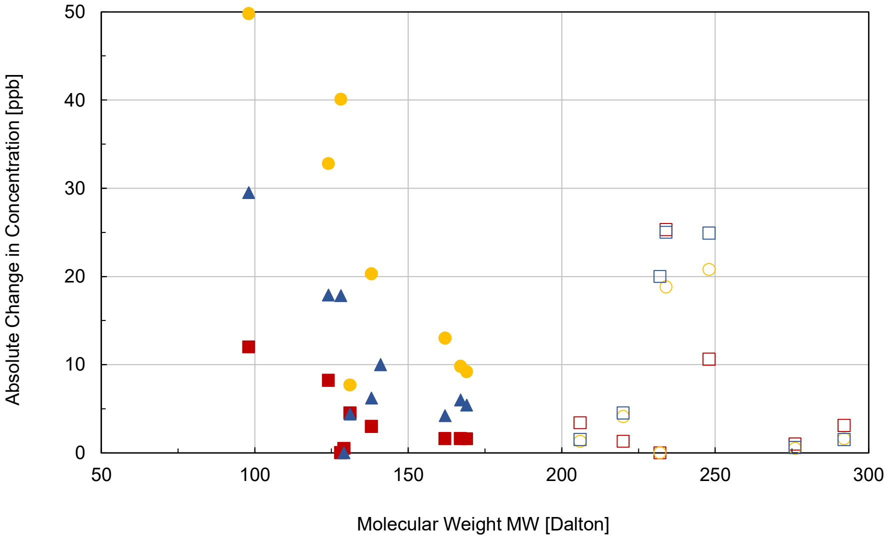


Figure 120: Relative (top) and absolute (bottom) change in concentrations (ppb)of fragments as a function of MW

Figure 120 illustrates the general trend for the addition of O-3 (**red**) and O-4 (**orange**) to a formulation containing AO-1 (**blue**). For absolute concentrations of fragments, the *addition of O-3 yields a general and non-specific reduction of fragments with a MW below ~175 g* mol^{-1}. On a relative scale, the reduction is in general in the range of ~50%. Below this MW, fragments are mainly oxidised-aliphatic compounds, while above 175 g mol^{-1} they are exclusively oxidised-aromatic compounds. In this range only the specific fragments F# 135 and F# 148 are reduced. The reason for this observation is not understood. Ironically, *O-4 seems to create more oxidised aliphatic fragments, but consistently reduces oxidised-aromatic fragments; the latter not formed by hydrolysis*.

O-3 (synthetic hydrotalcite) is an already known antacid in several PO applications where fatty acid salts (such as MS-1) cause problems [301]. As well as this neutralising function it can, by the same mechanism, scavenge LMW organic fragments up to a MW of ~175 g mol^{-1}. The latter effect is reported to be even stronger with activated carbon black [302]. This contrasts with the experimental results in this thesis for the zeolite O-4 (which is not PO quality and most likely comprises an insufficient surface treatment of the particle). Here there is in an increase in the number and concentration of fragments (especially below ~175 g mol^{-1}), yet zeolite is mentioned in literature as an effective scavenger [294,303-305]. Zeolite is though reported to be less effective than activated carbon [294]. Several additional scavengers have been reported [307-309][2].

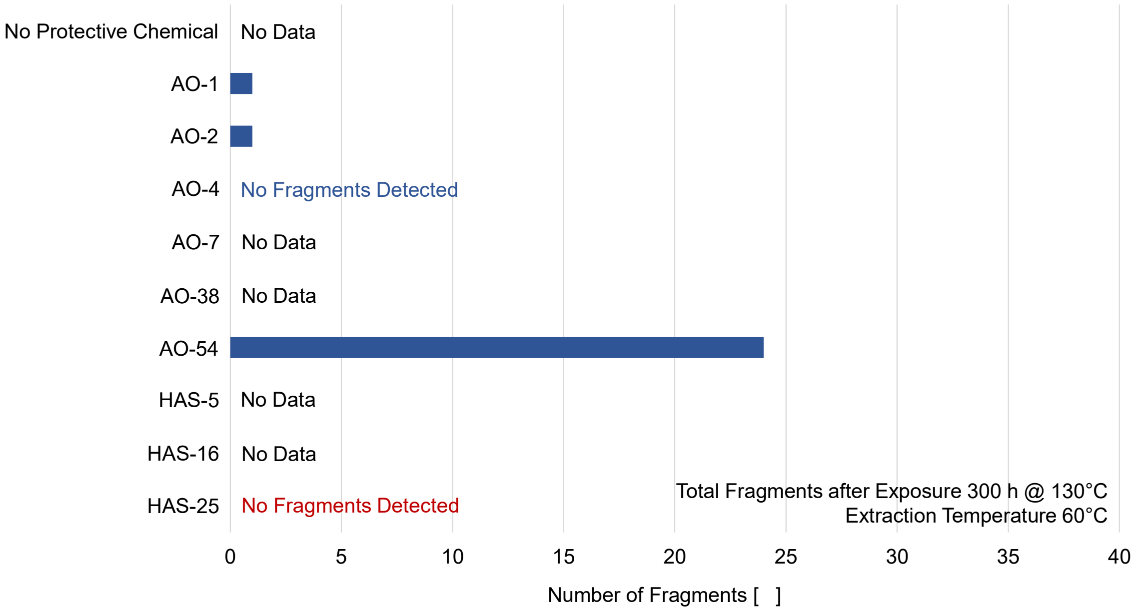
In order to reduce the high surface activity of many potential inorganic scavengers, a technology transfer from talc-filled PP is proposed [306], where an intentional surface treatment of the filler is carried out with carboxylic acid derivatives (such as benzoic acid, glycerol monostearate or 13-docosenamide); or alternatively with selected aliphatic amides (such as ethylene bisstearylamide, [ethylene bisstearylamide + oligomeric acrylester] or [ethylene bisstearylamide + dodecenylsuccinin anhydride]. In all these cases care has to be taken that no additional water-extractable fragments are generated via the surface treatment.

3.5.2 Thermal Treatment of LMW Fragments

The limit in **Figure 45** (between loss of LMW fragments via volatilization or extraction) can be moved to higher MW by a modest increase in temperature. In fact, it is reasonable for experiments described in this thesis many organic fragments below a MW of 100 g mol^{-1}, which are formed during melt-processing, *volatilise in an uncontrolled manner*. This is due to the 'open' set-up of the melt-processing equipment including subsequent cooling. Prior investigations where the gas-phase above the oxidising PP is controlled confirm this statement [129,130].

Selected samples (**Figure 100**, **Section 3.4.2**) were taken out of the oven after 300 hours of exposure at 130°C. The granular samples were analysed according to the extraction condition E-4 (at 60°C). A very low number and low concentration of fragments was detected for formulations which contained AO-1, AO-2, AO-4 or HAS-25 (**Figure 121).** In fact, the level is lower than the calculated (and hence expected minimum) concentration from **Figure 96** (data extrapolated from 20°C to 60°C). Overall, a reduction of water-extractable fragments is observed, despite the fact the PP substrate continues to oxidise. One explanation could be that the LMW fragments that already exist volatilise during the long timespan of 300 hours at 130°C (compared to several minutes residence time during melt-processing). Additionally, it is postulated that the rate of formation of new fragments that can volatilise is slower than the corresponding rate of volatilisation. In consequence, the concertation decreases.

The major exception is the formulation containing AO-54, which results in a high number and concentration of fragments. The majority (> 75%) of the fragments detected are of an oxidised-aliphatic nature; though some are different than those reported previously during melt-processing. In contrast to related work [129,130], the fragments detected cannot volatilise at 130°C. This observation corresponds with the established endpoint determination for the onset of (macroscopic) degradation of the PP sample. This is designated as ~290 hours (**Figure 100**); just before the sampling at 300 hours.



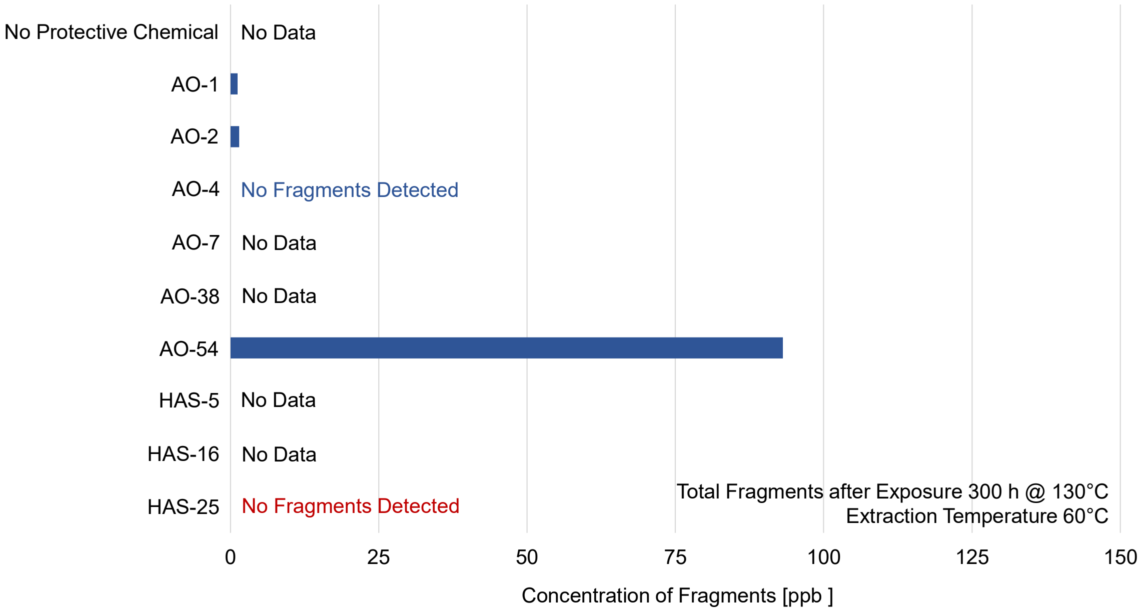


Figure 121: Number and concentration (ppb) of total fragments of selected protective chemicals after LTTS of 300 hours

Compounding Condition:	C-1
Exposure:	Granules from C-1 at 130°C in circulating hot air oven for 300 hours
Extraction Condition:	E-4 (60°C)
Formulation:	PP + 750 ppm MS-1 + 1000 ppm protective chemical

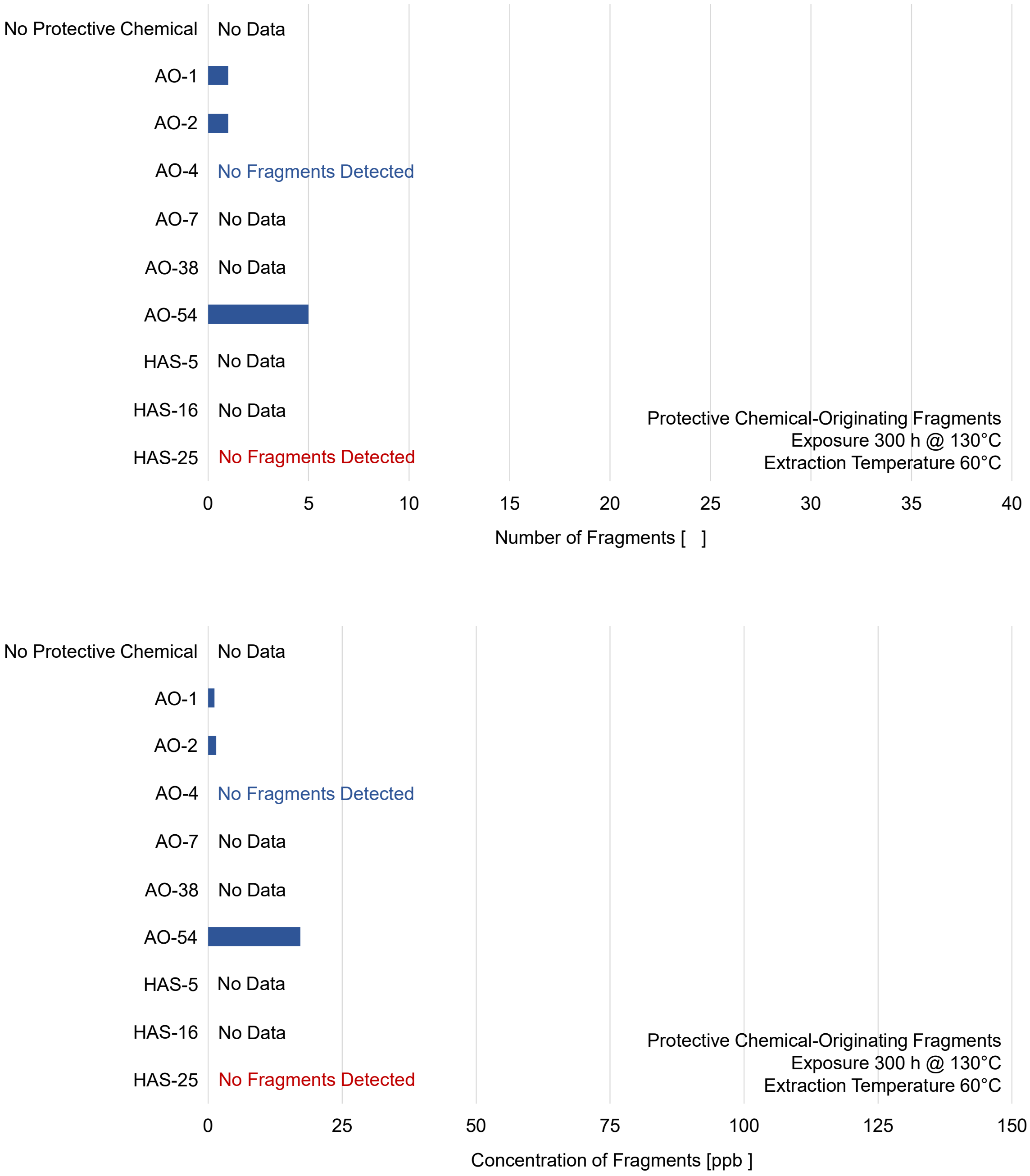


Figure 122: Number and concentration (ppb) of protective chemical-originating fragments after LTTS of 300 hours

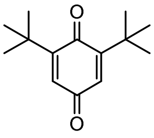
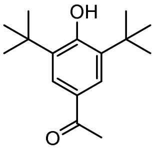
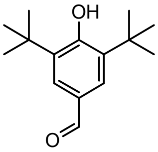
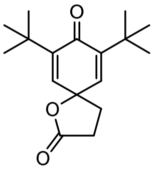
Compounding Condition:	C-1
Exposure:	Granules from C-1 at 130°C in circulating hot air oven for 300 hours
Extraction Condition:	E-4 (60°C)
Formulation:	PP + 750 ppm MS-1 + 1000 ppm protective chemical

It should be remembered that no fragments originating from protective chemicals are detected in the formulation containing AO-54 (at an extraction temperature of 20°C) directly after processing. After 300 hours exposure at 130°C, no fragments at all are detected for HAS-25 and AO-4. While for HAS-25, directly after melt-processing, several synthetic by-products but not transformation product are detected. One fragment (F# 148) is detected for both AO-1 and AO-2. For AO-54, a total of four fragments are identified (**Table 27**). The fragments are related, but not identical to, F# 135, F# 143 and F# 156. Only F# 148 is identical.

Two observations are worthy of attention. First, if the protective chemical is still active (and not yet consumed), very few fragments are detected during water-extraction. This is probably because volatilization of the fragments formed takes place at the testing temperature of 130°C. Secondly, in line with **Figure 45**, a thermal treatment of the PP granules in the solid state (below the melting range of PP) is proposed to decrease water-extract-able fragments. The suggested temperature should be slightly above room temperature in the range 50°C - ≤ 90°C. Below 50°C, no decrease of fragments is observed with these formulations [292]. Above 90°C, oxidative degradation of PP might accelerate so much, that too many transformation products of (in particular) Hindered Phenols are formed.

Another general approach is to volatilise or 'flush-off' and fragments formed. More volatile substances volatilise during melt conversion conditions (such as water, nitrogen, carbon dioxide) or specific stripping agents [294]. In addition, an *intentional and controlled* degassing or devolatilization step of the polyolefin product (mandatory degassing extruders) would lead to a reduction in the water-extractable fragments [295]. Previous work [208] implies that flushing of a PO pipe results in a significant decrease in water-extractable fragments (independent of their chemical nature). Here flushing increases the migration rate of the fragments to the surface of the plastic article and into the water, because fragments are below their solubility limit in the dynamic flow as opposed to stagnation

Table 27: Identified protective chemical-originating fragments after LTTS

Fragment	*AO-1*	*AO-2*	*AO-4*	*AO-54*	*HAS-25*
 F# 135				**5.0** Coelution of similar fragments	
 F# 148	**1.2**	**1.5**		**1.5**	
 F# 143				**5.0** Coelution of similar fragments	
 F# 156				**0.5** Coelution of similar fragments	

4 Hazard Assessment of Selected Fragments

In total more than 200 fragments were detected during this investigation, out of which ~20% have not yet been identified. It is beyond the scope of this research to assign all fragments and their hazard.

In this report several steps towards a preliminary self-assessment of hazard have been undertaken. In the first step, fragments with (suspected) CMR properties were identified. This was undertaken irrespective of the fact that concentration of such fragments should be zero in water (**Table 28**). **Table 28** is a shortlist of the overview of all fragments (**Appendix 7.3**). In total 29 fragments are listed as (suspected) CMR in the consulted sources of ECHA (EU) and the National Institute of Health (USA) [310,311]. Two fragments are solvents, two aliphatic, eighteen aliphatic-oxygenated and seven fragments (potentially) originating from protective chemicals. No further investigation or interpretation is carried out on these fragments other than the highlighting their possible presence.

In the second step, the 10 oxidised-aliphatic and 10 oxidised-aromatic fragments having the highest concentration (within the context of the investigation) are focussed on. **Figure 123** indicates the 10 oxidised-aliphatic fragments. The concentration range is 70 to 15 ppb. The concentrations refer to PP without or insufficient concentration (< 1000 ppm) of protective chemicals. It is of importance that most fragments can be completely suppressed via the addition of a protective chemical that is effective during melt-processing. This observation results in the conclusion that *PO cannot be processed without the presence of protective chemicals.* **Figure 124** illustrates the worst-case situation for oxidised aromatic fragments originating from protective chemicals. ***Figure 124*** *lists the highest concentration of the 10 specifically selected fragments quantified in this study. Here it should be noted, that within the scope of this investigation, formulations have been selected which are known to yield (high) concentrations of (specific) fragments.* Several formulations are intentionally not representative for formulations used in industrial practice. Given the nature of additives which are incorporated into PO, by adding less of the relevant parent protective chemicals, fragments can be easily minimized. Nevertheless, in this study, the observed range is from ~350 to 5 ppb.

In the third step, whether the fragments are intentionally added or are NIAS has been assessed as well as suspected CMR properties (**Table 30** and **Table 31**).

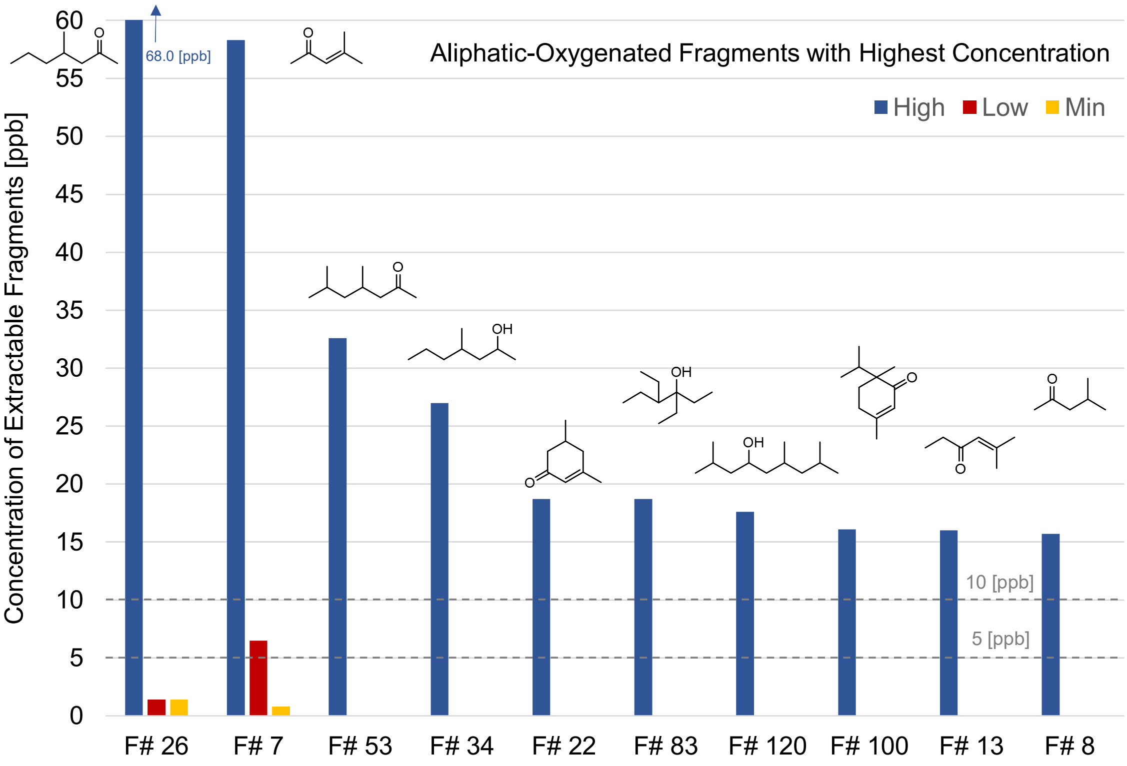


Figure 123: Concentration (ppb) of fragments from 10 key oxidised-aliphatic fragments
Highest concentration quantified in this study
Lowest concentration quantified within the same experiment than above
Minimum concentration quantified in the entire study

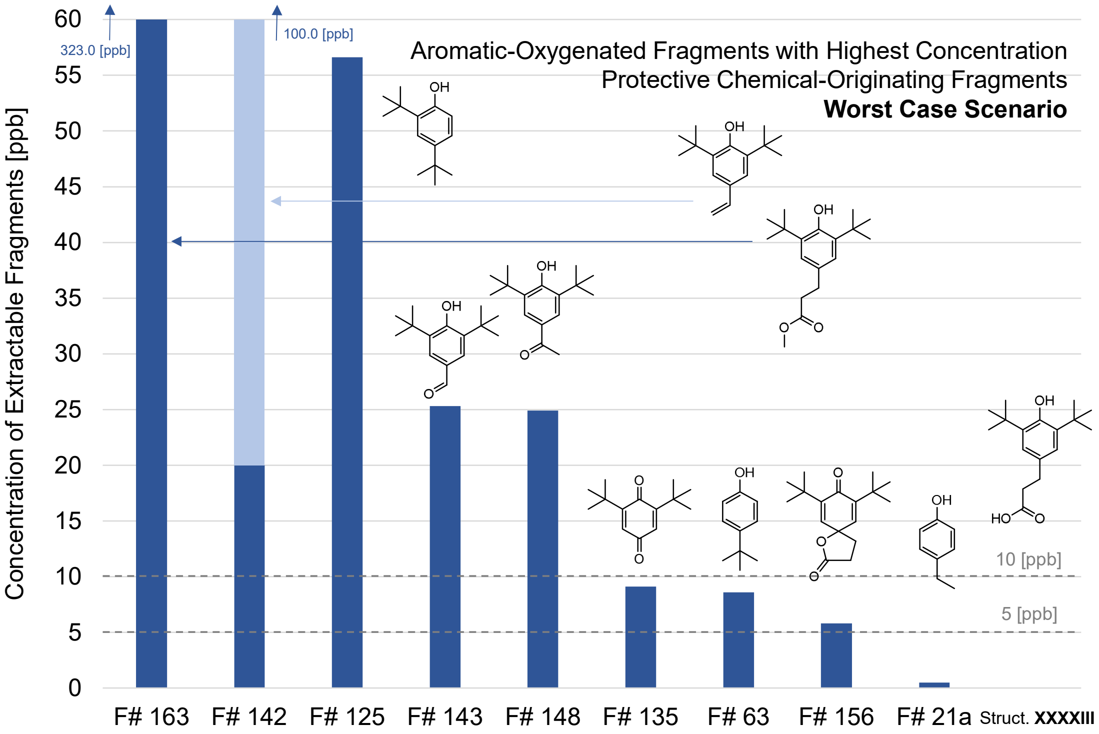


Figure 124: Concentration (ppb) of fragments from 10 key oxidised-aromatic fragments

All but two fragments are considered as NIAS. The fragments originating from protective chemicals F# 125 and F# 163 are considered NIAS as the fragments represent intermediates for the synthesis of the parent protective chemicals. Both are generally present in commercial qualities of the parent protective chemical (P-1 for F# 125 and AO-1 or AO-2 for F# 163). The oxidised-aliphatic fragments are listed neither in the draft of the positive list of the new European drinking water directive [312,317], nor in the positive list for indirect food contact of organic materials [313]. This is not a surprise, as the all the fragments are NIAS. In the absence of relevant information on the fragments, a **self-assessed the Cramer Class** has been made and from this classification the maximum allowed daily intake of the fragments has been derived; the so-called TTC (threshold of toxicological concern) [354]. This assessment is based on a generic person with an average body weight of 60 kg who drinks 4 litres of water per day (**Table 29**). The oxidised-aliphatic fragments not suspected as CMR are assigned to Cramer Class 1.

For all the oxidised-aromatic fragments and, fragments originating from protective chemicals, selected European countries have proposed a draft with concentration limits. The concentration limits are defined as MTC_{tap}, which is defined as maximum tolerable concentration at the tap [317]. *Note again, that the extraction conditions in this study (including a potential pre-treatment of samples) and in the proposed draft are significantly different. Any assessment is therefore relative, and a direct comparison of absolute values cannot be undertaken*.

Table 29: Cramer Class classification

Cramer	***Description***	***TTC*** [µg/day] [µg/kg of body weight/d]
Class 1	Substances of simple chemical structure with known metabolic pathways and innocuous end products which suggest a low order of oral toxicity	1800 30
Class 2	Substances that are intermediate. They possess structures that are less innocuous than those in Class 1 but they do not contain structural features that are suggestive of toxicity like those in Class 3	540 9
Class 3	Substances with chemical structures that permit no strong initial impression of safety and may even suggest a significant toxicity	90 1.5

Table 28a: Fragments with (suspected) CMR properties

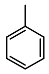
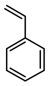
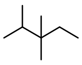
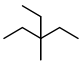
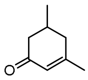
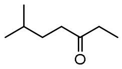
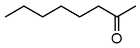
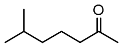
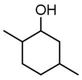
Fragment #	***Chemical Name***	***Molecular Weight*** *[g mol^{-1}]*	***Chemical Structure***	***Remark***
5	Toluene ***108-88-3*** C_7H_8	92		**H225**, **H304**, **H315**, H319, **H336**, **H361d**, **H373**, H412 Suspected **Toxic for Reproduction**
9	Styrene ***100-42-5*** C_8H_8	104		**H226**, **H315**,H304, **H319**, **H332**, H335, **H361d**, **H372**, H412 Suspected **Toxic for Reproduction**
16	Pentane,2,3,3-trimethyl- *or isomer* ***560-21-4*** C_8H_{18}	114		H225, H304, H315, H336, H400, H410 Suspected **cat. 1A or 1B CMR**
17	Pentane,3-ethyl-3-methyl- ***1067-08-9*** C_8H_{18}	114		H225, H304, H315, H336, H400, H410 Suspected **cat. 1A or 1B CMR**
22	2-Cyclohexen-1-one, 3,5-dimethyl- ***1123-09-7*** $C_8H_{12}O$	124		Suspected **cat. 1A or 1B CMR**
28	3-Heptanone,6-methyl- ***624-42-0*** $C_8H_{16}O$	128		Suspected **cat. 1A or 1B CMR**
29	2-Octanone ***111-13-7*** $C_8H_{16}O$	128		H226 Suspected **cat. 1A or 1B CMR**
30	2-Heptanone,6-methyl- ***928-68-7*** $C_8H_{16}O$	128		H226 Suspected **cat. 1A or 1B CMR**
31	2,5-Dimethyl cyclohexanol ***3809-32-3*** $C_8H_{16}O$	128		H225, H227, H315, H319, H335 Suspected **cat. 1A or 1B CMR**

Table 28b: Fragments with (suspected) CMR properties (cont.)

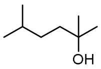
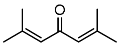
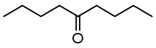
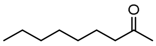
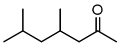
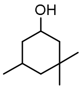
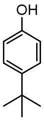
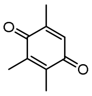
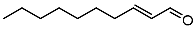
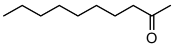
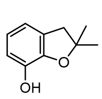
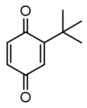
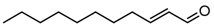
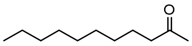
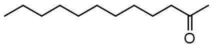
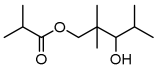
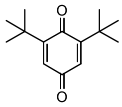
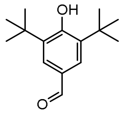
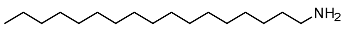
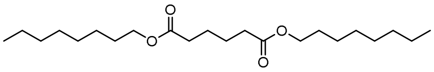
Fragment #	***Chemical Name***	***Molecular Weight*** *[g mol^{-1}]*	***Chemical Structure***	***Remark***
32	2-Hexanol,2,5-dimethyl-, (S) *or isomer* ***3730-60-7*** $C_8H_{18}O$	130		H226, H302, H315, H318, H335 Suspected **cat. 1A or 1B CMR**
40	Phorone ***504-20-1*** $C_9H_{14}O$	138		Suspected **cat. 1A or 1B CMR**
49	5-Nonanone ***502-56-7*** $C_9H_{18}O$	142		H226, H319, H335, H336, H372 Suspected **cat. 1A or 1B CMR**
50	2-Nonanone ***821-55-6*** $C_9H_{18}O$	142		H315, H319 Suspected **cat. 1A or 1B CMR**
53	2-Heptanone,4,6-dimethyl- ***19549-80-5*** $C_9H_{18}O$	142		H226, H335 Suspected **cat. 1A or 1B CMR**
55	Cyclohexanol,3,3,5-trimethyl-, trans- ***767-54-4*** $C_9H_{18}O$	142		H315, H319, H412 Suspected **cat. 1A or 1B CMR**
63	Tert.-butyl-phenol **ARVIN 2** ***98-54-4*** $C_{10}H_{14}O$	150		**H315**, **H318**, **H361f**, **H410** Suspected **Toxic for Reproduction** Suspected **Endocrine Disruptor**
66	2,3,6-Trimethyl-p-benzoquinone ***935-92-2*** $C_9H_{10}O_2$	150		**Skin sensitizer** Suspected **cat. 1A or 1B CMR**
75	2-Decenal, (E)- ***3913-81-3*** $C_{10}H_{18}O$	154		H315, H319 Suspected **cat. 1A or 1B CMR**
78	2-Decanone ***693-54-9*** $C_{10}H_{20}O$	156		H411 Suspected **cat. 1A or 1B CMR**

Table 28c: Fragments with (suspected) CMR properties (cont.)

Fragment #	***Chemical Name***	***Molecular Weight*** *[g mol^{-1}]*	***Chemical Structure***	***Remark***
88	2,3-di-hydro-2,2-dimethyl-7-benzo-furanol ***1563-38-8*** $C_{10}H_{12}O_2$	162		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
95	Tert-butyl-p-benzoquinone ***3602-55-9*** $C_{10}H_{12}O_2$	164		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
101	2-Undecenal ***2463-77-6*** $C_{11}H_{20}O$	168		H315, H317, H319, H411 Suspected **cat. 1A or 1B CMR**
106	2-Undecanone ***112-12-09*** $C_{11}H_{22}O$	170		H315, H400, H410 Suspected **cat. 1A or 1B CMR**
116	2-Dodecanone ***6175-49-1*** $C_{12}H_{24}O$	184		H411 Suspected **cat. 1A or 1B CMR**
134	2,2,4-Trimethyl-1,3-pentadiol-1-isobutyrate ***77-68-9*** $C_{12}H_{24}O_3$	216		Suspected **cat. 1A or 1B CMR**
135	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- **ARVIN 3** ***719-22-2*** $C_{14}H_{20}O_2$	220		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
143	3,5-di-tert-butyl-4-hydroxybenzaldehyde **ARVIN 6** ***1620-98-0*** $C_{15}H_{22}O_2$	234		H315, H319 Suspected **cat. 1A or 1B CMR**
152	Heptadecylamine ***4200-95-7*** $C_{17}H_{35}N$	256		H315, H319 Suspected **cat. 1A or 1B CMR**
174	Hexanedioic acid, dioctyl ester ***123-79-5*** $C_{22}H_{42}O_4$	370		H315, H319 Suspected **cat. 1A or 1B CMR**

Fragment	C_{60C} [ppb]	C_{70C} Calculated [ppb]	Type	CMR	ED	PBT vPvB	DW Positive List	DW-4MSI	Indirect Food Contact SML [mg/Kg]	Cramer Class [µg/d]
2-Heptanone,4-methyl- ***6137-06-0*** $C_8H_{12}O$ **F# 26**	68.0 Highest value 1.4 Lowest value	156.3 3.2 DI_{High} 624 DI_{Low} 13	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1000
3-Penten-2-one,4 -methyl- *or isomer* ***141-79-7*** $C_6H_{10}O$ **F# 7**	58.3 0.8	134.0 1.8 DI_{High} 536 DI_{Low} 7.2	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1800
2-Heptanone,4,6-dimethyl- ***19549-80-5*** $C_9H_{18}O$ **F# 53**	32.6 0.0	74.9 DI_{High} 300	NIAS	Suspected **cat. 1A/1B** **CMR**	No	No	Not listed	Not listed	Not listed	Class 3 ?
2-Heptanol, 4-methyl- ***56298-90-9*** $C_8H_{18}O$ **F# 34**	27.0 0.0	62.1 DI_{High} 248	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1800
2-Cyclohexen-1-one, 3,5-dimethyl- ***1123-09-7*** $C_8H_{12}O$ **F# 22**	18.7 0.0	43.0 DI_{High} 172	NIAS	Suspected **cat. 1A/1B** **CMR**	No	No	Not listed	Not listed	Not listed	Class 3 ?
3-Hexanol,3,4-diethyl- *or isomer* ***19398-78-8*** $C_{10}H_{22}O$ **F# 83**	18.7 0.0	43.0 DI_{High} 172	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1800

Table 30a: Hazard assessment of aliphatic-oxygenated fragments

Fragment	C_{60C} [ppb]	C_{70C} Calculated [ppb]	Type	CMR	ED	PBT vPvB	DW Positive List	DW-4MSI	Indirect Food Contact SML [mg/Kg]	Cramer Class [µg/d]
4-Nonanol,2,6,8-trimethyl- ***123-17-1*** $C_{12}H_{26}O$ **F# 120**	17.6 0.0	40.5 DI_{High} 162	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1000
2-Cyclohexene-1-one, 3,6-dimethyl-6-(1-methylethyl)- ***54410-58-1*** $C_{11}H_{18}O_4$ **F# 100**	16.1 0.0	37.0 DI_{High} 148	NIAS	?	?	?	Not listed	Not listed	Not listed	Class 1 ?
4-Hexen-3-one,5-methyl ***13905-10-7*** $C_7H_{12}O$ **F# 13**	16.0 0.0	36.0 DI_{High} 147	NIAS	?	?	?	Not listed	Not listed	Not listed	Class 1 ?
Methyl Isobutyl ketone ***108-10-1*** $C_6H_{12}O$ **F# 8**	15.7 0.0	30.1 DI_{High} 144	NIAS	No	No	No	Not listed	Not listed	Not listed	Class 1 1800

C_{60C}	Concentration of the fragment experimentally detected during this research. Extraction temperature 60°C
C_{70C}	Extrapolated concentration from 60°C to 70°C via equation 2
(N)IAS	Identification whether fragment is an intentionally added substance or a none intentionally added substance
CMR	**Ca**rcinogenic, **mu**tagenic or **re**protoxic substance
ED	**E**ndocrine **d**isruptor
PBT	**P**ersistent, **b**io-accumulative and **t**oxic substance (classification according to REACh)
vPvB	**V**ery **p**ersistent and **v**ery **b**io-accumulative substance (classification according to REACh)
DW Positive List	**Draft** of the positive list of additives which are allowed to be detected in drinking water. DIN EU 1420:2016-05 [312]
DW-4MSI	4 Member States Initiative on drinking water: Requirements and test methods for products made of organic materials in contact with drinking water – 4MSI **Draft** common approach on organic materials – part C [311]
Indirect Food Contact	Substance listed and SML specific migration limit assigned for use in indirect food contact according to DIN EU 12873-1:2014-09 [313]
Cramer Class	Concept for the cassification of unknown substance into 3 classes with different levels of maximum allowed daily intake DI. Class 1: 30 µg/kg body weight/d; Class 2: 9 µg/kg body weight/d; Class 3: 1.5 µg/kg body weight/d.

Table 30b: Hazard assessment of aliphatic-oxygenated fragments

Fragment	C_{60C} Worst Case [ppb]	C_{70C} Calculated [ppb]	Type	CMR	ED	PBT vPvB	DW Positive List	DW-4MSI MTC_{tap} [µg/l]	Indirect Food Contact SML [mg/Kg]	Cramer Class [µg/d]
Benzenepropoanoic acid,3,5-bis (1,1-dimethylethyl)-4-hycroxy-methyl ester **ARVIN 9** ***6386-38-5*** $C_{18}H_{28}O_3$ **F# 163**	323.0 Highest value	742 DI_{High} 2970	IAS	No	No	No	Not listed	50 (together with structure XXXXIII)	Not listed	Not applicable
3,5-di-tert-butyl-4-hydroxystyrene **ARVIN 5** ***52858-87-4*** ***19263-36-6*** $C_{16}H_{24}O$ F# 142	< 100.0	46-230 DI_{High} 184 020	NIAS	No	No	No	Not listed	0.1	Not listed	Not applicable
2,4-Di-tert-butyl phenol **ARVIN 4** ***96-76-4*** $C_{14}H_{22}O_2$ **F# 125**	56.6	130 DI_{High} 520	IAS	No	Suspected CoRAP	No	Not listed	250	0.05 Isomer	Not applicable
3,5-di-tert-butyl-4-hydroxybenzaldehyde **ARVIN 6** ***1620-98-0*** $C_{15}H_{22}O_2$ **F# 143**	25.3	58.1 DI_{High} 233	NIAS	Suspected **cat. 1A/1B CMR**	No	No	Not listed	2.5	Not listed	Not applicable
3,5-di-tert-butyl-4-hydroxyacetophenone **ARVIN 7** ***14035-33-7*** $C_{16}H_{24}O_2$ **F# 148**	24.9	57.2 DI_{High} 229	NIAS	No	No	No	Not listed	2.5	Not listed	Not applicable

Table 31a: Hazard assessment of aromatic-oxygenated fragments

Table 31b: Hazard assessment of aromatic-oxygenated fragments

Fragment	C_{60C} Worst Case [ppb]	C_{70C} Calculated [ppb]	Type	CMR	ED	PBT vPvB	DW Positive List	DW-4MSI MTC_{tap} [µg/l]	Indirect Food Contact SML [mg/Kg]	Cramer Class [µg/d]
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- **ARVIN 3** ***719-22-2*** $C_{14}H_{20}O_2$ **F# 135**	9.1	20.9 DI_{High} 84	NIAS	Suspected **cat. 1A/1B CMR**	No	No	Not listed	2.5	Not listed	No: applicable
Tert.-butyl-phenol **ARVIN 2** ***98-54-4*** $C_{10}H_{14}O$ **F# 63**	8.6	19.8 DI_{High} 79	NIAS	No	Suspected	Suspected	Not listed	2.5	0.05	No: applicable
7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione **ARVIN 8** ***82304-66-3*** $C_{17}H_{24}O_3P$ **F# 156**	5.8	13.3 DI_{High} 53	NIAS	No ?	No ?	No ?	Not listed	2.5	Not listed	No: applicable
4-Ethylphenol ***123-07-9*** $C_8H_{10}O$ **F# 21a**	0.5	1.2 DI_{High} 5	NIAS	No ?	No ?	No ?	Not listed	0.1	Not listed	No: applicable
Benzenepropoanoic acid,3,5 bis (1,1 dimethylethyl)-4-hydroxy- **ARVIN 10** ***20170-32-5*** $C_{17}H_{26}O_3$ **Structure XXXXIII**	0.0 Converted to F# 156 or F# 163 ?		NIAS	No	No	No	Not listed	50 (together with structure XXXXIII)	Not listed	No: applicable

The maximum concentrations detected for fragments F# 163 (counted as sum with structure XXXXIII) and F# 125 is exceptionally high; based on the specific experimental conditions selected (a detailed explanation is given in Section XXX). The conclusion being that the MTC_{tap} values can be matched. F# 21a and F# 63 seem to be generated only under exceptional conditions (see conclusions). *For the remaining fragments (F# 135, F# 142, F# 143, F# 148 and F# 156) it is suggested that the mixture of protective chemicals is adjusted in order to minimize the concentration of the fragments*.

When selecting the least hazardous option for materials and assessing the best available option, a holistic approach must be taken. For example, in attempting to centre the examination of fragments originating from protective chemicals in PO and more specifically PE pipes, it should be highlighted that crosslinked PE pipes have more contaminants than simple HDPE. Other pipes, namely PVC pipes contain very low concentrations of organic fragments [143]. PVC pipes contain non-neglectable concentrations of organotin fragments [314], while metal plumbing is susceptible to various metal ion contaminations [315].

5 Conclusions and Future Work

Since the first publication in 2002 [140], various studies have examined the type and concentration of fragments which can be extracted from PO pipes. Most studies focus on industrially made PO products (particularly pipes) and identify fragments (from, for example, pipes) which are leached or extracted to water. This limits interpretation of the data because the exact PO grade of material (e.g., pipes), as well as the initial composition of protective chemicals and modifiers, is not known Furthermore initial composition and formulation vary from manufacturer to manufacturer. Equally, manufacturing conditions are in general not known. In this study, the research topic is approached in a systematic manner. Known mixtures of protective chemicals and modifiers are incorporated into a standardised PO (namely, PP) with controlled melt-processing and extraction conditions. With this approach the impact of protective chemicals on the formation of LMW organic fragments may be better understood.

From the studies presented in this thesis, it can be concluded that the type, concentration, and presence of protective chemicals in PO have a major influence on the type, number, and concentration of organic compounds (fragments) detected in water.

During this investigation more than 200 fragments are detected from PO (namely, PP) of which more than 20 remain unidentified. Most of the fragments fall into a MW range of ~100 to 300 g mol^{-1}. Higher MW fragments are not extracted, while lower MW fragments are formed, but most likely lost due to volatilisation during the melt-processing operation for PP. The species detected (by GC-MS) can be classified into 7 categories:

- Aliphatic fragments
- Oxidised-aliphatic fragments
- Aromatic fragments
- Oxidised-aromatic fragments
- Unidentified fragments (from substrate or protective chemicals)
- Known contaminants
- Analytical contaminants

Extraction of aliphatic fragments is considered as an exception. Certain batches of PP contain aromatic fragments in the 25-50 ppb range; while other batches did not at all contain these fragments. The presence or absence of aromatic fragments does not depend on a (specific) protective chemical present in the formulation. Instead, variations apparently depend dependent on variations in the ‘work-up’ procedure after PP synthesis. The PP batches used were not of commercial quality and had to be isolated from the synthesis reactor in a manual operation.

However, two types of fragments depend strongly on the presence or absence of protective chemicals These are oxidised-aliphatic and oxidised-aromatic fragments. Oxidised-aliphatic fragments result from the oxidation of the organic material PP (PO). Due to their polymeric nature most oxidised-aliphatic fragments have a high enough MW to not be volatile or water extract-able. Only a fraction of the oxidised-aliphatic fragments can be found back in the water extracts and these fall into a MW range of ~100 to 200 g mol^{-1}. *The class of oxidised-aliphatic fragments in PP (PO) without protective chemicals forms by far the highest concentration of fragments in the entire study*. Oxidised-aliphatic fragments can be reduced significantly by the addition of a minimum concentration of appropriate protective chemicals. Though it should be stated that this reduction is achieved only at the expense of new fragments. The latter arise immediately on the addition of protective chemicals (depending on the exact chemical nature of the molecule), and many of these are of an oxidised-aromatic nature. *The total number and concentration of fragments, as well as the ratio between oxidised-aliphatic and oxidised-aromatic fragments results from the interplay between these two competing effects*. Optimal suppression of fragments is influenced by the chemical nature and concentration of protective chemicals as well as the presence of co-protective chemicals (synergistic effects). *Fundamentally it is not possible to achieve a complete suppression of the formation of both oxidised-aliphatic and oxidised-aromatic fragments, due to these parallel and competing reactions.*

The above statement has two direct implications. *Firstly, it is not possible to produce and use thermoplastic materials (such as PO) without the presence of protective chemicals.* The technology of thermoplastic melt-processing above 200°C accelerates the rate of oxidation so much, that during the short timespan of melt-processing uncontrolled changes in MW (and MWD), along with uncontrolled functionalisation of the polymer backbone with oxygenated groups, renders the material unsuitable for most end applications. Secondly, due to the mechanism of action of protective chemicals, oxidised-aromatic fragments can (at effective concentrations of protective chemicals) not be avoided. This is in particular true for CB-D structures, especially Hindered Phenols, which offer an alternative reaction pathway in a sacrificial. *The only realistic target to reduce fragments is to keep fragments below the concentration and resulting daily intake (into a human body), i.e., below the threshold of toxicological concern.*

One general technological approach suggested by the data assimilated in this study would be to minimize LMW organic fragments already in the polymer, without the use of modifiers. During melt-processing fragments already formed could be eliminated from the PO substrate by a controlled and reproduceable procedure which exposes the PO granules or the final PO article to an elevated temperature; or brings it proactively in contact with extractive media (such as water). In the first, de-volatilisation could take place at slightly elevated temperatures, for example, the conditions stipulated in test norms for interior automotive applications; e.g. a temperature of 90°C [316,317]. This would volatilise fragments up to a molecular weight of 200 to 250 g mol^{-1}. The temperature would still be low and would not be considered melt-processing or high enough to induce significant oxidation over the short time-period. One drawback of this approach would be that the procedure would have to be carried out after every melt-processing step. One advantage would be for crosslinked PE pipes, where a thermal post-treatment step is carried out to achieve the desired crosslinking density [318]. This step could be adjusted to include the best de-volatilisation conditions, thereby achieving two objectives in one step. Alternatively, PO granules or final PO products could be pre-extracted with water, e.g., by being stored for 24 hours at 20 or 60°C in stagnant water. After storage the water would be discarded. This procedure is used anyway in various tests to assess drinking water quality [312,313]. *As such, a modification of the melt-processing and* *finishing conditions is proposed*. For tap water piping, flushing the water inside the pipe for about 5 minutes should have a similar effect [319].

Conversely, another general technological approach would be to minimize LMW organic fragments already in the polymer, with the use of modifiers. Inorganic modifiers can adsorb LMW organic compounds at their surface and hence reduce the mobility of these compounds to migrate to the surface with subsequent water extraction. In the specific case of O-3 (synthetic hydrotalcite) it has been shown that this affects LMW fragments up to ~175 g mol-1. As the chemistry of formation of oxidised-aliphatic fragments is similar for extractable and for volatile fragments, a technology transfer from (filled) PP compounds for interior automotive applications, is suggested. In this application (in the interior of a car), VOC (volatile organic compounds) are reduced by various technologies [122,294,302-309].

An alternative technological approach would be to reduce oxidised-aliphatic fragments to a minimum. Oxidation of PP during melt-processing and the formation of water-extractable oxidised-aliphatic fragments can be reduced by the addition of a minimum concentration of a protective chemical which functions as PD. Within the chemical classes tested (Phosphite and Hydroxylamine), most individual molecules of protective chemicals do not display a performance that is strong enough to minimize oxidised-aliphatic fragments. Potentially, the only exception is P-19, which in fact is a bifunctional protective chemical, comprising PD and CB-D moieties within its structure. The intra-molecular synergistic effect between PD and CB-D functionality can be mimicked by combinations of [Hindered Phenol (CB-D) + Phosphite (PD)]. Various combinations are suggested [320-324] including Hindered Phenols (such as AO-1, AO-2, AO-3, AO-5, AO-5) and AO-6 and Phosphites (such as P-1, P-2, P-3, P-4, P-5 or P-9). A combination of any of the Hindered Phenols suggested with any of the Phosphites suggested, when used at a total concentration of at least 1500 ppm, does suppress to a high degree the formation of oxidised-aliphatic fragments. Nevertheless, differences in effectiveness exist, and only the most efficient were considered in this study when ranking relative performance [325]; namely:

[(AO-5 or AO-6) + (P-3 or P-5)]

On this basis it may be that the combinations stated above could be utilised at a lower concentration than 1500 ppm stipulated. The concept of very efficient mixtures of protective chemical for melt-processing can be further developed. An alternative approach (resulting in very low quantity of fragments overall) would be to use a fast CB-D radical scavenger for melt-processing (excluding intentional crosslinking reactions). The bond dissociation energy between the labile hydrogen of a CB-D radical scavenger and the corresponding hydrogen of a (Hindered Phenol) protective chemical needs to be as large as possible. This fast radical scavenger would react in a preferred manner during melt conversion and (at least partially) preserve the less reactive high Hindered Phenol for LTTS. The "ideal" fast CB-D has the following profile:

- Lipophilic character
- Weaker O-H bond dissociation energy than Hindered Phenols used for LTTS (and hence 2, 6 Di-tert-butyl hindered O-H bond)
- None-hazardous transformation products
- Melt compound-able

To fulfil this objective [327] natural antioxidants, more specifically *natural antioxidants with lipophilic character,* could be used. Here it would be logical to extend the search for suitable protective chemicals to the area of food science and cosmetic science [216]. Potential molecular structures for investigation could include:

- α-tocopherol AO-6 and its derivatives [217, 218]
- Tocotrienol [42]
- Ascorbyl palmitate AO-58 [268]
- Selected bi- and polyphenolic phenols with catecholic moiety [217] (caffeic acid, luteolin, quercetin, 3, 4-dihydroxy-chalcone, 6,7-dihydroxy-coumarine, 6,7-dihydroxy-4-methyl-coumarine … the latter being similar to F# 132 & F# 137)
- Hexadecxyl ester of AO-60 (gallic acid) [272]

It is recognised that some of the above-mentioned compounds have poor solubility in non-polar hydrocarbons. However, there is evidence in the literature of strategies to adjust the hydrophilicity/lipophilicity profile of phenols [216].

In conjunction with this combination of the selected fast CB-D with a synergistic co-protective chemical for melt-processing is suggested. This could be a synthetic Phosphite or another compound from the area of food and cosmetic science. Where a Phosphite is selected, the molecules should be:

- Lipophilic in character
- All transformation products (including those from hydrolysis) need to be approved
- Hydrolysis needs to be prevented as much as possible

Special care must be taken regarding the hydrolysis of the Phosphite. This study has demonstrated that onset of hydrolysis results in a significant increase of fragments beyond the Phosphite origin itself. Several technologies are proposed to retard the hydrolysis of Phosphite. The technologies involve:

- Micronised ZnO
- Hydrotalcite (e.g. O-3)
- HAS with alkaline character (e.g.HAS-3)
- Tri-isopronanol amine TIPA

Alternative synergists for the fast CB-D (in particular AO-6) outside phosphor-chemistry include:

- Queretin
- 6, 7-dihydroxy-coumarine
- Ascorbyl palmitate
- Ubiquinol
- Gallic acid esters
- β-carotene ± selected (fully regulated) phosphites

The disadvantage of most of these stabilisation systems is that they impart colour, though various technologies do exist to adjust colour. One approach to circumvent this, would be a processing stabilization system comprising [AO-1 + HYA-1].

In contrast to the previous conclusions and potential recommendations, it should be appreciated that the most often used mixture of protective chemicals is [AO-1 + P-1]. *It is specifically the use of this mixture which seems to result in additional protective chemical-originating fragments*. Two issues are particularly problematic. Firstly, the mixture [AO-1 + P-1] is less effective than e.g. [AO-6 + P-5]. Consequently, to give low MFI and a reduction in oxidised-aliphatic fragments, the mixture must be used at a concentration of 3000 to 5000 ppm. At this high concentration of P-1, the concentration of fragment F# 125 seems to increase in the water extract [143]. It was noted that only one specific fragment seems to increase at higher concentrations of the parent Phosphite P-1. The very large variation in of fragment F# 125 in water extracts from PO pipes manufactured by industry indicates different approaches to the protection of PO during melt-processing. Secondly, and more importantly, AO-1 by its size and the (2,6-di-*tert*-butyl-) substituent adjacent to the phenolic OH group is more suited as a protective chemical to increase LTTS. However, it was shown that AO-1 also reacted during conditions of melt-processing. Hence, transformation products of AO-1 are already formed during melt-processing (and AO-1 already partially consumed) before the start of the service life of the final PO product. *Hence, multiple fragmentation of AO-1 cannot be avoided with a formulation of the type [AO-1 + P-1 (**Figure 5.1**)]*.

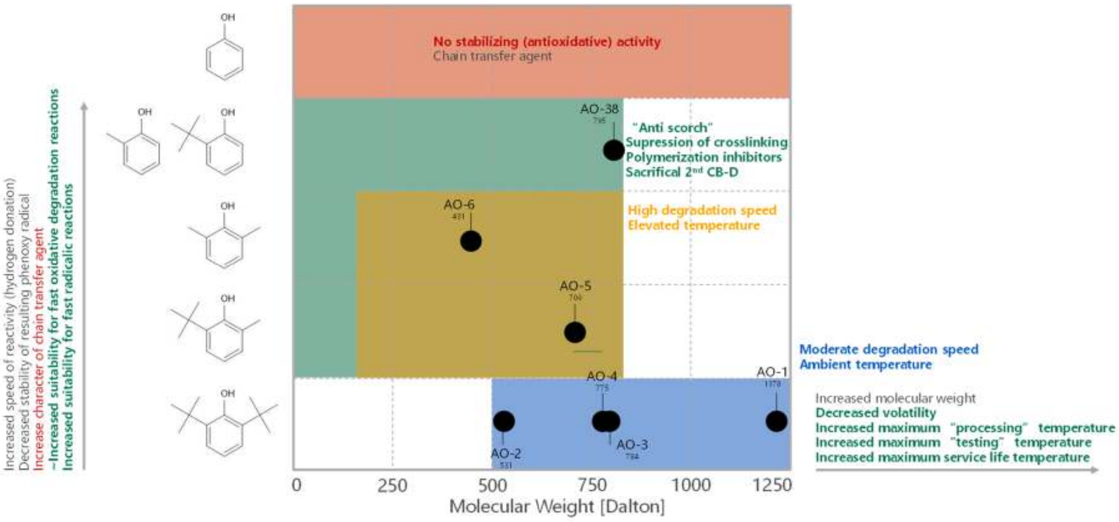


Figure 5-1: Classification of Hindered Phenols by hindrance (kinetics) and molecular weight 250

It is therefore recommended that the protective activity during melt-processing and the protective activity for LTTS are separated. Essentially this constitutes a proposal to avoid the dominant industrial scale mixture of protective chemicals (AO-1 + P-1] for PO applications of environmental concern that involve water contact. This can be achieved by a dedicated mixture of protective chemicals for melt-processing and a dedicated protective chemical to enhance LTTS, without the latter strongly interfering with melt-processing. Dedicated efficient mixtures of protective chemicals during melt-processing for water contact applications have been proposed in this study. The selection of protective chemicals to enhance LTTS, with limited effect on fragmentation during melt-processing, depends on two factors. The first one is whether or not the final PO product is under pressure (as e.g., in sanitary water supply piping). In the latter case HAS is suitable as protective chemical, while Hindered Phenol is suitable in both cases. Secondly, the service life temperature and/or the testing temperature influences the choice of protective chemicals. Only at temperatures below 80°C do all (suggested) protective chemicals (Hindered Phenol, Hydroxybenzoate and HAS) yield sufficient enhancement of LTTS. It should be noted that on an individual basis protective chemicals are active to a varying degree during melt-processing (**Figure 126**).

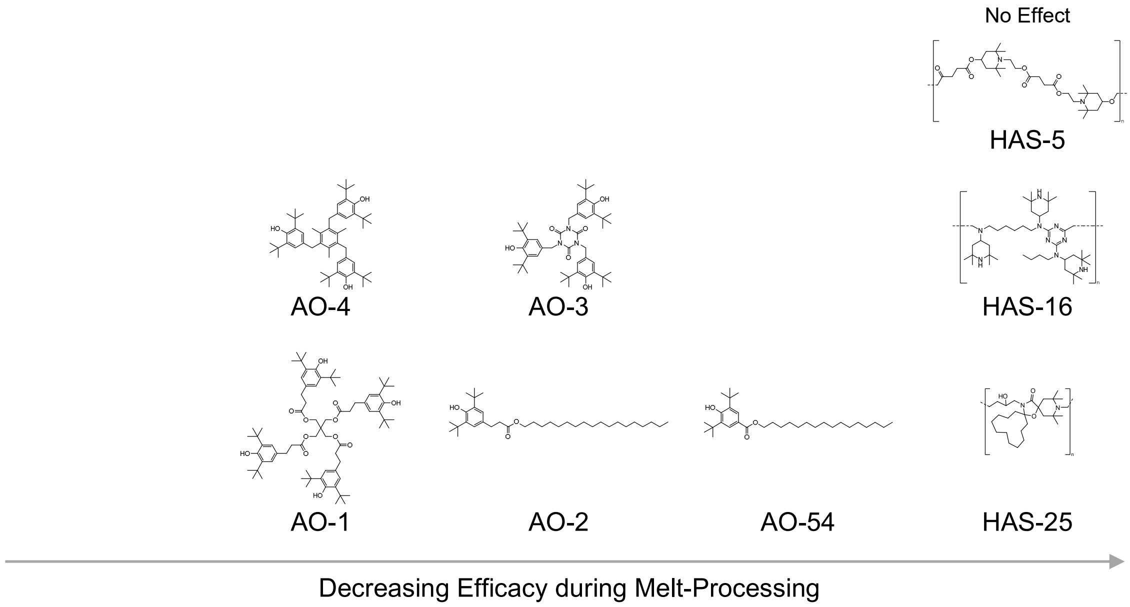


Figure 126: Protective chemicals with effect during service life and varying effect during melt-processing

A general decrease of oxidised aromatic and protective chemical-originating fragments is achieved by a selection from the right-hand side of **Figure 126**. No transformation products due to a protective effect are expected by the selection of HAS.

Finally, technologies to reduce oxidised aromatic fragments could be employed.

When discussing the reduction of oxidised aromatic fragments (originating from Hindered Phenol and/or Phosphite), it is suggested that they are *not* categorised tby GC retention time [140], but rather by *mechanism of formation*. This proposition points to different technologies being required to suppress the formation reactions of fragments. The following mechanisms of formation are proposed

- Hydrolysis
- Dealkylation
- Quinone methide transformation to cinnamate & hydrolysis
- Reaction pathways of cyclohexadienonyl radical
- Intermediates from synthesis

These warrant individual consideration as follows:

Hydrolysis (Mechanism 1)

Within the scope of this work, hydrolysis tends to lead to rather large fragments (200 to 300 g mol^{-1}) based on the positions of the hydrolyse-able functionality in the parent protective chemical. By the nature of the parent protective chemicals, the fragments are mainly of oxidised-aromatic nature. The fragments are considered as *first generation (hydrolysis) transformation products*. Hydrolysis is a fundamental weakness of the stabiliser class of Phosphites. Many Phosphites use as intermediate the structure F# 125 (for example in P-1, P-3 and P-4); which after hydrolysis constitutes the major fragment. As the hydrolysis of phosphites is autocatalytic, the onset of hydrolysis can yield rather high concentrations (at the ppb level of this study) of fragment F# 125. It is likely that its concentration is limited only by its solubility in water. [Note: although indirect food contact regulations do not apply directly to drinking water, the direct hydrolysis products of Phosphites do have a different regulatory status]. Fragment F# 125 (originating from P-1, P-3 or P-4) is not included in the granted indirect food contact status. In contrast for P-5, P-9, P-17 (among others) the granted indirect food contact status includes the parent Phosphite and likely transformation products [183]. Nevertheless, F# 125 is still considered as IAS.

Advanced hydrolysis of a Phosphite seems to enhance additional hydrolysis reactions which lead to additional fragments, such as fragments F# 156 and F# 163 (originating from “Metilox” based Hindered Phenols such as AO-1 or AO-2). F# 163 although an initial impurity is also formed via a hydrolysis and subsequent transesterification. The exact mechanism is not understood. F# 165 (isopropyl palmitate) originates from MS-1 (calcium stearate) or other metal soaps. It is was detected in every situation of advanced hydrolysis.

Hydrolysis reactions can also be induced by controlled external condition during an intentional procedure to modify the characteristics of PO. In this respect, crosslinking reactions of PE which use grafting of silane functionality onto a PE backbone and subsequent crosslinking via hydrolysis are of concern [162,163]. Silane crosslinked PE pipes show the highest levels of water odour and fragments [318]. The concentration of fragments F# 156 extracted from PP in this study seems an underestimate, compared with earlier studies by UBA (Umweltbundesamt; the German Federal Environmental Agency) on PE-Xb (silane crosslinked PE); while concentrations for other fragments are comparable [327,347].

Dealkylation (Mechanism 2)

Although dealkylation of hindered phenolic structures is an intentionally carried out industrial process [348,349], it is observed that there is an unintentional dealkylation of Hindered Phenol (and potentially alkylated aromatic Phosphite) under condition of high temperature, and/or severe processing condition (high temperature and high shear force); as well as the presence of surface active inorganic fillers or modifiers. Fragments F# 21a and F# 63 (and potentially its isomer F# 62) are therefore considered NIAS. F# 62 is also reported to fragment from mono-*ortho* unhindered Hindered Phenols such as AO-38 [285]. Fragments F# 21a, F# 62 or F# 63 can be reduced by surface treatment of inorganic materials in the formulation and/or by adjusting the “pH of the polymer substrate”. The prior general suggestion of addition of inorganic scavengers for LMW fragments would of course require a proper consideration of the surface activity of any inorganic modifier.

Quinone methide QM transformation to cinnamate & hydrolysis (Mechanism 3)

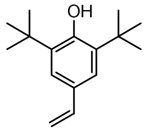
This reaction sequence concerns only Hindered Phenols base on “Metilox” (such as AO-1, AO-2) and results in the formation of fragment F# 156 [85,219,350]. F# 156 is considered a NIAS; its exact structure varies between F# 156 and the corresponding acid (**Structure XXXXIX** in **Scheme 15**) depending on pH [85]. F# 156 is considered a *4th generation transformation product of “Metilox”-based Hindered Phenol* (such as AO-1 and AO-2). A formation pathway was proposed in **Scheme 29**. F# 156 can be avoided by not using “Metilox”-based Hindered Phenol or by using HAS as protective chemical for LTTS. The formation of F# 156 can be reduced by addition of a kinetically fast CB-D (such as AO-5, AO-6) which would slow down <u>R 9.2</u> for high Hindered Phenols in general and AO-1 in particular.

The experimental results presented in this study also suggest a reduction in F# 156 concentration by a substitution of AO-1 with AO-2. The chemical nature of additional hydrolysis products of AO-1 versus AO-2 (on top of the formed cinnamate acid, **Structure XXXXVII**) is quite different. It is postulated that the co-formation of lipophilic stearyl alcohol (R 14.2 in **Scheme 14**) slows down the rate of hydrolysis. This argument is further developed later (see Protective chemicals with expected lipophilic transformation products)

Reaction pathways of cyclohexadienonyl radical (Mechanism 4)

This reaction pathway produces many fragments, the majority of which originates from Hindered Phenol. The reaction pathway to the formation of F# 135, F# 143 and F# 145 is well understood. The formation of F# 142 is less clear. F# 142 is only detected under severe melt-processing conditions. This suggests that its formation is favoured in oxygen deficiency conditions, but only for Hindered Phenols wih a present and accessible ɣ-carbon in the *para*-position of the phenolic group. *Therefore, F# 142 could only be formed by “Metilox”-based hindered phenols such as AO-1*. This hypthesis is supported by the fact that the complementary and non-extractable “main-body” (see **Figure 127**) of AO-1 has been identified in earlier studies [77]. In principle, F# 142 could also be formed via a cleavage between the β- and ɣ-carbon with subsequent hydrogen transfer.

F# 142



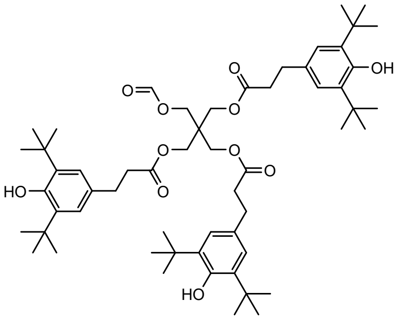


Figure 127: Complementary “main body” to F# 142 [77]

The peroxide formed from the macromolecular peroxy radical and the cyclohexadienonyl radical can further react via different reaction pathways. In the (*ortho*- and) *para*-position of fully Hindered Phenols. Hence, the tertiary α-carbon in *para*-

position, yields mainly reversible C-O coupling products and the formation of fragments F# 135, F# 143 and F# 148 is disfavoured. Only the presence of a secondary α-carbon allows the formation of fragments. However, it is the presence of a secondary β-carbon which renders possible only fragmentation to form F# 148 and strongly favours the formation of the corresponding aldehyde F# 143. Absence of a β-carbon and/or presence of a tertiary β-carbon and/or presence of a bulky group in β-position renders fragmentation to form F# 148 impossible and disfavours fragmentation to yield the corresponding aldehyde F# 143. The presence of "un-cleaved HMW ketones of AO-3 and AO-4 [73,77] (**Figure 110**) are reported and these prevent the formation of F# 148 for AO-3 and AO-4. The opposite is observed for fragment F# 135. Absence of a β-carbon, and/or presence of a tertiary β-carbon, and/or presence of a bulky group in β-position, favours a fragmentation between the phenolic system and it's α-carbon. Therefore, the formation of F# 135 is favoured in the case of AO-3 and AO-4 over AO-1. **Scheme 30** summarizes the various reaction pathways and **Tables 33-39** suggest technologies to minimize fragments F# 135, F# 143 and F# 148.

As a general strategy, the formation of F# 135, F# 142, F# 143, and F# 148 can be reduced by slowing down the formation of the cyclohexadienonyl radical via reaction R 6.2. This can be achieved via the introduction of a kinetically faster CB-D relative to the kinetics of the 2,6-di-tertiary-butyl Hindered Phenols AO-1, AO-2, AO-3 and AO-4. A synergistic effect of the fast CB-D with a Phosphite is expected to further decrease the concentration of these fragments and has already been discussed.

The category unreacted intermediates from synthesis (Mechanism 5) is not discussed further in detail. It is self-explanatory that a higher purity of the parent protective chemical can result in a lower number and concentration of water-extractable fragments.

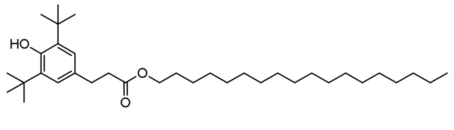
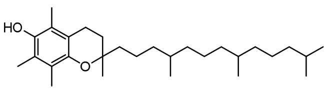
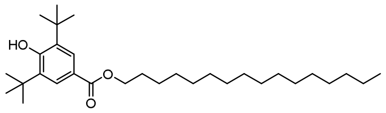
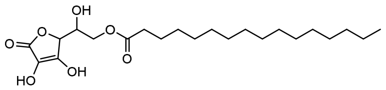
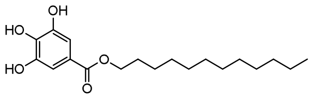
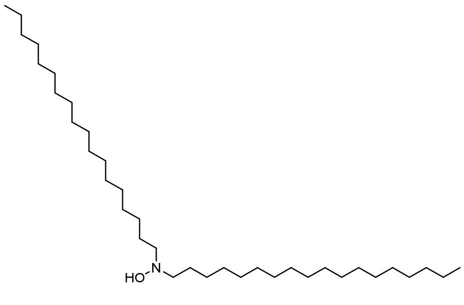
Protective Chemicals with Expected Lipophilic Transformation Products

The findings in this study also point to an auto-retardation of fragmentation where fragments of lipophilic nature are formed. This seems most noticeable during the formation of fragment F# 156 which involves a hydrolysis reaction. Hydrolytic fragmentation of AO-1 results in 4x **Structure XXXXVI** (**Scheme 14**) and ultimately one molecule of pentaerythritol with a Log K_{OW} of -1.69. In this case, the backbone structure of the protective chemical is also water soluble. In contrast, in the case of AO-2, on a molar basis, equal quantities of **Structure XXXXVI** and stearyl alcohol (R 14.2) are formed. With a Log K_{OW} of 8.22, stearyl alcohol is not very soluble in water and will accumulate at or in the surface layer of a PO manufactured product. With hydrolysis being an equilibrium reaction, this should slow down the overall rate of hydrolysis in the case of AO-2. The potential for 'scaling' on the inside of a pipe due to the accumulation of fatty acids and corresponding alcohols would need to be investigated. This hypothesis is supported by the lack of detection of C_{16}-C_{18} alcohol or carboxylic acid which originates from the metal soap MS-1 (present as antacid). Only under conditions of advanced hydrolysis F# 165 is detected and associated directly with MS-1. By analogy, a selection of protective chemicals, which are expected to yield lipophilic fragments, is listed in **Table 32**. It is noted that all listed protective chemicals (except AO-80, which is only evaluated as the corresponding acid AO-60) result in a very low number and concentration of fragments. *Three of the six protective chemicals listed are direct food contact additives*; the corresponding E number is indicated [186].

The limited solubility of AO-1 in impact-modified PP of ~1000 ppm is noted [351]. Extrapolation from this data point to PE suggest an again lower solubility. Additive solubility seems to decrease further with increasing MW of the PO substrate. The typical concentration of AO-1 for durable applications such as pipes are often ~5000 ppm. This fact would favour migration of AO-1 towards the interface PO article/water and further accelerate a potential hydrolysis reaction. AO-2 is reported to have a significantly higher solubility in PO.

The extraction temperature has a major impact on the findings of this research. Two regions can be defined; below and above ~40°C. Below 40°C, number and concentration of fragments are in general quite low. Above 40°C and particularly at 60°C, fragments increase significantly by ~ 50% (**Figure 38).** It is expected that extrapolation from 20°C to 60°C underestimates the number (and in consequence total concentration) of fragments, as selected fragments (of in in particular oxidised-aliphatic nature) cannot (yet) be detected at 20°C.

Table 32: Protective chemicals with expected lipophilic fragments

Protective Chemical	***Structure***	***Function***
AO-2		LTTS Slow CB-D
AO-6 E 306 – E 309		Melt-Processing Fast CB-D
AO-54		LTTS Very slow CB-D
AO-58 E 304		Melt-Processing Synergist for AO-6
AO-80 (Dodecyl ester of AO-60) E 312		Melt-Processing LTTS ?
HYA-1		Melt-Processing

This is important because formal testing on PO pipes manufactured at industrial scale is carried out at 70°C. Therefore, the findings in this study need to be extrapolated (increased) by ~50%. This temperature gap and the systematic but not industrial scale production of the PP granules (instead of PO pipes) and the different extraction procedure (relative to international standards [312,313]) does prohibit the comparison of absolute concentrations (relative to the described limits), but does allows an indication of trends and responsible variables.

In contrast, the conclusions can be extended to all PO which oxidatively degrade mainly via a chain scission mechanism. Care should be taken with selected HDPE grades where an intrinsic crosslinking reaction dominates and hence larger molecules rather than LMW fragments are formed.

This study is complementary to earlier studies with industrially manufactured PO articles but lacking knowledge on protective chemicals present and manufacturing conditions. To completely close the gap between the two approaches, it is suggested that a systematic evaluation be undertaken for a limited number of known mixtures of protective chemicals under industrial conditions of PE pipe manufacturing and subsequent crosslinking. The findings of this study could in this way be transferred to and verified under industrial scale conditions and standardised extraction testing. Two effects should be further investigated. Firstly, the external hydrolysis induced formation of F# 156 during the silane crosslinking procedure. Equally, the slower formation of F# 156 originating from AO-2 instead of AO-1 due to accumulation of lipophilic fragments at the interface PO/water needs to be proven.

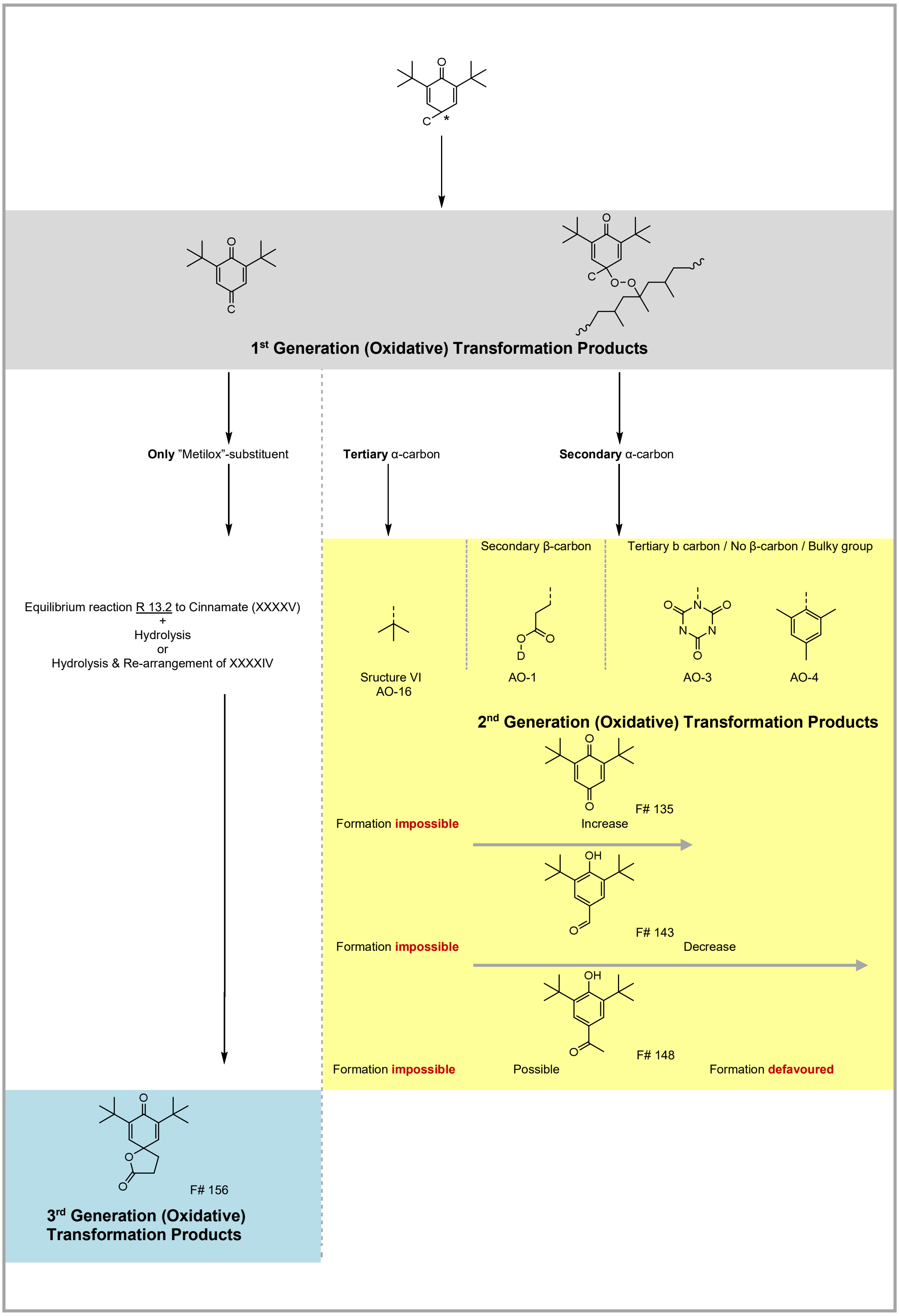
It is also suggested that a systematic evaluation of the impact of PO polymerisation technology on the formation of oxidised-aliphatic fragments should be undertaken. Selected HDPE grades (Cr-catalyst based HDPE manufactured in a slurry loop reactor without hydrogen response) have an inherent tendency to crosslink rather than to undergo chain scission. Hence oxidative degradation products can increase in MW. Equally the fundamental strategy to slow down such reaction differs from the one discussed and employed in this report; types of protective chemicals differ slightly.

As several alternative protective chemicals with effect on LTTS at or below 70°C are proposed, there is a need to solidify the few data sets with these alternatives, relative to the established protective chemicals AO-1 and AO-4.

A potential extension of this investigation into other extractive media is suggested. It is expected, depending on the chemical nature and polarity, to some degree there might be an inversion of some of our conclusions. Nevertheless, the fundamental issue of extractable fragments originating from the PO substrate and protective chemical is of equal importance in food and cosmetics applications

Lastly, the number of unidentified fragments is rather high. Further effort is needed to clarify the chemical identity and subsequent hazard assessment.

Finally, it should be recognised that this study has much wider implications than that of extraction of organic compounds of environmental concern into water from PO containers during service-life. Much of the research to identify markers that can characterize microplastics is hampered by an incomplete understanding of how additives in plastics are transformed and leach into rivers and oceans. Characterising extracts from these aged plastics could add to the body of data and our understanding of how to limit the impact of these important materials on our environment.



Scheme 30: 1st, 2nd & 3rd generation of transformation products

Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
Aliphatic-Oxygenated (mainly $\leq$ 200 Dalton)		Oxidation of PP R 1.11	Reduction of formation: Protective chemical	
			Reduction of already formed fragments:	
			Degassing & optimized melt-processing	352
			Thermal treatment after each melt-processing step (60-120 min @ 90-120°C)	
			Addition of inorganic scavengers	
			- Hydrotalcite	Figure 113
			- Carbon black	302
			- Zeolite	5304, 305
			- Porous silica	303
			(Unintentional) increase of formation: Advanced hydrolysis of additives (such as Phosphite)	
2-Ketones		Oxidation of PP R 1.11 R 24.1 R 25.3 R 27.3 Scheme 28	Reduction of formation: Protective chemical with strong PD effect during melt-processing	
Alcohols		Oxidation of PP	Reduction of formation: Addition of HAS	Figure 95

Table 33: Summary of strategies to decrease aliphatic-oxygenated fragments

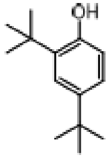
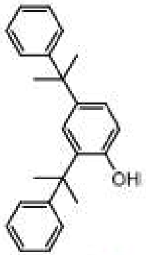
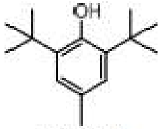
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 125** ARVIN 4	 From P-5  From P-9	Hydrolysis Scheme 18	Prohibition of formation: Use of aliphatic Phosphite a protective chemical with PD mechanism Use of another sub-class of PD, e.g. HYA-1 Reduction of formation: Limited concentration of P-1, P-3 or P-4 below solubility limit Abandon binary mixtures [AO-1 + P-1] Addition of inorganic scavengers to scavenge 1st generation hydrolysis transformation products Addition of alkaline substances (e.g. TIPA triisopropanol amine) to slow down rate of hydrolysis (Unintentional) increase of formation: Hydrolysis of Phosphite Hydrolysis of other chemicals in the formalution which induces Phosphite hydrolysis External conditions & procedures which induce hydrolysis (e.g. silane crosslinking of PE)	Figure 118 97, 99

Table 34: Summary of strategies to decrease fragment F# 125

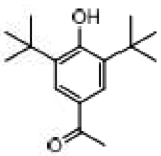
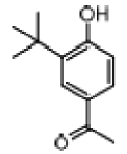
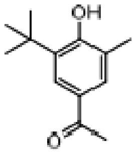
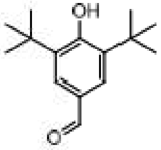
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 148** ARVIN 7	 	2nd Gen transformation product of HP	<u>Prohibition of formation:</u> Use of HAS instead of Hindered Phenol (for LTTS) Use of AO-54 (Hydroxybenzoate) instead of Hindered Phenol Use of AO-3 or AO-4 instead of AO-1 (and AO-2) No secondary β-carbon in para-position of phenolic group <u>Reduction of formation:</u> [Fast CB-D + PD] for melt-processing Reduction of AO-1 concentration < 2000 ppm Addition of inorganic scavengers	<u>Figure 69</u> <u>Figure 59</u>
 **F# 143** ARVIN 6			Same trend as for F# 148 but formation cannot be prohibited	

Table 35: Summary of strategies to decrease fragment F# 148

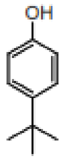
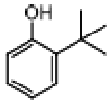
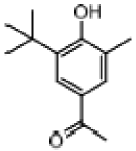
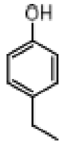
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 163** ARVIN 2		Dealkylation of 2,4 or 2,6 hindered HP	Prohibition of formation: Use of HAS instead of Hindered Phenol (for LTTS)	
		AO-38	Reduction of formation: Surface treatment of inorganic modifier Surface treatment of inorganic filler Modify "pH" of substrate	 258 258, 306 353
 **F# 21a** ARVIN 1			(Un-intentional) increase of formation: High temperature Catalyst residues Inorganic modifiers with high surface activity	

Table 36: Summary of strategies to decrease fragments F# 62, F# 63 and F# 21a

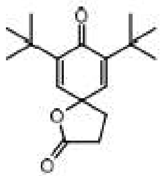
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 156** ARVIN 8		Metilox-based hindered HP AO-1, AO-2, … Scheme 29	Prohibition of formation: Do not use Metilox-based Hindered Phenol such as AO-1, AO-2, … Use of AO-3 or AO-4 instead of AO-1 Use of HAS instead of AO-1 for LTTS Reduction of formation: Slow down R 9.2 (formation of QM; structure XXVI or XXVII) in general Use of kinetically fast CB-D to slow down R 9.2 for AO-1 Use of AO-2 instead of AO-1 (Un-intentional) increase of formation: External hydrolysis conditions Severe processing conditions	

Table 37: Summary of strategies to decrease fragment F# 156

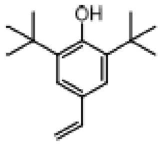
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 142** ARVIN 5		Unclear mechanism Oxygen deficiency ?	Prohibition of formation: Do not use Metilox-based Hindered Phenol such as AO-1, AO-2, … Use of AO-3 or AO-4 instead of AO-1 Use of HAS instead of AO-1 for LTTS Reduction of formation: Avoid sever processing conditions Slow down R 9.2 (formation of QM; structure XXVI or XXVII) in general Use of kinetically fast CB-D to slow down R 9.2 for AO-1 Use of AO-2 instead of AO-1 Presence of strong Phosphite (Un-intentional) increase of formation: Severe processing conditions Oxygen deficiency conditions	350

Table 38: Summary of strategies to decrease fragment F# 142

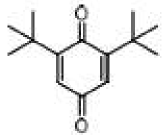
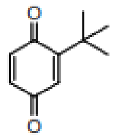
Fragment	Related Fragments	Mechanism of Formation	Control of the Fragment	Reference
 **F# 135** ARVIN 3	 F# 95	2^{nd} Gen transformation product of HP	Prohibition of formation: Use of HAS instead of Hindered Phenol (for LTTS) Use of AO-54 (Hydroxybenzoate) instead of Hindered Phenol Reduction of formation: [Fast CB-D + PD] for melt-processing Strong PD	Figure 71

Table 39: Summary of strategies to decrease fragment F# 135

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7 Appendices

7.1 Patents and Planned Publications

Selected data of this report has already been published in order to support intellectual property protection of one of the sub-topics, namely “polyolefin stabilizers with reduced fragmentation”. Two patent families have been filed on behalf of Songwon Industrial Corporation Ltd. (South Korea) in March 2017 and June 2018. The corresponding identifications are WO 2018/172934 A1 and WO 2020/003048 A1.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
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WIPO | PCT

(10) International Publication Number
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(51) International Patent Classification:
C08F 2/44 (2006.01) *C08K 5/3492* (2006.01)
C08K 5/00 (2006.01) *C08K 5/105* (2006.01)
C08K 5/13 (2006.01)

(21) International Application Number: PCT/IB2018/051861

(22) International Filing Date: 20 March 2018 (20.03.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
17162445.5 22 March 2017 (22.03.2017) EP

(71) Applicant: **SONGWON INDUSTRIAL CO., LTD.** [KR/KR]; 83 Jangsaenggpo-ro, Nam-Gu, Ulsan 680-090 (KR).

(72) Inventor: **KECK, Klaus**; Rue des Ecoles 28, 4031 Angleur (BE).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

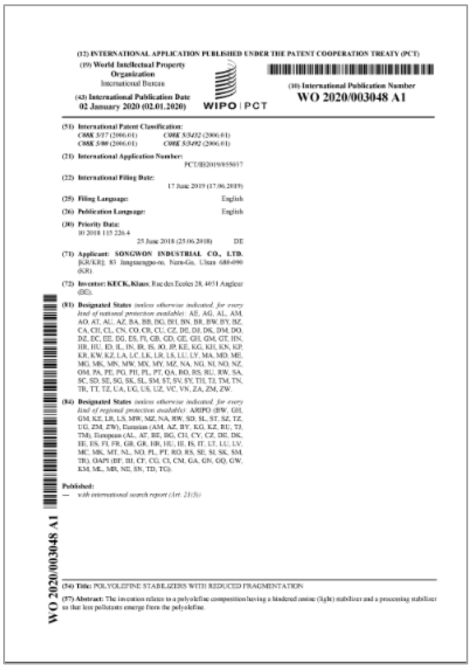
(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

WO 2018/172934 A1

(54) Title: POLYOLEFIN STABILIZERS WITH REDUCED FRAGMENTATION

(57) Abstract: The invention relates to a polyolefin composition having a selected thermal and processing stabilizer so that less pollutants emerge from the polyolefin.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
02 January 2020 (02.01.2020)

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(10) International Publication Number
WO 2020/003048 A1

(51) International Patent Classification:
C08K 5/17 (2006.01) *C08K 5/3432* (2006.01)
C08K 5/00 (2006.01) *C08K 5/3492* (2006.01)

(21) International Application Number: PCT/IB2019/055017

(22) International Filing Date: 17 June 2019 (17.06.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2018 115 226.4 25 June 2018 (25.06.2018) DE

(71) Applicant: **SONGWON INDUSTRIAL CO., LTD.** [KR/KR]; 83 Jangsaenggpo-ro, Nam-Gu, Ulsan 680-090 (KR).

(72) Inventor: **KECK, Klaus**; Rue des Ecoles 28, 4031 Angleur (BE).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report (Art. 21(3))*

WO 2020/003048 A1

(54) Title: POLYOLEFINE STABILIZERS WITH REDUCED FRAGMENTATION

(57) Abstract: The invention relates to a polyolefine composition having a hindered amine (light) stabilizer and a processing stabilizer so that less pollutants emerge from the polyolefine.

As this report is filled, 5 publication are in preparation by the author together with Dr. Michele Edge. Tentative titles are:

Reduction of water-extractable fragments from PO – Part 1: Impact of processing stabilization
Reduction of water-extractable fragments from PO – Part 2: Impact of the thermal stabilizer
Reduction of water-extractable fragments from PO – Part 3: Removal of formed fragments
Reduction of water-extractable fragments from PO – Part 4: Impact of standard processing stabilizer mixtures
Reduction of water-extractable fragments from PO – Part 5: Optimization of processing stabilization

7.2 Other Chemical Structures

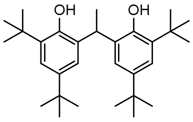
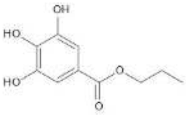
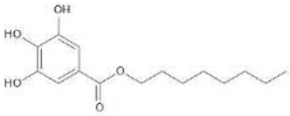
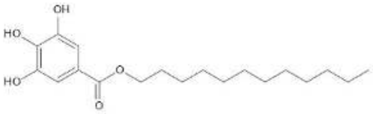
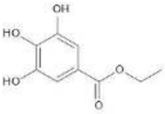
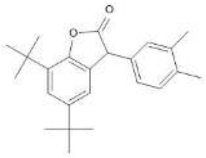
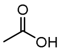
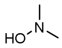
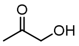
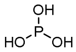
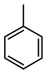
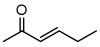
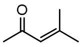
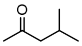
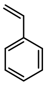
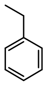
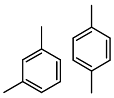
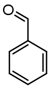
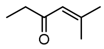
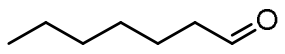
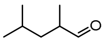
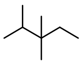
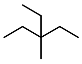
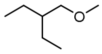
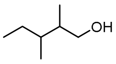
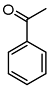
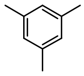
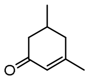
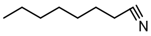
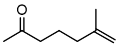
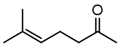
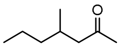
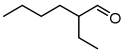
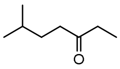
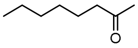
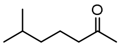
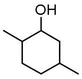
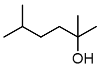
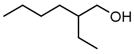
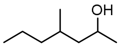
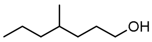
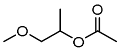
Code	Chemical Name	Chemical Structure	Class Description Reference
AO-16	**35958-30-6** 439 Dalton $C_{30}H_{46}O_2$		Fully hindered bisphenol
AO-78	Propylgallate **121-79-9** 212 Dalton $C_{10}H_{12}O_5$		Ester of gallic acid **E 310** Protective chemical
AO-79	Octylgallate **1034-01-1** 282 Dalton $C_{12}H_{22}O_5$		Ester of gallic acid **E 311** Protective chemical
AO-80	Dodecylgallate **1166-52-5** 338 Dalton $C_{19}H_{30}O_5$		Ester of gallic acid **E 312** Protective chemical
AO-94	Ethylgallate **831-61-8** 198 Dalton $C_{93}H_{108}O_5$		Ester of gallic acid **E 313** Protective chemical
L-1	5,7-Di-tert-butyl-“-(3,4-dimethylphenyl)-3H-benzofuran-2-one **181314-48-7** 350 Dalton $C_{24}H_{30}O_2$		“PO Lactone” Protective chemical

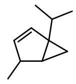
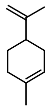
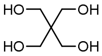
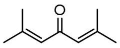
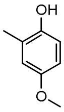
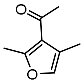
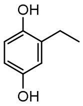
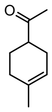
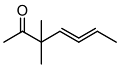
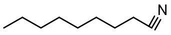
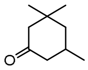
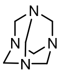
Table 40: Additional chemical structures

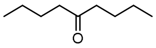
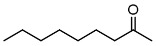
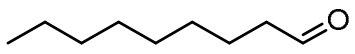
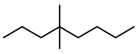
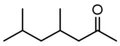
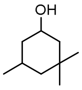
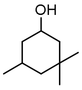
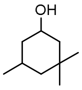
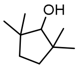
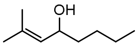
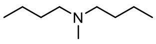
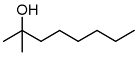
7.3 Overview over Water-Extractable Fragments

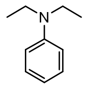
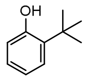
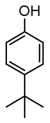
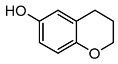
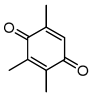
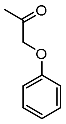
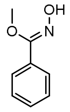
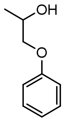
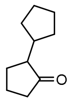
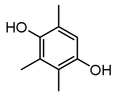
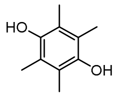
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
1	Acetic acid ***64-19-7*** $C_2H_4O_2$	60		**H226**, **H314**
2	Dimethyl hydroxylamine ***5725-96-2*** C_2H_7NO	61		
3	2-Propanone,1-hydroxy- ***116-09-6*** $C_3H_6O_2$	74		H226
4	Phosphoric acid ***10294-56-1*** H_3O_3P	82		H302, H314, (H318) Skin corrosion cat. 1A
5	Toluene ***108-88-3*** C_7H_8	92		**H225**, **H304**, **H315**, H319, **H336**, **H361d**, **H373**, H412 Suspected **Toxic for Reproduction**
6	3-Hexene-2-one or isomer ***763-93-9*** $C_6H_{10}O$	98		
7	3-Penten-2-one,4-methyl- *or isomer* ***141-79-7*** $C_6H_{10}O$	98		**H226**, **H302**, **H312**, H315, H319, **H332**, H331, H335
8	Methyl Isobutyl ketone ***108-10-1*** $C_6H_{12}O$	100		**H226**, **H319**, **H332**, **H335**
9	Styrene ***100-42-5*** C_8H_8	104		**H226**, **H315**,H304, **H319**, **H332**, H335, **H361d**, **H372**, H412 Suspected **Toxic for Reproduction**
10	Ethylbenzene ***100-41-4*** C_8H_{10}	106		**H225**, **H304**, **H332**, **H373**, H412
11	m- or p-Xylene ***108-38-3*** ***106-42-3*** C_8H_{10}	106		**H226**, **H312**, **H315**, **H332**, CoRAP

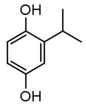
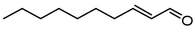
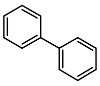
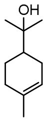
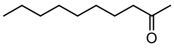
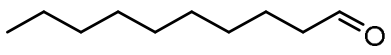
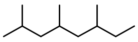
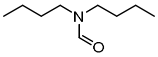
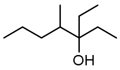
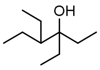
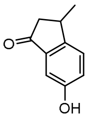
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
12	Benzaldehyde ***100-52-7*** C_7H_6O	106		❗ **H302**, H315, H317, H319, H332, H335, H373, H412
13	4-Hexen-3-one,5-methyl ***13905-10-7*** $C_7H_{12}O$	112		
14	Heptanal ***111-71-7*** $C_7H_{14}O$	114		🔥 ❗ **H226**, **H315**, H319, H412
15	Pentanal,2,4-dimethyl- ***27944-79-2*** $C_7H_{14}O$	114		
16	Pentane,2,3,3-trimethyl- *or isomer* ***560-21-4*** C_8H_{18}	114		🔥 ❗ ✴ 🐟 H225, H304, H315, H336, H400, H410 Suspected **cat. 1A or 1B CMR**
17	Pentane,3-ethyl-3-methyl- ***1067-08-9*** C_8H_{18}	114		🔥 ❗ ✴ 🐟 H225, H304, H315, H336, H400, H410 Suspected **cat. 1A or 1B CMR**
18	2-Ethyl-1-butanol, methyl ether ***No CAS# assigned*** $C_7H_{16}O$	116		
19	1-Pentanol,2,3-dimethyl- ***10143-23-4*** $C_7H_{16}O$	116		
20	Acetophenone ***98-86-2*** $C_8H_{18}O$	120		❗ **H302**, **H319**
21	Mesitylene ***108-67-8*** C_9H_{12}	120		🔥 ❗ 🐟 **H226**, **H335**, **H411**, H315, H319, H304
22	2-Cyclohexen-1-one, 3,5-dimethyl- ***1123-09-7*** $C_8H_{12}O$	124		Suspected **cat. 1A or 1B CMR**
23	Octanenitrile ***124-12-9*** $C_8H_{15}N$	125		❗ 🐟 H315, H400
24	1-Hepten-6-one,2-methyl- *or isomer* ***10408-15-8*** $C_8H_{12}O$	126		

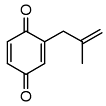
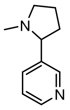
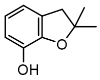
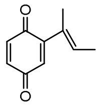
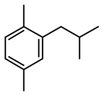
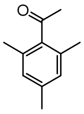
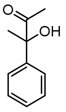
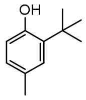
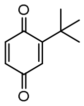
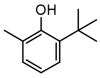
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
25	5-Hepten-2-one,6-methly- *or isomer* ***110-93-0*** $C_8H_{12}O$	126		H226, H319
26	2-Heptanone,4-methyl- ***6137-06-0*** $C_8H_{12}O$	128		
27	2-Ethylhexanal *or isomer* ***123-05-7*** $C_8H_{16}O$	128		H226, H317, H361
28	3-Heptanone,6-methyl- ***624-42-0*** $C_8H_{16}O$	128		Suspected **cat. 1A or 1B CMR**
29	2-Octanone ***111-13-7*** $C_8H_{16}O$	128		H226 Suspected **cat. 1A or 1B CMR**
30	2-Heptanone,6-methyl- ***928-68-7*** $C_8H_{16}O$	128		H226 Suspected **cat. 1A or 1B CMR**
31	2,5-Dimethyl cyclohexanol ***3809-32-3*** $C_8H_{16}O$	128		H225, H227, H315, H319, H335 Suspected **cat. 1A or 1B CMR**
32	2-Hexanol,2,5-dimethyl-, (S) *or isomer* ***3730-60-7*** $C_8H_{18}O$	130		H226, H302, H315, H318, H335 Suspected **cat. 1A or 1B CMR**
33	2-Ethyl-1-hexanol ***104-76-7*** $C_8H_{18}O$	130		H315, H319, H332, H335 CoRAP
34	2-Heptanol, 4-methyl- ***56298-90-9*** $C_8H_{18}O$	130		
35	1-Heptanol, 4-methyl- ***817-91-4*** $C_8H_{18}O$	130		H227, H315, H319, H335
36	1-Methoxy-2-propyl acetate ***108-65-6*** $C_6H_{12}O_3$	132		**H226**, H336

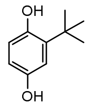
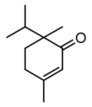
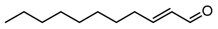
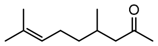
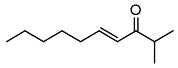
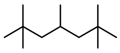
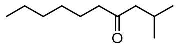
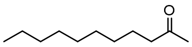
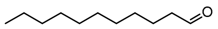
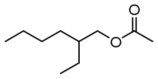
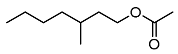
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
37	Bicyclo[3.10] hex-2-ene, 4-methyl-1-(1-methylethyl)- β-Thyjene ***28634-89-1*** $C_{10}H_{16}$	136		
38	Limonene ***138-86-3*** $C_{10}H_{16}$	136		**H226**, H304, **H315**, **H317**, H318, **H400**, **H410**, H411 **Skin sensitizer** Suspected **cat. 1A or 1B CMR**
39	Pentaerythritol ***115-77-5*** $C_5H_{12}O_4$	136		
40	Phorone ***504-20-1*** $C_9H_{14}O$	138		Suspected **cat. 1A or 1B CMR**
41	Phenol, 4-methoxy-3-methyl- *or isomer* ***14786-82-4*** $C_8H_{10}O_2$	138		
42	1-(2,4-Dimethyl-furan-3-yl)-ethanone ***32933-07-6*** $C_8H_{10}O_2$	138		H226
43	*Derivative of* Tert-butyl hydroquinone w/o 1 or 2 methyl groups	138		
44	4-Acetyl-1-methylcyclohexene ***6090-09-1*** $C_9H_{14}O$	138		H227, H315, H319, H335
45	3,3-Dimethyl-hepta-4,5-dien-2-one ***No CAS# assigned***	138		
46	Nonanenitrile ***2243-27-8*** $C_9H_{17}N$	139		H315, H319
47	Cyclohexanone,3,3,5-trimethyl- ***873-94-9*** $C_9H_{16}O$	140		H315, H319, H332, H335
48	Methenamine ***100-97-0*** $C_6H_{12}N_4$	140		H228, H317 **Skin sensitizer**

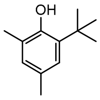
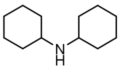
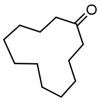
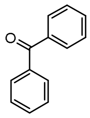
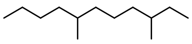
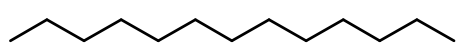
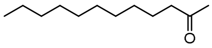
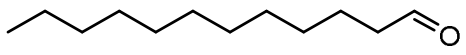
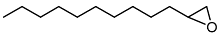
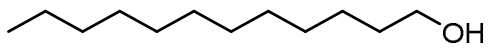
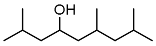
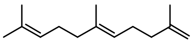
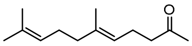
Fragment #	*Chemical Name*	*Molecular Weight* *[Dalton]*	*Chemical Structure*	*Remark*
49	5-Nonanone ***502-56-7*** $C_9H_{18}O$	142		H226, H319, H335, H336, H372 Suspected **cat. 1A or 1B CMR**
50	2-Nonanone ***821-55-6*** $C_9H_{18}O$	142		H315, H319 Suspected **cat. 1A or 1B CMR**
51	Nonanal ***124-19-6*** $C_9H_{18}O$	142		H315, H319, H412
52	4,4-dimethyl octane *or isomer* ***15869-95-1*** $C_{10}H_{22}$	142		H226, H304
53	2-Heptanone,4,6-dimethyl- ***19549-80-5*** $C_9H_{18}O$	142		H226, H335 Suspected **cat. 1A or 1B CMR**
54	Cyclohexanol,3,3,5-trimethyl-, cis- ***933-48-2*** $C_9H_{18}O$	142		H315, H319, H412
55	Cyclohexanol,3,3,5-trimethyl-, trans- ***767-54-4*** $C_9H_{18}O$	142		H315, H319, H412 Suspected **cat. 1A or 1B CMR**
56	Cyclohexanol,3,3,5-trimethyl- ***116-02-9*** $C_9H_{18}O$	142		H315, H319
57	2,2,5,5-Tetramethyl-cyclopentanol ***15231-50-2*** $C_9H_{18}O$	142		
58	2 -Octen-4-ol, 2-methyl- ***65885-49-6*** $C_9H_{18}O$	142		
59	1-Butanamine, N-butyl-N-methyl- *3405-45-6* $C_9H_{21}N$	143		H226, H302, H311, H312, H332
60	2-Octanol,2-methyl- ***628-44-4*** $C_9H_{20}O$	144		H226, H315, H318, H335

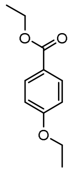
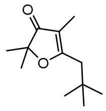
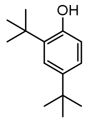
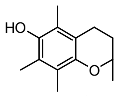
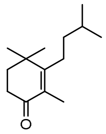
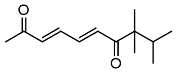
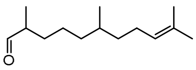
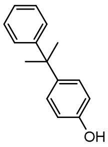
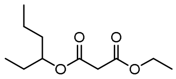
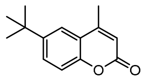
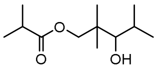
Fragment #	*Chemical Name*	*Molecular Weight* *[Dalton]*	*Chemical Structure*	*Remark*
61	N, N-Diethylaniline ***91-66-7*** $C_{10}H_{15}N$	149		**H301**, **H311**, **H331**, **H373**, **H411**
62	Phenol, 2-(1,1-dimethylethyl)- ***88-18-6*** $C_{10}H_{14}O$	150		H302, H311, H312, H314, H318, H332, H411
63	Tert.-butyl-phenol **ARVIN 2** ***98-54-4*** $C_{10}H_{14}O$	150		**H315**, **H318**, **H361f**, **H410** Suspected **Toxic for Reproduction** Suspected **Endocrine Disruptor**
64	*Derivative of* Phenol, 2-(1,1-dimethylethyl)-		*See Fragment 62*	
65	3,4-Dihydro-2H-1-benzopyran-6-ol phenol (6-Chromanol) ***5614-78-8*** $C_9H_{10}O_2$	150		H302, H315, H319, H335
66	2,3,6-Trimethyl-p-benzoquinone ***935-92-2*** $C_9H_{10}O_2$	150		**Skin sensitizer** Suspected **cat. 1A or 1B CMR**
67	*Derivatives of* 1-phenoxypropan-2-ol *resp.* 1-phenoxy-propan-2-one	150		
68	Oxime-, methoxy-phenyl-	151		
69	1-Phenoxypropan-2-ol ***770-35-4*** $C_9H_{12}O_2$	152		H319
70	2-cyclopentyl cyclopentanone ***4864-24-6*** $C_{10}H_{16}O$	152		H315, H319, H335
71	Trimethylhydroquinone ***700-13-0*** $C_9H_{12}O_2$	152		**H315**, **H317**, **H318**, **H332**, **H335**, **H400**, **H410**
72	Tetramethylhydro-quinone ***527-18-4*** $C_{10}H_{14}O_2$	**166**		

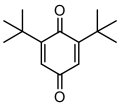
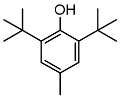
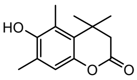
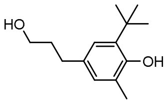
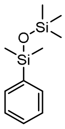
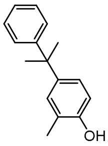
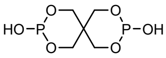
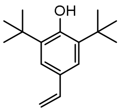
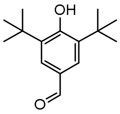
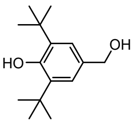
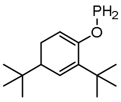
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
73	*Derivative of* Tert-butyl hydroquinone w/o 1 or 2 methyl groups	152		
74	*Derivatives of* 1-phenoxypropan-2-ol resp. 1-phenoxypropan-2-one	152	*See Fragment 69*	
75	2-Decenal, (E)- ***3913-81-3*** $C_{10}H_{18}O$	154		⚠ H315, H319 Suspected **cat. 1A or 1B CMR**
76	Bi-phenyl ***92-54-4*** $C_{12}H_{10}$	154		⚠ 🐟 **H315**, **H319**, **H335**, **H400**, **H410** CoRAP (Suspected **PBT**)
77	Alpha-Terpineol ***98-55-5*** $C_{10}H_{18}O$	154		🐟 H315, H319
78	2-Decanone ***693-54-9*** $C_{10}H_{20}O$	156		🐟 H411 Suspected **cat. 1A or 1B CMR**
79	Decanal ***112-31-2*** $C_{10}H_{20}O$	156		⚠ 🐟 H315, H319, H412
80	Octane,2,4,6-trimethyl *or isomer* ***62016-37-9*** $C_{11}H_{24}O$	156		
81	Formamidine, N,N-dibutyl- ***761-65-9*** $C_9H_{19}NO$	157		🧪 ⚠ H302, H312, H317, H318, H412 **PBT**
82	3-Ethyl-4-methyl-3-heptanol ***66719-39-9*** $C_{10}H_{22}O$	158		
83	3-Hexanol,3,4-diethyl- *or isomer* ***19398-78-8*** $C_{10}H_{22}O$	158		⚠ H227, H315, H319, H335
84	*Isomer of* 3-Ethyl-4-methyl-3-heptanol	158	*See Fragment 82*	
85	5-Hydroxy-3-methyl-1-inadone ***57878-30-5*** $C_{10}H_{10}O_2$	162		

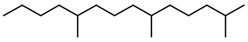
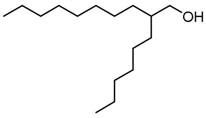
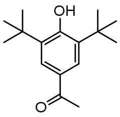
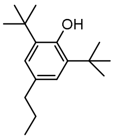
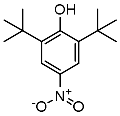
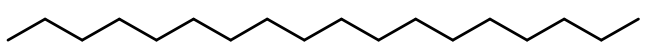
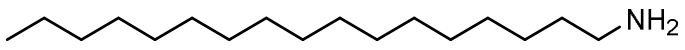
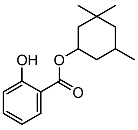
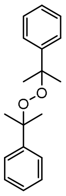
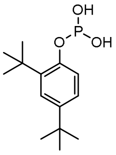
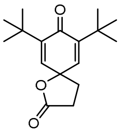
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
86	$C_{10}H_{10}O_2$	162		
87	Pyridine-3-(1-methyl-2-pyrrodinyl)-, (S)- ***54-11-5*** ***22083-74-5*** $C_{10}H_{14}N_2$	162		H301, H310, H411
88	2,3-di-hydro-2,2-dimethyl-7-benzo-furanol ***1563-38-8*** $C_{10}H_{12}O_2$	162		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
89	*"Dehydrogenated derivative" of* Tert.-butyl-p-benzoquinone *(partially co-elution)*	162	 *See Fragment 99*	
90	Benzene,1,4-dimethyl-2-(2-methylpropyl) ***55669-88-0*** $C_{12}H_{18}$	162		
91	Ethanone,1-(2,4,6-trimethylphenyl) ***1667-01-2*** $C_{11}H_{14}O$	162		
92	3-Hydroxy-3-phenylbutan-2-one ***3155-01-9*** $C_{10}H_{12}O_2$	164		H315, H318, H335
93	Phenol, 2-(1,1-dimethylethyl)-4-methyl ***2409-55-4*** $C_{11}H_{16}O$	164		H302, H312, H314, H315, H318, H319, H335, H411 **Skin sensitizer**
94	*Derivative of* 7-Benzofuranol, 2,3-dihydro-2,2-dimethyl-	164	*See Fragment 88*	
95	Tert-butyl-p-benzoquinone ***3602-55-9*** $C_{10}H_{12}O_2$	164		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
96	*Derivative of* Tert-butyl hydroquinone	164	See Fragment # 99	
97	2-tert-butyl-6-methyl phenol ***2219-08-1*** $C_{11}H_{16}O$	164		H314, H318

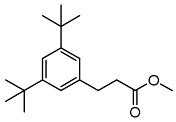
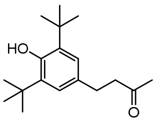
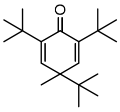
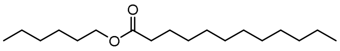
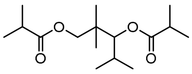
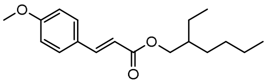
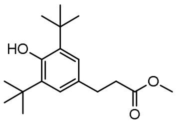
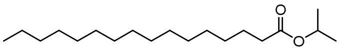
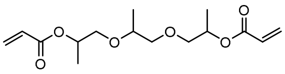
Fragment #	Chemical Name	Molecular Weight [Dalton]	Chemical Structure	Remark
98	*Isomer of* 2,3-di-hydro-2,2-dimethyl-7-benzo-furanol	164	*2 additional isomers detected*	
99	Tert-butyl hydroquinone ***1948-33-0*** $C_{10}H_{14}O_4$	166		H302, H319, H400, H312, H317, H315, H410
100	2-Cyclohexene-1-one, 3,6-dimethyl-6-(1-methylethyl)- ***54410-58-1*** $C_{11}H_{18}O_4$	166		
101	2-Undecenal ***2463-77-6*** $C_{11}H_{20}O$	168		H315, H317, H319, H411 Suspected **cat. 1A or 1B CMR**
102	7-Nonen-2-one, 4, 8-dimethyl- ***3664-64-0*** $C_{11}H_{20}O$	168		
103	Isobutyl-2-heptenone ***No CAS# assigned*** $C_{11}H_{20}O$	168		
104	Heptane,2,2,4,6,6-pentamethyl- ***13475-82-6*** $C_{12}H_{26}$	170		H226, H304, H319, H336, H400, H410, H413
105	2-Methyl-4-decanone *or isomer* ***6628-25-7*** $C_{11}H_{22}O$	170		H412
106	2-Undecanone ***112-12-09*** $C_{11}H_{22}O$	170		H315, H400, H410 Suspected **cat. 1A or 1B CMR**
107	Undecanal ***112-44-7*** $C_{11}H_{22}O$	170		H315, H412
108	Acetic acid, 2-ethylhexyl ester ***103-09-3*** $C_{10}H_{20}O_2$	172		H315 CoRAP
109	3-Methylheptyl acetate ***72218-58-7*** $C_{10}H_{20}O_2$	172		

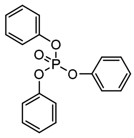
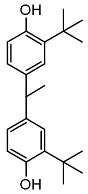
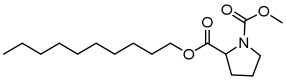
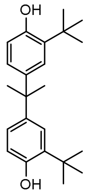
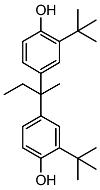
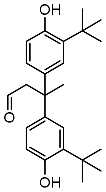
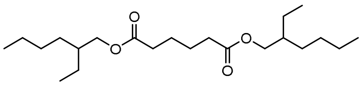
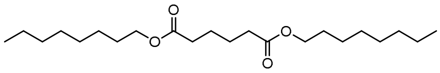
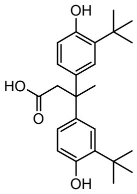
Fragment #	*Chemical Name*	*Molecular Weight* *[Dalton]*	*Chemical Structure*	*Remark*
110	6-Tert-butyl-2,4-dimethyl phenol ***1879-09-0*** $C_{12}H_{18}O$	178		H301, H302, H310, H315, H319, H373, H411
111	Dicyclohexylamine ***101-83-7*** $C_{12}H_{23}N$	181		H301, **H302**, H311, **H314**, **H400**, **H410**
112	Cyclododecanone ***830-13-7*** $C_{12}H_{22}O$	182		H411
113	Benzophenone ***119-61-9*** $C_{13}H_{10}O$	182		H373, H411, H412 CoRAP
114	Undecane, 3,7-dimethyl- *or isomer* ***17301-29-0*** $C_{13}H_{28}$	184		
115	Tridecane ***629-50-5*** $C_{13}H_{28}$	184		H304
116	2-Dodecanone ***6175-49-1*** $C_{12}H_{24}O$	184		H411 Suspected **cat. 1A or 1B CMR**
117	Dodecanal ***112-54-9*** $C_{12}H_{24}O$	184		H315, H317, H319, H411 **Skin sensitizer**
118	Oxirane, decyl- ***2855-19-8*** $C_{12}H_{24}O$	184		H315, H319, H335, H400, H411
119	1-Dodecanol ***112-53-8*** $C_{12}H_{26}O$	186		H319, H400, H410, H411
120	4-Nonanol,2,6,8-trimethyl- ***123-17-1*** $C_{12}H_{26}O$	186		
121	1,5,9-Undecatriene,2, 6,10-trimethyl-, (Z)- ***62951-96-6*** $C_{14}H_{24}$	192		
122	5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)- ***3879-26-3*** $C_{13}H_{22}O$	194		H315, H411

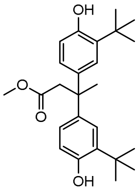
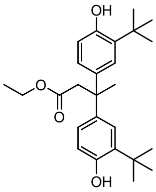
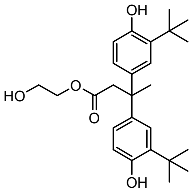
Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
123	Benzoic acid, 4-ethoxy-, ethyl ester ***23676-09-7*** $C_{11}H_{14}O_3$	194		⚠ ⚠ H302, H315, H319, H335
124	Derivative of Dimethylpropyl, trimethyl-furanone ***No CAS# assigned*** $C_{12}H_{20}O_2$	196		
125	2,4-Di-tert-butyl phenol **ARVIN 4** ***96-76-4*** $C_{14}H_{22}O_2$	206		⚠ ⚠ ⚠ ⚠ H302, H315, H318, H319, H335, H400, H410 CoRAP (Suspected **ED**)
126	2,5,7,8-Tetramethyl-6-chromanol $C_{13}H_{18}O_2$	206		
127	2, 4, 4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone ***88725-82-0*** $C_{14}H_{24}O$	208		
128	8,8,9-Trimethyl-deca-3,5-diene-2,7-dione ***No CAS# assigned*** $C_{13}H_{20}O_2$	208		
129	Undecanal,2,6,10-trimethyl- ***141-13-9*** $C_{14}H_{26}O_2$	210		⚠ ⚠ H317, H400, H410 **Skin Sensitizer**
130	4-Cumyl phenol ***599-64-4*** $C_{15}H_{16}O$	212		⚠ H302, H315, H318, H319, H335, H373, H400, H410, H411
131	Malonic acid, ethyl 3-hexyl ester ***1000349-11-7*** $C_{11}H_{20}O_4$	216		
132	6-tert-butyl-4-methylcoumarin ***17874-32-7*** $C_{14}H_{16}O_2$	216		
133	*Isomer of* 2,2,4-Trimethyl-1,3-pentadiol-1-isobutyrate	216	*See Fragment 134*	
134	2,2,4-Trimethyl-1,3-pentadiol-1-isobutyrate ***77-68-9*** $C_{12}H_{24}O_3$	216		Suspected **cat. 1A or 1B CMR**

Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
135	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- **ARVIN 3** ***719-22-2*** $C_{14}H_{20}O_2$	220		H315, H319, H335 Suspected **cat. 1A or 1B CMR**
136	Butylhydroxy Toluene **128-37-0** $C_{15}H_{24}O$	220		H400, H410 CoRAP (Suspected **ED**)
137	Dihydrocoumarin tetramethyl ***50442-68-7*** $C_{13}H_{16}O_3$	220		
138	3-(3,tert-butyl-4-hydroxy-5-methylphenyl) propanol ***75546-54-2*** $C_{14}H_{22}O_2$	224		
139	Phenyl-pentamethyl-disiloxane ***14920-92-4*** $C_{11}H_{20}OSi_2$	224		
140	*Isomer of* 2-Methyl,4-cumyl phenol ***2675-76-5*** $C_{18}H_{18}O$	226		
141	$C_5H_{10}O_6P_2$	228		
142	3,5-di-tert-butyl-4-hydroxystyrene **ARVIN 5** ***52858-87-4*** ***19263-36-6*** $C_{16}H_{24}O$	232		
143	3,5-di-tert-butyl-4-hydroxybenzaldehyde **ARVIN 6** ***1620-98-0*** $C_{15}H_{22}O_2$	234		H315, H319 Suspected **cat. 1A or 1B CMR**
144	$C_{15}H_{24}O_2$	236		
145	(2,4-di-tert-butyl cyclohexa-1,3-dien-1-yl) oxyphosphane ***No CAS# assigned*** $C_{14}H_{25}OP$	240		

Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
146	Tetradecane, 2,6-10-trimethyl- ***14905-56-7*** $C_{17}H_{36}$	240		
147	1-Decanol, 2-hexyl- ***2425-77-6*** $C_{16}H_{34}O$	242		Suspected **PBT**
148	3,5-di-tert-butyl-4-hydroxyacetophenone **ARVIN 7** ***14035-33-7*** $C_{16}H_{24}O_2$	248		⚠ H315, H319, H335, H413
149	*Proposed structure* 2,6-di-tert-butyl-4-propylphenol ***4973-24-4*** $C_{17}H_{28}O$	248		
150	2,6-Di-tert-Butyl-4-nitrophenol ***728-40-5*** $C_{14}H_{21}NO_3$	251		
151	n-Octadecane ***593-45-3*** $C_{18}H_{38}$	255		⚠ H304
152	Heptadecylamine ***4200-95-7*** $C_{17}H_{35}N$	256		⚠ H315, H319 Suspected **cat. 1A or 1B CMR**
153	Homosalate ***118-56-9*** $C_{16}H_{22}O_3$	262		H315, H319, H335, (H413) Suspected **Endocrine Disruptor**
154	Dicumyl peroxide ***80-43-3*** $C_{18}H_{22}O_2$	270		⚠ ⚠ ⚠ H242, H315, H319, H411 CoRAP (Suspected **PBT**)
155	$C_{14}H_{23}O_3P$	270		
156	7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione **ARVIN 8** ***82304-66-3*** $C_{17}H_{24}O_3P$	276		

Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
157	*Derivative of **ARVIN 9***	276		
158	*Derivative of **ARVIN 9***	276		
159	2,4,6-Tris (1,1-dimethyl ethyl)-4-methylcyclohexa-2,5-dien-1-one ***19687-22-0*** $C_{19}H_{32}O$	277		
160	Dodecanoic acid, hexyl ester ***34316-64-8*** $C_{18}H_{36}O_2$	285		
161	2,2,4-Trimethyl-1,3-pentanediol diisobutyrate ***6846-50-0*** $C_{16}H_{30}O_4$	286		H315, H319, H361, H373, H412
162	2-Ethylhexyl trans-4-methoxycinnamate ***83834-59-7*** $C_{18}H_{26}O_3$	290		H411 CoRAP (Suspected **PBT** & **ED**)
163	Benzenepropoanoic acid,3,5-bis (1,1-dimethylethyl)-4-hydroxy-, methyl ester **ARVIN 9** ***6386-38-5*** $C_{18}H_{28}O_3$	292		H302, H411
164	*Derivative of ARVIN 9*		*See Fragment 163*	
165	Isopropyl palmitate ***142-91-6*** $C_{19}H_{38}O_2$	299		
166	2-Propenoic acid, (1-methyl-1,2-ethanediyl) bis [oxy(methyl-2,1-etahndiyl)] Tripropyleneglycol diacrylate ***71412-35-6*** $C_{15}H_{24}O_6$	300		

Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
167	Triphenylphosphate ***115-86-6*** $C_{18}H_{15}O_4P$	326		E400, E410 CoRAP (Suspected **ED**)
168	$C_{22}H_{30}O_2$	326		
169	*Derivative of* 1-Proline, N-methoxycarbonyl-, decyl ester	327	*Derivative of* 	
170	$C_{23}H_{32}O_2$	340		
171	$C_{24}H_{34}O_2$	354		
172	$C_{24}H_{32}O_3$	368		
173	Hexanedioic acid, bis(2-ethylhexyl) ester ***103-23-1*** $C_{22}H_{42}O_4$	370		CoRAP
174	Hexanedioic acid, dioctyl ester ***123-79-5*** $C_{22}H_{42}O_4$	370		H315, H319 Suspected **cat. 1A or 1B CMR**
175	$C_{24}H_{32}O_4$	384		

Fragment #	***Chemical Name***	***Molecular Weight*** *[Dalton]*	***Chemical Structure***	***Remark***
176	$C_{25}H_{34}O_4$	399		
177	$C_{26}H_{36}O_4$	413		
178	$C_{26}H_{36}O_5$	429		

7.4 Individual Data on In-Polymer Performance

Individual data to characterize PP samples after melt-processing are grouped by common processing window. Formulations were melt-processed in batches; the entire timeframe covered nearly 5 years.

Polymer: PP-A
Extrusion: C-1, M-1

Formulation	**MFI**				**YI**			
750 ppm MS-1+ 750 ppm P-1 + 750 ppm AO-1	7.3	12.9	26.9	40.9	-3.8	4.7	7.4	7.9

Polymer: PP-B
Extrusion: C-1, M-1

Formulation	**MFI**				**YI**			
750 ppm MS-1	9.0	13.9	25.4	35.8	-4.2	-3.3	-2.2	-0.1
750 ppm MS-1+ 750 ppm P-1	4.0	5.4	8.3	12.3	-4.1	-2.7	-1.1	0.0
750 ppm MS-1+ 750 ppm P-1 + 1000 ppm AO-1	3.8	4.3	5.5	7.0	-3.1	-1.5	-0.1	0.8
750 ppm MS-1+ 750 ppm P-1 + 2500 ppm AO-1	2.4	2.5	2.8	2.9	-2.2	-0.2	2.3	4.9
750 ppm MS-1+ 750 ppm P-1 + 5000 ppm AO-1	2.4	2.4	2.5	2.7	-1.8	-0.6	2.2	4.4
750 ppm MS-1+ 750 ppm P-1 + 5000 ppm AO-3	2.7	2.7	3.5	3.7	0.8	5.3	10.1	14.3
750 ppm MS-1+ 750 ppm P-1 + 5000 ppm AO-4	2.4	2.5	2.6	2.8	1.5	4.7	11.6	14.8
750 ppm MS-1+ 750 ppm P-1 + 5000 ppm AO-38	2.5	2.8	3.5	4.6	-2.2	2.2	7.2	9.8
750 ppm MS-1+ 750 ppm P-1 + 5000 ppm AO-39	2.4	2.5	2.7	2.8	5.2	9.9	18.7	29.1

Polymer: PP-C
Extrusion: C-1, M-1

Formulation	**MFI**				**YI**			
750 ppm MS-1	15.8	22.6	35.2	38.4	-0.1	1.0	4.3	6.3
750 ppm MS-1 + 5000 ppm AO-1	7.1	7.8	8.9	10.2	0.2	11.1	18.6	23.2
750 ppm MS-1+ 5000 ppm AO-1 + 1000 ppm P-1	2.9	3.0	3.1	3.2	-1.6	0.6	2.3	4.5
750 ppm MS-1+ 5000 ppm AO-1 + [1000 ppm P-1 + 250 ppm AO-6]	3.0	3.0	3.1	3.2	0.3	0.9	2.6	4.1
750 ppm MS-1+ 5000 ppm AO-1 + [500 ppm P-1 + 250 ppm AO-6]	3.0	3.0	3.2	3.3	-0.3	0.1	1.8	3.0
750 ppm MS-1+ 5000 ppm AO-1 + 1000 ppm P-1$_{HYD}$	8.0	9.1	10.4	11.9	0.6	6.2	11.3	15.1

Polymer: PP-A
Extrusion:C-1, M-1

Formulation	MFI				YI			
750 ppm MS-1	8.7	13.9	24.6	41.5	-3.9	-2.8	-0.9	0.3
750 ppm MS-1+ 1000 ppm P-1	3.6	5.3	6.1	12.0	-3.5	-3.7	-3.9	-3.1
750 ppm MS-1+ 1000 ppm P-3	3.0	3.2	3.9	4.1	-3.8	-1.4	-1.3	0.7
750 ppm MS-1+ 1000 ppm P-4	3.2	3.3	4.2	5.1	-2.9	-3.8	-3.2	-2.4
750 ppm MS-1+ 1000 ppm P-5	3.1	3.8	4.1	4.6	-3.9	-3.9	-2.7	-2.7
750 ppm MS-1+ 1000 ppm P-9	3.1	3.2	3.8	4.3	-3.2	-2.6	0.0	2.3
750 ppm MS-1+ 1000 ppm P-19	2.4	2.5	2.7	2.9	-2.2	-2.3	-0.8	0.6
750 ppm MS-1+ 1000 ppm AO-6	3.3	3.5	4.3	5.4	9.2	17.3	26.4	33.7
750 ppm MS-1+ 1000 ppm AO-36	3.5	3.8	4.0	5.7	-1.6	0.6	3.4	9.9
750 ppm MS-1+ 1000 ppm AO-53	2.4	2.6	3.3	6.8	24.0	28.2	30.6	31.5
750 ppm MS-1+ 1000 ppm AO-58	4.1	5.2	8.9	11.7	50.8	50.5	49.7	48.5
750 ppm MS-1+ 1000 ppm AO-60	2.4	2.5	2.7	2.9	20.2	8.5	1.8	-0.2
750 ppm MS-1+ 1000 ppm HYA-1	3.1	3.6	5.8	7.4	-3.8	-3.0	-1.6	-0.6
750 ppm MS-1+ 1000 ppm L-2	2.7	3.2	3.9	4.6	7.9	11.2	14.3	15.7

Polymer: PP-A
Extrusion:C-1, M-1

Formulation	MFI				YI			
750 ppm MS-1	10.8	16.8	34.0	57.7	-3.0	-3.3	-2.6	-1.8
750 ppm MS-1 + 500 ppm AO-1 + 500 ppm P-1	4.1	4.7	6.8	9.7	-1.6	0.5	2.8	4.5
750 ppm MS-1+ 1000 ppm AO-1	5.4	6.7	9.6	13.3	-1.6	-0.3	2.3	4.8
750 ppm MS-1+ 1000 ppm AO-2	6.9	9.0	14.7	20.6	-0.9	-1.0	1.4	2.5
750 ppm MS-1+ 1000 ppm AO-4	4.8	5.8	7.6	10.0	0.6	1.8	5.0	7.9
750 ppm MS-1+ 1000 ppm AO-7	4.3	4.8	6.3	8.3	8.4	11.4	20.7	25.5
750 ppm MS-1+ 1000 ppm AO-38	5.7	7.1	10.8	15.4	-0.2	-0.7	2.4	5.2
750 ppm MS-1+ 1000 ppm AO-54	9.1	12.0	20.6	32.8	-2.3	-2.1	-1.1	0.0
750 ppm MS-1+ 1000 ppm HAS-5	10.3	15.0	28.3	39.8	-3.3	-2.9	-2.2	-1.4
750 ppm MS-1+ 1000 ppm HAS-16	9.7	13.3	25.2	39.8	-3.1	-3.2	-2.8	-2.2
750 ppm MS-1+ 1000 ppm HAS-25	9.9	13.7	28.5	43.3	-3.1	-3.3	-2.4	-1.9

Polymer: PP-A
Extrusion: C-1, M-1

Formulation	MFI				YI			
750 ppm MS-1 + 750 ppm P-1	8.9	14.6	24.8	36.0	-2.3	-1.1	0.7	2.7
750 ppm MS-1 + 750 ppm P-1 + 5000 ppm AO-1	3.9	4.5	5.4	6.5	0.6	5.0	13.9	20.4
750 ppm MS-1 + 750 ppm P-1 + 5000 ppm AO-1 + 5000 ppm O-3	3.0	3.1	3.2	3.4	3.8	7.9	11.0	13.0
750 ppm MS-1 + 750 ppm P-1 + 5000 ppm AO-1 + 5000 ppm O-4	5.4	6.0	7.2	8.9	11.3	17.1	26.2	30.2
750 ppm MS-1 + 750 ppm P-1 + 5000 ppm AO-4	4.5	4.9	6.3	7.3	3.1	10.9	19.8	24.7
750 ppm MS-1 + 750 ppm P-1 + 5000 ppm AO-4 + 5000 ppm O-3	3.4	3.5	4.5	5.2	14.6	19.6	26.5	30.9

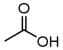
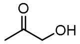
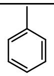
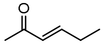
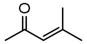
7.5 Individual Analytical Data

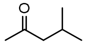
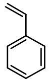
Below listed table comprises all individual analytic data points on fragments identified. The table is compiled by increasing molecular weight of fragments and corresponds therefore to **Appendix 7.3**. A colour coding is introduced for better readability

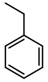
Blue (S)	PP substrate-originating fragment
Red (PC)	Protective chemical originating fragment
Green (M)	Modifier-originating fragment
Light Blue (Syn)	Fragment originating from synthesis or process chemical
Brown (?)	Fragment with unclear origin
Black	Unidentified fragments

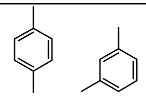
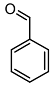
For each fragment the highest concentration detected (within the scope of this investigation) is highlighted in yellow. The highest concentration is listed independent of the experimental conditions which created it an whether the conditions are representative of industrial practice. The following abbreviations are used in the table:

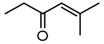
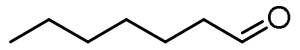
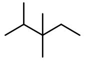
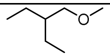
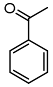
F#	Fragment number
Chemical Name	Identity of the fragment including formula and CAS# in case assigned
MW	Molecular weight of fragment in [Dalton]
Chemical Structure	Proposed target structure
Match [%]	Probability of identification from MS spectra library
RT [min]	Retention time under employed GC conditions
Origin	See above colour coding
Chapter	Chapter of the report where the data is discussed
T [°C]	Extraction temperature
C [ppb]	Concentration of fragment
PP	PP batch
Remark	Formulation utilized which yield the fragments
Ref.	Analytical file referenced in chapter 6

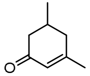
F #	Chemical Name	MW [Dalton]	Chemical Structure	Match [%]	RT [min]	Origin	Chapter	T [°C]	C [ppb]	PP	Remark	Ref.
1	Acetic acid ***64-19-7*** $C_2H_4O_2$	60		97	4.71	**S**	3.1	20°C	**0.6**	PP-A	None	237
3	2-Propanone,1-hydroxy- ***116-09-6*** $C_3H_6O_2$	74		87	5.63	**S**	3.1	20°C	**0.9**	PP-A	None	237
				94	5.63		3.1	20°C	**0.9**	“	[AO-1+P-1] [750+750]	“
5	Toluene ***108-88-3*** C_7H_8	92		96	7.24	**Syn**	3.3.5	20°C	4.2	PP-A	1000 P-1	263
				91	7.09		3.3.5	20°C	1.3	“	1000 P-3	“
				93	7.23		3.3.5	20°C	1.7	“	1000 P-4	“
				92	7.24		3.3.5	20°C	2.7	“	1000 P-5	“
				92	7.23		3.3.5	20°C	1.9	“	1000 P-9	“
				92	7.23		3.3.5	20°C	2.3	“	1000 P-19	“
				96	7.25		3.3.5	20°C	3.5	“	1000 AO-6	“
				97	7.07		3.3.5	20°C	4.5	“	1000 AO-36	“
				98	7.08		3.3.5	20°C	3.7	“	1000 AO-53	“
				95	7.24		3.3.5	20°C	2.6	“	1000 AO-58	“
				96	7.24		3.3.5	20°C	6.2	“	1000 AO-60	“
				92	7.24		3.3.5	20°C	2.2	“	1000 HYA-1	“
				92	7.09		3.3.5	20°C	3.6	“	1000 L-2	“
				96	7.08		3.4	20°C	2.6	PP-A	None	279
				97	7.06		3.4	20°C	**9.0**	“	1000 AO-1	“
				92	7.20		3.4	20°C	1.5	“	1000 AO-2	“
				96	7.17		3.4	20°C	2.5	“	1000 AO-4	“
				97	7.19		3.4	20°C	4.8	“	1000 AO-7	“
				91	7.17		3.4	20°C	2.0	“	1000 AO-38	“
				97	7.21		3.4	20°C	5.1	“	1000 AO-54	“
				93	7.19		3.4	20°C	1.7	“	1000 HAS-5	“
				95	7.22		3.4	20°C	2.4	“	1000 HAS-16	“
				98	7.22		3.4	20°C	5.1	“	1000 HAS-25	“
				95	7.18		3.4	20°C	3.9	“ “	[AO-1+P-1] [500+500]	“
6	3-Hexene-2-one or isomer ***763-93-9*** $C_6H_{10}O$	98		89	8.41	**S**	3.1	60°C	**1.7**	PP-A	None	238
7	3-Penten-2-one,4-methyl- *or isomer* ***141-79-7*** $C_6H_{10}O$	98		88	8.42	**S**	3.1	60°C	0.8	PP-A	[AO-1+P-1] [750+750]	238
				97	8.35		3.5	60°C	33.2	PP-A	750 P-1	229
				97	8.34		3.5	60°C	29.5	“	[AO-1+P-1] [5000+750]	“
				97	8.37		3.5	60°C	12.0	“	[AO-1+P-1+O-3]	“

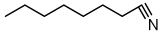
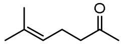
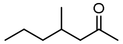
											[5000+750+5000]	
				97	8.32		3.5	60°C	49.8	“	[AO-1+P-1+O-4] [5000+750+5000]	“
				97	8.33		3.5	60°C	42.2	“	AO-4+P-1] [5000+750]	“
				97	8.35		3.5	60°C	43.8	“	[AO-4+P-1+O-3] [5000+750+5000]	“
				97	8.29		3.2	60°C	**58.3**	PP-B	None	243
				97	8.28		3.3.3	60°C	48.0	PP-B	5000 AO-1	“
				94	8.36		3.3.3	60°C	6.5	PP-B	[AO-1+P-1] [5000+1000]	“
				97	8.35		3.3.3	60°C	8.9	PP-B	[AO-1+P-1+AO-6] [5000+1000+250]	“
				96	8.37		3.3.3	60°C	7.2	PP-B	AO-1+P-5+AO-6] [5000+500+250]	“
				96	8.34		3.3.4	60°C	47.8	PP-B	[AO-1+P-1_{HYD}] [5000+1000]	“
				97	8.33		3.2	60°C	25.7	PP-C	None	246
				94	8.37		3.3	60°C	12.9	“	[P-1] [750 ppm]	“
				92	8.37		3.3	60°C	8.8	“	[AO-1+P-1] [1000+750]	“
				82	8.37		3.3	60°C	3.7	“	[AO-1+P-1] [2500+750]	“
				80	8.42		3.3	60°C	2.3	“	[AO-1+P-1] [5000+750]	“
				91	8.38		3.4	60°C	4.0	“	[AO-3+P-1] [5000+750]	“
				83	8.43		3.4	60°C	3.2	“	[AO-4+P-1] [5000+750]	“
				88	8.39		3.4	60°C	3.6	“	[AO-38+P-1] [5000+750]	“
				79	8.41		3.4	60°C	3.0	“	[AO-39+P-1] [5000+750]	“
8	Methyl Isobutyl ketone ***108-10-1*** $C_6H_{12}O$	100		86	6.35	**S**	3.2	60°C	**15.7**	PP-C	None	246
				93	6.38		3.4	60°C	2.5	“	[AO-3+P-1] [5000+750]	“
				96	6.39		3.4	60°C	4.2	“	[AO-38+P-1] [5000+750]	“
9	Styrene ***100-42-5*** C_8H_8	104		99	11.91	**Syn**	3.3.5	20°C	21.0	PP-A	1000 P-1	263
				98	11.92		3.3.5	20°C	15.4	“	1000 P-3	“
				99	11.89		3.3.5	20°C	17.9	“	1000 P-4	“
				99	11.91		3.3.5	20°C	20.4	“	1000 P-5	“
				89	11.90		3.3.5	20°C	12.1	“	1000 P-9	“
				98	11.91		3.3.5	20°C	16.3	“	1000 P-19	“

				99	11.91		3.3.5	20°C	18.8	“	1000 AO-6	“
				99	11.91		3.3.5	20°C	29.6	“	1000 AO-36	“
				99	11.91		3.3.5	20°C	19.4	“	1000 AO-53	“
				99	11.90		3.3.5	20°C	16.6	“	1000 AO-58	“
				99	11.91		3.3.5	20°C	25.8	“	1000 AO-60	“
				99	11.90		3.3.5	20°C	15.4	“	1000 HYA-1	“
				99	11.92		3.3.5	20°C	17.7	“	1000 L-2	“
				99	11.89		3.4	20°C	30.4	PP-A	None	279
				99	11.90		3.4	20°C	34.9	‘	1000 AO-1	“
				99	11.89		3.4	20°C	25.4	‘	1000 AO-2	“
				99	11.88		3.4	20°C	17.3	‘	1000 AO-4	“
				99	11.89		3.4	20°C	30.7	‘	1000 AO-7	“
				99	11.88		3.4	20°C	25.2	‘	1000 AO-38	“
				99	11.89		3.4	20°C	34.2	‘	1000 AO-54	“
				99	11.89		3.4	20°C	19.8	‘	1000 HAS-5	“
				99	11.89		3.4	20°C	19.9	‘	1000 HAS-16	“
				99	11.89		3.4	20°C	38.4	‘	1000 HAS-25	“
				99	11.89		3.4	20°C	23.0	‘	[AO-1+P-1] [500+500]	“ “
				92	11.86		3.2	60°C	4.5	PP-C	None	246
				94	11.87		3.3	60°C	3.6	“	P-1] [750 ppm]	“
				93	11.86		3.3	60°C	3.0	“	[AO-1+P-1] [1000+750]	“
				95	11.86		3.3	60°C	4.1	“	[AO-1+P-1] [2500+750]	“
				95	11.87		3.3	60°C	2.7	“	[AO-1+P-1] [5000+750]	“
				94	11.85		3.4	60°C	2.1	“	[AO-3+P-1] [5000+750]	“
				95	11.87		3.4	60°C	2.0	“	[AO-4+P-1] [5000+750]	“
				95	11.86		3.4	60°C	2.4	“	[AO-38+P-1] [5000+750]	“
				95	11.86		3.4	60°C	1.5	“	[AO-39+P-1] [5000+750]	“
10	Ethylbenzene ***100-41-4*** C_8H_{10}	106		97	10.71	**Syn**	3.3.5	20°C	0.5	PP-A	1000 P-1	263
				96	10.71		3.3.5	20°C	0.6	“	1000 P-3	“
				96	10.71		3.3.5	20°C	0.6	“	1000 P-4	“
				94	10.71		3.3.5	20°C	0.5	“	1000 P-5	“
				94	10.71		3.3.5	20°C	0.5	“	1000 P-9	“
				95	10.70		3.3.5	20°C	0.5	“	1000 P-19	“
				96	10.72		3.3.5	20°C	0.6	“	1000 AO-6	“
				98	10.70		3.3.5	20°C	1.0	“	1000 AO-36	“
				98	10.71		3.3.5	20°C	0.6	“	1000 AO-53	“

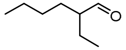
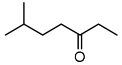
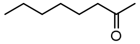
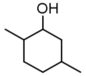
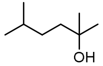
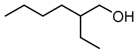
				95	10.71		3.3.5	20°C	0.5	“	1000 AO-58	“
				97	10.71		3.3.5	20°C	0.6	“	1000 AO-60	“
				92	10.70		3.3.5	20°C	0.5	“	1000 HYA-1	“
				96	10.72		3.3.5	20°C	0.5	“	1000 L-2	“
				89	10.71		3.3.5	20°C	2.6	PP-A	None	279
				98	10.70		3.3.5	20°C	1.2	“	1000 AO-1	“
				96	10.69		3.3.5	20°C	0.5	“	1000 AO-2	“
				93	10.69		3.3.5	20°C	1.5	“	1000 AO-54	“
				93	10.68		3.3.5	20°C	1.7	“	1000 HAS-5	“
				98	10.73		3.3.5	20°C	0.9	“	1000 HAS-25	“
				96	10.72		3.3.5	20°C	0.7	“	[AO-1+P-1] [500+500]	“ “
11	m- or p-Xylene ***108-38-3*** ***106-42-3*** C_8H_{10}	106		97	10.78	**Syn**	3.3.5	20°C	1.2	PP-A	1000 P-1	263
				94	10.78		3.3.5	20°C	0.7	“	1000 P-3	“
				96	10.76		3.3.5	20°C	0.9	“	1000 P-4	“
				96	10.77		3.3.5	20°C	1.2	“	1000 P-5	“
				91	10.76		3.3.5	20°C	0.6	“	1000 P-9	“
				96	10.77		3.3.5	20°C	0.9	“	1000 P-19	“
				96	10.78		3.3.5	20°C	0.8	“	1000 AO-6	“
				98	10.78		3.3.5	20°C	1.6	“	1000 AO-36	“
				97	10.78		3.3.5	20°C	1.0	“	1000 AO-53	“
				95	10.77		3.3.5	20°C	1.0	“	1000 AO-58	“
				98	10.78		3.3.5	20°C	1.4	“	1000 AO-60	“
				94	10.76		3.3.5	20°C	0.8	“	1000 HYA-1	“
				95	10.79		3.3.5	20°C	0.9	“	1000 L-2	“
				99	10.77		3.4	20°C	1.6	PP-A	1000 AO-1	279
				97	10.75		3.4	20°C	1.3	“	1000 AO-2	“
				96	10.73		3.4	20°C	1.3	“	1000 AO-4	“
				99	10.75		3.4	20°C	2.3	“	1000 AO-7	“
				95	10.74		3.4	20°C	1.8	“	1000 AO-38	“
				96	10.75		3.4	20°C	2.2	“	1000 AO-54	“
				95	10.75		3.4	20°C	1.0	“	1000 HAS-5	“
				95	10.75		3.4	20°C	1.3	“	1000 HAS-16	“
				99	10.75		3.4	20°C	2.0	“	1000 HAS-25	“
				95	10.76		3.4	20°C	0.9	“	[AO-1+P-1] [500+500]	“
12	Benzaldehyde ***100-52-7*** C_7H_6O	106		69	14.60	?	3.3.5	20°C	0.5	PP-A	None	263
				98	14.58		3.4	20°C	0.8	PP-A	None	279
				89	14.59		3.4	20°C	0.5	“	1000 HAS-5	“
				75	14.53		3.2	60°C	7.9	PP-C	None	246
				96	14.54		3.3	60°C	2.6	“	[P-1] [750 ppm]	“
				98	14.55			60°C	2.0	“	[AO-1+P-1]	“

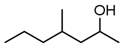
							3.3				[1000+750]	
				98	14.55		3.3	60°C	1.7	“	[AO-1+P-1] [2500+750]	“
				98	14.55		3.3	60°C	2.5	“	[AO-1+P-1] [5000+750]	“
				98	14.55		3.4	60°C	1.8	“	[AO-3+P-1] [5000+750]	“
				99	14.55		3.4	60°C	2.4	“	[AO-4+P-1] [5000+750]	“
				96	14.55		3.4	60°C	2.5	“	[AO-38+P-1] [5000+750]	“
				98	14.55		3.4	60°C	2.1	“	[AO-39+P-1] [5000+750]	“
13	4-Hexen-3-one,5-methyl or isomer ***13905-10-7*** $C_7H_{12}O$	112		91	11.34	**S**	3.5	60°C	7.3	PP-A	[AO-1+P-1+O-4] [5000+750+5000]	229
				85	12.09		3.2	60°C	7.5	PP-B	None	243
				82	12.08		3.3.3	60°C	6.6	PP-B	5000 AO-1	“
				83	12.10		3.3.4	60°C	**16.0**	PP-B	[AO-1+P-1$_{HYD}$] [5000+1000]	“
14	Heptanal ***111-71-7*** $C_7H_{14}O$	114		83	12.38	**S**	3.3.5	20°C	1.0	PP-A	1000 P-3	263
				87	12.36		3.3.5	20°C	**1.9**	“	1000 P-9	“
15	Pentanal,2,4-dimethyl- ***27944-79-2*** $C_7H_{14}O$	114		92	9.18	**S**	3.4	60°C	**1.8**	PP-A	[AO-38+P-1] [5000+750]	246
16	Pentane,2,3,3-trimethyl- *or isomer* ***560-21-4*** C_8H_{18}	114		79	16.68	**S**	3.2	60°C	**4.8**	PP-C	None	246
18	2-Ethyl-1-butanol, methyl ether ***No CAS# assigned*** $C_7H_{16}O$	116		86	14.45	**S**	3.1	40°C	**1.1**	PP-A	None	238
19	1-Pentanol,2,3-dimethyl- ***10143-23-4*** $C_7H_{16}O$	116		85	12.07	**S**	3.4	60°C	**1.6**	PP-A	[AO-38+P-1] [5000+750]	246
20	Acetophenone ***98-86-2*** $C_8H_{18}O$	120		84	18.43	**?**	3.1	60°C	2.2	PP-A	None	238
				93	18.45		3.1	40°C	0.9	“	“	“
				96	18.43		3.1	60°C	1.0	“	[AO-1+P-1]	“
				91	18.46		3.1	40°C	0.8	“	[750+750]	“
				87	18.45		3.3.5	20°C	0.5	“	None	263
				87	18.47		3.3.5	20°C	0.5	“	1000 P-4	“

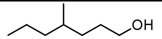
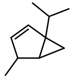
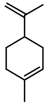
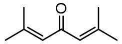
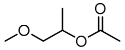
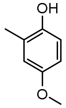
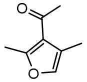
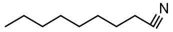
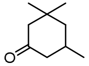
				90	18.46		3.3.5	20°C	0.5	“	1000 P-5	“
				90	18.46		3.3.5	20°C	0.5	“	1000 AO-6	“
				90	18.46		3.3.5	20°C	0.5	“	1000 AO-36	“
				90	18.47		3.3.5	20°C	0.5	“	1000 AO-60	“
				90	18.46		3.3.5	20°C	0.5	“	1000 HYA-1	“
				90	18.46		3.3.5	20°C	0.5	“	1000 L-2	“
				96	18.45		3.4	20°C	0.6	PP-A	None	279
				91	18.46		3.4	20°C	0.5	“	1000 AO-1	“
				92	18.45		3.4	20°C	0.5	“	1000 AO-2	“
				91	18.47		3.4	20°C	0.5	“	1000 AO-7	“
				88	18.46		3.4	20°C	0.5	“	1000 AO-38	“
				95	18.45		3.4	20°C	0.5	“	1000 AO-54	“
				93	18.45		3.4	20°C	0.5	“	1000 HAS-5	“
				90	18.46		3.4	20°C	0.5	“	1000 HAS-16	“
				87	18.45		3.4	20°C	0.5	“	1000 HAS-25	“
				91	18.45		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“
				72	18.41		3.2	60°C	**5.7**	PP-C	None	246
				89	18.42		3.3	60°C	1.7	“	[P-1] [750 ppm]	“
				91	18.43		3.3	60°C	1.6	“	[AO-1+P-1] [1000+750]	“
				90	18.43		3.3	60°C	1.0	“	[AO-1+P-1] [2500+750]	“
				93	18.43		3.3	60°C	1.7	“	[AO-1+P-1] [5000+750]	“
				93	18.42			60°C	1.1	“	[AO-3+P-1] [5000+750]	“
				94	18.43			60°C	0.9	“	[AO-4+P-1] [5000+750]	“
				90	18.43			60°C	1.5	“	[AO-38+P-1] [5000+750]	“
				95	18.42			60°C	1.6	“	[AO-39+P-1] [5000+750]	“
22	2-Cyclohexen-1-one, 3,5-dimethyl- ***1123-09-7*** $C_8H_{12}O$	124		95	19.81	**S**	3.1	60°C	5.2	PP-A	None	238
				89	19.78		3.2	60°C	18.1	PP-B	None	243
				85	19.78		3.3.3	60°C	13.8	“	5000 AO-1	“
				95	19.79		3.2	60°C	**18.7**	PP-C	None	246
				85	19.87		3.3	60°C	7.0	“	[P-1] [750 ppm]	“
				95	19.83		3.3	60°C	1.8	“	[AO-1+P-1] [1000+750]	“
				86	19.84		3.4	60°C	1.3	“	[AO-3+P-1]	“

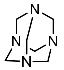
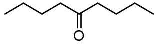
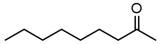
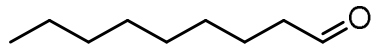
											[5000+750]	
23	Octanenitrile ***124-12-9*** $C_8H_{15}N$	125		76	19.01	**?**	3.3.5	20°C	4.9	PP-A	None	263
				93	19.01		3.4	20°C	**11.4**	PP-A	None	279
				89	19.01		3.4	20°C	0.6	“	1000 AO-1	“
				78	19.01		3.4	20°C	3.4	“	1000 AO-54	“
				93	19.01		3.4	20°C	4.3	“	1000 HAS-5	“
25	5-Hepten-2-one,6-methly- *or isomer* ***110-93-0*** $C_8H_{14}O$	126		69	15.77	**S**	3.1	20°C	0.6	PP-A	None	237
				76	15.76		3.1	20°C	0.7	“	[AO-1+P-1] [750+750]	“
				86	15.62		3.3.5	20°C	0.5	PP-A	None	263
				94	15.62		3.3.5	20°C	0.9	“	1000 P-3	“
				< 70	15.61		3.3.5	20°C	0.5	“	1000 P-4	“
				81	15.63		3.3.5	20°C	0.5	“	1000 P-5	“
				80	15.60		3.3.5	20°C	**1.6**	“	1000 P-9	“
				79	15.62		3.3.5	20°C	0.5	“	1000 AO-60	“
				< 80	15.62		3.4	20°C	0.5	PP-A	1000 AO-1	279
				80	15.62		3.4	20°C	0.5	“	1000 AO-2	“
				80	15.62		3.4	20°C	0.5	“	1000 AO-4	“
				78	15.62		3.4	20°C	0.5	“	1000 AO-7	“
				80	15.61		3.4	20°C	0.5	“	1000 AO-38	“
				98	15.62		3.4	20°C	0.5	“	1000 HAS-5	“
				81	15.62		3.4	20°C	0.5	“	1000 HAS-16	“
				82	15.62		3.4	20°C	0.5	“	1000 HAS-25	“
				80	15.62		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“
26	2-Heptanone,4-methyl- ***6137-06-0*** $C_8H_{12}O$	128		97	13.77	**S**	3.1	60°C	3.7	PP-A	None	238
				98	13.78		3.1	40°C	1.5	“	“	“
				97	13.77		3.1	60°C	2.8	“	[AO-1+P-1] [750+750]	“
				97	13.80		3.1	40°C	1.3	“		“
				97	13.75		3.5	60°C	24.5	PP-A	750 P-1	229
				97	13.75		3.5	60°C	17.8	“	[AO-1+P-1] [5000+750]	“
				97	13.74		3.5	60°C	40.1	“	[AO-1+P-1+O-4] [5000+750+5000]	“
				97	13.74		3.5	60°C	29.5	“	AO-4+P-1] [5000+750]	“
				97	13.76		3.5	60°C	10.6	“	[AO-4+P-1+O-3] [5000+750+5000]	“
				92	13.81		3.3.5	20°C	0.5	PP-A	None	263
				87	13.82		3.3.5	20°C	0.5	“	1000 P-1	“
				87	13.83		3.3.5	20°C	0.5	“	1000 P-3	“
				90	13.81		3.3.5	20°C	0.5	“	1000 P-4	“

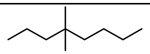
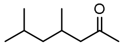
				90	13.82		3.3.5	20°C	0.5	“	1000 P-5	“
				84	13.81		3.3.5	20°C	0.5	“	1000 P-9	“
				98	13.81		3.3.5	20°C	0.7	“	1000 AO-6	“
				87	13.83		3.3.5	20°C	0.5	“	1000 AO-36	“
				93	13.82		3.3.5	20°C	0.5	“	1000 AO-53	“
				84	13.82		3.3.5	20°C	0.5	“	1000 AO-58	“
				79	13.83		3.3.5	20°C	0.5	“	1000 AO-60	“
				99	13.81		3.3.5	20°C	0.7	“	1000 HYA-1	“
				89	13.83		3.3.5	20°C	0.5	“	1000 L-2	“
				98	13.81		3.4	20°C	0.5	PP-A	None	279
				97	13.81		3.4	20°C	0.6	“	1000 AO-1	“
				98	13.80		3.4	20°C	0.5	“	1000 AO-2	“
				99	13.80		3.4	20°C	0.8	“	1000 AO-4	“
				97	13.80		3.4	20°C	0.8	“	1000 AO-7	“
				98	13.79		3.4	20°C	0.7	“	1000 AO-38	“
				99	13.81		3.4	20°C	0.5	“	1000 AO-54	“
				98	13.80		3.4	20°C	0.5	“	1000 HAS-5	“
				98	13.81		3.4	20°C	0.5	“	1000 HAS-16	“
				92	13.81		3.4	20°C	0.5	“	1000 HAS-25	“
				99	13.81		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“ “
				98	13.73		3.2	60°C	27.5	PP-B	None	243
				97	13.72		3.3.3	60°C	39.4	“	5000 AO-1	“
				90	13.77		3.3.3	60°C	1.5	“	[AO-1+P-1] [5000+1000]	“
				85	13.77		3.3.3	60°C	1.4	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				82	13.79		3.3.3.	60°C	1.4	“	AO-1+P-5+AO-6] [5000+500+250]	“
				96	13.75		3.3.4	60°C	**68.0**	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				97	13.74		3.2	60°C	29.1	PP-C	None	246
				97	13.76		3.3	60°C	15.2	“	[P-1] [750 ppm]	“
				97	13.75		3.3	60°C	15.6	“	[AO-1+P-1] [1000+750]	“
				98	13.77		3.3	60°C	3.2	“	[AO-1+P-1] [2500+750]	“
				99	13.78		3.3	60°C	1.8	“	[AO-1+P-1] [5000+750]	“
				97	13.75		3.4	60°C	11.0	“	[AO-3+P-1] [5000+750]	“
				98	13.77		3.4	60°C	2.8	“	[AO-4+P-1] [5000+750]	“

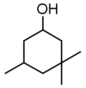
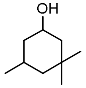
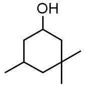
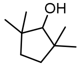
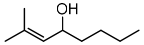
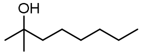
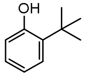
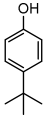
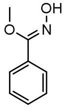
				97	13.75		3.4	60°C	18.3	“	[AO-38+P-1] [5000+750]	“
				98	13.77		3.4	60°C	2.9	“	[AO-39+P-1] [5000+750]	“
27	2-Ethylhexanal *or isomer* ***123-05-7*** $C_8H_{16}O$	128		< 80	14.38		3.4	20°C	0.8	PP-A	None	279
				< 80	14.39		3.4	20°C	0.5	“	1000 AO-1	“
				< 80	14.38		3.4	20°C	0.5	“	1000 AO-54	“
				< 80	14.39		3.4	20°C	0.5	“	1000 HAS-5	“
28	3-Heptanone,6-methyl- ***624-42-0*** $C_8H_{16}O$	128		74	15.62	**S**	3.3.5	20°C	0.5	PP-A	1000 P-19	263
29	2-Octanone ***111-13-7*** $C_8H_{16}O$	128		83	15.75	**S**	3.3.5	20°C	0.9	PP-A	1000 P-9	263
31	2,5-Dimethyl cyclohexanol ***3809-32-3*** $C_8H_{16}O$	128		72	17.23	**S**	3.2	60°C	6.2	PP-B	None	243
32	2-Hexanol,2,5-dimethyl-, (S) *or isomer* ***3730-60-7*** $C_8H_{18}O$	130		82	10.64	**S**	3.4	20°C	1.9	PP-A	None	279
				84	10.63		3.4	20°C	0.9	“	1000 AO-54	“
33	2-Ethyl-1-hexanol ***104-76-7*** $C_8H_{18}O$	130		98	17.11	**S**	3.1	60°C	10,7	PP-A	None	238
				94	17.11		3.1	40°C	5,7	“	“	“
				98	17.11		3.1	60°C	13,2	“	[AO-1+P-1] [750+750]	238
				95	17.12		3.1	40°C	7.0	“		“
				97	17.14		3.3.5	20°C	3.7	“	None	263
				96	17.15		3.3.5	20°C	0.7	“	1000 P-3	“
				99	17.15		3.3.5	20°C	4.0	“	1000 P-9	“
				98	17.15		3.3.5	20°C	1.3	“	1000 AO-60	“
				99	17.18		3.4	20°C	58.3	PP-A	None	279
				99	17.18		3.4	20°C	48.3	“	1000 AO-1	“
				99	17.16		3.4	20°C	37.8	“	1000 AO-2	“
				99	17.14		3.4	20°C	3.3	“	1000 AO-7	“
				99	17.14		3.4	20°C	2.8	“	1000 AO-38	“
				99	17.16		3.4	20°C	40.3	“	1000 AO-54	“
				99	17.14		3.4	20°C	6.5	“	1000 HAS-5	“
				99	17.14		3.4	20°C	2.8	“	1000 HAS-16	“
				98	17.14		3.4	20°C	2.6	“	1000 HAS-25	“
				99	17.14		3.4	20°C	12.4	“	[AO-1+P-1] [500+500]	“
				95	17.10		3.5	60°C	6.2	PP-A	750 P-1	229

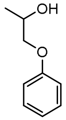
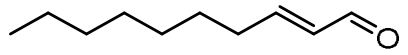
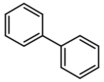
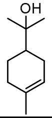
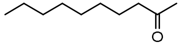
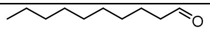
				96	17.10		3.5	60°C	4.4	“	[AO-1+P-1] [5000+750]	“
				98	17.10		3.5	60°C	4.4	“	[AO-1+P-1+O-3] [5000+750+5000]	“
				96	17.10		3.5	60°C	7.7	“	[AO-1+P-1+O-4] [5000+750+5000]	“
				96	17.09		3.5	60°C	4.4	“	AO-4+P-1] [5000+750]	“
				97	17.10		3.5	60°C	4.8	“	[AO-4+P-1+O-3] [5000+750+5000]	“
				94	17.09							
				96	17.09		3.2	60°C	6.1	PP-B	None	243
				97	17.09		3.3.3	60°C	5.3	“	5000 AO-1	“
							3.3.3	60°C	4.5	“	[AO-1+P-1] [5000+1000]	“
				97	17.09							
							3.3.3	60°C	4.1	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				98	17.09							
							3.3.3	60°C	4.4	“	AO-1+P-5+AO-6] [5000+500+250]	“
				94	17.09							
							3.3.4	60°C	7.5	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				96	17.11							
				91	17.11		3.2	60°C	4.1	PP-C	None	246
							3.3	60°C	4.7	“	[P-1] [750 ppm]	“
				98	17.11							
							3.3	60°C	11.0	“	[AO-1+P-1] [1000+750]	“
				97	17.11							
							3.3	60°C	3.5	“	[AO-1+P-1] [2500+750]	“
				96	17.11							
							3.3	60°C	2.9	“	[AO-1+P-1] [5000+750]	“
				94	17.11							
							3.4	60°C	4.0	“	[AO-3+P-1] [5000+750]	“
				98	17.11							
							3.4	60°C	11.2	“	[AO-4+P-1] [5000+750]	“
				98	17.10							
							3.4	60°C	10.8	“	[AO-38+P-1] [5000+750]	“
				98	17.10							
							3.4	60°C	10.0	“	[AO-39+P-1] [5000+750]	“
34	2-Heptanol, 4-methyl- ***56298-90-9*** $C_8H_{18}O$	130		95	14.39	**S**	3.1	60°C	4.7	PP-A	None	238
				94	14.41		3.5	60°C	15.2	PP-A	750 P-1	229
				93	14.39		3.2	60°C	**27.0**	PP-B	None	243
				85	14.39		3.3.3	60°C	8.2	“	5000 AO-1	“
				82	14.41		3.3.4	60°C	10.6	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“

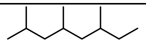
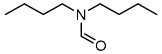
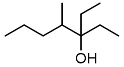
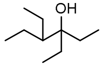
				94 92 86 88	14.41 14.42 14.43 14.44		3.2 3.3 3.3 3.4	60°C 60°C 60°C 60°C	19.3 2.5 1.2 1.2	PP-C “ “ “	None [P-1] [750 ppm] [AO-1+P-1] [1000+750] [AO-38+P-1] [5000+750]	246 “ “ “
35	1-Heptanol, 4-methyl- ***817-91-4*** $C_8H_{18}O$	130		75	18.65	**S**	3.3.3	60°C	2.7	PP-B	5000 AO-1	243
37	Bicyclo[3.10] hex-2-ene, 4-methyl-1-(1-methylethyl)- β-Thyjene ***28634-89-1*** $C_{10}H_{16}$	136		83	13.57	**S**	3.3.5	20°C	**0.5**	PP-A	None	263
38	Limonene ***138-86-3*** $C_{10}H_{16}$	136		95 70	17.27 17.27	**S**	3.1 3.1	20°C 20°C	**2.0** 0.8	PP-A “	None [AO-1+P-1] [750+750]	237 “
40	Phorone ***504-20-1*** $C_9H_{14}O$	138		86	20.24	**PC**	3.4	20°C	**0.5**	PP-1	1000 HAS-25	279
36	1-Methoxy-2-propyl acetate ***108-65-6*** $C_6H_{12}O_3$	132		?	11.43	?	3.1	20°C	**0.6**	PP-A	[AO-1+P-1] [750+750]	237
41	Phenol, 4-methoxy-3-methyl- *or isomer* ***14786-82-4*** $C_8H_{10}O_2$	138		84 85 85 85	19.38 19.38 19.38 19.38	?	3.1 3.2 3.3.3 3.3.4	60°C 60°C 60°C 60°C	1.6 18.5 13.7 **30.8**	PP-A PP-B “ “	None None 5000 AO-1 [AO-1+P-1$_{HYD}$] [1000+750]	238 243 “ “
42	1-(2,4-Dimethyl-furan-3-yl)-ethanone ***32933-07-6*** $C_8H_{10}O_2$	138		85	19.40	?	3.2	60°C	**14.7**	PP-C	None	246
46	Nonanenitrile ***2243-27-8*** $C_9H_{17}N$	139		83	27.37	PC	3.4	20°C	**0.5**	PP-A	1000 HAS-5	279
47	Cyclohexanone,3,3,5-trimethyl- ***873-94-9*** $C_9H_{16}O$	140		70 93 92	17.46 17.46 17.46	S	3.3.5 3.4 3.4	20°C 20°C 20°C	0.5 **1.8** 1.0	PP-A PP-A “	None None 1000 AO-54	263 279 “

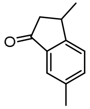
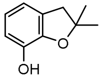
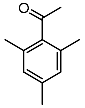
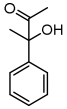
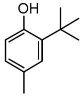
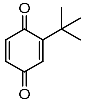
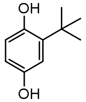
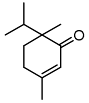
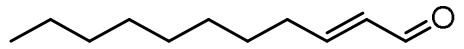
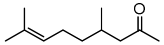
48	Methenamine ***100-97-0*** $C_6H_{12}N_4$	140		86	25.48	**?**	3.3.5	20°C	0.9	PP-A	None	263
				95	25.47		3.3.5	20°C	0.5	"	1000 P-1	"
				78	25.49		3.3.5	20°C	0.5	"	1000 P-9	"
				85	25.49		3.3.5	20°C	0.5	"	1000 AO-53	"
				97	25.46		3.3.5	20°C	**1.3**	"	1000 AO-60	"
				92	25.45		3.4	20°C	**1.1**	PP-A	1000 AO-2	279
49	5-Nonanone ***502-56-7*** $C_9H_{18}O$	142		87	18.68	**S**	3.3.5	20°C	**0.9**	PP-A	1000 P-9	263
50	2-Nonanone ***821-55-6*** $C_9H_{18}O$	142		87	19.41	**S**	3.3.5	20°C	0.5	PP-A	1000 P-9	263
				76	17.97		3.2	60°C	**7.7**	PP-B	None	243
				82	17.97		3.3.3	60°C	2.1	"	5000 AO-1	"
				81	17.97		3.3.4	60°C	3.3	"	[AO-1+P-1$_{HYD}$] [5000+1000]	"
51	Nonanal ***124-19-6*** $C_9H_{18}O$	142		65	20.10	**S**	3.1	20°C	0.8	PP-A	None	237
				85	20.10		3.1	20°C	0.8	"	[AO-1+P-1] [750+750	"
				97	19.92		3.3.5	20°C	1.2	"	None	263
				96	19.92		3.3.5	20°C	1.1	"	1000 P-1	"
				98	19.92		3.3.5	20°C	3.7	"	1000 P-3	"
				97	19.92		3.3.5	20°C	1.2	"	1000 P-4	"
				97	19.92		3.3.5	20°C	1.3	"	1000 P-5	"
				96	19.92		3.3.5	20°C	0.9	"	1000 P-9	"
				96	19.92		3.3.5	20°C	0.9	"	1000 AO-6	"
				99	19.92		3.3.5	20°C	5.6	"	1000 AO-36	"
				95	19.92		3.3.5	20°C	0.8	"	1000 AO-53	"
				96	19.92		3.3.5	20°C	1.0	"	1000 AO-58	"
				97	19.92		3.3.5	20°C	1.3	"	1000 AO-60	"
				97	19.92		3.3.5	20°C	1.3	"	1000 HYA-1	"
				95	19.92		3.3.5	20°C	0.8	"	1000 L-2	"
				95	19.92		3.4	20°C	1.1	PP-A	None	279
				94	19.92		3.4	20°C	0.9	"	1000 AO-1	"
				92	19.92		3.4	20°C	0.6	"	1000 AO-54	"
				93	19.92		3.4	20°C	0.6	"	1000 HAS-5	"
				97	19.92		3.4	20°C	1.3	"	[AO-1+P-1] [500+500]	"
				79	19.86		3.3.3	60°C	2.6	PP-B	AO-1+P-5+AO-6] [5000+500+250]	243
				84	19.87		3.3	60°C	3.5	PP-C	[AO-1+P-1] [1000+750]	246
				89	19.87		3.3	60°C	4.1	PP-C	[AO-1+P-1]	"

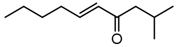
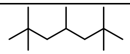
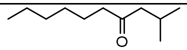
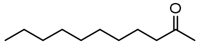
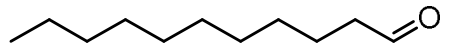
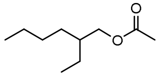
				95	19.87		3.3	60°C	**5.7**	PP-C	[2500+750] [AO-1+P-1] [5000+750]	“
52	4,4-dimethyl octane *or isomer* ***15869-95-1*** $C_{10}H_{22}$	142		83	23.26	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
53	2-Heptanone,4,6-dimethyl- ***19549-80-5*** $C_9H_{18}O$	142		76	15.70	**S**	3.1	60°C	2.9	PP-A	None	238
				87	15.71		3.1	60°C	1.1	“	[AO-1+P-1] [750+750]	“
				88	15.68		3.5	60°C	12.0	PP-A	750 P-1	229
				94	15.68		3.5	60°C	10.0	“	[AO-1+P-1] [5000+750]	“
				90	15.68		3.5	60°C	20.3	“	[AO-1+P-1+O-4] [5000+750+5000]	“
				93	15.68		3.5	60°C	13.5	“	[AO-4+P-1] [5000+750]	“
				94	15.69		3.5	60°C	5.0	“	[AO-4+P-1+O-3] [5000+750+5000]	“
				83	15.56		3.2	60°C	16.9	PP-B	None	243
				90	15.66		3.3.3	60°C	18.7	“	5000 AO-1	“
				92	15.68		3.3.4	60°C	**32.6**	“	[AO-1+P-1_{HYD}] [5000+1000]	“
				85	15.69		3.2	60°C	15.8	PP-C	None	246
				84	16.52		3.2	60°C	3.4	“	“	“
				92	15.70		3.3	60°C	7.5	“	[P-1] [750 ppm]	“
				93	15.69		3.3	60°C	5.8	“	[AO-1+P-1] [1000+750]	“
				90	15.70		3.3	60°C	2.0	“	[AO-1+P-1] [2500+750]	“
				84	15.70		3.3	60°C	1.5	“	[AO-1+P-1] [5000+750]	“
				96	15.69		3.4	60°C	5.1	“	[AO-3+P-1] [5000+750]	“
				96	15.79		3.4	60°C	1.5	“	[AO-4+P-1] [5000+750]	“
				96	15.69		3.4	60°C	9.0	“	[AO-38+P-1] [5000+750]	“
				93	15.70		3.4	60°C	1.6	“	[AO-39+P-1] [5000+750]	“

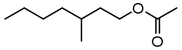
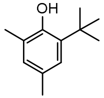
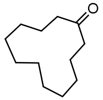
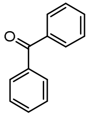
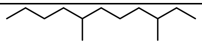
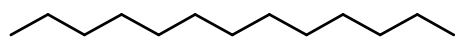
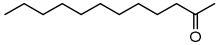
54	Cyclohexanol,3,3,5-trimethyl-, cis- ***933-48-2 / 111-13-7*** $C_9H_{18}O$	142		82 71	16.99 16.99	**S**	3.1 3.2	60°C 60°C	1.9 **5.3**	PP-A PP-C	None None	238 246
55	Cyclohexanol,3,3,5-trimethyl-, trans- ***767-54-4*** $C_9H_{18}O$	142		78	18.69	**S**	3.1	60°C	**2.2**	PP-A	None	238
56	Cyclohexanol,3,3,5-trimethyl- ***116-02-9*** $C_9H_{18}O$	142		83 77 73	18.64 18.65 18.67	**S**	3.2 3.3.4 3.2	60°C 60°C 60°C	**9.0** 3.1 5.6	PP-B “ PP-C	None [AO-1+P-1$_{HYD}$] [5000+1000] None	243 “ 246
57	2,2,5,5-Tetramethyl-cyclopentanol ***15231-50-2*** $C_9H_{18}O$	142		77	17.25	**S**	3.2	60°C	**5.0**	PP-C	None	246
58	2 -Octen-4-ol, 2-methyl- ***65885-49-6*** $C_9H_{18}O$	142		73	16.30	**S**	3.2	60°C	**4.0**	PP-C	None	243
60	2-Octanol,2-methyl- ***628-44-4*** $C_9H_{20}O$	144		85 76 87	15.27 15.28 15.30	**S**	3.2 3.3.3 3.3.4	60°C 60°C 60°C	**3.6** 1.3 2.0	PP-B “ “	None 5000 AO-1 [AO-1+P-1$_{HYD}$] [5000+1000]	243 “ “
61	N, N-Diethylaniline ***91-66-7*** $C_{10}H_{15}N$	149		90	25.51	Impurity	3.4	60°C	**3.0**	PP-C	[AO-39+P-1] [5000+750]	246
62	Phenol, 2-(1,1-dimethylethyl)- ***88-18-6*** $C_{10}H_{14}O$	150		91	27.08	**PC**	3.4	20°C	**0.6**	PP-A	1000 AO-38	279
63	Tert.-butyl-phenol **ARVIN 2** ***98-54-4*** $C_{10}H_{14}O$	150		83 96 98 96	27.66 27.59 27.04 27.02	**PC**	3.3.5 3.3.4 3.4 3.4	20°C 60°C 60°C 60°C	0.5 8.6 **159.2** 6.2	PP-A PP-B PP-C “	1000 P-4 [AO-1+P-1$_{HYD}$] [5000+1000] [AO-38+P-1] [5000+750] [AO-39+P-1] [5000+750]	263 243 246 “
68	Oxime-, methoxy-phenyl-	151		84 84 83 84 84 82 83	12.99 13.07 13.09 13.06 13.05 13.03 13.07	**?**	3.3.5 3.3.5 3.3.5 3.3.5 3.3.5 3.3.5 3.3.5	20°C 20°C 20°C 20°C 20°C 20°C 20°C	2.6 5.0 3.9 4.0 5.3 0.8 4.5	PP-A “ “ “ “ “ “	None 1000 P-1 1000 P-3 1000 P-4 1000 P-5 1000 P-9 1000 P-19	263 “ “ “ “ “ “

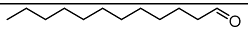
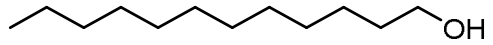
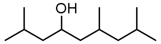
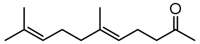
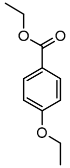
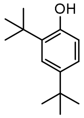
				83	13.03		3.3.5	20°C	2.1	“	1000 AO-6	“
				83	13.06		3.3.5	20°C	3.8	“	1000 AO-36	“
				84	13.07		3.3.5	20°C	6.4	“	1000 AO-53	“
				84	13.10		3.3.5	20°C	4.4	“	1000 AO-58	“
				84	12.94		3.3.5	20°C	2.6	“	1000 HYA-1	“
				84	13.13		3.3.5	20°C	4.6	“	1000 L-2	“
				84	13.12		3.4	20°C	7.6	PP-A	None	279
				84	13.14		3.4	20°C	5.5	“	1000 AO-1	“
				83	13.05		3.4	20°C	6.0	“	1000 AO-2	“
				84	13.09		3.4	20°C	5.4	“	1000 AO-4	“
				84	13.05		3.4	20°C	5.3	“	1000 AO-7	“
				83	13.12		3.4	20°C	5.6	“	1000 AO-38	“
				84	12.94		3.4	20°C	3.6	“	1000 AO-54	“
				84	13.01		3.4	20°C	1.2	“	1000 HAS-5	“
				82	13.05		3.4	20°C	0.9	“	1000 HAS-16	“
				84	13.14		3.4	20°C	8.0	“	1000 HAS-25	“
				81	12.98		3.4	20°C	1.5	“	[AO-1+P-1] [500+500]	“
69	1-Phenoxypropan-2-ol ***770-35-4*** $C_9H_{12}O_2$	152		88	25.25	**?**	3.3.5	20°C	0.6	PP-A	None	263
75	2-Decenal, (E)- ***3913-81-3*** $C_{10}H_{18}O$	154		84	26.69	**S**	3.3.5	20°C	0.5	PP-A	1000 P-9	263
76	Bi-phenyl ***92-54-4*** $C_{12}H_{10}$	154		91	29.68	**PC**	3.3.5	20°C	0.5	PP-A	1000 P-4	263
77	Alpha-Terpineol ***98-55-5*** $C_{10}H_{18}O$	154		95	24.16	**S**	3.3	60°C	4.8	PP-C	[P-1] [750 ppm]	246
				96	24.16		3.4	60°C	2.4	“	[AO-38+P-1] [5000+750]	“
78	2-Decanone ***693-54-9*** $C_{10}H_{20}O$	156		82	24.24	**S**	3.3.5	20°C	0.8	PP-A	1000 P-9	263
79	Decanal ***112-31-2*** $C_{10}H_{20}O$	156		96	24.78	**S**	3.3.5	20°C	1.6	PP-A	None	263
				98	24.78		3.3.5	20°C	2.5	“	1000 P-3	“
				95	24.78		3.3.5	20°C	0.6	“	1000 P-4	“
				94	24.78		3.3.5	20°C	0.5	“	1000 P-5	“
				99	24.77		3.3.5	20°C	3.4	“	1000 P-9	“
				95	24.78		3.3.5	20°C	0.9	“	1000 AO-60	“

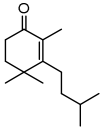
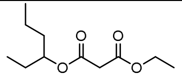
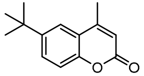
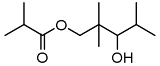
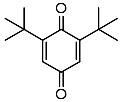
				95	24.78		3.4	20°C	0.7	PP-A	None	279
				93	24.78		3.4	20°C	0.5	“	1000 AO-1	“
				92	24.78		3.4	20°C	0.5	“	1000 AO-54	“
				95	24.78		3.4	20°C	0.5	“	1000 HAS-5	“
				95	24.78		3.4	20°C	0.6	“	1000 HAS-25	“
				96	24.78		3.4	20°C	1.1	“	[AO-1+P-1] [500+500]	“
80	Octane,2,4,6-trimethyl *or isomer* ***62016-37-9*** $C_{11}H_{24}O$	156		88	29.97	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
81	Formamidine, N,N-dibutyl- ***761-65-9*** $C_9H_{19}NO$	157		96	28.14		3.3.4	60°C	**5.3**	PP-B	[AO-1+P-1$_{HYD}$] [1000+750]	243
82	3-Ethyl-4-methyl-3-heptanol ***66719-39-9*** $C_{10}H_{22}O$	158		82	22.97	**S**	3.3.5	20°C	0.8	PP-A	None	263
				88	22.97		3.4	20°C	0.8	PP-A	None	279
				77	22.96		3.4	20°C	0.5	“	1000 AO-2	“
				71	22.97		3.4	20°C	0.5	“	1000 AO-38	“
				79	22.97		3.4	20°C	0.5	“	1000 AO-54	“
				84	22.96		3.4	20°C	0.6	“	1000 HAS-5	“
				79	22.97		3.4	20°C	0.5	“	1000 HAS-16	“
				81	22.97		3.4	20°C	0.5	“	1000 HAS-15	“
				88	22.98		3.2	60°C	**14.3**	PP-B	None	243
				80	22.98		3.3.3	60°C	3.6	“	5000 AO-1	“
				80	22.99		3.3.4	60°C	5.7	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				83	22.90		3.2	60°C	10.2	PP-C	None	246
				85	23.02		3.2	60°C	8.5	“	“	
83	3-Hexanol,3,4-diethyl- *or isomer* ***19398-78-8*** $C_{10}H_{22}O$	158		87	22.92	**S**	3.1	60°C	7.5	PP-A	None	238
				86	22.90		3.1	40°C	3.7	“	“	“
				86	23.09		3.3.5	20°C	0.9	“	“	263
				82	23.09		3.4	20°C	0.9	PP-A	None	279
				79	23.09		3.4	20°C	0.5	“	1000 AO-2	“
				79	23.08		3.4	20°C	0.5	“	1000 AO-38	“
				82	23.09		3.4	20°C	0.5	“	1000 AO-54	“
				85	23.08		3.4	20°C	0.6	“	10000 HAS-5	“
				84	23.08		3.4	20°C	0.5	“	1000 HAS-16	“
				84	23.08		3.4	20°C	0.5	“	1000 HAS-25	“
				>83	22.90		3.2	60°C	**18.7**	PP-C	None	246

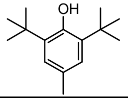
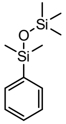
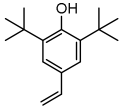
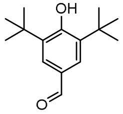
85	5-Hydroxy-3-methyl-1-inadone ***57878-30-5*** $C_{10}H_{10}O_2$	162		85	33.41	**PC**	3.3.5	20°C	**2.9**	PP-A	1000 AO-53	263
88	2,3-di-hydro-2,2-dimethyl-7-benzo-furanol ***1563-38-8*** $C_{10}H_{12}O_2$	162		93	30.30	**PC**	3.3.5	20°C	**6.8**	PP-A	1000 AO-53	263
91	Ethanone,1-(2,4,6-trimethylphenyl) ***1667-01-2*** $C_{11}H_{14}O$	162		89 86 91	27.86 27.85 27.86	**S?**	3.2 3.3.3 3.3.4	60°C 60°C 60°C	7.1 5.9 **18.4**	PP-B " "	None 5000 AO-1 [AO-1+P-1$_{HYD}$] [1000+750]	243 " "
92	3-Hydroxy-3-phenylbutan-2-one ***3155-01-9*** $C_{10}H_{12}O_2$	164		81	26.90	**?**	3.3.5	20°C	**0.5**	PP-A	None	263
93	Phenol, 2-(1,1-dimethylethyl)-4-methyl ***2409-55-4*** $C_{11}H_{16}O$	164		89 70 96	29.07 29.08 29.08	**PC**	3.3.5 3.3.5 3.4	20°C 20°C 20°C	0.5 0.5 **1.1**	PP-A " PP-A	1000 AO-36 1000 P-9 1000 AO-7	263 " 279
95	Tert-butyl-p-benzoquinone ***3602-55-9*** $C_{10}H_{12}O_2$	164		97 80	24.72 24.58	**PC**	3.3.5 3.4	20°C 60°C	**136.7** 1.3	PP-A PP-C	1000 AO-53 [AO-38+P-1] [5000+750]	263 246
99	Tert-butyl hydroquinone ***1948-33-0*** $C_{10}H_{14}O_4$	166		96	32.66	**PC**	3.3.5	20°C	**2.1**	PP-A	1000 AO-53	263
100	2-Cyclohexene-1-one, 3,6-dimethyl-6-(1-methylethyl)- ***54410-58-1*** $C_{11}H_{18}O_4$	166		79	19.79	**S**	3.3.4	60°C	**16.1**	PP-B	[AO-1+P-1$_{HYD}$] [5000+1000]	243
101	2-Undecenal ***2463-77-6*** $C_{11}H_{20}O$	168		82	29.27	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
102	7-Nonen-2-one, 4, 8-dimethyl- ***3664-64-0*** $C_{11}H_{20}O$	168		71 75 76 < 80	32.82 32.82 32.83 32.84	**S**	3.2 3.3.3 3.3.4 3.2	60°C 60°C 60°C 60°C	2.7 5.1 **6.6** 4.9	PP-B " " PP-C	None 5000 AO-1 [AO-1+P-1$_{HYD}$] [5000+1000] None	243 " " 246

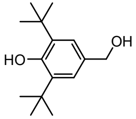
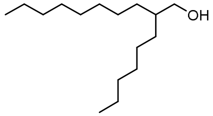
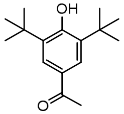
				< 80	32.84		3.3	60°C	1.6	“	[P-1] [750 ppm]	“
				< 80	32.84		3.3	60°C	1.2	“	[AO-1+P-1] [1000+750]	“
				< 80	32.97		3.4	60°C	1.5	“	[AO-3+P-1] [5000+750]	“
				< 80	32.85		3.4	60°C	1.2	“	[AO-38+P-1] [5000+750]	“
				< 80	32.84		3.4	60°C	0.6	“	[AO-39+P-1] [5000+750]	“
103	Isobutyl-2-heptenone ***7225-67-4*** $C_{11}H_{20}O$	168		73	32.95	**S**	3.2	60°C	3.4	PP-B	None	243
				77	32.95		3.3.3	60°C	5.5	“	5000 AO-1	“
				76	32.96		3.3.4	60°C	**7.2**	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				< 80	32.97		3.2	60°C	6.1	PP-C	None	246
				< 80	32.97		3.3	60°C	2.2	“	[P-1] [750 ppm]	“
				< 80	32.96		3.3	60°C	2.2	“	[AO-1+P-1] [1000+750]	“
				< 80	32.97		3.4	60°C	1.7	“	[AO-3+P-1] [5000+750]	“
				< 80	32.97		3.4	60°C	1.2	“	[AO-38+P-1] [5000+750]	“
				< 80	32.96		3.4	60°C	1.2	“	[AO-39+P-1] [5000+750]	“
104	Heptane,2,2,4,6,6-pentamethyl- ***13475-82-6*** $C_{12}H_{26}$	170		86	15.71	**S**	3.3.5	20°C	0.6	PP-A	None	263
				74	15.71		3.4	20°C	1.0	PP-A	None	279
				81	15.70		3.4	20°C	**1.4**	“	1000 AO-54	“
105	2-Methyl-4-decanone *or isomer* ***6628-25-7*** $C_{11}H_{22}O$	170		78	27.00	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
106	2-Undecanone ***112-12-09*** $C_{11}H_{22}O$	170		79	27.59	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
107	Undecanal ***112-44-7*** $C_{11}H_{22}O$	170		91	27.94	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-3	263
				94	27.94			20°C	**0.5**	“	1000 P-9	“
108	Acetic acid, 2-ethylhexyl ester ***103-09-3*** $C_{10}H_{20}O_2$	172		73	22.10	**S**	3.3.5	20°C	0.5	PP-A	None	263
				87	22.10		3.3.5	20°C	0.5	“	1000 P-1	“
				88	22.10		3.3.5	20°C	0.5	“	1000 P-3	“
				92	22.10		3.3.5	20°C	0.5	“	1000 P-4	“
				88	22.10		3.3.5	20°C	0.6	“	1000 P-5	“
				65	22.09		3.3.5	20°C	0.5	“	1000 P-9	“
				83	22.10		3.3.5	20°C	0.5	“	1000 P-19	“

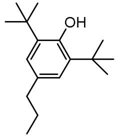
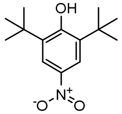
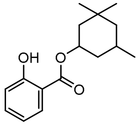
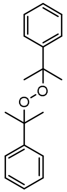
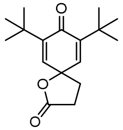
				93	22.10		3.3.5	20°C	0.5	“	1000 AO-6	“
				93	22.10		3.3.5	20°C	0.5	“	1000 AO-36	“
				84	22.10		3.3.5	20°C	0.5	“	1000 AO-58	“
				81	22.10		3.3.5	20°C	0.7	“	1000 AO-60	“
				93	22.10		3.3.5	20°C	0.6	“	1000 HYA-1	“
				93	22.10		3.3.5	20°C	0.6	“	1000 L-2	“
				85	22.10		3.4	20°C	0.9	PP-A	None	279
				92	22.11		3.4	20°C	0.7	“	1000 AO-1	“
				86	22.10		3.4	20°C	0.5	“	1000 AO-2	“
				80	22.10		3.4	20°C	0.5	“	1000 AO-4	“
				90	22.10		3.4	20°C	0.7	“	1000 AO-7	“
				84	22.10		3.4	20°C	0.9	“	1000 AO-38	“
				76	22.10		3.4	20°C	0.5	“	1000 AO-54	“
				93	22.10		3.4	20°C	0.6	“	1000 HAS-5	“
				93	22.10		3.4	20°C	0.5	“	1000 HAS-16	“
				94	22.10		3.4	20°C	0.9	“	1000 HAS-25	“
				89	22.10		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“
109	3-Methylheptyl acetate ***72218-58-7*** $C_{10}H_{20}O_2$	172		90	22.08	**S**	3.1	40°C	0.6	PP-A	None	238
				88	22.07		3.1	60°C	0.7	“	[AO-1+P-1] [750+750]	“
				93	22.07		3.1	40°C	0.8	“		
110	6-Tert-butyl-2,4-dimethyl phenol ***1879-09-0*** $C_{12}H_{18}O$	178		81	29.82	**PC**	3.3.5	20°C	0.5	PP-A	1000 AO-36	263
112	Cyclododecanone ***830-13-7*** $C_{12}H_{22}O$	182		98	32.14	**PC**	3.4	20°C	3.2	PP-A	1000 HAS-25	279
113	Benzophenone ***119-61-9*** $C_{13}H_{10}O$	182		99	33.90	**PC**	3.3.5	20°C	1.8	PP-A	None	263
114	Undecane, 3,7-dimethyl- *or isomer* ***17301-29-0*** $C_{13}H_{28}$	184		87	27.23	**S**	3.3.5	20°C	0.5	PP-A	1000 AO-60	263
115	Tridecane ***629-50-5*** $C_{13}H_{28}$	184		88	27.74	**S**	3.3.5	20°C	0.5	PP-A	1000 P-9	263
116	2-Dodecanone ***6175-49-1***	184		68	29.89	**S**	3.3.5	20°C	0.5	PP-A	1000 P-9	263

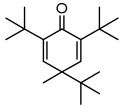
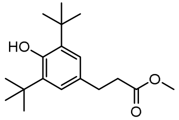
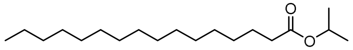
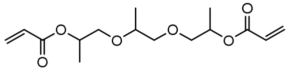
	$C_{12}H_{24}O$											
117	Dodecanal ***112-54-9*** $C_{12}H_{24}O$	184		87	30.17	**S**	3.3.5	20°C	**0.5**	PP-A	None	263
				88	30.17		3.3.5	20°C	**0.5**	“	1000 AO-60	“
				89	30.17		3.3.5	20°C	**0.5**	“	1000 P-3	“
				86	30.17		3.3.5	20°C	**0.5**	“	1000 P-9	“
119	1-Dodecanol ***112-53-8*** $C_{12}H_{26}O$	186		75	32.25	**S**	3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
120	4-Nonanol,2,6,8-trimethyl- ***123-17-1*** $C_{12}H_{26}O$	186		81	22.86	**S**	3.2	60°C	**17.6**	PP-B	None	243
				77	22.84		3.3.3	60°C	6.3	“	5000 AO-1	“
				79	22.86		3.3.4	60°C	6.2	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
122	5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)- ***3879-26-3*** $C_{13}H_{22}O$	194		84	31.00	**S**	3.3.5	20°C	**0.5**	PP-A	None	263
				84	30.99		3.3.5	20°C	**0.5**	“	1000 P-3	“
				84	31.00		3.3.5	20°C	**0.5**	“	1000 P-9	“
123	Benzoic acid, 4-ethoxy-, ethyl ester ***23676-09-7*** $C_{11}H_{14}O_3$	194		85	3225	**?**	3.3.5	20°C	**0.5**	PP-A	None	263
125	2,4-Di-tert-butyl phenol **ARVIN 4** ***96-76-4*** $C_{14}H_{22}O_2$	206		96	32.00	**PC**	3.1	60°C	3.9	PP-A	[AO-1+P-1]	238
				95	32.00		3.1	40°C	1.5	“	[750+750]	“
				74	32.14		3.1	20°C	0.7	“	“	237
				95	32.02		3.3.5	20°C	0.6	“	1000 P-1	263
				96	32.03		3.3.5	20°C	9.4	“	1000 P-3	“
				88	32.02		3.3.5	20°C	0.5	“	100 P-4	“
				96	32.02		3.3.5	20°C	0.6 ?	“	1000 P-5	“
				94	32.02		3.4	20°C	0.5	PP-A	[AO-1+P-1] [500+500]	279
				94	31.97		3.3.3	60°C	1.4	PP-B	[AO-1+P-1] [5000+1000]	243
				95	31.97		3.3.3	60°C	2.4	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				95	32.07		3.3.4	60°C	**56.6**	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				96	31.99		3.3	60°C	3.2	PP-C	[P-1] [750 ppm]	246
				94	31.99		3.3	60°C	3.6	“	[AO-1+P-1] [1000+750]	“

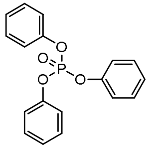
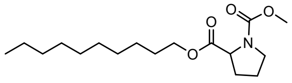
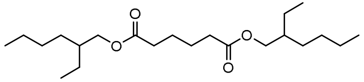
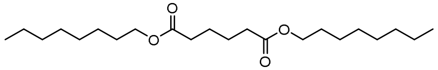
				96	31.99		3.3	60°C	3.6	“	[AO-1+P-1] [2500+750]	“
				95	31.99		3.3	60°C	3.3	“	[AO-1+P-1] [5000+750]	“
				96	31.99		3.4	60°C	8.2	“	[AO-3+P-1] [5000+750]	“
				95	31.99		3.4	60°C	6.0	“	[AO-4+P-1] [5000+750]	“
				95	32.00		3.4	60°C	11.8	“	[AO-38+P-1] [5000+750]	“
				95	31.99		3.4	60°C	4.8	“	[AO-39+P-1] [5000+750]	“
127	2, 4, 4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone ***88725-82-0*** $C_{14}H_{24}O$	208		77	28.84	**PC**	3.1	60°C	**2.4**	PP-A	[AO-1+P-1] [750+750]	238
				74	28.84		3.1	40°C	1.1	“		
131	Malonic acid, ethyl 3-hexyl ester ***1000349-11-7*** $C_{11}H_{20}O_4$	216		77	27.73	**PC**	3.4	20°C	**0.5**	PP-A	1000 HAS-5	279
132	6-tert-butyl-4-methylcoumarin ***17874-32-7*** $C_{14}H_{16}O_2$	216		79	36.56	**PC**	3.4	20°C	**0.5**	PP-A	1000 AO-38	279
				92	36.53		3.4	60°C	**4.3**	PP-C	[AO-38+P-1] [5000+750]	246
134	2,2,4-Trimethyl-1,3-pentadiol-1-isobutyrate ***77-68-9*** $C_{12}H_{24}O_3$	216		?	29.63	**S**	3.1	20°C	0.5	PP-A	None	237
				85	29.63		3.1	20°C	**0.6**	“	[AO-1+P-1] [750+750]	“
135	2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)- **ARVIN 3** ***719-22-2*** $C_{14}H_{20}O_2$	220		95	31.32	**PC**	3.1	60°C	1.2	PP-A	[AO-1+P-1] [750+750]	238
				86	31.34		3.4	20°C	0.5	PP-A	1000 AO-4	279
				93	31.29		3.3.3	60°C	1.4	PP-B	5000 AO-1	243
				95	31.29		3.3.3	60°C	1.2	“	[AO-1+P-1] [5000+1000]	“
				90	31.29		3.3.3	60°C	0.8	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				85	31.29		3.3.3	60°C	0.5	“	AO-1+P-5+AO-6] [5000+500+250]	“
				81	31.33		3.3.4	60°C	1.0	“	[AO-1+P-1$_{HYD}$] [1000+1000]	“
				86	31.32		3.3	60°C	1.3	PP-C	[AO-1+P-1] [1000+750]	246
				89	31.31		3.3	60°C	1.7	“	[AO-1+P-1]	“

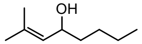
											[2500+750]	
				92	31.31		3.3	60°C	1.9	“	[AO-1+P-1] [5000+750]	“
				97	31.31		3.4	60°C	3.8	“	[AO-3+P-1] [5000+750]	“
				97	31.31		3.4	60°C	3.4	“	[AO-4+P-1] [5000+750]	“
				97	31.31		3.4	60°C	**4.6**	“	[AO-39+P-1] [5000+750]	“
136	Butylhydroxy Toluene **128-37-0** $C_{15}H_{24}O$	220		93	32.07		3.3.5	20°C	**0.5**	PP-A	1000 P-9	263
139	Phenyl-pentamethyl-disiloxane ***14920-92-4*** $C_{11}H_{20}OSi_2$	224	 Miss-assigned peak?	72	14.67		3.3.5	20°C	**0.9**	PP-A	1000 P-5	263
142	3,5-di-tert-butyl-4-hydroxystyrene **ARVIN 5** ***52858-87-4*** $C_{16}H_{24}O$	232		?	33.76		3.3.3	60°C	**20-100**	PP-B	[AO-1+P-1] [5000+1000]	243
143	3,5-di-tert-butyl-4-Hydroxybenzaldehyde **ARVIN 6** ***1620-98-0*** $C_{15}H_{22}O_2$	234		97	35.61	**PC**	3.1	60°C	12.5	PP-A	[AO-1+P-1] [750+750]	238
				96	35.60		3.1	40°C	3.8			
				95	35.62		3.4	40°C	0.5	PP-A	1000 AO-1	279
				95	35.62		3.4	40°C	0.5	“	[AO-1+P-1] [500+500]	“
				96	35.57		3.3.3	60°C	7.8	PP-B	5000 AO-1	243
				96	35.58		3.3.3	60°C	8.2	“	[AO-1+P-1] [5000+1000]	“
				96	35.57		3.3.3	60°C	6.1	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				96	35.57		3.3.3	60°C	4.0	“	AO-1+P-5+AO-6] [5000+500+250]	“
				95	35.57		3.3.4	60°C	8.1	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				96	35.59		3.3	60°C	1.5	PP-C	[AO-1+P-1] [1000+750]	246
				96	35.61		3.3	60°C	14.8	“	[AO-1+P-1] [2500+750]	“
				96	35.61		3.3	60°C	**17.6**	“	[AO-1+P-1]	“

											[5000+750]	
				85	35.60		3.4	60°C	6.3	“	[AO-3+P-1] [5000+750]	“
				84	35.59		3.4	60°C	1.0	“	[AO-4+P-1] [5000+750]	“
				91	35.59		3.4	60°C	0.6?	“	[AO-38+P-1] [5000+750]	“
				97	35.59		3.4	60°C	4.7	“	[AO-39+P-1] [5000+750]	“
144	$C_{15}H_{24}O_2$	236		85	35.60		3.4	60°C	**8.4**	PP-C	[AO-3+P-1] [5000+750]	246
147	1-Decanol, 2-hexyl- ***2425-77-6*** $C_{16}H_{34}O$	242		97	35.81	**S**	3.2	60°C	**1.5**	PP-C	None	246
148	3,5-di-tert-butyl-4-hydroxyacetophenone **ARVIN 7** ***14035-33-7*** $C_{16}H_{24}O_2$	248		96	36.20	**PC**	3.1	60°C	8.8	PP-A	[AO-1+P-1] [750+750]	238
				96	36.20		3.1	40°C	2.6	“		“
				94	36.30		3.1	20°C	1.0	“	“	237
				96	36.22		3.4	20°C	0.6	PP-A	1000 AO-1	279
				94	36.22		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“
				96	36.18		3.3.3	60°C	10.0	PP-B	5000 AO-1	243
				95	36.17		3.3.3	60°C	6.3	“	[AO-1+P-1] [5000+1000]	“
				96	36.17		3.3.3	60°C	5.6	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				95	36.17		3.3.3	60°C	2.9	“	AO-1+P-5+AO-6] [5000+500+250]	“
				96	36.18		3.3.4	60°C	9.7	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
				95	36.19		3.3	60°C	0.9	PP-C	[AO-1+P-1] [1000+750]	246
				96	36.20		3.3	60°C	10.8	“	[AO-1+P-1] [2500+750]	“
				96	36.20		3.3	60°C	**13.3**	“	[AO-1+P-1] [5000+750]	“
				< 80	36.22		3.4	60°C	16.7	“	[AO-39+P-1] [5000+750]	“

149	Proposed structure 2,6-di-tert-butyl-4-propylphenol ***4973-24-4*** $C_{17}H_{28}O$	248		< 80	35.45	**PC ?**	3.3	60°C	0.5	PP-C	[AO-1+P-1] [2500+750]	246
				< 80	35.45		3.3	60°C	0.5	PP-C	[AO-1+P-1] [5000+750]	“
150	2,6-Di-tert-Butyl-4-nitrophenol ***728-40-5*** $C_{14}H_{21}NO_3$	251		89	37.24	**PC**	3.1	60°C	2.9	PP-A	[AO-1+P-1] [750+750]	238
				75	37.24		3.1	40°C	0.9	“		“
153	Homosalate ***118-56-9*** $C_{16}H_{22}O_3$	262		< 80	37.02	**S**	3.2	60°C	0.9	PP-B	None	243
				< 80	37.01		3.3.3	60°C	0.9	“	5000 AO-1	“
				94	37.02		3.3.4	60°C	1.9	“	[AO-1+P-1_{HYD}] [5000+1000]	“
154	Dicumyl peroxide ***80-43-3*** $C_{18}H_{22}O_2$	270		85	26.90	**?**	3.4	20°C	0.7	PP-A	None	279
				75	26.90		3.4	20°C	0.5	“	1000 AO-54	“
				76	26.90		3.4	20°C	0.5	“	1000 HAS-5	“
156	7,9-di-tert-butyl-1-oxaspiro (4,5) deca-6,9-diene-2,8-dione **ARVIN 8** ***82304-66-3*** $C_{17}H_{24}O_3P$	276		84	37.33	**PC**	3.1	60°C	0.8	PP-A	[AO-1+P-1] [750+750]	238
				93	37.33		3.1	40°C	1.1	“		“
				85	37.35		3.4	20°C	0.5	PP-A	1000 AO-1	279
				69	37.36		3.4	20°C	0.5	“	[AO-1+P-1] [500+500]	“
				84	37.31		3.3.3	60°C	4.3	PP-B	5000 AO-1	243
				100	37.31		3.3.3	60°C	2.3	“	[AO-1+P-1] [5000+1000]	“
				100	37.31		3.3.3	60°C	2.2	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				100	37.31		3.3.3	60°C	2.0	“	AO-1+P-5+AO-6] [5000+500+250]	“
				94	37.31		3.3.4	60°C	5.8	“	[AO-1+P-1_{HYD}] [5000+1000]	“
				96	37.33		3.3	60°C	0.6	PP-C	[AO-1+P-1] [2500+750]	246
				96	37.33		3.3	60°C	0.9	“	[AO-1+P-1] [5000+750]	“
				93	37.40		3.4	60°C	0.7	“	[AO-39+P-1]	“

											[5000+750]	
159	2,4,6-Tris (1,1-dimethyl ethyl)-4-methylcyclohexa-2,5-dien-1-one ***19687-22-0*** $C_{19}H_{32}O$	277		78	38.47	**PC**	3.1	60°C	**0.9**	PP-A	[AO-1+P-1] [750+750]	238
163	Benzenepropoanoic acid,3,5-bis (1,1-dimethylethyl)-4-hydroxy-, methyl ester **ARVIN 9** ***6386-38-5*** $C_{18}H_{28}O_3$	292		87	37.52	**PC**	3.1	60°C	0.5	PP-A	[AO-1+P-1] [750+750]	238 “
				94	37.49		3.3.3	60°C	2.6	PP-B	5000 AO-1	243
				93	37.49		3.3.3	60°C	1.8	“	[AO-1+P-1] [5000+1000]	“
				93	37.49		3.3.3	60°C	1.8	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				88	37.49		3.3.3	60°C	1.4	“	AO-1+P-5+AO-6] [5000+500+250]	“
				96	37.49		3.3.4	60°C	4.0	“	[AO-1+P-1_{HYD}] [5000+1000]	“
				95	37.51		3.3	60°C	0.8	PP-C	[AO-1+P-1] [2500+750]	246
				94	37.51		3.3	60°C	1.4	“	[AO-1+P-1] [5000+750]	“
				96	36.69		3.4	60°C	**323.0**	“	[AO-39+P-1] [5000+750]	“
164	*Derivative of ARVIN 9*			< 80	38.00		3.4	60°C	**2.9**	PP-C	[AO-39+P-1] [5000+750]	246
165	Isopropyl palmitate ***142-91-6*** $C_{19}H_{38}O_2$	299		85	38.20	**M**	3.3.4	60°C	1.2	PP-B	[AO-1+P-1_{HYD}] [5000+1000]	243
				89	38.22		3.4	60°C	0.7	PP-C	[AO-3+P-1] [5000+750]	“
				87	38.22		3.4	60°C	**1.6**	PP-C	[AO-39+P-1] [5000+750]	“
166	2-Propenoic acid, (1-methyl-1,2-ethanediyl) bis [oxy(methyl-2,1-etahndiyl)] Tripropyleneglycol diacrylate ***71412-35-6*** $C_{15}H_{24}O_6$	300		84	31.54	**S**	3.3.5	20°C	**1.1**	PP-A	None	263

167	Triphenylphosphate ***115-86-6*** $C_{18}H_{15}O_4P$	326		94	42.28	**PC**	3.1	20°C	**2.6**	PP-A	[AO-1+P-1] [750+750]	5-3
169	*Derivative of* 1-Proline, N-methoxycarbonyl-, decyl ester	327 ?		84	41.17	?	3.1	20°C	**10.8**	PP-A	None	237
173	Hexanedioic acid, bis(2-ethylhexyl) ester ***103-23-1*** $C_{22}H_{42}O_4$	370		84	41.92	**S**	3.1	20°C	0.7	PP-A	None	237
				84	41.83		3.1	60°C	1.0	“	[AO-1+P-1]	238
				86	41.92		3.1	20°C	**1.2**	“	[750+750]	237
174	Hexanedioic acid, dioctyl ester ***123-79-5*** $C_{22}H_{42}O_4$	370		94	41.81	**S**	3.2	60°C	**0.6**	PP-C	None	246
	Unidentified (m/z 31, 61, 91)			< 70	13.29		3.3.5	20°C	**1.4**	PP-A	1000 P-3	263
				< 70	13.24		3.3.5	20°C	0.5	“	1000 P-5	“
				< 80	13.25		3.3.5	20°C	0.5	“	1000 P-9	“
				< 70	13.23		3.3.5	20°C	0.8	“	1000 AO-60	
	Unidentified (m/z 43, 72, 114, 156)		Oxygenated	< 60	15.57	**S**	3.4	20°C	1.0	PP-A	None	279
				< 70	15.61		3.4	20°C	0.5	“	1000 AO-54	“
				< 80	15.56		3.2	60°C	3.2	PP-B	None	243
				< 80	15.56		3.3.3	60°C	2.6	“	5000 AO-1	“
				< 80	15.58		3.3.4	60°C	**3.3**	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
	Unidentified		Oxygenated	< 70	15.77	**S?**	3.3.5	20°C	0.5	PP-A	1000 P-3	263
				< 70	15.75		3.3.5	20°C	0.5	“	1000 P-4	“
				< 70	15.77		3.3.5	20°C	0.5	“	1000 P-5	“
				< 70	15.77		3.3.5	20°C	0.5	“	1000 P-19	“
				< 80	15.74		3.3.5	20°C	**0.7**	“	1000 AO-6	“
				< 70	15.78		3.3.5	20°C	0.5	“	1000 AO-36	“
				< 70	15.74		3.3.5	20°C	0.5	“	1000 AO-53	“
				?	15.77		3.3.5	20°C	0.5	“	1000 AO-58	“
				< 70	15.76		3.3.5	20°C	0.5	“	1000 AO-60	“
				< 70	15.74		3.3.5	20°C	0.5	“	1000 HYA-1	“
				< 70	15.75		3.3.5	20°C	0.5	“	1000 L-2	“
				< 70	15.76		3.4	20°C	0.5	PP-A	1000 AO-1	279
				< 60	15.75		3.4	20°C	0.5	“	1000 AO-2	“
				< 80	15.74		3.4	20°C	0.5	“	1000 AO-4	“

				< 80	15.74		3.4	20°C	0.5	“	1000 AO-7	“
				< 80	15.74		3.4	20°C	0.5	“	1000 AO-38	“
				< 70	15.74		3.4	20°C	0.5	“	1000 HAS-5	“
				< 70	15.75		3.4	20°C	0.5	“	1000 HAS-16	“
				< 70	15.75		3.4	20°C	0.5	“	1000 HAS-25	“
				< 60	15.74		3.4	20°C	0.6	“	[AO-1+P-1] [500+500]	“
	Unidentified oxygenated		 (Proposed structure) F# 58?	< 80	16.30	**S**	3.1	60°C	1.5	PP-A	None	238
				< 80	16.32		3.5	60°C	3.6	PP-A	750 P-1	229
				73	16.30		3.2	60°C	4.0	PP-B	None	238
				< 80	16.32		3.2	60°C	**4.5**	PP-C	None	246
	Unidentified (m/z 71, 109)			?	17.26	**S**	3.1	60°C	**2.5**	PP-A	None	238
	Unidentified			< 80	18.67	**S**	3.1	40°C	0.7	PP-A	None	238
	Oxygenated		Cyclohexanol,3,3,5-trimethyl- ***116-02-9*** ***?***	< 80	18.67		3.1	40°C	0.5	“	[AO-1+P-1] [750+750]	“
				< 80	18.68		3.3	60°C	**1.7**	PP-C	[P-1] [750 ppm]	246
				< 80	18.64		3.3	60°C	1.5	PP-C	[AO-1+P-1] [1000+750]	“
	Unidentified (m/z 43, 77, 99, 123)			< 80	19.21	?	3.2	60°C	**4.6**	PP-C	None	246
	Unidentified (m/z 31, 61, 91)			< 70	21.19	?	3.3.5	20°C	**0.5**	PP-A	AO-60	246
				< 80	21.16		3.3.5	20°C	**0.5**	“	P-3	“
	Unidentified			< 90	24.19	?	3.3.5	20°C	0.6	PP-A	1000 P-1	263
				< 80	24.20		3.3.5	20°C	0.5	“	1000 P-3	“
				< 80	24.20		3.3.5	20°C	0.5	“	1000 P-4	“
				< 80	24.20		3.3.5	20°C	0.5	“	1000 P-5	“
				< 85	24.20		3.3.5	20°C	0.5	“	1000 P-19	“
				< 90	24.19		3.3.5	20°C	**0.9**	“	1000 AO-60	“
				< 90	24.20		3.3.5	20°C	0.5	“	1000 L-2	“
	Unidentified (m/z 61, 89, 143, 172)			< 80	24.89		3.1	60°C	2.8	PP-A	None	238
				< 80	24.91		3.1	60°C	2.4	“	[AO-1+P-1] [750+750]	“
	(m/z 43, 61, 89, 113, 143, 172)			< 80	24.99		3.2	60°C	**5.5**	PP-C	None	246
				?	24.89		3.3	60°C	2.0	“	[P-1] [750 ppm]	“
				?	24.89		3.3	60°C	1.9	“	[AO-1+P-1] [1000+750]	“
				?	24.89		3.3	60°C	1.8	“	[AO-1+P-1]	“

											[2500+750]	
				?	24.89		3.3	60°C	1.8	“	[AO-1+P-1] [5000+750]	“
				?	24.90			60°C	1.4	“	[AO-3+P-1] [5000+750]	“
				?	24.89			60°C	1.5	“	[AO-4+P-1] [5000+750]	“
				?	24.89			60°C	1.7	“	[AO-38+P-1] [5000+750]	“
				< 80	24.89			60°C	1.6	“	[AO-39+P-1] [5000+750]	“
	Unidentified (m/z 121, 136) Co-elution with Decanal			?	24.94	?	3.1	20°C	**0.6**	PP-A	[AO-1+P-1] [750+750]	237
	Unidentified (m/z 150)			< 70	25.09	?	3.3.5	20°C	0.5	PP-A	1000 AO-6	263
				< 80	25.02		3.3.3	60°C	**1.4**	PP-B	[AO-1+P-1+AO-6] [5000+1000+250]	243
				< 80	25.03		3.3.3	60°C	1.2	“	AO-1+P-5+AO-6] [5000+500+250]	“
	Unidentified (m/z 57, 85, 143)		Oxygenated	< 80	25.25	?	3.4	60°C	**0.9**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 57, 111, 125, 140, 181, 196)			< 80	25.56		3.3.3	60°C	3.1	PP-B	5000 AO-1	243
				< 80	25.56		3.3.4	60°C	**5.7**	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
	Unidentified (m/z 57, 111, 125, 140, 181, 196)			< 80	25.58		3.4	60°C	**6.7**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified		$C_{10}H_{12}O_2$	< 80	26.02	**PC**	3.3.5	20°C	**1.8**	PP-A	1000 AO-53	263
	Unidentified		$C_{10}H_{10}O_2$	< 80	26.62	**PC**	3.3.5	20°C	**2.3**	PP-A	1000 AO-53	263
	Unidentified (m/z 43, 61, 113, 155)			< 80	26.68		3.2	60°C	**3.3**	PP-C	None	246
	Unidentified		$C_{10}H_{13}O_2$	< 80	27.54		3.3.5	20°C	**0.5**	PP-A	1000 AO-53	263
	Unidentified		Oxygenated	< 80	27.94		3.3.5	20°C	**0.5**	PP-A	None	263
	Unidentified (m/z 57, 125, 140, 162, 181)			< 80	28.24		3.3.4	60°C	**9.5**	PP-B	[AO-1+P-1$_{HYD}$] [5000+1000]	243
	Unidentified (m/z 43, 85, 127)			< 80	28.56	**S**	3.1	60°C	1.8	PP-A	None	238
				< 80	28.67		3.1	60°C	1.0	“	[AO-1+P-1] [750+750]	“
	(m/z 43, 69, 85, 109, 127, 142)			< 80	28.64		3.2	60°C	4.2	PP-B	None	243

	(m/z 43, 69, 85, 91, 127, 145)			< 80	28.64		3.3.3	60°C	3.7	“	5000 AO-1	“
				< 80	28.56		3.3.4	60°C	3.5	“	[AO-1+P-1_{HYD}] [5000+1000]	“
				< 80	28.66		3.2	60°C	**5.7**	PP-C	None	246
				?	28.66		3.3	60°C	2.6	“	[P-1] [750 ppm]	“
				< 80	28.67		3.3	60°C	1.2	PP-C	[AO-1+P-1] [1000+750]	“
				?	28.66		3.4	60°C	1.2	“	[AO-3+P-1] [5000+750]	“
				?	28.66		3.4	60°C	0.9	“	[AO-38+P-1] [5000+750]	“
	Unidentified (m/z 57,95,123,138,193, 208)			< 80	28.81		3.3.3	60°C	3.3	PP-B	5000 AO-1	243
				< 80	28.81		3.3.3	60°C	2.7	“	[AO-1+P-1] [1000+750]	“
				< 80	28.81		3.3.3	60°C	1.7	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				< 80	28.81		3.3.3	60°C	0.9	“	AO-1+P-5+AO-6] [5000+500+250]	“
				< 80	28.81		3.3.4	60°C	**3.4**	“	[AO-1+P-1_{HYD}] [5000+1000]	“
	Unidentified			< 70	29.08		3.3.5	20°C	**0.5**	PP-A	1000 AO-53	263
	Unidentified (m/z 195, 210)		Oxygenated	< 70	29.68		3.3.4	20°C	0.5	PP-A	1000 P-9	263
				< 80	29.68		3.4	60°C	**1.2**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified		Oxygenated	< 80	30.29	**S**	3.1	60°C	**1.0**	PP-A	None	238
				< 80	30.29		3.1	60°C	0.6	“	[AO-1+P-1] [750+750]	“
	Unidentified		Hydrocarbon	< 80	30.33		3.3.5	20°C	**0.5**	PP-A	Npne	263
	Unidentified		Oxygenated	< 80	30.34	**S**	3.1	60°C	**1.4**	PP-A	None	5-4
				< 80	30.35		3.1	60°C	0.7	“	[AO-1+P-1] [750+750]	“
	Unidentified (m/z 57, 131, 183)			< 70	30.92		3.3.5	20°C	**0.5**	PP-A	1000 AO-60	263
				< 70	30.92		3.3.5	20°C	**0.5**	“	1000 P-3	“
	Unidentified (m/z 129, 173, 213)			< 70	31.24		3.3.5	20°C	**0.5**	PP-A	1000 AO-36	263
				< 70	31.24		3.3.5	20°C	**0.5**	“	1000 P-3	“
				< 70	31.24		3.3.5	20°C	**0.5**	“	1000 P-4	“
				< 70	31.24		3.3.5	20°C	**0.5**	“	1000 P-9	“
	Unidentified		Potentially CAS# 39170-97-3	< 80	31.51		3.4	60°C	**2.7**	PP-C	[AO-3+P-1]	246

											[5000+750]	
	Unidentified (m/z 58)			< 70 < 80 < 80 < 80	31.81 31.81 31.84 31.81		3.3.5 3.3.5 3.3.5 3.3.5	20°C 20°C 20°C 20°C	**0.5** **0.5** **0.5** **0.5**	PP-A “ “ “	1000 AO-60 1000 P-1 1000 P-3 1000 P-5	263 “ “ “
	Unidentified (m/z 57, 125, 140, 161, 181, 203)			< 80	32.20		3.3.3	60°C	**2.9**	PP-B	5000 AO-1	243
	Unidentified (m/z 57, 125, 140)			< 80	32.34		3.3.4	60°C	**4.9**	PP-B	[AO-1+P-1$_{HYD}$] [5000+1000]	243
	Unidentified		$C_{10}H_{12}O_2$	< 70	32.42		3.3.5	20°C	**0.5**	PP-A	1000 AO-53	263
	Unidentified		$C_{10}H_{12}O_2$	< 70	32.50		3.3.5	20°C	**0.9**	PP-A	1000 AO-53	263
	Unidentified (m/z 151, 165, 180, 208)			< 80	32.52		3.3.4	60°C	**2.7**	PP-B	[AO-1+P-1$_{HYD}$] [5000+1000]	243
	Unidentified			< 80 < 80	32.63 32.63		3.4 3.4	60°C 60°C	**37.3** 0.8	PP-C “	[AO-38+P-1] [5000+750] [AO-39+P-1] [5000+750]	246 “
	Unidentified oxygenated			< 80 < 80	32.85 32.85	S	3.1 3.1	60°C 60°C	**1.6** 1.3	PP-A “	None [AO-1+P-1] [750+750]	238 “
	Unidentified oxygenated			< 80 < 80	32.98 32.98	S	3.1 3.1	60°C 60°C	**2.0** 1.6	PP-A “	None [AO-1+P-1] [750+750]	238 “
	Unidentified oxygenated (m/z 43, 69, 85, 95, 110, 151)			< 80 < 80 < 80	33.16 33.16 33.16	S	3.2 3.3.3 3.3.4	60°C 60°C 60°C	1.6 2.6 **3.6**	PP-B “ “	None 5000 AO-1 [AO-1+P-1$_{HYD}$] [5000+1000]	243 “ “
	Unidentified (m/z 151 166, 222)			< 80	33.41		3.3.4	60°C	**2.1**	PP-B	[AO-1+P-1$_{HYD}$] [5000+500]	243
	Unidentified (m/z 79, 106, 134, 167, 194, 227, 251)			< 80	34.16		3.4	60°C	**0.5**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 41, 57, 67, 95, 138, 167, 181, 191, 209)			< 80	34.35		3.4	60°C	**0.5**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified			< 80	34.72		3.4	60°C	**1.8**	PP-C	[AO-38+P-1] [5000+750]	246
	Unidentified (m/z 161, 189, 204)			< 80	35.19		3.4	60°C	**0.5**	PP-C	[AO-38+P-1] [5000+750]	246
	Unidentified (m/z 193, 275)			< 80 < 80	35.78 35.77	S	3.2 3.3.3	60°C 60°C	**0.8** 0.9	PP-B “	None 5000 AO-1	243 “

				< 80	35.77		3.3.3	60°C	0.8	“	[AO-1+P-1] [5000+1000]	“
				?	35.78		3.3.3	60°C	0.9	“	[AO-1+P-1+AO-6] [5000+1000+250]	“
				< 80	35.77		3.3.3	60°C	0.8	“	AO-1+P-5+AO-6] [5000+500+250]	“
				<80	35.77		3.3.4	60°C	1.0	“	[AO-1+P-1$_{HYD}$] [5000+1000]	“
	Unidentified (m/z 225, 240)			< 70	36.02	**PC**	3.3.5	20°C	**0.5**	PP-A	1000 P-19	243
	Unidentified (m/z 161, 177, 207, 222)			< 70	36.15	**PC**	3.3.5	20°C	**0.5**	PP-A	1000 P-19	243
	Unidentified (m/z 181, 197, 255, 270)			< 80	36.56		3.4	60°C	**2.6**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 203, 261, 276)		Potentially F# 157 or F# 158 Derivative of F# 163 ?	< 80	37.16		3.3.3	60°C	0.8	PP-B	[AO-1+P-1] [5000+1000]	243
				< 80	37.18		3.3	60°C	0.6	PP-C	[AO-1+P-1] [2500+750]	246
				< 80	37.18		3.3	60°C	**0.9**	PP-C	[AO-1+P-1] [5000+750]	“
	Unidentified (m/z 233, 275, 290)			< 80	38.33		3.4	60°C	**1.1**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 57, 177, 205, 220, 236, 273, 306)			< 80	38.50		3.4	60°C	**0.7**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 147, 199, 217, 233, 263, 277, 291, 306)			< 80	38.65		3.4	60°C	**8.8**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 161, 175, 201, 235, 250, 272, 290, 308)			< 80	39.61		3.4	60°C	**4.2**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 275, 290)			< 80	39.81		3.4	60°C	**1.9**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 57, 161, 203, 235, 247, 275, 291, 307)			< 80	40.25		3.4	60°C	**0.7**	PP-C	[AO-39+P-1] [5000+750]	246
	Unidentified (m/z 41, 69, 346)			?	40.76	**S**	3.1	20°C	1.0	PP-A	None	237
				?	40.75		3.1	20°C	**1.1**	“	[AO-1+P-1] [750+750]	“
	Unidentified (m/z 219, 299, 331)			< 80	41.66		3.4	60°C	**0.5**	PP-C	[AO-39+P-1] [5000+750]	246