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DOES THE IN-PACKAGING FOOD PRESERVATION TECHNIQUE, RETORTING, AFFECT THE MIGRATION OF FOOD PACKAGING?

A thesis presented in partial fulfilment of the requirements for the degree of Master of Engineering in Chemical and Bioprocess Engineer at Massey University, New Zealand.

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Abstract

The effects of retort treatments on chosen monolayer plastic films commonly used in the food industry were studied. Changes occurring in the plastic monolayers and the leachates into the food system, and post-retort treatments were monitored. Three industry-relevant retort settings were trialled: 110 °C for 51 mins, 115 °C for 25 mins, and 121 °C for 16 mins. The monolayer plastic films studied were polyethylene, polyethylene terephthalate, and polyamide; common components of multi-layer retort pouches. The key areas for this research project were to investigate how different retort time-temperature profiles affect the monolayer physically and the overall and specific migration from monolayer films into different food simulants. This was used to determine whether a significant change in migration from the monolayer films was associated with retort processing. The plastic was tested using EU standards of compliance and using 10 % ethanol and 3 % acetic acid as food simulants to represent retort products. The materials were visually inspected straight after retorting, followed by an in-depth internal surface investigation to monitor changes via microscopy. The overall and specific migration was assessed, and compounds putatively identified were assigned a Cramer class.

Overall, the retort treatment at 110° C for 51 mins created the most changes in terms of migration on most of the samples. The results of this research were for the simulants: ethanol triggered significantly more changes in PE and PET. For PA films the results revealed that both simulants had a similar number of changes, due to long processing time.

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Abbreviation Table

Name	Abbreviations
Acetaldehyde	AA
Antimony	Sb
Clostridium Botulinum	*C.Botulinum*
Ethyleneglycol	EG
Gas Chromatography Mass Spectroscopy	GCMS
High Density Polyethylene	HDPE
Hydroxylamine Sulphate Oxidation	HSO
Intentionally Added Substances	IAS
Inductively Coupled Plasma Mass Spectroscopy	ICPMS
Liquid Chromatography Mass Spectroscopy	LCMS
Low Density Polyethylene	LDPE
Linear Low Density Polyethylene	LLDPE
Medium Density Polyethylene	MDPE
Non-Intentionally Added Substances	NIAS
Overall Migration	OML
Polyamide	PA
Polyethylene	PE
Polyethylene Terephthalate	PET
Polypropylene	PP
Read-to-eat meals	MRE
Scanning Electron Microscopy	SEM
Slowest Heating Point	SHP
Specific Migration Limit	SML
Poly(2,6,-Diphenyly-P-Phenylene Oxide)	TENAX
Ultra Low Density Polyethylene	ULDPE
Water Activity	Aw
Zinc	Zn

1.0 Introduction

Food packaging is an essential part of life. It has multiple roles: but primary it is to preserve food freshness and characteristics and to ensure consumer safety. Packaging must comply with international food contact regulations, which limit the release of substances from component materials into the food systems it protects. Food preservation techniques are used to meet the increased consumer demand for ambient temperature stable products with longer shelf life, while maintaining their high quality. Food is packaged fresh and treated in packaging to minimise food spoilage, whilst retaining nutritional components usually destroyed in conventional processing or cooking preservation techniques. Extensive studies have been focused on food properties and modifications in food characteristics post in-packaging treatment (Akbarian et al., 2014). These focus on food spoilage, overlooking any potential effects on food packaging properties (mechanical and chemical). Additionally only**,** very preliminary studies have been performed on leaching of specific migrates from the packaging into the food system, due to treatment of food already packaged and no attempts have been made to confirm the structure and concentration of putatively identified compounds (O'Connor, 2020). It is commonly known that chemical changes are observed in materials due to ageing and use (Yates et al., 2021). These chemical changes lead to leaching of breakdown products and additives from food packaging into food systems. It is not yet understood whether food preservation treatments lead to release of unwanted compounds from packaging materials. As part of previous research, there has been a proof-of-concept study to determine compounds released during retorting from commonly used multi-layer packaging films, a commonly used high temperature food treatment (O'Connor, 2020). The packaging materials used still complied with regulations based on the commonly required food contact compliance tests. Further investigations showed that a large number of compounds were released post-retorting, most of them identified as potentially hazardous. However, due to the multi-layer material used, there was no possible identification of the monolayer contributing the most to the increased leaching. It is essential to gain an understanding of the behaviour of different monomaterials under the strain of in-packaging treatment parameters.

The main constituents of multi-layer food packaging are polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), and polyamide (PA). Although discrete studies on physical and chemical changes of packaging and food safety post processing have been reported, no coordinated approach to assess individual monolayers of food packaging materials in novel preservation techniques has been attempted (O'Connor, 2020).

The purpose of this research was to investigate the effects of retorting treatments on chosen types of monolayer materials. Material changes and trends associated with retorting were investigated.

The plastics chosen as representative were PE, PET, and PA, in their monolayer forms.

Regulations governing plastic packaging materials were reviewed and used as a basis for experimental design. This included the simulants most suitable to replicate food systems commonly encountered in retort pouches. A critical review of current use of monolayer and multilayer materials in food packaging was used as a starting point for material choice.

The results for the three plastic films using two food simulants and three retort setting were compared and conclusions were drawn regarding their suitability.

2.0 Literature Review

This literature review was used to investigate the reported effects of retorting on specific types of plastic packaging used in the food industry. The retorting is the most commonly used sterilization techniques. Relevant food contact regulations outlining the testing required for a packaging material in contact with food are discussed. The compliance and hazard assessment process required by regulation to determine whether plastic is safe to be used for food contact is presented. Compliance and hazard assessments completed on retort pouches, as well as modelling of migration is briefly reviewed.

2.1 Retort Processing

Food that is not perishable is either acidic (pH value < 4.6) or has a low water activity (Aw <0.6), or has been treated to allow a long-term shelf life. Water activity (Aw) is a measure of how "free" or "available" the water in a food is; the higher the water activity, the more available that water is to support reactions (e.g. microbial growth and other deteriorative reactions) (Maltini et al., 2003). Aw is accepted as one of the most important factors that affect bacteria growth. A retort is used as a key technique in the food industry to create shelf-stable food via an in-packaging sterilization process. This uses high temperatures (between 110 to 135°C) for a calculated amount of time needed to kill bacteria. This time is known as thermal death time.

The principle of retorting products is to destroy microorganisms through thermal processing creating a first order logarithmic rate of destruction (Awuah et al., 2007). In industry, the primary focus microorganism is *Clostridium Botulinum* (*C. Botulinum*) spores. The death of this bacteria is what the parameters for thermal processing/sterilization are based around. *C.Botulinum* is a spore-forming mesophilic bacteria of concern due to its toxicity and heat resistance; it can be aerobic, anaerobic, or microaerobic (Awuah et al., 2007; Lund & Peck, 2013). The retort requirements for sterilization ($F_o/F_{121.1°C}$=3 min) are based on the destruction of *C. Botulinum* because of its toxicity (MPI, 2021). F is a function used to describe all temperatures and all times during the treatment (Frank, 1987). F is the minimum sterilization required to bring the number of bacteria down to a safe level, which is by 90% or one log order. According to good manufacturing practice its concentration needs to be reduced by a factor of 10^{12} (Awuah et al., 2007). F_o = 3 mins, means the retort is heated to 121 °C, then held at that temperature for three mins-cycle used to achieve the 10^{12} reduction. The come-up temperature/time profile is a part of achieving F_o value as well as the hold time (come-up means the time for the product to reach the set temperature). The F_o value is affected by thermal properties and mass of the food packaging system. There are predictive measures that can be used to predict heat

transfer like Gillespy's mathematical model. The temperature is always measured at the slowest heating point (SHP) of the product inside the packaging, to ensure all the food receives the required thermal treatment.

Traditionally, packaging used for thermal processing of food was metal cans or glass containers. In the 1970s plastic retort pouches became globally available. They were developed for Ready-to-Eat Meals (RTE) used by the military (Frank, 1987; Jun et al., 2006; Lalpuria et al., 2012). Most commercially available retort pouches use a multi-layer film. Some of the most common materials used in the multilayer pouches are PP, PET, PE, and PA. Plastic pouches offer advantages over traditional packaging; they are significantly lighter, so are more economical to transport and store; they are cheaper, easier to dispose of at end of use, and are significantly better for heat transfer throughout the product. This in turn means the product can achieve sterilisation much faster and maintain higher quality (Jun et al., 2006). This creates a better product as it has less time cooking, which means the product will remain closer to its original state (Jun et al., 2006).

Most retorts fall into two categories with two modes of operation: static or agitating, and batch or continuous. These retorts can be used for all different types of packaging. All retorts use water or steam; the required temperature is achieved via controlling the pressure. The temperature is maintained for a specific time to achieve the F_o value. The retort is cooled down by releasing the pressure.

- Static retorts were one of the first retorts made (Vatankhah et al., 2023). These retorts use water/steam in multiple ways to heat: these can be cascading, spraying, showering, or raining; steam is used in combination with air.
- Agitating retorts are the newest technological advance in retorting; the agitation helps improve heat transfer in foods that do not have a high viscosity, as the agitation allows the product to get more even heat distribution from the retort (Vatankhah et al., 2023; Walden, 2008). There are four different ways the agitating: axial, bi-axial, end-over-end, and reciprocating, displayed in Figure 1 (Singh et al., 2016).
- Batch retorts were ones of the first retorts made and they are used due to their ability to process products in many ways, using different methods, different types of food, and packaging types simultaneously (Vatankhah et al., 2023). These have less maintenance compared to their counterpart, however they require more manual labour during loading and unloading (Holdsworth et al., 2016).
- Continuous retorts are characterised by the product conveyed through rather than being operated in a batch process. They generally have much higher capital costs but have

advantages of higher throughput efficiency. As a result they are only encountered in large scale commercial manufacturers (Jimenez et al., 2023).

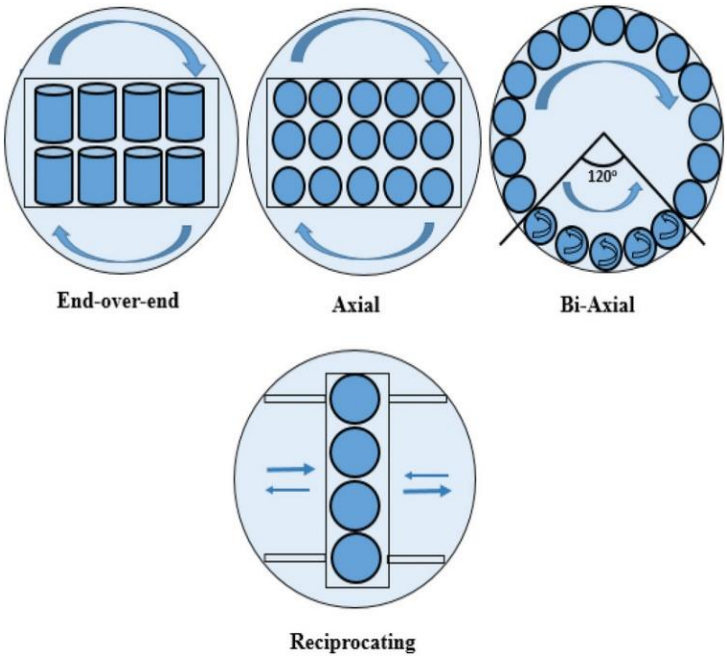


Figure 1: *Types of agitating retorts (from (Singh et al., 2016)*

2.2 Food Contact Compliance

Food contact regulations are mostly country specific, but some countries reference generally accepted regulations in their own. For example, in New Zealand both the European and US/American Food Contact Regulations can be used to show compliance for food packaging materials (Sotomayor et al., 2007). This review investigated the European regulations for food contact plastics, also known as Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food in Europe (COMMISSION, 2011).

All plastics allowed to be used in food contact must undergo risk assessment testing, under their worst "foreseen" conditions when they are first proposed as a food contact substance (COMMISSION, 2011). If the manufacturer uses a material that has not been assessed yet for use in contact with food, compliance with legislation must be shown the material should be assessed and the rules followed for testing should be set out. For this research a compliance assessment was completed using: overall migration limits (OML), metal migration, and specific migration limit (SML), followed by an hazard evaluation using toxicology assessment. The compliance tests can only be done by certified laboratories. The compliance for the SML is a maximum amount of a substance permitted to be in a food as set out in regulations. This is based on ensuring that the food contact material does not pose a potential risk to health. It is difficult to study migration using real foods as most foods are a complex matrix which makes isolating and identifying migrants difficult. Moreover, many foods are not

compatible with the analysis equipment used. To ensure reproducibility of results, the European Commission introduced a set of simulants to replace food in compliance testing which overcomes these issues.

2.2.1 Food Simulants and Conditions of Use

There are currently six simulants that the Commission uses: 10% ethanol, 3% acetic acid, 20% ethanol, 50% ethanol, vegetable oil, and poly (2,6,-diphenyly-p-phenylene oxide) (TENAX). Table 1 lists the simulants and what food categories they represent.

Table 1: *List of food simulants as stated in Commission Regulation (EU) No 10/2011 (COMMISSION, 2011)*

Characteristics	Food simulant	Purpose
Hydrophilic	10 % ethanol	Simulant for aqueous food with an alcohol content of up to 10 %.
	3 % acetic acid	Simulant for acidic food with a pH <4.5
	20 % ethanol	Simulant for alcoholic food with an alcohol content of up to 20 %
Lipophilic	50 % ethanol	Simulant for alcoholic food with an alcohol content above 20 % and for oil in water emulsions
	Vegetable oil	Simulant for food which contain free fats on the surface
Dried	TENAX, particle size 60-80 mesh, pore size 200nm	Simulant for dry foods

To identify the appropriate simulants for this research, the types of food products commonly retorted in pouches were identified and were then compared to the Commission Regulation (EU) No 10/2011 for each product. The main areas retort pouches are used in the market, alongside the proposed food simulant suitable under EU, are listed in Table 2.

Table 2: *Commonly retorted food products with the recommended simulant (Caspak; COMMISSION, 2011)*

Product	Solution	Food simulant recommendation
Seafood	In fat/oil	10% ethanol and vegetable oil
	In aqueous	3% acetic acid and 20% ethanol
Sauces	In fat/oil	10% ethanol and 3% acetic acid
	In aqueous	3% acetic acid, 10% ethanol and vegetable oil
Condiments Spices and seasoning	In fat/oil	Vegetable oil
Ready Meals/Soups Soups, broths, sauces, in liquid, solid or powder form	In oil/fat	10% ethanol and 3% acetic acid
	Other/aqueous	3% acetic acid, 10% ethanol and vegetable oil
Petfood Preserved Meats	In oil/fat	3% acetic acid and vegetable oil
	In aqueous	10% ethanol and 50% ethanol
Meat of all zoological species Marinated meat products	In oil/fat	3% acetic acid and vegetable oil

The European Commission also sets guidelines for test conditions to match real life processing conditions for food, to create standardised testing conditions. These are listed in Table 3. These conditions are deemed to be accelerated versions of the worst situation these foods would normally foresee.

Table 3: *Standardised food testing conditions (COMMISSION, 2011),*

Food conditions	**Recommend testing condition (set time and set temperature)**
Frozen and/or refrigerated food	10 days at 20 °C
Long term stored food at room temperature or below, can include heating up to 70 °C for up to 2 hours, or up to 100 °C for up to 15 minutes	10 days at 40 °C
Food that only involves heating up to 70 °C for up to 2 hours, or up to 100 °C for up to 15 minutes	2 hours at 70 °C
Food that only involves heating to high temperatures of up to 100 °C	1 hour at 100 °C
Food that only involves heating to high temperatures of up to 121 °C	2 hours at 100 °C, or 1 hour at 121 °C, or At reflux
Foods that have conditions exceeding 40 °C and the use the simulants: 10 % ethanol, 3 % acetic acid, and 20 % ethanol	4 hours at 100 °C, or At reflux
Fatty foods which involve cooking temperature exceeding 121 °C	2 hours at 175 °C

2.2.2 Packaging Migration – Overall Migration

One of the major functions of packaging is to protect the food from the environment. It is also imperative that the packaging poses no risk through migration of hazardous compounds. Intentionally added substances (IAS), for example, plastic additives, are used in packaging production. They are known to migrate, break down, and/or react with other substances, both from food or packaging, which is why this risk assessment is required (Bradley et al., 2009). A risk assessment is used to evaluate how the plastic may change during the storage or in-package cooking process, and the potential migration of monomers, additives, and breakdown products. The compliance assessment uses OML which measures the inertness of packaging, and SML of IAS, Non-intentionally added substances (NIAS) and metals that can potentially migrate from packaging. Chemical migration is monitored on Liquid Chromatography Mass spectroscopy (LCMS) or Gas Chromatography Mass Spectroscopy (GCMS). The compounds putatively identified via LCMS or GCMS are assessed for possible toxicity based on structure and functional classes and assigned to one of the three Cramer classes. Metal migration can be measured through Inductively Coupled Plasma Mass Spectroscopy (ICPMS).

OML is one of the compliance assessments used: it is a gravimetric determination of the sum of all substances/leachates which migrate into food/food simulant from the packaging (Bradley et al., 2009; Caner et al., 2004; Grob et al., 2007; Júnior et al., 2019). These substances include NIAS and metals. However, OML does not differentiate between individual compounds; for substances that are deemed a potential risk, their concentrations are measured as part of SML, which is done using NIAS and metals migration (Caner, 2011; Júnior et al., 2019). The measure of overall migration value from a product is assessed against the OML as set in the Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food. Generally, OML for plastic materials is defined as a migration of maximum 10 mg/dm^2 packaging material or 6 mg/kg food for food consumed by adults. (COMMISSION, 2011; Grob et al., 2007).

2.2.3 Packaging Migration – Specific Migration

SML are the limits applied to individual substances or groups of substances based on functional groups and structure that migrate out of the packaging. The migration limits are created based on toxicological hazards that could occur from the substances when they breach the limit. SML includes NIAS, IAS, and metal migration.

IAS and NIAS are chemicals that are regulated by the SML; these are discussed in more depth in the next section. SML also includes metals which can also migrate.

NIAS

There are a lot of potential sources for NIAS (e.g., production process, equipment, transportation) but the main one is from the packaging material itself (Nerin et al., 2013). NIAS occur due the interactions within packaging material components and ingredients in a particular set of storage or treatment conditions. NIAS can also occur due to material degradation, material processing, and contact with food matrices. NIAS in food contact materials represent a possible safety issue for the food industry. NIAS studies are needed to screen, identify, and quantify these substances to assess the safety and compliance of the materials. Food simulants (please refer to Table 1) are used to investigate what NIAS and IAS are migrating into food. There are a myriad of techniques available for detecting NIAS and IAS, depending on the individual substance and its characteristics. Some of the analytical techniques are LCMS and GCMS. This a hazard assessment is performed based on the chemical structures. This is done in two different ways: firstly, the European Commission has a list of substances which are considered potentially harmful that must be kept under a set concentration to minimise the risk to consumers. Other NIAS that are of concern may also be identified. Their hazard potential must be assessed, mainly via theoretical toxicological assessment.

The difficulty with NIAS is that it is are hard to accurately identify, and to assess which material they have been generated in, because of the complexities introduced by multi-layered packaging. NIAS could be plasticizers, monomers, low molecular weight breakdown products, antioxidants, organic solvents, and reaction by-products (Nerin et al., 2013). Table 4 shows a small selection of the most common NIAS (Arvanitoyannis & Kotsanopoulos, 2014).

Table 4: *Examples of NIAS and IAS encountered from polymer migration*

NIAS and IAS	Function/source	Examples
Plasticizers	Additives used to increase flexibility and help processing	Phthalates Adipic acid
Monomers Oligomers	They are used to make polymers They make up the base of many different types of plastic packaging	Caprolactam (monomer for Nylon 6) Tetracaprolactam (oligomer)
Antioxidants	Additives used to enhance stability and reduce the rate of oxidation which can cause degradation of the plastic	Cyanox
Light stabilizers	Additives used to extend the ability of plastics to withstand harsh weathering conditions	Polymeric hindered amines
Thermal stabilizers	Additives used to reduce breakdown due to heat	Titanium dioxide
Epoxy resins	Additives used for binding plastic together	Bisphenol compounds
Slip additives	Additives used to create certain characteristic in plastic, like reducing the static charge or creating lubrication to prevent the finished plastic products from sticking together	Erucamide
Benzene	This substance is not an additive, but it is a common contaminate which migrates out of packaging after high temperature applications.	Benzene
Heavy metals	Catalysts used in polymerisation	Antimony (Sb), Zinc (Zn)

2.2.4 Toxicological Hazard Assessment

One way to determine the probability of potential toxicity of a chemical compound is to determine its Cramer class. This is done via an assessment tool which looks at the chemical structure and functional groups and uses that to assess the potential toxicity of the identified chemical. This is performed through a decision tree approach. Based on the decision tree answers, compounds are classified into three classes based on their structure:

- class I is assumed to be low toxicity,
- class II is assumed to be moderately toxic,
- class III is assumed to be very toxic (Bhatia et al., 2015).

The decision tree contains 33 questions: each question leads to either another question or a final classification of one of the three classes (García Ibarra et al., 2018). The 33-questions decision tree is presented in the 7.1 Appendix. The Cramer class classification was originally designed for assessing the potential toxicity of substances based on oral consumption, so it is considered a suitable tool for assessing whether compounds migrating from plastic could pose a problem (Roberts et al., 2015).

When using the Cramer class as an assessment tool, there are two common freely available website based systems that are widely available: Toxtree and OECD QSAR toolbox (Roberts et al., 2015). These tools, however, are not always suitable at assessing the structure based on the questions. 17-23% of the time these programs misclassify the substances compared to expert judgements (Roberts et al., 2015). However, despite this limitation, they are a valuable tool because using the decision tree was designed to be used by experts with experience in organic chemistry and biochemistry. Toxtree is employed as a useful initial assessment tool of identified migrating compounds.

2.2.5 Migration Diffusion Modelling

To better understand the process of migration, modelling was reviewed. Modelling is a good way to understand the way a system works and what environmental factors influence it. However, it is a simplification of the systems it is attempting to explain. Migration is a mass transfer process where migrants diffuse from the polymer and get then absorbed into the food system. This process is shown schematically in Figure 2.

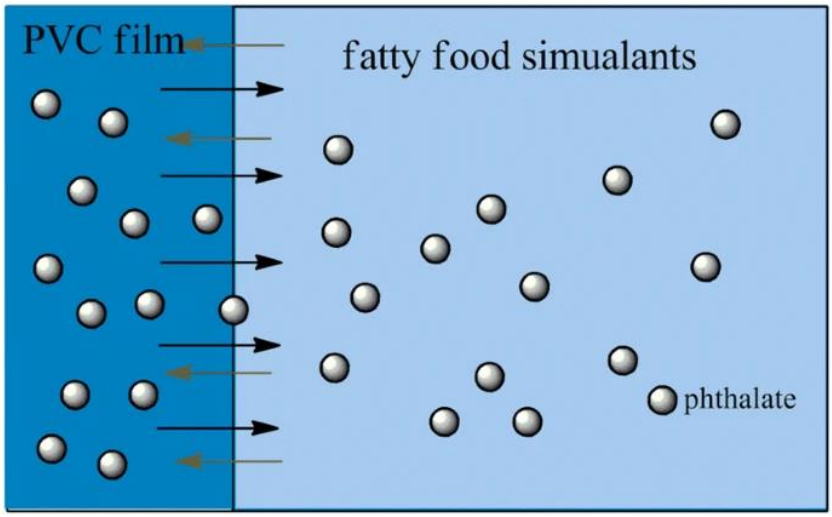


Figure 2: *Schematic representation of migration in a food packaging system, where phthalate is migrating from a PVC film into a food simulant (Yuan et al., 2020)*

Migration models for packaging typically uses Fick's laws of diffusion. The mathematical models can be used for predictive purposes and in some instances to demonstrate food contact compliance (Begley et al., 2005; Brandsch et al., 2002; Pocas et al., 2012). Fick's second law of diffusion is used to model migration, which is expressed by equation 1 below (Begley et al., 2005; Brandsch et al., 2002).

This model must make several assumptions, which is why models are considered simplifications of reality. The assumptions made for this model were including the migrant being initially homogeneously distributed in the plastic, *P*, no boundary resistance for mass transfer between the food and the packaging, and the migrant being evenly distributed in the food, *F* (Begley et al., 2005; Yuan et al., 2020).

$$\frac{m_{F,t}}{A} = c_{p,o}\rho_p d_p \left(\frac{\alpha}{1+\alpha}\right) * \left[1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} exp\left(-D_p t \frac{q_n^2}{d_n^2}\right)\right] \quad \text{Eq 1}$$

$$\text{With } \alpha = \frac{1}{K_{P,F}}\frac{V_F}{V_P} = \frac{c_{F,\infty}}{c_{P,\infty}}\frac{\rho_F}{\rho_P}\frac{V_F}{V_P};$$

$$\text{With } D_p = 10^4 \exp\left(A_p - 0.1351 m_r^{\frac{2}{3}} + 0.003 m_r - \left(\frac{10454}{T}\right)\right)$$

$$K_{P,F} = \frac{c_{F,\infty}}{c_{P,\infty}}\frac{\rho_F}{\rho_P} \text{ and } \tan q_n = -\alpha q_n$$

Where:

- $m_{F,t}/A$ is the amount of migrant per unit area of packaging after some time *t,*
- *A* is the contact area between the food system and packaging,
- $c_{P,0}$ is the initial concentration of the migrant in the packaging, *P,*
- ρ_P and ρ_F are the density of the migrant in the packaging and food system respectively,
- d_p is the packaging film thickness,
- D_P is the diffusion coefficient of the migrant in the plastic film,
- V_P and V_F are the volumes of the packaging and food system,
- $K_{P,F}$ is the partition coefficient which is the ratio of the migrant concentrations (w/v) in the packaging and food system at equilibrium,
- q_n is the positive root of $\tan q_n = -\alpha q_n$,
- *T* is the temperature during migration,
- A_p the diffusion effect on the packaging,
- M_r is the migrates molecular weight,

The amount of migration over time depends on numerous factors, including but not limited to: the initial concentration of the migrants in the material, properties of the food or simulant and the

contact between the food and packaging, properties of the packaging material including its polarity and structure, and the packaging surface area-to-volume ratio of the food (Pocas et al., 2012, Cruz et al., 2019). The purpose of this work was not to use models to try predicting migration; this study investigated migration from monolayer materials in retort processing which has not been reported in literature previously. However, Fick's model of diffusion could provide insight into what trends observed in this research. A key input parameter in Fick's model is the diffusion coefficient which increases with temperature. However, with retort processing, different set point temperatures result in different processing times to achieve the required F_o value (as discussed in section 2.1). The expected migration could increase at the highest retort temperature, but the shorter processing time may negate the temperature somewhat.

2.3 Retort Packaging

2.3.1 Multilayer Packaging Materials

Currently plastic pouches used for retorting are multi-layer materials, since they better handle retort conditions and subsequent shelf-life requirements.

Previous work was done at Scion and Massey on this topic "Effect of Retort Processing on Packaging Materials: The Changes in the Migration and Physiochemical Properties of Two Polymer Films" (O'Connor, 2020). The research investigated the effects of retorting on multilayer packaging pouches. It specifically reviewed two pouch types using commercially available multi-layer films, two different food simulants and three different thermal treatments. The most interesting results were related to OML and NIAS. In all the conditions the OML was below the EU limit, so the packaging was deemed safe. However, the LCMS results showed some potentially toxic chemicals migrating. The work raised questions, mainly around which layer was responsible for the migrating substances. To address this, existing literature was explored to see how much was known about how migration is affected by the retorting process, and what is known about the origin of the migrants from multi-layered films. Research revealed that retort pouches made with PP and PE and filled with an oil simulant, had effects on migration properties; as temperatures increased, migration increased (Limm & Hollifield, 1995). Migration of the antioxidants from the packaging material was highlighted. However, another study found there was minimal migration due to retorting, and concluded that the small amount of migration that did occur, was not due to high heat (Dhawan et al., 2014). Another study investigated the migration of silicone and aluminium from multi-layer pouches made from PA/PET/PP and PA/PA/PP, with water and 3% acetic acid as simulant. Only 1.3 mg/kg of migration occurred, and the greatest occurred during pasteurization temperature (70 – 90 °C). Other researchers have shown that the OML was within the EU guidelines (Galotto & Guarda, 2004; Mohan et al., 2008; Rijk & de Kruijf,

1993). These findings aligned with the work of O'Connor (2020) that OML from retort processing was below the EU limits.

There is a clear gap in the literature with respect to migration assessment during retort processing. Specifically, little is known about SML and what is migrating from the individual layers in a multi-layered material. An investigation into the migration from each layer is warranted. It is essential to identify the layers producing the potential substances considered hazardous, especially if the presence of certain hazardous materials is only associated with certain processing temperatures or treatments. This can become the basis of new research linking contaminant migration and usefulness of certain polymeric layers in different applications. There is existing literature on pharmaceutical extractables and leachables and also in environmental science, however, those were not considered due to not having the same high temperature seen in retorting.

2.3.2 Monolayer Packaging Materials

PET, PA, and PE monolayer films were investigated to better understand the effect of the retort processing conditions on the material. The physical properties and possible migration from each individual material were investigated.

PET

PET is a thermoplastic polymer: it is part of the polyester family, which are known for their ester functional groups. It is a fossil-based plastic that is not biodegradable. It is highly inert in comparison to other plastics (Nisticò, 2020). In the food industry PET is commonly used in bottled drinks due to its functional properties, as a transparent, lightweight, elastic, and stable over a wide heat range (Tsironi et al., 2022).

PET is created by a prepolymerization of the diol ethyleneglycol (EG), followed by a polycondensation using one of the following reactions: a transesterification with dimethyl ester, or esterification using terephthalic acid. The transesterification uses antimony (Sb) as a catalyst, and it needs an excess of EG. The esterification is a heterogeneous reaction and needs the side product (methanol) to be removed (Nisticò, 2020).

Literature on PET bottles could be used as a guide for what NIAS are to be expected from the retort process. Research showed that, when PET filled with 3 % acetic acid or 20 % ethanol was stored for 10 days at 60 °C, it leached 4-cumylphenol, bisphenol S and A, and octocrylene (Aigotti et al., 2022). Other studies showed that acetaldehyde (AA) and formaldehyde were released from PET during the melting process. However, the industry has been reducing the production of these by using AA scavengers and antimony trioxide (Tsironi et al., 2022).

PA

PA is also known as Nylon. PA is most available in two forms: PA 6 and PA 66 (Ebnesajjad, 2013; Kim et al., 2014). The main difference between the two is in their physical properties: PA 66 has a higher melting point, higher glass transition, higher tensile modulus, a triclinic crystallinity structure. PA 6 has a lower melting point, lower glass transition, lower tensile modulus, a monoclinic crystallinity structure. PA is often used as an outer layer in a multi-layer system due to its great properties such as its temperature resistance, impact strength, and puncture resistance. These properties occur because of its intrinsic hydrogen bonds. These are created by amide linkages and intermolecularity (Kim et al., 2014). PA is commonly used in the packaging of fish, cheese, and meat.

The PA for this project is a biaxially oriented film, which is made from PA 6. PA is typically made from caprolactam going through the process of hydrolysis polymerization (Zhang et al., 2023). Caprolactam can be processed by hydroxylamine sulphate oxidation (HSO), which is one of the oldest methods for creating PA 6 (Herps, 2020). The start of this process involves the hydrogenation of benzene to cyclohexane; the cyclohexane is subsequently oxidised to cyclohexanone. Ammonia is oxidised to ammonium nitrite which produces hydroxylamine. This is then reduced to hydroxylamine disulphonate with sulphur dioxide. The product then needs to be hydrolysed, to make hydrolysed sulphate. Cyclohexanone is added to the hydrolysed sulphate, and it undergoes oxidation, which causes the cyclohexanone to become neutralised cyclohexanone oxime. This is followed to rearranging and neutralization to caprolactam using ammonia creating a by-product of ammonium sulphate. Only about 90 % converts from the caprolactam to the polymer, so filtration or vacuum occurs to remove the residual caprolactam; however, small amounts are still found in PA (Song et al., 2018). During this whole process, cyclic monomers and oligomers are created and make up about 2 % of the total PA (Heimrich et al., 2015).

Cyclic monomer, caprolactam, and oligomers are known to migrate from PA. PA is affected by thermal treatment as it can cause small amounts of PA to revert to caprolactam (Heimrich et al., 2015; Song et al., 2018). It also causes the number of oligomers in PA to increase when thermally treated (Heimrich et al., 2015; Hu et al., 2021). Investigations into the migration of NIAS and IAS out of PA found a range of compounds migrated out of the PA (Table 5).

Table 5: Oligomers found to migrate from a PA film into different simulants (Hu et al., 2021)

PA Oligomer	PA roasting bag (mg/dm²)	PA6 film (mg/dm²)		
	Oil	Water	50 % Ethanol	95 % Ethanol
PA 6 dimer	338	0.47	0.47	0.50
PA 6 Trimer	379	1.19	1.22	1.30
PA 6 Tetramer	480	1.69	1.73	1.76
PA 6 Pentamer	508	1.80	1.87	1.73
PA 6 Hexamer	591	1.66	1.73	1.12
PA 6 Heptamer	341	1.22	1.30	0.79
PA 6 Octamer		0.68	0.76	0.40
PA 6 Nonamer		0.40	0.43	0.18

Hu's research used roasting bags filled with water, oil, 50 % ethanol, and 95 % ethanol. Additional migrants were plasticizers, phthalates, antioxidants, slip agents, and fatty acids (Hu et al., 2021). Research also showed that caprolactam is lost during by OML, the testing is not reliable or feasible, as it is lost to the drying process (Heimrich et al., 2015).

PE

In the food industry there are several different types of PE used: low-density PE (LDPE), medium-density PE (MDPE), high-density PE (HDPE), ultra low-density PE (ULDPE), and linear low-density PE (LLDPE) (Ebnesajjad, 2013; Kim et al., 2014). PE is part of the plastic group known as polyolefins, which also includes PP. Therefore, the group is expected to have similar properties, production, and migration results. PE is used due to its versatility. PE is used as an inner layer in retort pouches due to its water vapour barrier properties and ability to heat seal (Zhong et al., 2018).

The PE used for this project was LDPE, so that its production method this review was focused on. To create LDPE, the following conditions are used: temperature of 190 – 210 °C, peroxide catalytic conditions, free radical polymerization, and pressure between 100 - 300 MPa. This process is most commonly done in an autoclave and high-pressure tube method (Zhong et al., 2018). The peroxide is used as an initiator and is most commonly organic. The process starts by placing ethylene into a tubular and kettle reactor. The polymerization of ethylene occurs under high pressure with high temperature, using peroxide or oxygen. Any ethylene that was not reacted is separated out in the reactor and recycled.

Benzaldehyde dimethyl acetal has been identified as a common NIAS pertaining to PE. Commonly encountered IAS have been reported to migrate: benzaldehyde, 3,4-dimethyl-methylpalmitate, and erucamide (Lahimer et al., 2017). Other research showed the migration of substances such as: aromatic compounds, cyclic amides, alkanes, phenolic compounds, alkenes, alcohols, cycloalkanes,

phthalate phthalate esters, and cycloalkanes from PE as an inner layer in multilayer film (Ibarra et al., 2019).

2.4 Research Questions

The key areas for this research project are:

- To investigate how different retort time-temperature profiles affect overall and specific migration of substances from PET, PE and PA monolayer films (common constituents of multilayer commercial pouches) in different food simulants.
- To determine if there is a significant difference in migration due to retort processing from PET, PE and PA materials.

3.0 Materials and Methods

The materials chosen are PET, PA, and PE for the monolayer pouches, as they are most common constituents of multi-layer retort pouches. The specification sheets are in the 7.2 Appendix. PE did not have a specification sheet.

3.1 Retort Treatments

3.1.1 Simulant Preparation

Based on the research shown in Table 2, 3% (w/v) acetic acid is the most common simulant recommended for different types of retort products, appearing seven times. This is followed by 10% (v/v) ethanol, six times, and vegetable oil, six times; 50% and 20% ethanol appear only once each. The monolayer films used in the research are 20-30 µm thick. Based on most common simulants and film resistance and thickness, it was decided 3% (w/v) acetic acid, and 10% (v/v) ethanol would be used as simulant (standards BS EN 1186-1:2002 and BS EN 1186-3:2022). Vegetable oil was discounted because it requires a different setup for LCMS and OML analysis; the procedures for working in oil had not been developed and tested and doing that would not be within the scope of the project.

The ethanol was made as a 10% (v/v) aqueous solution with Milli-Q water and the acetic acid was made as a 3% (w/v) aqueous solution with Milli-Q water. Each of the bottles was made up using the standards above, in volumetric flasks. The chemicals used for the simulant were both purchased from Bio-Strategy: Ethanol absolute, multi-solvent HPLC grade, and Acetic acid glacial, HPLC grade.

3.1.2 Pouch Preparation

Pouches were made according to EU standards to OML Testing: BS EN 1186-1:2002 and BS EN 1186-3:2022. A metal template (140 x 251 mm) was used for cutting the plastic films for making the pouches. This template makes a full pouch where one edge is folded over, and all sides have been made to allow an edge for the 10 mm seal. Then a second template was used at 100 x 100 mm for the inner layer pouch (see Figure 3).

Figure 3: *Inner layer of pouch with template on the inside*

Pouches were made from PET, PA, and PE respectively. A hand impulse sealer (Mercier, ME-300HI, Figure 4) was used to seal the pouches.

Figure 4: *Mercier hand impulse sealer, ME-300HI*

All pouches were made with two layers. The inner layer had the dimension of 100 x 100 mm and an outer layer was created to protect the inner layer. As the material is very thin, double layering of pouches was used for all three monolayer materials. All pouches were filled with 100 mL and sealed as described below.

To create the pouch seals, the sealer was set on an eight second timer. The arm of the sealer was held down until the sealer clicked and then lifted lightly and pushed back down again until it clicked. The arm was then held down for an additional 12 seconds.

3.1.3 Treatments

To investigate the effect of the retorting process on migration from pouches, it was decided to replicate industry-relevant conditions to achieve commercial sterility (F_o of 3 minutes or greater). All retorting was done in a Microflow-911R (Steriflow) retort (see Figure 5)(MPI, 2021).

Figure 5: *Retort Microflow 911R from Steriflow thermal processing, which was used for treatment*

The maximum and minimum temperatures were 121 °C and 110 °C respectively. The middle temperature was 115 °C. The times for each of these were estimated using Gillespy Method so that they reached a F_o = 3 mins.

The retort used was a batch retort with the option to use agitation. Because of the delicate nature of the pouches, it was used in static mode. Internal probe temperature was measured for 6 pouches which were filled with simulants (3 per simulant). The probes were internally fitted and lined up to be in the position where the SHP was. These pouches were made of a multi-layer film because the monolayers were too thin to withstand the weight of the probes. Due to the pouch material providing a low resistance to heat transfer, it was assumed that these would closely match the temperature inside the monolayer pouches. The temperature data from the probes was fed in real time into a program for the retort called Calsoft, which calculated the F_o values in real time using a trapezoidal integration method. The retort was run until the slowest pouch reached F_o = 3 mins.

Temperature-Time Profiles of Treatments

The temperature-time profiles of the three treatments are shown in Figures 6, 7, and 8. The times calculated for F_o in each of the treatments are listed in Tables 6, 7, and 8.

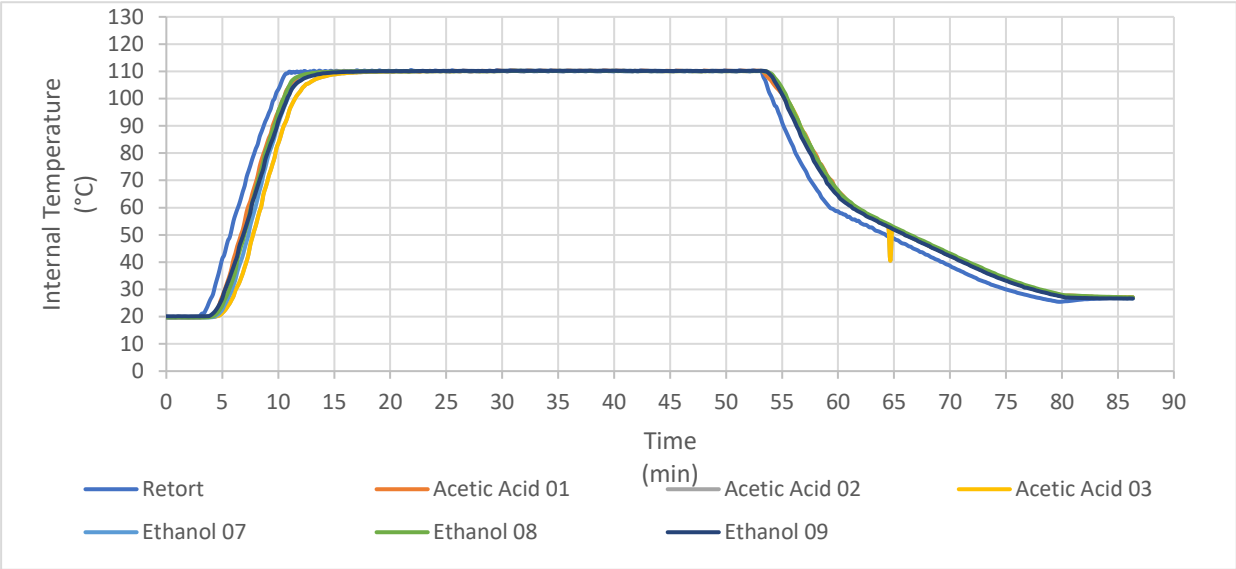


Figure 6: *'Low' treatment, internal pouch temperatures (at 110°C for 51 mins)*

Table 6: *F_o values calculated during retorting for 'Low' treatment*

	Retort/Baseline	**Acetic acid 01**	**Acetic acid 02**	**Acetic acid 03**	**Ethanol 07**	**Ethanol 08**	**Ethanol 09**
F_o	3.40	3.30	3.04	3.14	3.27	3.28	3.26

After this first treatment it was found that acetic acid is the slowest heating simulant, so it was the only simulant used to determine F_0 for the 'Medium' and 'High' treatments. The F_o seen above was calculated using trapezoidal integration method. The values matched the data seen from Calsoft during the process. It took 51 minutes for the 'Low' treatment to reach F_o = 3 minutes, from ambient temperature.

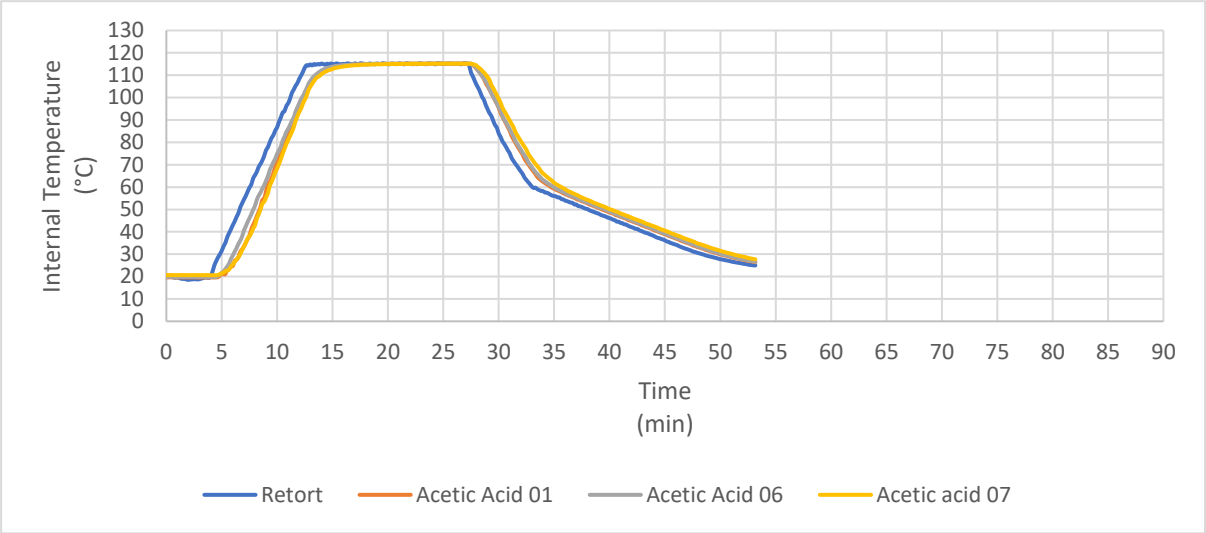


Figure 7: *'Medium' treatment internal pouch temperatures (at 115°C for 25 mins)*

Table 7: *F_o values calculated during retorting for 'Medium' treatment*

	Retort/Baseline	**Acetic acid 01**	**Acetic acid 06**	**Acetic acid 07**
F_o	3.72	3.22	3.27	3.08

It took 25 minutes for the 'Medium' treatment to reach F_o = 3 minutes, from ambient temperature.

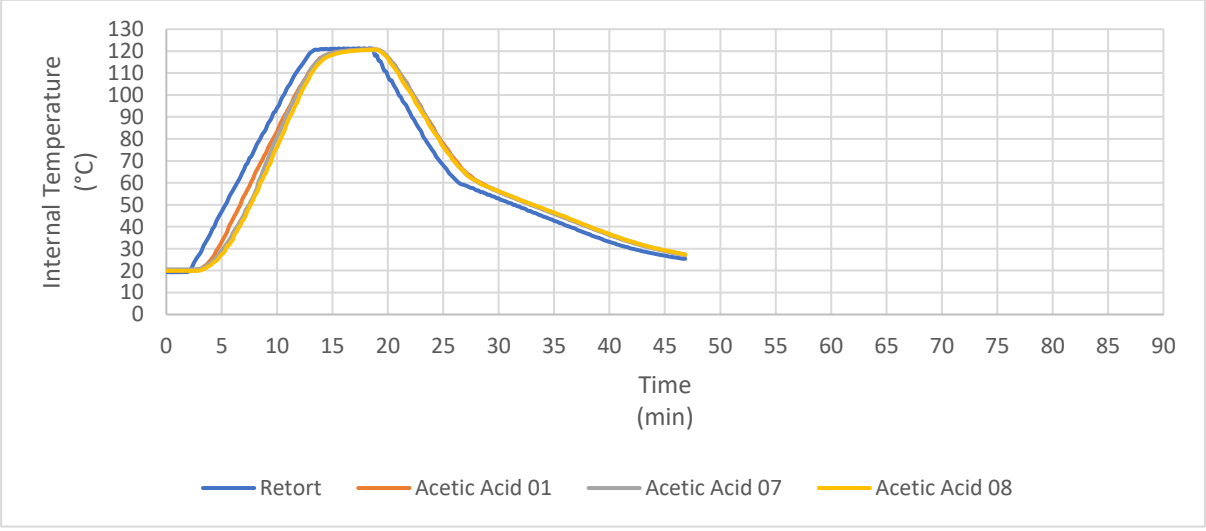


Figure 8: *'High' teatment internal pouch temperatures (at 121 °C for 16 mins)*

Table 8: *F_o Values Calculated during Retorting for 'High' treatment*

	Retort	**Acetic acid 01**	**Acetic acid 07**	**Acetic acid 08**
F_o	5.78	3.80	3.77	3.31

It took 16 minutes for the 'High' treatment to reach F_o= 3 minutes, from ambient temperature.

Incubations

The liquid was fully drained from pouches and kept for analysis post-treatment. The pouches were flipped inside-out, then placed inside their bottles so that the inner material was in contact with the simulant. The Schott bottles containing the liquid were then placed into an incubator for 10 days at 40 °C (see Figure 9), as per the recommendations in EU legislation 10/2011 which specifies the compliance testing requirements in EU for food contact plastics.

Pouches that were not retort treated were also incubated. These were considered control samples.

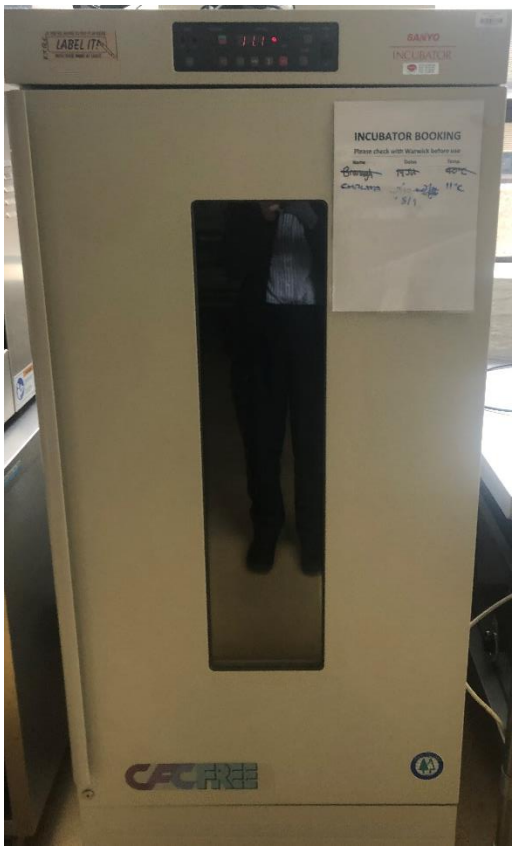


Figure 9: *Sanyo Incubator*

Table 9 presents all treatments that each material was subjected to:

Table 9: *Treatments that each different material were subjected to.*

Name of treatment	Retort temperature, ˚C	Retort time, min	Incubation time
'Control' (C)	Not retorted		10 days, 40 ˚C
'Low' (L)	110	51	10 days, 40 ˚C
'Medium' (M)	115	25	10 days, 40 ˚C
'High' (H)	121	16	10 days, 40 ˚C

The treatments will be referred to by their name in this thesis.

3.2 Material Evaluation

In total, there were 126 pouches made, as shown in Table 10. 18 pouches were kept as a control and 108 pouches were incubated. The 126 pouches made were split between the 3 materials.

Table 10: *Pouches made for retort treatment*

Material	Simulant	Control	'Low' treatment	'Medium' treatment	'High' treatment
PET	Ethanol	3	6	3	3
	Acetic acid	3	6	3	3
PE	Ethanol	3	9*	6*	6*
	Acetic acid	3	9*	6*	6*
PA	Ethanol	3	9*	6*	6*
	Acetic acid	3	9*	6*	6*

*Extra samples for 'Low', 'Medium', and 'High' treatment for PA and PE were made as the materials was much more unpredictable when early trial work was done.

3.2.1 Overall Migration (Gravimetric Analysis)

Glassware Preparation

The glassware was thoroughly cleaned following standard BS EN 1186-1:2002 – (Materials and articles in contact with foodstuffs - Plastics - Part 1: Guide to the selection of conditions and test methods for OML) and BS EN 1186-3:2022 – (Materials and articles in contact with foodstuffs - Plastics - Part 3: Test methods for OML in evaporable simulants).

The glassware and metalware were soaked in hot water. Each piece of equipment was thoroughly rinsed three times with analyst grade isopropanol, then analyst grade acetone, then MilliQ water. All metal and all non-graduated glassware were wrapped in foil and placed into a furnace at 400 °C, then held at temperature for 4 hours. Any glassware with a maximum temperature rating of 20 °C and the plastic lids were not furnaced.

Testing

This test was completed in sets of 9 samples at a time from the Schott bottles. At the same time 2 samples are taken straight from the simulant bottle, to be used as a blank. The simulants were placed into a 100 mL round bottom flask and reduced to about 20 mL by rotatory evaporation. The water bath was set at 50 °C – 60 °C and the rotation was set at 100 rpm.

The initial weight of the dried evaporating dishes was determined (1 per sample). To ensure evaporating dishes were dry, they were placed into an oven at 107.5 ± 2.5 °C for 30 ± 5 mins followed by transfer into a desiccator for the same amount of time, to settle the weight. The dishes were then

weighed. The process was repeated as many times as necessary to get the weight of each dish within 0.5 mg of its previous weight.

The simulant was then transferred into thus prepared evaporating dishes, then placed on a hot plate. The hot plate was set on a temperature to allow them to boil very slowly until approximately 1 mL of simulant was left. The drying process was completed in an oven at 40 °C, to avoid burning. The final weight of the evaporating dishes was determined following the drying/weighing procedure described above.

3.2.2 NIAS Migration (LCMS)

An LCMS was used to measure the NIAS migration. The LCMS used was 66545XT AdvanceBio LC/Q-TOF, Agilent, California. A 50 mm Zorbax Eclipse column with 1.8 µm particle size and 2.7 mm internal diameter was used, placed in a column oven at 35° C, a photo diode array to monitor the input at 250 nm, and a mass spectrometer in both positive and negative ionisation mode. The LCMS and equipment were set to a drying gas flow rate of 12 Lmin (positive) or 8 L/min (negative), capillary voltage 3500 V, skimmer 65 V, fragmentor voltage 175 V, temperature 320 °C, no collision energy, octupole 750 V, nozzle voltage 1000 V, and acquisition 50-3000 mz^{-1}. All simulant samples were tested. 1 mL of each was individually pipetted into the 2 mL HPLC vials using single use glass pipettes. The vials were placed into the LCMS. The flow rate was set at 0.3 mL/min, pump A water- 0.1 % formic acid, and pump B- acetonitrile- 0.1 % formic acid. 2 µL injection volume was used. A gradient was used: 0 min pump B 2 %, over 20 mins to pump B 100 %. A post-treatment of 5 min re-equilibrated the column after each injection. The data was assessed using MassHunter Qualitative Analysis, and compounds were monitored against Mass Hunter Extractables and Leachables database. For assessment, mass tolerance was set at +-5ppm, scoring >80%, area >25,000, Precursor ion +- (10.0ppm +_ 2.000mDa).

3.2.3 Metal Analysis (ICPMS)

Microwave Digestion

Before any testing on simulants was done, the plastic monolayers were digested using a microwave to measure the identify and quantify of metals in the samples. All 3 plastics were analysed at this stage.

For digestion of the plastic, 0.25 g of plastic was weighed into microwave digestion vessels. 2 mL of hydrochloric acid 36 % and 3 mL of nitric acid 63 % were added to the vessel and left to predigest. The vessels were then capped and placed into a Mars 6 CEM microwave digestor, set to ramp up to 200 °C over 20 min, held at the temperature for 20 min, then cooled over a 20 min period. The

samples were then made up to 25 mL in volumetric tubes. The samples were diluted 1:10 in 1 % nitric acid prior to ICPMS analysis. They were run against standards for each element. The ICPMS used was Perkin NexION 2000 with an autosampler, with a glass concentric nebulizer with a flow rate of 0.85 L/min, plasma gas flow was 16 L/min, Auxiliary gas flow 1.2 L/min, Nickel cones, 1500 W RF power, and Quartz cyclonic used in the spray chamber and run with Perkin Elmer Syngistix software (Version 2.2).

Migration

For the samples from the simulant: 0.8 mL was pipetted out into 10 mL volumetric tube and made up with 1 % nitric acid/0.5 % HCl. They were run against standards for each element. The ICPMS used was Perkin NexION 2000 with autosampler, with a glass concentric nebulizer with a flow rate of 0.85 $Lmin^{-1}$, plasma gas flow was 16 $Lmin^{-1}$, Auxiliary gas flow 1.2 $Lmin^{-1}$, Nickel cones, 1500 W RF power, and Quartz cyclonic was used in the spray chamber and run with Perkin Elmer Syngistix software (Version 2.2).

3.2.4 Internal Surface Evaluation- Scanning Electron Microscope (SEM)

Only the films perceived as the worst based following retort treatment on the visual inspection were analysed via SEM. The samples were prepared drying any simulant drops off with Chem wipes. The plastic is cut into 10 mm squares (Stubs had a 10 mm diameter). The most damaged section of the pouch was selected for each sample. Only the internal side of the pouch was used for inspection (the side in contact with the simulant). The samples were then placed onto a stub, inspection side up. The stub had tape on it which is used to adhere it to the stub. Samples were then coated with gold, using a “BAL-TEC” Sputter Coater, SCD 050,” for 160 seconds. Samples were then analysed using JEOL 6700F Field emission scanning electron microscope (SEM). It was set at a base of voltage of 3 kV and an acceleration of 10 µA. A set of photos were taken for all samples at a low magnification of x25 to obtain an image of the whole sample to help interpret what surface damage was occurring. The remaining pictures were taken of the individual defects/damages. Each was magnified until the defect could be identified, using magnifications ranging from x25 - x5000.

3.2.5 Toxicological Hazard Assessment (Toxtree Software)

The toxicological assessment for the substances was performed using Toxtree software “AMBIT: chemical substance database”. This system uses Cramer classification to assess the potential hazard

nature of the compounds. For the substances that were not available to be assessed on the online program, they were assessed using the 33-decision tree scheme. The decision tree applied is available in the Appendix.

4.0 Results and Discussion

In this section, the outcome of the various retort treatments on the different monolayer pouches is discussed individually for each material. Firstly, visual material observations after retorting are given, followed by in-depth surface evaluations, migration testing results (overall and specific) as well as toxicological hazard assessments of the determined migrants.

Based on the literature review findings, films were fully digested to assess the presence of heavy metals in their composition prior to any retorting. If metals were found in the digests, the films were assessed for metal leaching.

Table 11 presents the results for the total heavy metal content after microwave digestion. The microwave digestion results were considered first before deciding which simulant samples to take further for specific metal migration testing.

Table 11: *Heavy metal results after microwave digestion*

Sample	Zinc (ppm)	Antimony (ppm)
PA	0.8	<0.05
PE	44.4	<0.05
PET	0.4	279

No heavy metals were detected in PA film after microwave digestion in concentrations that would be detectable from a leaching sample. Zinc (Zn) and antimony (Sb) were detected in concerning concentration for both PE for Zn and PET for Sb films after microwave digestion. Given these results, the simulants for PE and PET after various retort treatments were analysed for their specific metal migration. Only the specific migration of zinc was measured for PE and only the specific migration of antimony was analysed for PET. For both materials, the digestion results were in agreement with the outcome of the literature review.

The visual material observations after retort treatments build the foundation for deciding which samples (films and simulants) to consider for further analysis. Figure 10 shows retort pouch examples before and after retort treatments.

Figure 10: *Example of pre- (left) and post- (right) retort pouches (all materials, 'High' treatment, both simulants)*

Pouches that showed visible changes post-treatment were further examined with SEM. All leaching solutions were analysed for NIAS presence by LCMS. OML was assessed for the worst case changes for each different material. ICPMS was performed for metal leaching from PE and PET, decided based in the initial digestion tests. Chemicals identified were assessed for toxicity via Toxtree software.

Finally, the results obtained in this study were compared to results reported in literature (see Section 4.4). The results obtained could only be compared to reported trends for multi-layer materials, as no literature exists on retorting monolayer packaging. Trends of temperature and time exposure are established, building an understanding of the contributions of each layer to the overall migration. A conclusion was drawn about how migration might affect food and indirectly potential consumers. Selected chemicals which migrated and were classified as Cramer class III are highlighted and discussed.

4.1 Retorting of PET Monolayer Pouches

No visible changes were observed after the 'Low' retort treatment of PET using both acetic acid and ethanol as simulants. Additionally, no visible changes were observed after the 'Medium' retort treatment of PET using either of the simulants. However, when using ethanol, the pouches only had an average fluid retention of 68/100 mL. No visible changes were observed after 'High' retort treatment of PET with acetic acid and ethanol. However, when using ethanol, the pouches had an average fluid retention of 45/100 mL. There was no loss of the acetic acid simulant after any of the retort treatments.

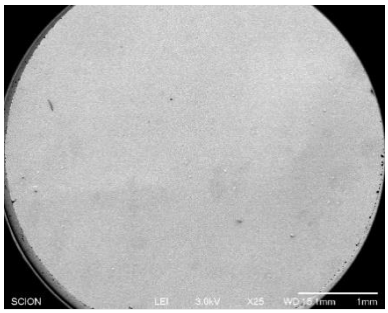
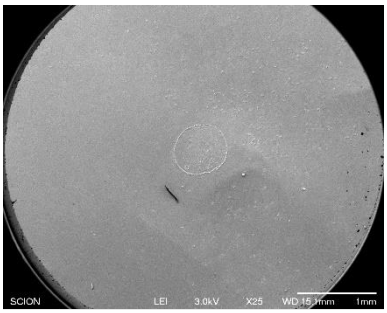
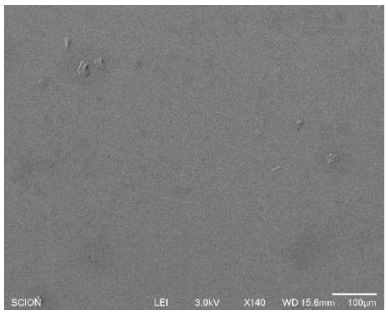
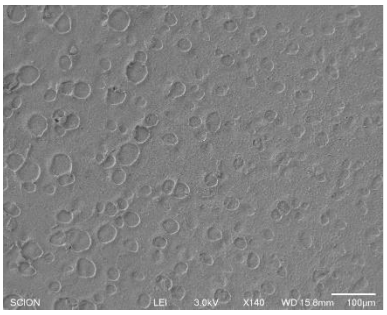
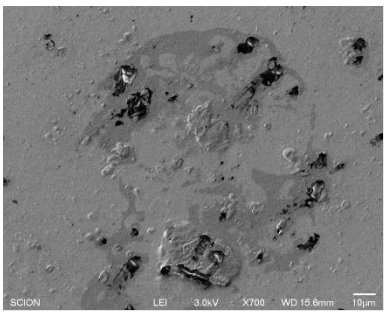
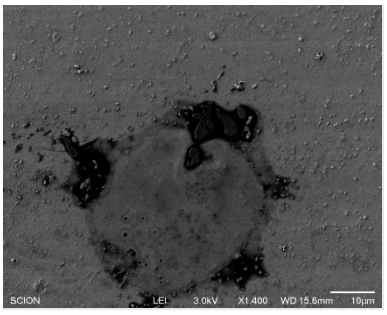
It was decided to take a closer look (SEM and OML analysis) at the potential structural damage seen in ethanol after 'High' treatment, because of the increased fluid leak when the temperature is increased. No decision could be made based on these results for the simulant acetic acid. Therefore, after checking the peak height and patterns in LCMS profiles it was decided to investigate PET pouches with filled acetic acid after 'Low' treatment, because the number of compounds present in the LCMS chromatograms was considerably increased.

4.1.1 Internal Surface Damage

The internal surface damage for PET pouches was assessed using SEM imaging after two different retort treatments as well as using two simulants. The pictures were shown of the treatment sample were taken of the individual defects/damages. Each was magnified until the defect could be identified, using magnifications ranging from x25 - x5000.

Figure 11 presents SEM imaging for PET pouches filled with ethanol after 'High' treatment using various magnifications.

Figure 11: *PET post ethanol treatment, virgin on left and 'High' treatment on the right*

Control	Ethanol 'High' treatment	Magnification
		x 25 (low)
		x 140
		x 700
		x 1400

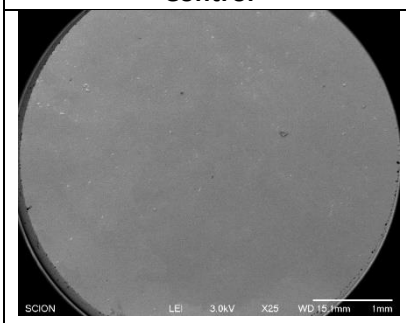
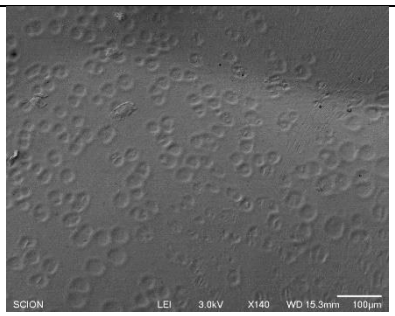
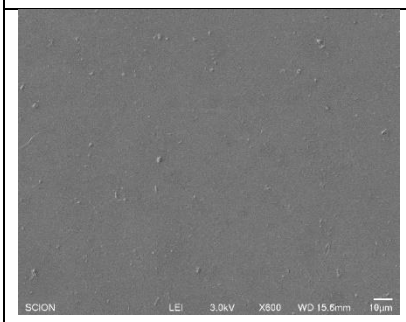
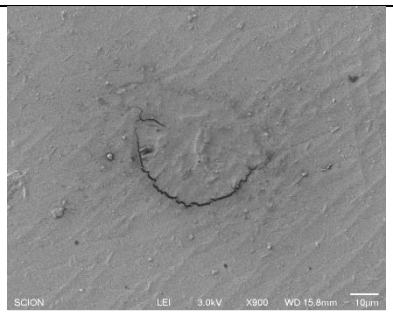
The images on the left are of the control PET sample in ethanol and are used for comparison only. The ridges/bumps observed at x 140 magnification are caused by particles of dust.

The images on the right were of damage observed on the PET pouches filled with ethanol post 'High' treatment. The first image at low magnification in Figure 11 provides an overview of the damage

observed on the surface of the pouches. The x 140 magnification photo shows pitting, and the x 700 magnification photo shows cracking. The x 1400 magnification photo is a close-up of the cracking observed. There are holes, alongside micro-pitting around the seams.

Figure 12 shows SEM images for PET pouches filled with acetic acid after 'Low' treatment using various magnifications.

Figure 12: *PET post acetic acid treatment, virgin on left and 'Low' treatment on the right*

Control	Acetic acid 'Low' treatment	Magnification
		x 25 (low)
		x 140
		x 600
		x 900

The images on the left are of the control PET sample in acetic acid and are used for comparison only. The bumps observed at x 600 magnification are caused by dust particles.

The images on the right were of damage observed on the PET pouches filled with acetic acid post 'Low' treatment. The first image at low magnification in Figure 12 provides an overview of the damage observed on the surface of the pouches. The x 140 magnification photo shows the amount of damage that was observed on the surface of the pouches, and the x 900 magnification photo shows cracking associated with the pitting.

The damage shown in these photos validated the observations after retorting. The pouches filled with acetic acid post 'Low' treatment showed more pitting than the pouches filled with ethanol post 'High' treatment.

The ethanol simulant from the 'Medium' treatment and the acetic acid simulant from the 'Low' treatment were further assessed via gravimetric analysis to determine the OML.

4.1.2 Overall Migration

OML was determined on both PET pouches filled with ethanol after the 'High' retort treatment and on PET pouches filled with acetic acid after the 'Low' retort treatment. The OML results for the PET pouches are summarised in Figure 13.

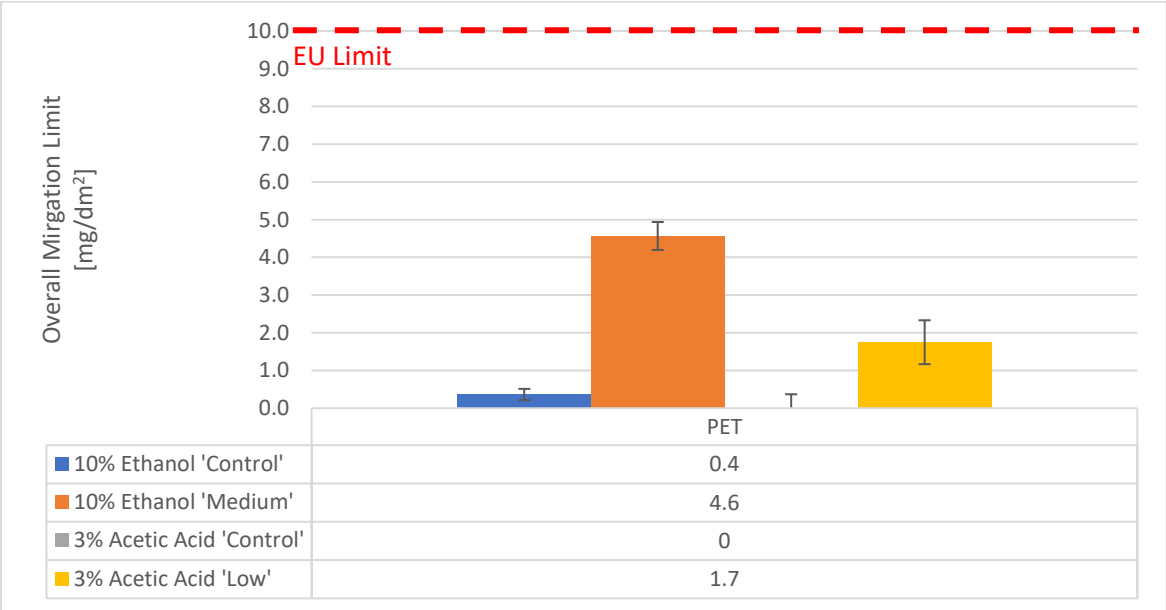


Figure 13: *OML test for PET of the control and the worst case situation for each simulant (mean and standard deviation of three replicates): please note the EU limit bar)*

PET in ethanol at 'High' treatment had an average OML of 4.6 ±0.2 mg/dm^2, compared with 0.4 ± 0.0 mg/dm^2. in the control. PET in acetic acid at 'Low' treatment had an average OML of 1.7 ± 0.6 mg/dm^2, while the acetic acid control experienced very minor migration of 0.0 ± 0.4 mg/dm^2. As expected, the heat treatment increased the overall migration significantly. When comparing the two

simulants, the total migration is much greater in ethanol, both before and post-treatment; however, both are below the limit set by the EU Regulation on food contact plastics of 10 mg/dm^2 (COMMISSION, 2011). Ethanol has been noted in literature to cause higher OML rates in PET with acetic acid (Cai et al., 2014). The results for PET in ethanol at 'High' treatment seem to support that, for ethanol, the increase in OML, hence the degradation, is directly influenced by the temperature.

4.1.3 Specific Migration - NIAS

Simulants from all pouches were analysed on LCMS. For all identified compounds trends were established on increases or decreases in peak height (corresponding to concentration). The full list of compounds found migrating from PET pouches in both ethanol and acetic acid across all treatments is presented in the Appendix. The discussion here focuses on the most important compounds identified (highest Cramer Class, III) in each simulant. Table 12 presents a list of substances identified as Cramer class III migrating from PET into 10% ethanol across all treatments.

Table 12: *Cramer class III compounds in PET pouches in ethanol found to occur due to retorting, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	Name	Change	Source
542-44-9	Glycerol monopalmitate	C<**M=H**	Food contaminant
120-40-1	N,N-bis(2-hydroxyethyl) dodecanamide	C<**H=M=L**	Cleaning agent
6386-38-5	Methylester analog of Irganox 1310	C<H=M=L	Antioxidant used in PE
72629-94-8	PFTrDA / Perfluorotridecanoic acid	C=M=H<**L**	non-polymer PFAS
603-48-5	LCV / Leucocrystal violet (Leucomethyl green)	C=M=H<**L**	Dye
3648-21-3	DHEPP / Diheptyl phthalate (DHP)	C=M=H<**L**	Breakdown from phthalate
3524-68-3	PETA / Pentaerythritol triacrylate	C=M=H<**L**	Used as a crosslinker to create better properties for plastic
99-09-2	MNA / m-Nitroaniline (3-Nitroaniline)	C<M<H<**L**	Used as a diazo component in azo dyes

A total of 78 compounds were detected across all analysis of PET materials in the 10 % ethanol. It was found that 27% were produced due to retorting (not present in the control samples) and the other 73% were present in both control and retorted samples. More than half of the compounds associated with retorting only were classed as Cramer class III, so overall retorting increased the amount of Cramer class III compounds found. The highest LCMS peak was measured for PET filled with ethanol after 'Medium' retort treatment. The substance was identified as glycerol monopalmitate, which is a Cramer class III. However, the 'Low' treatment was associated with the most migrants in Cramer class III. Overall, 71% of Cramer class III compounds were found after 'Low' treatment. This suggests that although higher treatment temperatures caused the most amount of physical damage to the pouch,

as seen by visual observations and SEM imaging, the 'Low' treatment produced the most migration of Cramer class III chemical.

Table 13 shows a list of substances migrating from PET into 3 % acetic acid.

Table 13: *Cramer class III compounds in PET pouches in acetic acid found to occur due to retorting, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	Name	Change	Source
52829-07-9	Tinuvin 770	C=M=H<**L**	Light stabilizer used in plastic
120-40-1	N,N-bis(2-hydroxyethyl) dodecanamide	C=M=H<**L**	Cleaning agent
3524-68-3	PETA / Pentaerythritol triacrylate	C=M=H<**L**	Used as a Crosslinker to create better properties for plastic
81-88-9	Rhodamine B (C.I. Pigment Violet 1)	C=M=H<**L**	Dye

The highest peak (Tinuvin 770) and the most migration at Cramer Class III are seen after the 'Low' treatment. All the Cramer class III compounds were found at 'Low' treatment. This agrees with visual observations, SEM imaging and OML assessment, that have all pointed to longer retorting time causing the most damage and migration for PET pouches with acetic acid.

The results for PET in ethanol and acetic acid, as seen in LCMS, across all treatments indicate that the degradation seemed to increase with treatment time, as the number of LCMS compounds and their intensity is increased in the 'Low' treatment.

4.1.4 Specific Migration – Metal

As previously stated in Section 4.0, Table 11, only antimony migration was measured for PET pouches given the total heavy metal migration results after PET sample digestion.

Metal migration for PET pouches filled with ethanol before and after retort treatments is shown in Figure 14.

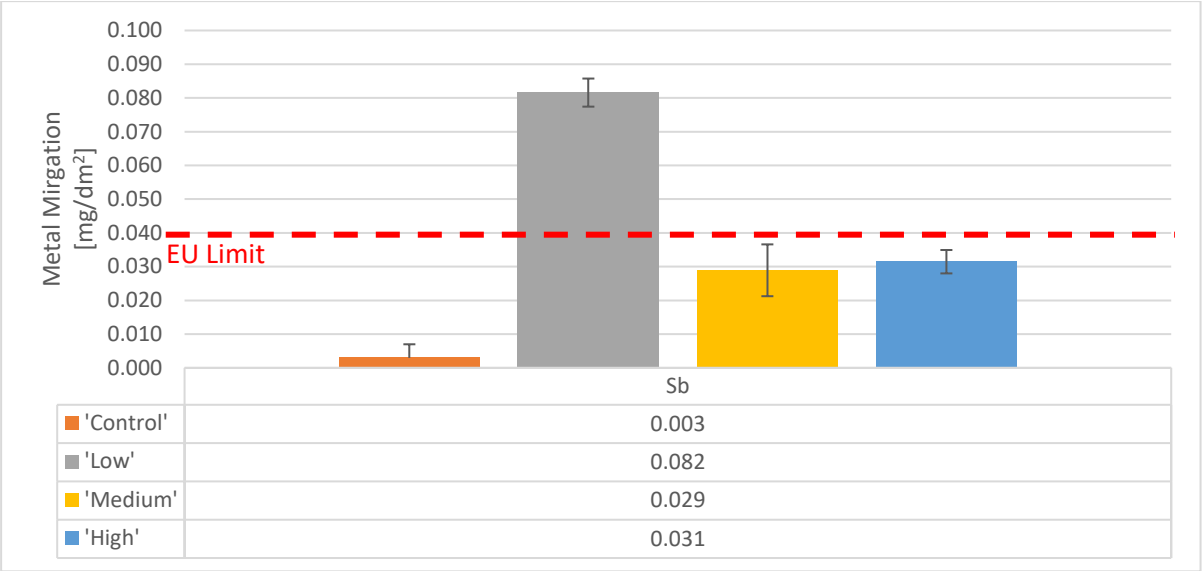


Figure 14: *Antimony released from PET pouches filled with ethanol pre- and post-treatment (mean and standard deviation of three replicates): please note the EU limit bar*

Metal migration from PET pouches filled with acetic acid before and retort treatments is shown in Figure 15.

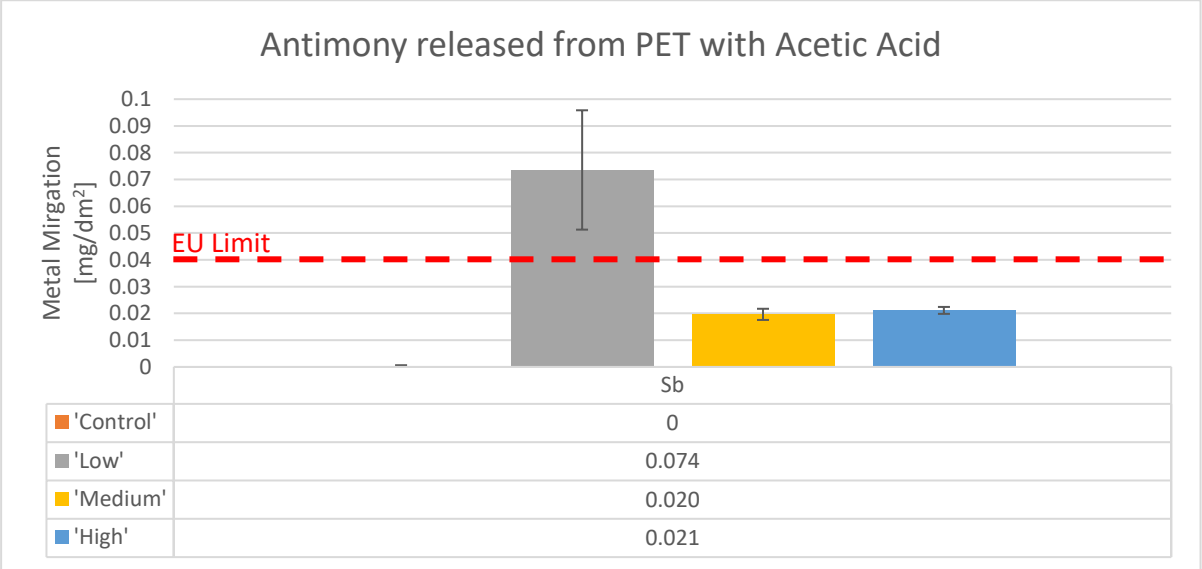


Figure 15: *Antimony released from PET pouches filled with acetic acid pre- and post-treatment; please note the EU limit bar*

For both simulants, the results followed the same trend. Retorting did cause antimony to be released, which can be seen in Figure 14 and Figure 15. It was also found that the 'Low' treatment was associated with the largest release of antimony, which was 0.082 ± 0.004 mg/dm^2 for ethanol and 0.07 ± 0.02 mg/dm^2 for acetic acid, respectively. The same trends have been previously observed in literature (Sánchez-Martínez et al., 2013) and the values for 'Low' treatment were above the limit set in EU regulation of food contact plastics of 0.04 mg/dm^2 (COMMISSION, 2011). The other two

treatments produce statistically the same amount of antimony, higher than the controls, but below the EU limit.

4.1.5 Discussion of PET Results

PET filled with 10% ethanol exhibited most physical damage at 'High' treatment, as observed in the SEM imaging and by the fluid loss from the bags. However, ICPMS results showed higher metal migration at 'Low' treatments; in this case Sb exceeded the EU admitted limit. Migration (NIAS) also seemed to be higher for 'Medium' and 'Low' treatments. OML was only performed for the 'High' treatment and proved to increase 10-fold over the non-retort treated materials, although staying under the admitted EU limits. Overall, PET pouches filled with ethanol seemed to be affected by both temperature and time of treatment; whereas physical damage was visibly increased by increased temperature of the retorting, migration of metals of concern and migration of Cramer class III chemicals seemed to worsen with increasing treatment time.

PET filled with 3% acetic acid exhibited the worst physical damage (both visual and SEM), and worst metal and organic compounds in the 'Low' treatment. The results were consistent across all analyses and seemed to indicate that time, rather than temperature, has a more significant effect on PET pouches filled with an acidic simulant.

When comparing the effects of the two different simulants on PET post-retorting:

- Physical observation: only the ethanol pouches lost fluid at 'Medium' and 'High' retort treatments.
- Microscopy observation: SEM imaging showed more damage in acetic acid, with an increase in pitting appearance and definition.
- Overall migration: value increased for both simulants after retorting, but values were still below the legal limit of 10 mg/dm^2 (average OML is 4.6mg/dm^2 at 'High' and 1.7 mg/dm^2 at 'Low' in ethanol and acetic acid respectively).
- Metal migration: for both simulants, the 'Low' treatment caused the Sb value to exceed the EU limit, making the material unsuitable.
- Chemical migration: the number of compounds migrating in both simulants increased post-treatment; however, the increase was more notable (almost 1000-fold by identical peak height) in ethanol than in acetic acid.

PET pouches filled with both acetic acid and ethanol simulants were damaged by retort treatments. Although the PET material mainly withstood the 'Low' treatment conditions with both simulants, the

film was proven to become unsuitable as food contact material, due to physical damage and leaching exceeding limits associated with treatments.

4.2 Retorting of PA Monolayer Pouches

No visible changes were observed after the 'Low' and 'Medium' treatment of PA using both acetic acid and ethanol as simulants. However, when using ethanol, the pouches with 'High' treatment had no fluid retention and when using acetic acid, half the pouches with 'High' treatment had no fluid retention.

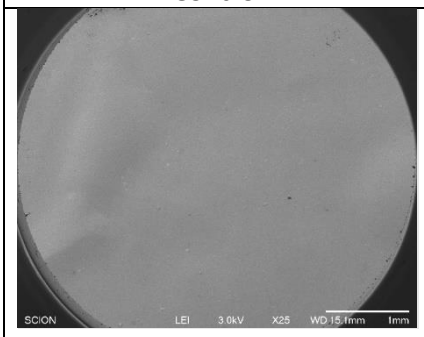
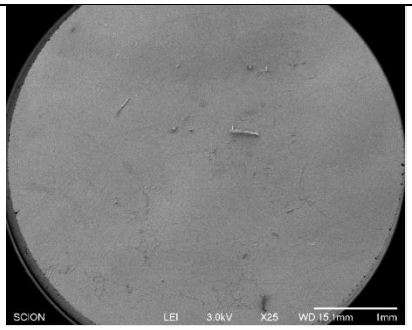
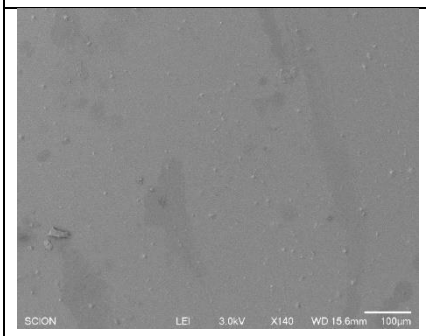
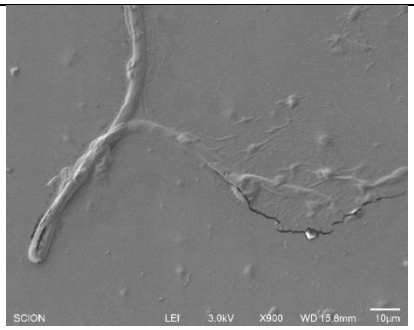
As a result, it was decided to take a closer look (SEM and OML analysis) at the potential structural damage seen in acetic acid after 'High' treatment, because of the increased fluid leak when the temperature is increased. It was decided to take a closer look (SEM and OML analysis) at the potential structural damage seen in Ethanol after 'Medium' treatment, because there was no 'High' treatment left, due to the increased fluid leak when the temperature was increased.

4.2.1 Internal Surface Damage

The internal surface damage for PA pouches was assessed using SEM imaging after two different retort treatments as well as using two simulants. The pictures were shown of the treatment sample were taken of the individual defects/damages. Each was magnified until the defect could be identified, using magnifications ranging from x25 - x5000.

Figure 16 presents SEM imaging for PA pouches filled with ethanol after 'Medium' treatment using various magnifications.

Figure 16: *PA pouches filled with ethanol, control on left and 'Medium' treatment on the right*

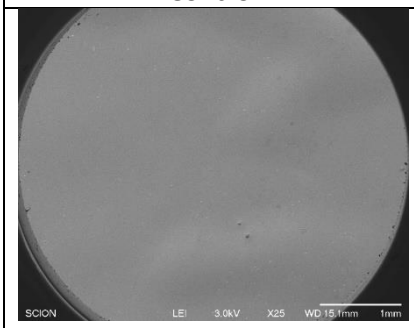
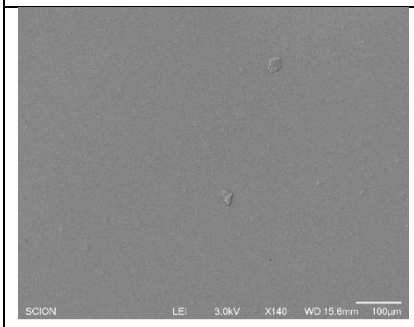
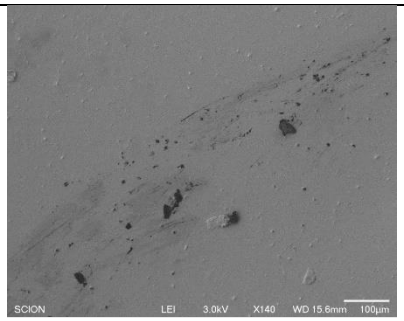
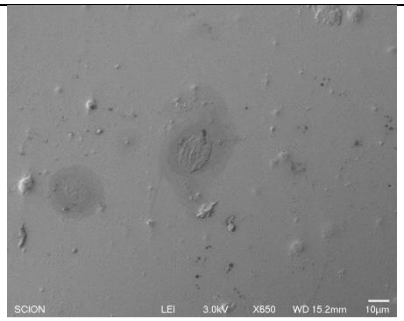
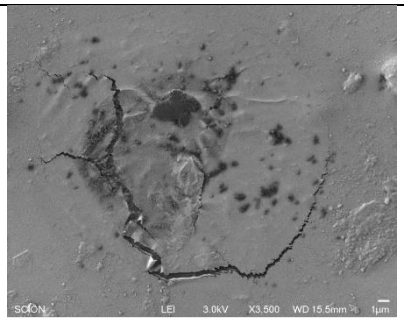
Control	Ethanol with 'Medium' treatment	Magnification
		x 25 (low)
		x 140
		x 900

The images on the left are of the control PA sample in ethanol and are used for comparison only. The ridges/bumps observed at x 140 magnification are caused by particles of dust.

The images on the right were of damage observed on the PA pouches filled with ethanol post 'Medium' treatment. The first image at low magnification in Figure 16 provides an overview of the damage observed on the surface of the pouches. The x 900 photo is a close up shot of damage: a fold on the plastic with cracks lines.

Figure 17 shows SEM images for PA pouches filled with acetic acid after 'High' treatment using various magnifications:

Figure 17: *PA filled with acetic acid, control on left and 'High' treatment on the right*

Control	Acetic acid 'High' treatment	Magnification
		x 25 (low)
		x 140
		x 900
		x 3500

The images on the left are of the control PA sample with acetic acid and are used for comparison only. The bumps observed at x 140 magnification are caused by dust particles.

The images on the right were of damage observed on the PA pouches filled with acetic acid post 'High' treatment. The first image at low magnification in Figure 17 provides an overview of the damage observed on the surface of the pouches. The x 140 magnification photo shows the amount of damage that was observed of scratches and pinholes on the surface of the pouches, and the x 900

magnification photo shows cracking. The x 3,500 magnification photo showed cracking at higher magnification.

The damage shown in these photos supported the visual observations seen after retorting, in the section above.

The ethanol simulant from the 'Medium' treatment and the acetic acid simulant from the 'High' treatment were further assessed via gravimetric analysis to determine the OML.

4.2.2 Overall Migration

OML was determined on both PA pouches filled with ethanol after the 'Medium' treatment and on PA pouches filled with acetic acid after the 'High' treatment. The OML results for the PA pouches are summarised in Figure 18.

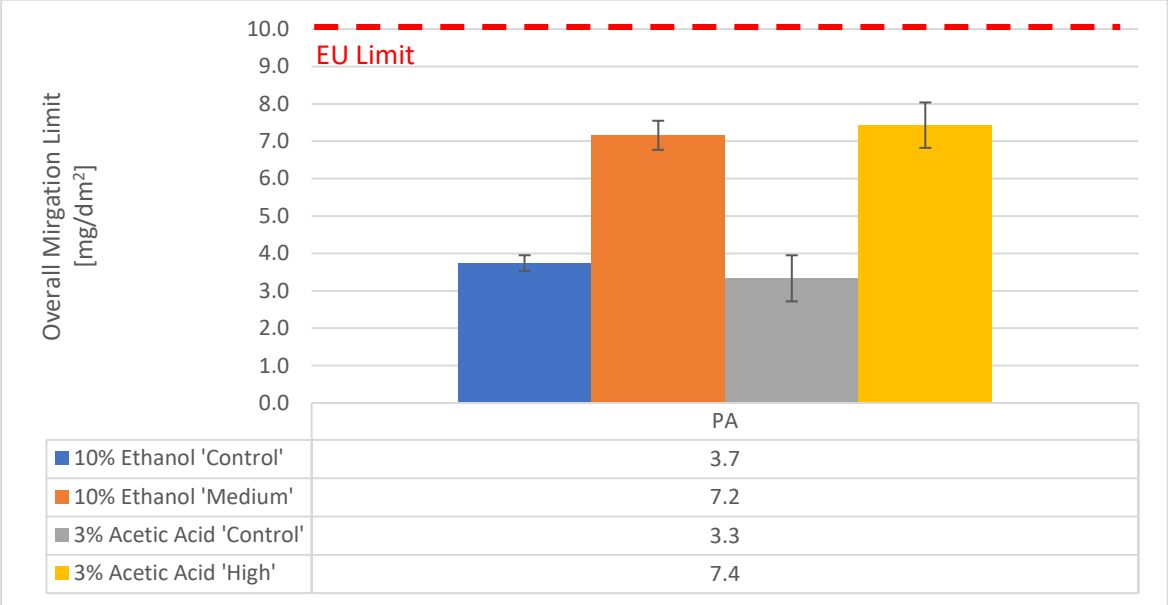


Figure 18: *OML test for PA of control and the worst-case situation for each simulant*

PA in ethanol at 'Medium' treatment had an average OML of 7.2 ± 0.4 mg/dm^2, compared with 3.7 ± 0.0 mg/dm^2. in the control. PA in acetic acid at 'High' treatment had an average OML of 7.4 ± 0.6 mg/dm^2, while the acetic acid control experienced a similar migration of 3.3 ± 0.6 mg/dm^2. As expected, the heat treatment increased the overall migration significantly. When comparing the two simulants the total migration is similar in ethanol as acetic acid, both before and post-treatment; however, both are below the limit set by the EU Regulation on food contact plastics of 10 mg/dm^2 (COMMISSION, 2011). The results for PA in ethanol at 'Medium' treatment and in acetic acid at 'High' treatment seem to support that, the increase in OML, hence degradation, is directly influenced by the temperature. However more analysis needed.

4.2.3 Specific Migration - NIAS

Simulants from all pouches were analysed on LCMS and identified. For all identified compounds trends were established on increases or decreases in peak height (corresponding to concentration). The full list of compounds found migrating from PA pouches in both ethanol and acetic acid across all treatments is presented in the Appendix. The discussion here focuses on the most significant compounds identified in each simulant. Table 14 presents a list of substances identified as Cramer class III migrating from PA into ethanol across all treatments.

Table 14: *Cramer class III compounds in ethanol found to occur due to retorting of PA pouches, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	**Name**	**Change**	**Sources**
542-44-9	Glycerol monopalmitate	C=H<**L=M**	Food contamination
3648-21-3	DHEPP / Diheptyl phthalate (DHP)	C=M=H<**L**	Breakdown from phthalate
375-22-4	PFBA / Perfluorobutanoic acid (Heptafluorobutyric acid)	C=M=H<**L**	This is a breakdown product from PFAS which are used as a building block for the synthesis of perfluoroalkyl substituted and surfactant in emulsion polymerization of fluoropolymers
2235-00-9	Vinyl caprolactam	C=M=H<**L**	Breakdown from Nylon
40601-76-1	Cyanox 1791	C=M=H<**L**	Antioxidant and/or stabilizer (only supposed to be used for room temperature or below)
36443-68-2	Irganox 245 (Antioxidant 245)	M=H<C<**L**	Antioxidant/stabilizer in adhesives
27676-62-6	Irganox 3114	C=M=H<**L**	Antioxidant/stabilizer in polyolefin
184649-96-5	Irgacure 1800	C=M=H<**L**	UV photoinitiator, it is often a mixture of aryl ketone and phosphineoxide
32687-78-8	Irganox MD1024	C=M=H<**L**	Antioxidant
100-75-4	N-Nitrosopiperidine	C=M=H<**L**	Food contaminates found in products with sodium nitrite
6386-38-5	Methylester analog of Irganox 1310	C=M=H<**L**	Antioxidant used in PE
31570-04-4	Irgafos 168 (Antioxidant 168)	C=M=H<**L**	Antioxidant
5650-10-2	Isopropyl diphenylamine	C=M=H<**L**	Antioxidant
107-50-6	Tetradecamethylcycloheptasiloxane (D7)	C=M=H<**L**	Slip agent
495-54-5	Chrysoidine	C=M=H<**L**	Dye
90-66-4	Irganox 1081 (Thioalkofen BP)	C=L=H<**M**	Stabilizer
CAS	**Name**	**Change**	**Sources**
108-95-2	Phenol	C=M=H<**L**	Used for making nylon

CAS	Name	Change	Sources
5888-33-5	Isobornyl acrylate	C=M=H<**L**	Used in the plastic as it is monofunctional

Glycerol monopalmitate was also found with the largest peak in ethanol. 70 % of the Cramer class III compounds identified were found in the 'Low' treatment.

A total of 95 compounds were detected across all analysis of PA materials. It was found that 72 % were produced due to retorting (not present in the control samples) and the other 28 % were present in both control and retorted samples. Exactly half of the compounds associated with retorting only were classed as Cramer class III, so overall retorting increased the amount of Cramer class III compounds. The highest LCMS peak was measured for PA filled with ethanol after 'Low' treatment. The substance was identified as glycerol monopalmitate, which is a Cramer class III. Overall, 93 % of Cramer class III compounds were found after 'Low' treatment. This suggests that although higher treatment temperatures caused the most amount of physical damage to the pouch, the 'Low' treatment produced more chemical migration in class III and higher peaks, corresponding to an increase in concentration. Table 15 shows a list of substances migrating from PA into 3 % acetic acid.

Table 15: *Cramer class III compounds in acetic acid found to occur due to retorting of PA pouches, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	Name	Change	Sources
3648-21-3	DHEPP / Diheptyl phthalate (DHP)	C=M=H <**L**	Breakdown from phthalate
162881-26-7	Phenyl-bis-(2,4,6-trimethylbenzoyl)-phosphine oxide	C=M=L <**H**	Production of plastic
375-22-4	PFBA / Perfluorobutanoic acid (Heptafluorobutyric acid)	C=M=H <**L**	This is a breakdown product from PFAS which are used as a building block for the synthesis of perfluoroalkyl substituted and surfactant in emulsion polymerization of fluoropolymers
40601-76-1	Cyanox 1790	C=M=H <**L**	Antioxidant and/or stabilizer (only supposed to be used for room

			temperature or below)
CAS	**Name**	**Change**	**Sources**
36443-68-2	Irganox 245 (Antioxidant 245)	C<M<H<**L**	Antioxidant/stabilizer in adhesives
2235-00-9	Vinyl caprolactam	C=M=H<**L**	Breakdown from nylon
120-40-1	N,N-bis(2-hydroxyethyl) dodecanamide	C<M=H<**L**	Cleaning agent
603-48-5	LCV / Leucocrystal violet (Leucomethyl green)	C=M=H<**L**	Dye
119-47-1	BKF (Cyanox 2246) (2,2â€²-methylene-bis(6-tert-butyl-4-methylphenol))	C=M=H<**L**	Antioxidant/stabilizer
184649-96-5	Irgacure 1800	C=M=H<**L**	UV photoinitiator, it is often a mixture of aryl ketone and phosphineoxide
6386-38-5	Methylester analog of Irganox 1310	C=H<**M=L**	Antioxidant used in PE
78-42-2	TEHP / Tris(2-ethylhexyl)phosphate	C=L=H<**M**	Plasticizer in polymer
100-75-4	N-Nitrosopiperidine	C=M=H<**L**	Food contaminant found in products with sodium nitrite
100-97-0	Methenamine	C=M=H<**L**	Used for curing formaldehyde
14426-25-6	Crystal Violet (Methyl violet) (Basic Violet 3)	C=L=H<**M**	Breakdown compound from phenyl
107-50-6	Tetradecamethylcycloheptasiloxane (D7)	C=M=H<**L**	Slip agent
31570-04-4	Irgafos 168 (Antioxidant 168)	C=M=H<**L**	Antioxidant/stabilizer
26347-98-8	Monoester analog of Irganox 1010	C=M=H<**L**	Antioxidant/stabilizer

The highest peak diheptyl phthalate (DHP) and the most migration of Cramer Class III compounds are seen in the 'Low' treatment. 70 % of the Cramer class III compounds were found at 'Low' treatment. Similar to the findings for the ethanol simulant, this suggests that although higher treatment temperatures caused the most amount of physical damage to the pouch, the 'Low' treatment produced more chemical migration in Cramer class III and higher peaks.

The results for PA in ethanol and acetic acid, as seen in LCMS, across all treatments indicated that the degradation seemed to increase with treatment time, as the number of LCMS compounds and their intensity is increased in the 'Low' treatment.

4.2.4 Specific Migration – Metal

As stated in Section 4.0 of the discussion the concentration of metals post- PA digestion did not justify metal migration studies. Hence no metal migration studies were performed.

4.2.5 Discussion on PA Results

PA filled with ethanol exhibited most physical damage at 'High' treatment but 'Medium' was investigated, as observed in the SEM imaging and the fluid loss from the bags at 'High'. However, migration (NIAS) seemed to be increased for 'Low' treatments. OML was only performed for the 'Medium' treatment and proved to increase two-fold over the non-retort treated materials, although still staying under the admitted EU limits. Overall, PA pouches filled with ethanol seemed to be affected by both temperature and time of treatment: whereas physical damage was visibly increased by increased temperature of the retorting, migration of Cramer class III chemicals seemed to worsen with increasing treatment time.

PA filled with acetic acid exhibited most physical damage at 'High' treatment, as observed in the SEM imaging and the fluid loss from the pouches. However, migration (NIAS) seemed to be increased for 'Low' treatments. OML was only performed for the 'High' treatment and proved to increase two-fold over the non-retort treated materials, although staying under the admitted EU limits. Overall, PA pouches filled with acetic acid seemed to be affected by both temperature and time of treatment: whereas physical damage was visibly increased by increased temperature of the retorting, migration of Cramer class III chemicals seemed to worsen with increasing treatment time.

When comparing the effects of the two different simulants on PA post-retorting:

- Physical observation: the ethanol and acetic acid pouches lost fluid at 'High' treatments.
- Microscopy observation: SEM imaging showed similar damage in acetic acid as ethanol.
- Overall migration: value increased for both simulants after retorting, but values are still below the legal limit of 10 mg/dm^2 (average OML is 7.2 ± 0.4 mg/dm^2 at 'Medium' and 7.4 ± 0.6 mg/dm^2 at 'High' in ethanol and acetic acid respectively).
- Metal migration: no migration studies were performed.

- Chemical migration: the number of compounds migrating in both simulants increased post-treatment.

PA pouches filled with both acetic acid and ethanol simulants were damaged by retort treatments.

4.3 Retorting of PE Monolayer Pouches

During retorting of PE pouches filled with both simulants, some pouches did not survive the treatment. The 'High' treatment pouches (see Figure 19) were very warped, and only one pouch for each simulant still contained fluid, which was not considered enough for consistency. No fluid loss was noted in 'Low' or 'Medium' treatments for either simulant. The physical damage noted in the 'High' treatment was believed to have happened due to the melting point of LDPE being 110 °C.

No checks could be done on the 'High' treatment samples from pouches filled with ethanol. After checking the peak height and patterns in LCMS profiles it was decided to investigate PE in ethanol at 'Medium' treatment and in acetic acid at 'Low' treatment.

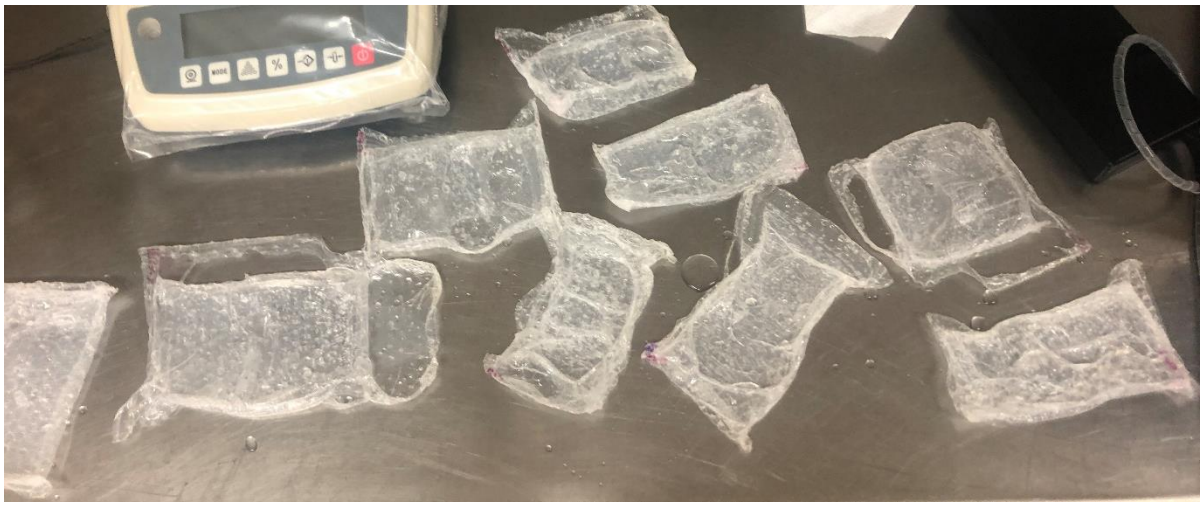


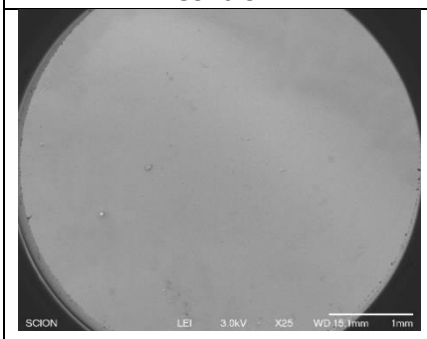
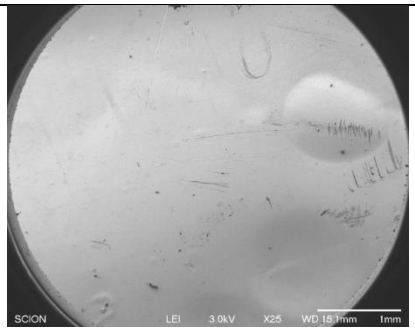
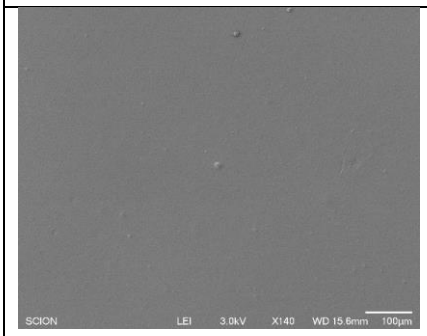
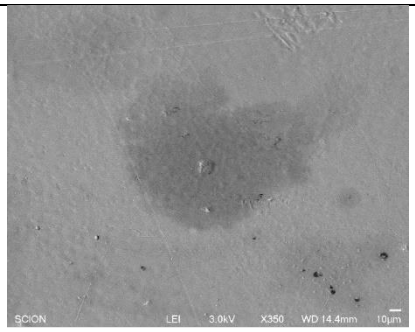
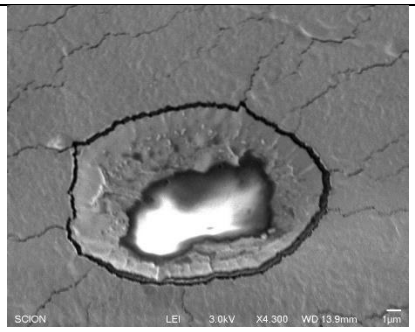
Figure 19: *PE pouches filled with both ethanol and acetic acid, after 'High' Treatment*

4.3.1 Internal Surface Damage

The internal surface damage for PE pouches was assessed using SEM imaging after two different retort treatments and two simulants. The pictures were shown of the treatment sample were taken of the individual defects/damages. Each was magnified until the defect could be identified, using magnifications ranging from x25 - x5000.

Figure 20 presents SEM images for PE pouches filled with ethanol after 'Medium' treatment using various magnifications. For PE filled with ethanol, the simulant and treatment caused damage to the surface of the pouch.

Figure 20: *PE post ethanol treatment, virgin on left and 'Medium' treatment on the right*

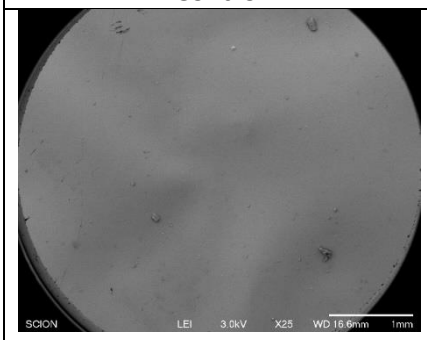
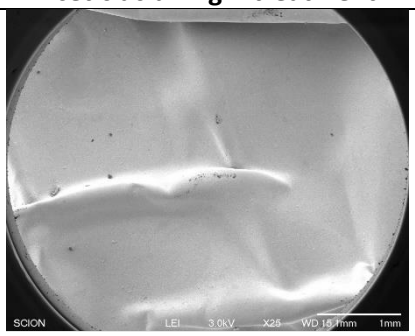
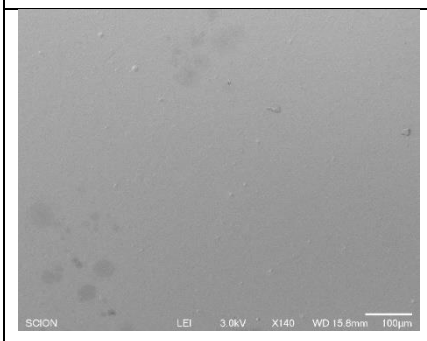
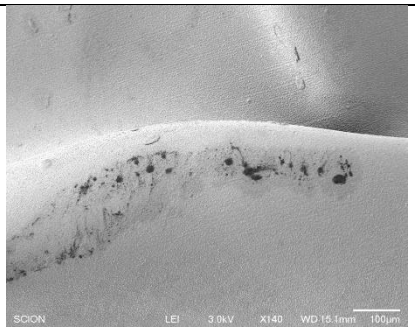
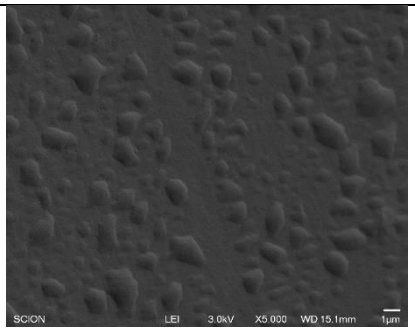
Control	Ethanol 'Medium' treatment	Magnification
		x 25 (low)
		x 140
		x 350
		x 4300

The images on the left are the control PE samples and the images on the right are the PE samples filled with ethanol post 'Medium' treatment. The first image at low magnification in Figure 20 provides an overview of the damage associated with retorting. The ridges/bumps observed at

magnification x 140 are dust particles. The rest of the photos on the right (x 350 and x 4300 magnification) are magnifications of the scratches and pinholes observed post-treatment.

Figure 21 shows SEM images for PE pouches filled with acetic acid after 'High' treatment using various magnifications.

Figure 21: *PE post acetic acid treatment, virgin on left and 'High' treatment on the right*

Control	Acetic acid 'High' treatment	Magnification
		x 25 (low)
		x 140
		x 5000

The images on the left are of the control PE sample in acetic acid and are used for comparison only. The ridges observed at low magnification are caused by dust particles in both control and treated samples.

The images on the right were of damage observed on the PE pouches filled with acetic acid post 'High' treatment. The pouches filled with acetic acid post 'High' treatment showed material breakdown. Fold lines are observed post-treatment from low magnification. The x 350 and x 900 magnification images show bubbling that appeared across the whole material post- 'High' treatment in the pouch filled with acetic acid.

The ethanol simulant from the 'Medium' treatment was further assessed. Based on material breakdown and the acetic acid simulant loss from the 'High' treatment, samples from the 'Low' treatment for acetic acid were further assessed via gravimetric analysis to determine the OML.

4.3.2 Overall Migration

OMLs was determined on both PE pouches filled with ethanol after the 'Medium' treatment and on PE pouches filled with acetic acid after the 'Low' treatment. The OML results for the PE pouches are summarised in Figure 22.

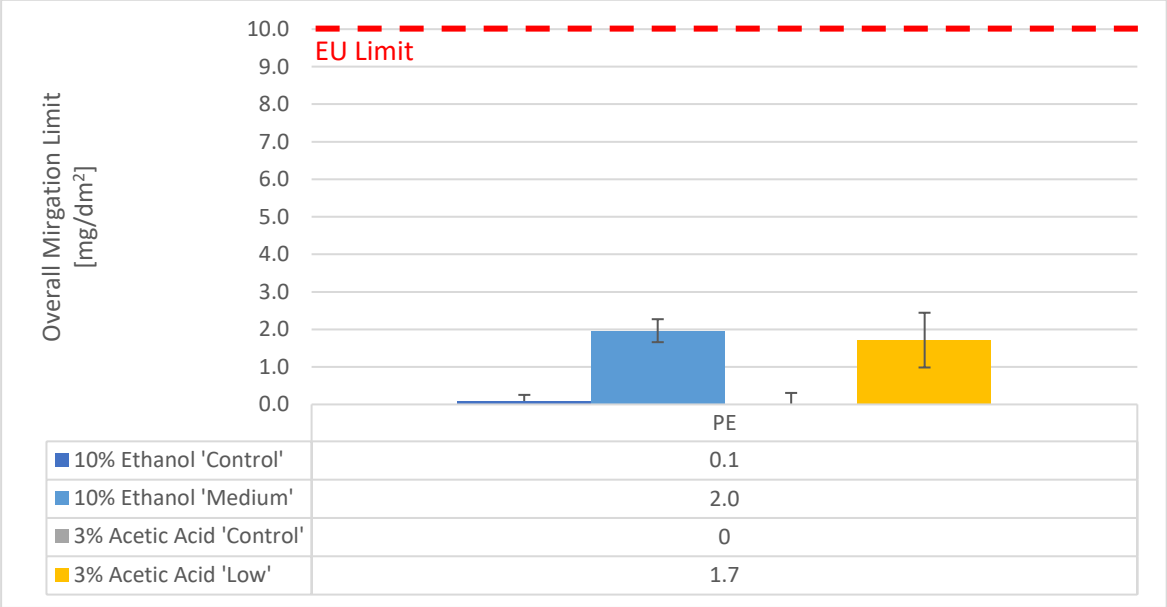


Figure 22: *OML test for PE of the control and the worst case situation for each simulant (mean and standard deviation of three replicates): please note the EU limit bar*

PE with ethanol after 'Medium' treatment had an average OML of 2.0 ± 0.2 mg/dm^2, compared to only 0.1 ± 0.1 mg/dm^2 in the control. PE in acetic acid after 'Low' treatment had an average OML of 1.7 ± 0.8 mg/dm^2, while the control in acetic acid had 0.0 ± 0.2 mg/dm^2. When comparing the two simulants and treatments, retorting increased the OML in both simulants and treatments. No conclusion could be drawn between the two simulants as the two values are very similar. However, they are both under the EU limit of 10 mg/dm^2.

4.3.3 Specific Migration - NIAS

Simulants from all pouches were analysed on LCMS and identified. For all identified compounds trends were established on increases or decreases in peak height (corresponding to concentration). The full list of compounds found migrating from PE pouches in both ethanol and acetic acid across all treatments is presented in the Appendix. The discussion here focuses on the most important

compounds identified (highest Cramer class, III) in each simulant. Table 16 presents a list of substances identified as Cramer class III migrating from PE into 10 % ethanol across all treatments.

Table 16: *Cramer class III compounds in PE pouches in ethanol found to occur due to retorting, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	Name	Change	Source
90-66-4	Irganox 1081 (Thioalkofen BP)	C=L=H<**M**	Phenol antioxidant
67362-76-9	2-Butoxyethyl 4-(dimethylamino)benzoate	C<H<L<**M**	Uv protectant
119-42-6	2-Cyclohexylphenol	C=L=H<**M**	Stabilizers from bisphenol group
10527-11-4	1H-Inden-5-ol, 2,3-dihydro-3-(4-hydroxyphenyl)-1,1,3-trimethyl-	C=L<H<**M**	Breakdown from bisphenol A
115-86-6	TPPA / Triphenyl phosphate	M=L<C<**H**	it is a plasticizer
6386-38-5	Methylester analog of Irganox 1310	H<**M=L**	Antioxidant used in PE
901-44-0	Bisphenol A ethoxylate	C=L<**M=H**	It is used in adhesives
72629-94-8	PFTrDA / Perfluorotridecanoic acid	C=M=H<**L**	non-polymer PFAS
120-40-1	N,N-bis(2-hydroxyethyl) dodecanamide	C=H<M=**L**	Cleaning agent
28675-80-1	6-Methylheptyl methacrylate	C=M=L<**H**	monomer
26347-98-8	Monoester analog of Irganox 1010	C=H<**M**	Antioxidant/stabilizr
1620-98-0	3,5-di-tert-butyl-4-hydroxybenzaldehyde	C=M=H<**L**	I is a food contamination, BHT is a common food additive
5888-33-5	Isobornyl acrylate (Isomer 2) (Class II)	C=M=H<**L**	Used in the plastic as it is monofunctional
5888-33-5	Isobornyl acrylate (Class II)	L<H<C<**M**	Used in the plastic as it is monofunctional
105-76-0	DBM / Dibutylmaleate	C=L=H<**M**	Liquid plasticizer used for emulsion polymerization

78 compounds were detected and identified across the ethanol treatments in the PE materials. The 'Medium' treatment produced the most compounds identified as Cramer class III, contributing to an increase in concentration of 49% of the Cramer class III compounds. The 'Low' treatment produces the highest concentrations across most peaks for ethanol, however the compounds contributing to the overall increase are mainly Cramer class I. Once those are removed, the highest LCMS peak was measured for PE filled with ethanol at 'Medium' and 'Low' retort treatment. The substance was identified as N,N-bis(2-hydroxyethyl) dodecanamide, which is a Cramer class III. The next highest LCMS peak was measured for PE filled with ethanol at 'Low' retort treatment. The substance was identified as PFTrDA / Perfluorotridecanoic acid, Cramer class III. These observations suggest that retorting time, rather than temperature, caused an increase in total number and concentration in compounds migrating from PE in ethanol.

Table 17 shows a list of Cramer class II and III compounds migrating from PE in acetic acid.

Table 17: *Cramer class III compounds in PE pouches in acetic acid found to occur due to retorting, measured on LCMS; C = control, L = 'Low', M = 'Medium', H = 'High'; the value in bold is the highest observedd value across all treatments*

CAS	Name	Change	Source
5888-33-5	Isobornyl acrylate (Isomer 2) (**Class II)**	C=M=H<**L**	Used in the plastic as it is monofunctional
120-40-1	N,N-bis(2-hydroxyethyl) dodecanamide	C<H<**M=L**	Cleaning agent
6386-38-5	Methylester analog of Irganox 1310	C=H<L<**M**	Antioxidant used in PE

Considerably less compounds were identified in the acetic acid samples than in ethanol. However, the same trend as in ethanol was observed post-treatment in acetic acid: the 'Medium' treatment presented the most Class III compounds, but the 'Low' treatment had the most peaks overall.

As for ethanol, the LCMS results seem to point to retorting time, rather than temperature, tending to an increase in the amount of migration.

4.3.4 Specific Migration - Metal

As stated in Section 4.0, Table 11, only zinc (Zn) migration was measured for PE pouches, given the total heavy metal migration results from the PE material post-digestion.

Metal migration from PE pouches filled with ethanol before and after retort treatments is presented in Figure 23.

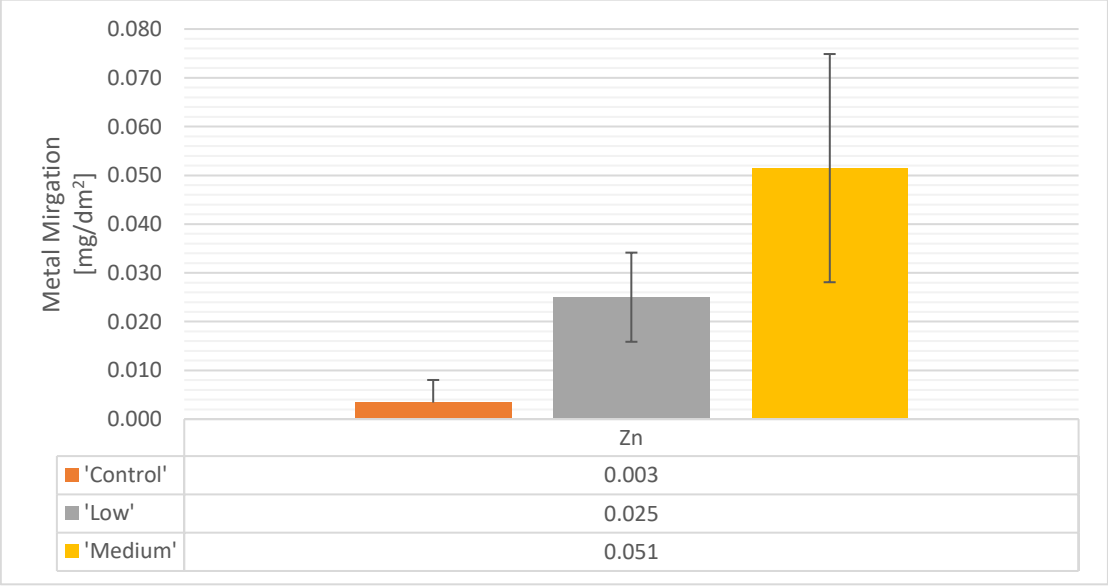


Figure 23: *Zn released from PE pouches filled with Ethanol pre and post treatment (mean and standard deviation of three replicates)*

Metal migration from PE pouches filled with acetic acid before and after retort treatments is presented in Figure 24.

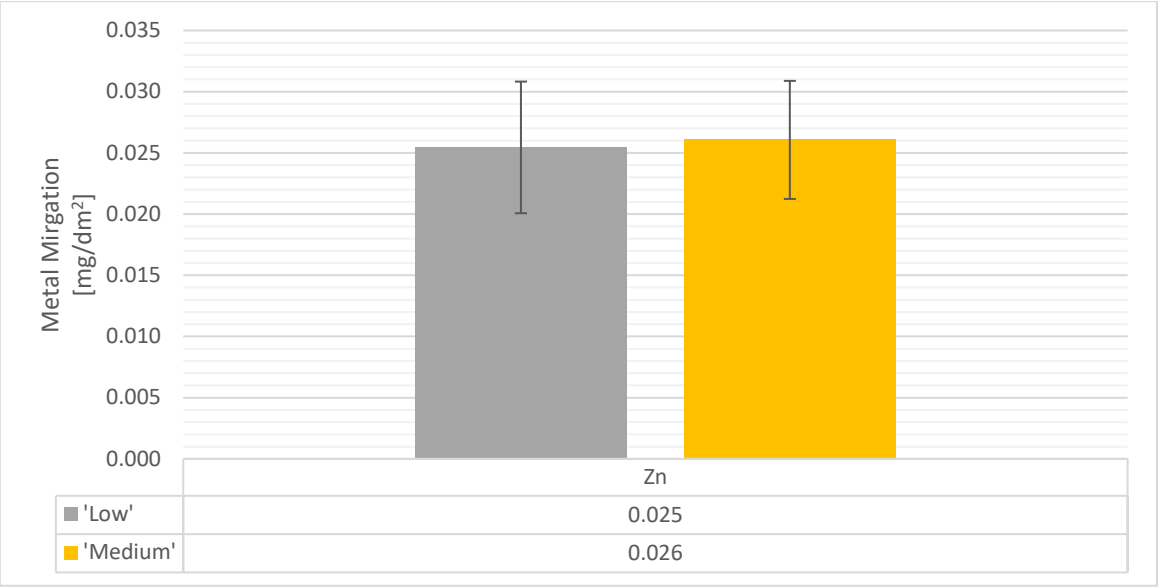


Figure 24: *Zn released from PE pouches with acetic acid pre and post treatment (mean and standard deviation of three replicates)*

The control value is not represented in the acetic acid graph (Figure 24) as the value was below the detection limit of the instrument. For both simulants, the retorting causes Zn to be released. For both simulants Zn increases and there is no statistical significance between 'Low' and 'Medium' treatments. However, both are well below the limit of 5 mg/dm^2 which is set by the EU (COMMISSION, 2011).

4.3.5 Discussion of PE results

PE filled with 10% ethanol exhibited most physical damage at 'High' treatment, but this was caused by the material melting. No fluid could be collected from the 'High' treatment pouches. ICPMS results showed zinc was released from the packaging in both 'Low' and 'Medium' treatments, but the differences in values were not statistically significant. Migration (NIAS) was increased for 'Medium' and 'Low' treatments when compared to the control. Whereas most Cramer class III compounds were observed in the 'Medium' treatment, overall, the largest number of compounds was found in the 'Low' treatment. OML was only performed for the 'Medium' treatment and proved to increase 20-fold over the non-retort treated materials, although staying under the admitted EU limits. Overall, PE pouches filled with ethanol seemed to be affected by both temperature and time of treatment: whereas physical damage was visibly increased by increased temperature of the retorting, migration of metals of concern and migration of overall chemicals seemed to worsen with increasing treatment time.

PE filled with acetic acid exhibited the worst physical damage (both visual and SEM) in the 'High' treatment. As no fluid could be collected from the pouches, the 'High' treatment could not be further

investigated. Overall, highest metal and general organic compounds were found in the simulant of the 'Low' treatment. The results were consistent across all analyses and seemed to indicate that time, rather than temperature, had a more significant effect on PE pouches filled with an acidic acid simulant.

When comparing the effects of the two different simulants on PE post-retorting:

- Physical observation: ethanol and acetic acid filled pouches did not survive the 'High' treatments; the 'Low' and 'Medium' treatments had no fluid loss.
- Microscopy observation: SEM imaging showed more damage in acetic acid, with an increase in pitting appearance and definition.
- Overall migration: value increased for both simulants after retorting, but values were still below the legal limit of 10 mg/dm^2 (average OML is 2.0 mg/dm^2 at 'Medium' and 1.7 mg/dm^2 at 'Low' in ethanol and acetic acid respectively).
- Metal migration: for both simulants, Zn was released in both 'Low' and 'Medium' treatments but stays well below the 5.0 mg/dm^2 EU limit.
- Chemical migration: the number of compounds migrating in both simulants increased post-treatment; however, the increase in number of compounds was more in ethanol than in acetic acid.

PE pouches filled with both acetic acid and ethanol simulants were damaged by retort treatments. The PE material did not withstand the 'High' treatment conditions with either of the simulants. The films were proven to still be suitable for use in food contact packaging material post 'Low' and 'Medium' treatments as no migrant compounds exceeded the EU limits imposed. However, the concentration and number of compounds released from the material increased post-treatment.

4.4 Comparison of pouches and treatments

The visual damage observed in the monolayer pouches made from PA, PET, and PE could be one of the many reasons these are not used as single layer retort pouches in industry. However, these materials were much thinner than typical retort pouches and tend to make up one of the layers in a multilayer film. This damage could be occurring and not be noticeable, however, the functional properties of the material were not quantified so it is not known how these visual observations from SEM might relate to a decrease in WVTR, OTR, or mechanical properties such as the tensile strength. The physical damage in multilayer films may not be as apparent or pronounced especially for middle layers such as; PA and PET where the damage is expected to be worse at the surface because of interactions with the food or simulant at the surface. This research focused on chemical and metal migration as this could lead to safety and compliance concerns. Table 18 summarises the most

concerning visual observations and chemical and metal migration found in for the three films used in this work.

Table 18: Summary of which treatments and simulants gave the most extreme visual observations and migration for the each of the three monolayer films. In each square of the table it compares the resulst of the test and which treatment with the simulant which caused the biggest change.

	Observations	**SEM**	**OML**	**LCMS**	**ICPMS**
PET	Fluid loss in ethanol at 'Medium'- 'High'	Pitting, cracking, and pinholes	'Medium' with ethanol	'Low' – 'Medium' with ethanol	'Low' with both simulants
PA	Fluid loss at 'High'	Fold lines, pinholes and cracking	Both simulants causing Increase OML	'Low' with Both simulants	NA
PE	Melting at 'High'	Pinholes, folds, cracking, and bubbling	Both stimulants causing increased OML	'Low' – 'Medium' with ethanol	'Low' – 'Medium' with both simulants

Material characteristics pre- and post-retort treatments were critically analysed to assess how the different retort temperature/time profiles influenced the monolayers. The 'Low' treatment, of 110° C for 51 min, had the most effect on NIAS migration in PA with both simulants, PET with acetic acid, and PE with acetic acid. 'Medium' treatment, of 115° C for 25 min, affected the PE pouches filled with ethanol. However, no conclusions could be drawn about the migration for the 'High' treatment on PET filled with ethanol because the pouches all burst or leaked all the simulant in the retort. PET exhibited the highest peaks of NIAS migration at 'Medium' treatment. However, the most Cramer Class III were produced in 'Low' treatments and ICPMS results showed more metal migration at 'Low' treatments; in this case antimony exceeded the EU admitted limit. Using quantitative techniques for PET with ethanol would potentially help confirm which treatment was causing the most specific migration, OML, and damage. One conclusion from the PET trials is that PET at 'Low' treatment creates a concerningly high level of antimony.

The 'Low' treatment with longer time and lower temperature caused more NIAS and metal migration than the 'Medium' and 'High' treatments in PA with both simulants, in PET and PE with acetic acid. The 'Low' treatment of 110 °C had on an associated time of 51 mins. The 'Medium' treatment of 115 °C had a time of 25 mins, and the 'High' treatment of 121 °C had a time of 16 min. Fick's equation shows that migration is proportional to the diffusion coefficient D_p (for more detailed explanation see section 2.2.5 "Migration Diffusion Modelling"). The diffusion coefficient is temperature dependant, however, over the temperature ranges used in this work the extended time in the 'Low' treatment outweighed the temperature effect of a lower diffusion coefficient in most instances. Migration

modelling was out of scope of this work as time intensive experiments are required to measure the specific migration of compounds of interest.

When comparing the effects of the simulants on the materials, ethanol caused significantly more physical damage and NIAS migration than acetic acid for PE and PET, which correlates with the work previously undertaken by Massey and Scion on multilayer retort pouches (O'Connor, 2020). Both simulants caused a similar amount of migration in PA. When comparing all the materials, most of the Cramer class III and II compounds were identified in PA (36), followed by PE (17), and then PE (12).

4.4.1 NIAS of Concern

The most important Cramer class III chemicals detected in this research are discussed in this section. Although Cramer class III chemicals are classed as substances of high concern, it is important to realise that concentration and exposure are key factors in whether a chemical is toxic to humans. In this research NIAS chemicals were identified but not quantified, therefore no conclusions could be drawn on the toxicity of leachates. A brief review due to consumed and contaminated food is presented on the potential toxicity of the most important compounds identified, as provided by the European Chemicals Agency (*ECHA- European Chemicals Agency*).

Diheptyl phthalate

Diheptyl phthalate (CAS No 3648-21-3) (Figure 25) was found in PA filled with both ethanol and acetic acid and in PET filled with ethanol only. It produced the largest peak in PA with acetic acid, and the second largest peak in PA with ethanol.

Diheptyl phthalate is a breakdown product from a bigger phthalate compound series (*ECHA- European Chemicals Agency*). Once the diheptyl phthalate forms, it is potentially harmful if at the right concentration: it is a skin irritant, an eye irritant, it is suspected it may cause respiratory irritation, and it may cause damage to fertility or the unborn child. It is also suspected to meet the criteria for carcinogenic, mutagenic, and reproductive toxicity properties.

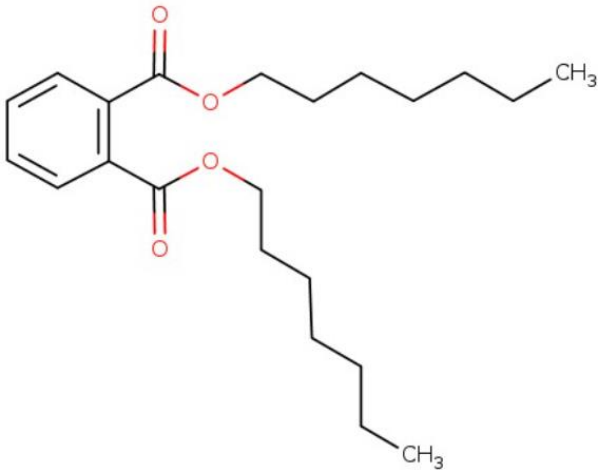


Figure 25: *Diheptyl Phthalte (ECHA- European Chemicals Agency)*

2 N,N,-bis(2-hydroxyethyl) Dodecanamide

N, N- bis(2-hydroxyethyl) dodecanamide (CAS No 120-40-1) (Figure 26) was found in PET filled with both simulants, PA filled with acetic acid, and PE with both simulants.

This chemical is part of a cleaning agent used in both food and plastic industry. It is classified as a skin irritant and an eye irritant. Although it was classed as a Cramer class III, hence toxic, no known hazards via oral route were listed for this chemical. There is a single study on its carcinogenic effect, which was completed on mice (*ECHA- European Chemicals Agency*).

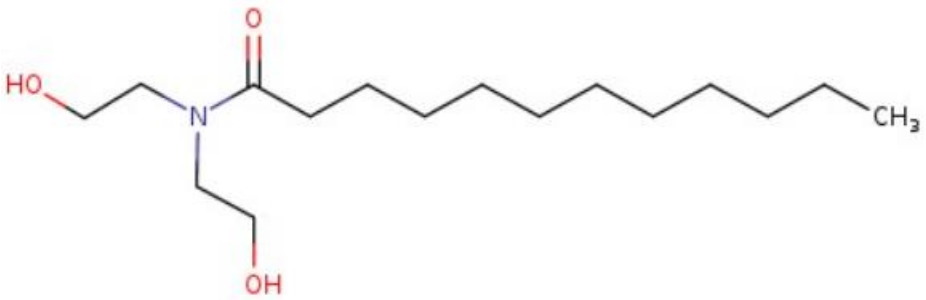


Figure 26: *N,n,-bis(2-hydroxyethyl) Dodecanamide (ECHA- European Chemicals Agency)*

Methylester analog of Irganox 1310

Methylester analog of Irganox 1310 (CAS No 6386-38-5) (Figure 27) was found in PA filled with both simulants, in PE with both simulants, and in PET with ethanol.

The chemical is an antioxidant which is used in the production of the plastic, which is a classified as harmful if swallowed, a skin irritant, serious eye irritant, and potential respiratory irritant.

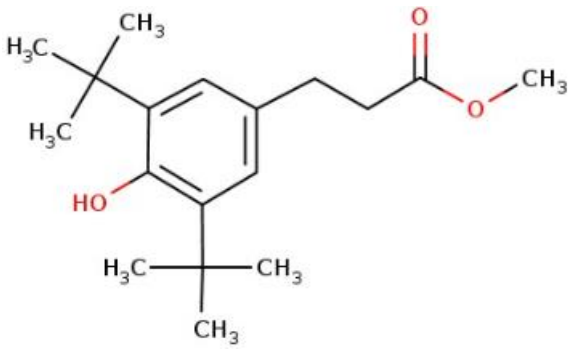


Figure 27: *Methylester analog of Irganox 1310 (ECHA- European Chemicals Agency)*

PFBA / Perfluorobutanoic acid (Heptafluorobutyric acid)

PFBA (CAS No 375-22-4), (Figure 28) was only found in PA filled in both ethanol and acetic acid.

This chemical is a breakdown of PFAS which is used in the production of the plastics. It is classified as skin corrosive, and serious eye irritant. It is also suspected to meet the criteria for carcinogenic, mutagenic, and reproductive toxicity properties.

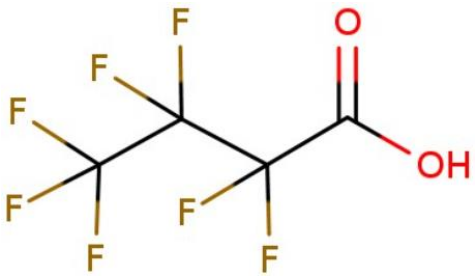


Figure 28: *4 PFBA / Perfluorobutanoic acid (ECHA- European Chemicals Agency)*

Glycerol monopalmitate,

Glycerol monopalmitate (CAS No 542-44-9) (Figure 29) only appeared when the simulant is ethanol. However, it is found leaching from all the materials. It also produced the largest peak in PET and PA, in Ethanol.

The chemical is a breakdown of food contamination from the environment, which is an example where even things that are considered safe, can breakdown into things that are considered potentially toxic. It is suspected to meet the criteria for carcinogenic, mutagenic, and reproductive toxicity properties.

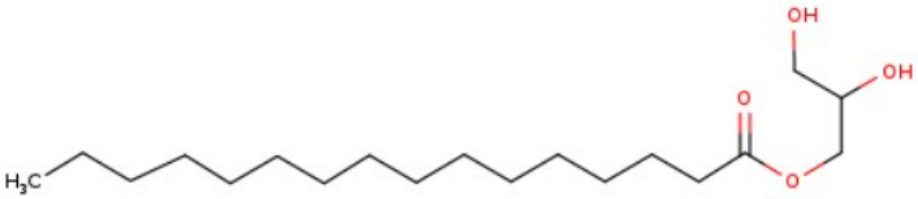


Figure 29: *Glycerol Monopalmitate (ECHA- European Chemicals Agency)*

5.0 Conclusion and Recommendations

This research focused on the effects of retort treatments on plastic films commonly used in the food industry. Changes occurring in the plastic monolayer and in the leachates post-retort treatments were monitored. Three different retort settings: 110 °C for 51 minutes, 115 °C for 25 minutes, and 121 °C for 16 minutes were used based on industry requirements to achieve an of F_o value of 3 minutes. The monolayer plastic films studied were PE, PET, and PA, common components of multi-layer retort pouches. The key areas for this research project were to investigate how different retort time-temperature profiles affect overall and specific migration from monolayer films in different food simulants. This was used to determine whether a significant difference in migration from the monolayer films was associated with retort processing. The plastic was tested using EU standards of compliance with 10 % ethanol and 3 % acetic acid as food simulants. The materials were visually inspected straight after retorting, followed by an in-depth internal surface test using SEM to view changes at the micro level. The overall and specific migration was assessed, and compounds putatively identified were assigned a Cramer class.

The 'Low' treatment, of 110 °C for 51 minutes, had the most effect on specific migration in PA with both simulants, PET with acetic acid, and PE with acetic acid. 'Medium' treatment, of 115 °C for 25 minutes, affected the specific migration of PE pouches with ethanol because of the melting point of PE; high could not be measured. However, no conclusions could be drawn about the effects of specific migration due to the treatment, on PET filled with ethanol without calibration curves, apart from the concerningly high levels of antimony in 'Low' treatment.

It is recommended that quantitation of leachates is completed for PET filled with ethanol, and then completed for the rest of the samples. Quantitation was outside the scope of this research, but it would enable further insights into toxicity of leachates and materials suitability. It is highly recommended that more metal migration tests for PET are completed due to the concerning levels of antimony at the 'Low' treatment, as they breached the legation limits set by EU. The findings in this research has highlighted that more research is essential to ensure multi-layer films used in industry are suitable in new and existing in package processing techniques. This research also raises questions about other in-packaging food preservation techniques used (for example: High Pressure Processing, Assistant Microwave Treatment, UV treatment, and Cold Plasma), and whether any compliance testing is being done, down to the individual monolayers.

6.0 Bibliography

Aigotti, R., Giannone, N., Asteggiano, A., Mecarelli, E., Dal Bello, F., & Medana, C. (2022). Release of Selected Non-Intentionally Added Substances (NIAS) from PET Food Contact Materials: A New Online SPE-UHPLC-MS/MS Multiresidue Method. *Separations*, *9*(8), 188. https://doi.org/10.3390/separations9080188

Akbarian, M., Aghamohammadi, B., Akbarian, A., Poursharif, Z., Ghasemkhani, N., & Moayedi, F. (2014). Effect of different nonthermal processings on food packaging: A review. *Indian Journal of Fundamental and Applied Life Sciences*, *4*(2), 420-426.

Arvanitoyannis, I. S., & Kotsanopoulos, K. V. (2014). Migration phenomenon in food packaging. Food–package interactions, mechanisms, types of migrants, testing and relative legislation—a review. *Food and Bioprocess Technology*, *7*, 21-36.

Awuah, G., Ramaswamy, H. S., & Economides, A. (2007). Thermal processing and quality: Principles and overview. *Chemical Engineering and Processing: Process Intensification*, *46*(6), 584-602. https://doi.org/10.1016/j.cep.2006.08.004

Begley, T., Castle, L., Feigenbaum, A., Franz, R., Hinrichs, K., Lickly, T., Mercea, P., Milana, M., O'Brien, A., & Rebre, S. (2005). Evaluation of migration models that might be used in support of regulations for food-contact plastics. *Food Additives and Contaminants*, *22*(1), 73-90.

Bhatia, S., Schultz, T., Roberts, D., Shen, J., Kromidas, L., & Api, A. M. (2015). Comparison of cramer classification between toxtree, the OECD QSAR Toolbox and expert judgment. *Regulatory Toxicology and Pharmacology*, *71*(1), 52-62. https://doi.org/10.1016/j.yrtph.2014.11.005

Bradley, E., Castle, L., Jickells, S., Mountfort, K., & Read, W. (2009). Use of overall migration methodology to test for food-contact substances with specific migration limits. *Food Additives and Contaminants*, *26*(4), 574-582.

Brandsch, J., Mercea, P., Rüter, M., Tosa, V., & Piringer, O. (2002). Migration modelling as a tool for quality assurance of food packaging. *Food Additives & Contaminants*, *19*(S1), 29-41.

Cai, R., Nthoiwa, K. K. M., & Ge, C. (2014). Effect of microwave heating on the migration of additives from PS, PP and PET container into food simulants. *Journal of Applied Packaging Research*, *6*(1), 3.

Caner, C. (2011). Sorption phenomena in packaged foods: factors affecting sorption processes in package–product systems. *Packaging Technology and Science*, *24*(5), 259-270. https://doi.org/10.1002/pts.935

Caner, C., Hernandez, R., Pascall, M., Balasubramaniam, V., & Harte, B. (2004). The effect of high-pressure food processing on the sorption behaviour of selected packaging materials. *Packaging Technology and Science: An International Journal*, *17*(3), 139-153. https://doi.org/10.1002

Commission Regulation (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food (Text with EEA relevance)Text with EEA relevance, (2011). https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32011R0010

Dhawan, S., Sablani, S. S., Tang, J., Barbosa-Cànovas, G. V., Ullman, J. L., & Bhunia, K. (2014). Silicon Migration from High-barrier Coated Multilayer Polymeric Films to Selected Food Simulants after Microwave Processing Treatments. *Packaging Technology and Science*, *27*(8), 625-638. https://doi.org/10.1002/pts.2055

Ebnesajjad, S. (2013). *Plastic films in food packaging : matertials, technology, and applications* (S. Ebnesajjad, Ed.). William Andrew. https://doi.org/10.1016/B978-1-4557-3112-1.00002-8

ECHA- European Chemicals Agency. An agency of the European Union. https://echa.europa.eu/home

Frank, A. P. (1987). *Modern Processing, Packaging and Distribution Systems for Food* (B. a. S. Limited, Ed. 1st ed.). Springer. https://doi.org/10.1007/978-1-4684-8592-9

Galotto, M. J., & Guarda, A. (2004). Suitability of alternative fatty food simulants to study the effect of thermal and microwave heating on overall migration of plastic packaging. *Packaging Technology and Science*, *17*(4), 219-223. https://doi.org/10.1002/pts.660

García Ibarra, V., Rodríguez Bernaldo de Quirós, A., Paseiro Losada, P., & Sendón, R. (2018). Identification of intentionally and non-intentionally added substances in plastic packaging materials and their migration into food products. *Analytical and Bioanalytical Chemistry*, *410*, 3789-3803.

Grob, K., Pfenninger, S., Pohl, W., Laso, M., Imhof, D., & Rieger, K. (2007). European legal limits for migration from food packaging materials: 1. Food should prevail over simulants; 2. More realistic conversion from concentrations to limits per surface area. PVC cling films in contact with cheese as an example. *Food Control*, *18*(3), 201-210.

Heimrich, M., Nickl, H., Bönsch, M., & Simat, T. J. (2015). Migration of cyclic monomer and oligomers from polyamide 6 and 66 food contact materials into food and food simulants: direct food contact. *Packaging Technology and Science*, *28*(2), 123-139. https://doi.org/10.1002/pts.2094

Herps, H. H. T. (2020). *Modelling and Comparative Assessment of Polyamide-6 Manufacturing towards a Sustainable Chemical Industry* Utrecht University].

Holdsworth, S. D., Simpson, R., & Ramirez, C. (2016). *Thermal processing of packaged foods. [electronic resource]* (Third edition ed.). Springer. https://ebookcentral.proquest.com/lib/massey/reader.action?docID=4182199

Hu, Y., Du, Z., Sun, X., Ma, X., Song, J., Sui, H., & Debrah, A. A. (2021). Non-targeted analysis and risk assessment of non-volatile compounds in polyamide food contact materials. *Food Chem*, *345*, 128625. https://doi.org/10.1016/j.foodchem.2020.128625

Ibarra, V. G., De Quirós, A. R. B., Losada, P. P., & Sendón, R. (2019). Non-target analysis of intentionally and non intentionally added substances from plastic packaging materials and their migration into food simulants. *Food Packaging and Shelf Life*, *21*, 100325. https://doi.org/10.1016/j.fpsl.2019.100325

Jimenez, P. S., Bangar, S. P., Suffern, M., & Whiteside, W. S. (2023). Understanding retort processing: A review. *Food Science & Nutrition*.

Jun, S., Cox, L. J., & Huang, A. (2006). Using the flexible retort pouch to add value to agricultural products. https://scholarspace.manoa.hawaii.edu/server/api/core/bitstreams/7bf18f19-0319-4bdf-aba3-61888b4465e7/content

Júnior, L. M., Cristianini, M., Padula, M., & Anjos, C. A. R. (2019). Effect of high-pressure processing on characteristics of flexible packaging for foods and beverages. *Food Research International*, *119*, 920-930. https://doi.org/10.1016/j.foodres.2018.10.078

Kim, Y. T., Min, B., & Kim, K. W. (2014). General characteristics of packaging materials for food system. In *Innovations in food packaging* (pp. 13-35). Elsevier. https://doi.org/10.1016/B978-0-12-394601-0.00002-3

Lahimer, M. C., Ayed, N., Horriche, J., & Belgaied, S. (2017). Characterization of plastic packaging additives: food contact, stability and toxicity. *Arabian journal of chemistry*, *10*, S1938-S1954. https://doi.org/10.1016/j.arabjc.2013.07.022

Lalpuria, M., Anantheswaran, R., & Floros, J. (2012). *Packaging technologies and their role in food safety*. Elsevier. https://eds-p-ebscohost-com.ezproxy.massey.ac.nz/eds/ebookviewer/ebook/ZTAwMHh3d19fNjgwNTA0X19BTg2?sid=3e230510-7295-423d-a779-c106134ba7b3@redis&vid=0&format=EB&rid=1

Limm, W., & Hollifield, H. C. (1995). Effects of temperature and mixing on polymer adjuvant migration to corn oil and water. *Food Addit Contam*, *12*(4), 609-624. https://doi.org/10.1080/02652039509374349

Lund, B. M., & Peck, M. W. (2013). Clostridium botulinum. *Guide to foodborne pathogens*, 91-111. https://doi.org/10.1002/9781118684856.ch6

Maltini, E., Torreggiani, D., Venir, E., & Bertolo, G. (2003). Water activity and the preservation of plant foods. *Food Chemistry*, *82*(1), 79-86.

Mohan, C. O., Ravishankar, C. N., Srinivasa Gopal, T. K., & Bindu, J. (2008). Thermal processing of prawn 'kuruma'in retortable pouches and aluminium cans. *International Journal of Food Science & Technology*, *43*(2), 200-207. https://doi.org/10.1111/j.1365-2621.2006.01369.x

MPI. (2021). *Guidance Document on further processing*. Wellington Retrieved from https://www.mpi.govt.nz/dmsdocument/32007-Guidance-document-Further-processing

Nerin, C., Alfaro, P., Aznar, M., & Domeno, C. (2013). The challenge of identifying non-intentionally added substances from food packaging materials: a review. *Anal Chim Acta*, *775*, 14-24. https://doi.org/10.1016/j.aca.2013.02.028

Nisticò, R. (2020). Polyethylene terephthalate (PET) in the packaging industry. *Polymer Testing*, *90*, 106707. https://doi.org/10.1016/j.polymertesting.2020.106707

O'Connor, S. L.-Q. (2020). *Effect of Retort Processing on Packaging Materials: The Changes in the Migration and Physiochemical Properties of Two Polymer Films*.

Pocas, M. F., Oliveira, J. C., Brandsch, R., & Hogg, T. (2012). Analysis of mathematical models to describe the migration of additives from packaging plastics to foods. *Journal of Food Process Engineering*, *35*(4), 657-676.

Rijk, R., & de Kruijf, N. (1993). Migration testing with olive oil in a microwave oven. *Food Addit Contam*, *10*(6), 631-645. https://doi.org/10.1080/02652039309374190

Roberts, D. W., Aptula, A., Schultz, T. W., Shen, J., Api, A. M., Bhatia, S., & Kromidas, L. (2015). A practical guidance for Cramer class determination. *Regulatory Toxicology and Pharmacology*, *73*(3), 971-984.

Sánchez-Martínez, M., Pérez-Corona, T., Cámara, C., & Madrid, Y. (2013). Migration of antimony from PET containers into regulated EU food simulants. *Food Chemistry*, *141*(2), 816-822.

Singh, A., Pratap Singh, A., & Ramaswamy, H. S. (2016). A controlled agitation process for improving quality of canned green beans during agitation thermal processing. *Journal of Food Science*, *81*(6), E1399-E1411. https://doi.org/10.1111/1750-3841.13308

Song, H. J., Chang, Y., Lyu, J. S., Yon, M. Y., Lee, H.-s., Park, S.-J., Choi, J. C., Kim, M., & Han, J. (2018). Migration study of caprolactam from polyamide 6 sheets into food simulants. *Food science and biotechnology*, *27*, 1685-1689. https://doi.org/10.1007/s10068-018-0403-4

Regulatory Report: Assessing the Safety of Food Contact Substances, (2007). http://wayback.archive-it.org/7993/20171114191242/https://www.fda.gov/Food/IngredientsPackagingLabeling/PackagingFCS/ucm064166.htm#authors

Tsironi, T. N., Chatzidakis, S. M., & Stoforos, N. G. (2022). The future of polyethylene terephthalate bottles: Challenges and sustainability. *Packaging Technology and Science*, *35*(4), 317-325. https://doi.org/10.1002/pts.2632

Vatankhah, H., Sidhu, L. S., & Ramaswamy, H. S. (2023). Retorts in the food industry. In *Thermal Processing of Food Products by Steam and Hot Water* (pp. 325-335). Elsevier. https://doi.org/10.1016/B978-0-12-818616-9.00011-0

Walden, R. (2008). The Zinetec Shaka™ retort and product quality. In *In-Pack Processed Foods* (pp. 86-101). Elsevier. https://doi.org/10.1533/9781845694692.2.86

Yates, J., Deeney, M., Rolker, H. B., White, H., Kalamatianou, S., & Kadiyala, S. (2021). A systematic scoping review of environmental, food security and health impacts of food system plastics. *Nature Food*, *2*(2), 80-87. https://doi.org/10.1038/s43016-021-00221-z

Yuan, H., Hao, Q., Su, R., Qi, W., & He, Z. (2020). Migration of phthalates from polyvinyl chloride film to fatty food simulants: experimental studies and model application. *Journal of Consumer Protection and Food Safety*, *15*, 135-143.

Zhang, S., Wu, Y., Ji, P., Ran, Q., Wang, H., Chen, B., & Wang, C. (2023). Sustainable Production of Polyamide 6 Fibers: Direct Melt Spinning and Efficient Reuse of Residual Oligomers during Polymerization. *ACS Sustainable Chemistry & Engineering*, *11*(9), 3789-3800. https://doi.org/10.1021/acssuschemeng.2c06974

Zhong, X., Zhao, X., Qian, Y., & Zou, Y. (2018). Polyethylene plastic production process. *Insight-Material Science*, *1*(1), 1-8. https://doi.org/10.18282/ims.v1i1.104

7.0 Appendix

7.1 Original Cramer Class Decision Tree from Roberts work (Roberts et al., 2015)

Number	Questions	Indepth Description
1	Is the substance a normal constituent of the body, or an optical isomer of such? If YES Class I; If NO Q2	This question throws into Class I all normal constituents of body tissues and fluids, including normal metabolites. Hormones are excluded, as are, by implication, the metabolites of environmental and food contaminants or those resulting from disease state.
2	Does the substance contain any of the following functional groups: an aliphatic secondary amine or a salt thereof, cyano, N-nitroso, diazo (e.g. CH2N2), triazeno (RN ¼ NNH2) or quaternary nitrogen, except in any of the following forms: >C]N þ R2, >C]N þH2 or the hydrochloride or sulphate salt of a primary or tertiary amine? If YES Class III; If NO Q3	Questions 2, 3 and 4 are a means of placing in Class III those structures that contain elements or valency states often associated with enhanced toxicity. Halo-, nitro-, Nnitroso- and diazocompounds, organophosphates, quaternary nitrogen compounds and similar xenobiotic structures should cause 'yes' answers to Question 2 and 3 and a 'no' answer to Question 4.
3	Does the structure contain elements other than C, H, O, N or divalent S? If YES Q4; If NO Q5	
4	Do all elements not listed in Q3 occur only as (a) a Na, K, Ca, Mg or ammonium salt of a carboxylic acid, or (b) a sulphate or hydrochloride of an amine, or (c) a Na, K, or Ca sulphonate, sulphamate or sulphate? (If the answer is yes, treat as free acid, amine, unsulphonated or unsulphated compound, except for the purposes of Q24 and Q33, and proceed). If YES Q7; If NO Class III	This is intended to let through, for further consideration, certain acid, amine, sulphonate and sulphate salts. Sulphamate salts are treated as such because they are not readily hydrolysed.
5	Is it a simply branched acyclic aliphatic hydrocarbon or a common carbohydrate? If YES Class I; If NO Q6	
6	Is the substance a benzene derivative bearing substituents consisting only of (a) hydrocarbon chains or 1' -hydroxy or hydroxy estersubstituted hydrocarbon chains and (b) one or more alkoxy groups, one of which must be para to the hydrocarbon chain in (a)? If YES Class III; If NO Q7	This places in Class III safrole, myristicin and related substances
7	Is the substance heterocyclic? If YES Q8; If NO Q16	
8	Is it a lactone or cyclic diester? If YES Q9; If NO Q10	This question separates the lactones and cyclic diesters from other heterocyclic compounds.

9	Is it a Lactone, fused to another ring, or 5- or 6-membered a,bunsaturated lactone? If YES Class III; If NO it is a lactone, from this point on, treat the structure as if it were the hydroxy acid in the form of its more stable tautomer and proceed to Q20 if it is open chain, to 10 if it is heterocyclic and to Q23 if it is carbocylic; if it is a cyclic diester, treat as the separate components.Q2. This places certain lactones known or suspected to be of unusual toxicity in Class III.	
10	Is it a 3-membered heterocycle? If YES Class III; If NO Q11	This places such substances as epoxides and ethylenimine in Class III.
11	Disregarding only the heteroatoms on any one ring, does that heterocyclic ring contain or bear substituents other than simply branched hydrocarbons (including bridged chains and monocyclic aryl or alkyl structures), alkyl alcohols, aldehydes, acetals, ketones, ketals, acids, esters (including cyclic esters other than lactones), mercaptans, sulphides, methyl ethers, hydroxy or single rings (hetero or aryl) with no substituents other than those just listed? If YES Q33; If NO Q12	Questions 11-15 separate out various categories of heteroaromatic substances. Under Q11, set aside and do not consider the atom(s), usually O, N and S, making the ring heterocyclic. If there is more than one hetero ring, regard each ring separately, with the remainder of the structure as substituents of that hetero ring. Other than the heterocyclic atom(s), does the ring carry anything besides the simple groups listed? If so, the answer is YES, and the next Question 33. If not, then classify further by Q12 et seq. Bridged-chain derivatives may be represented by structures like the bicyclic ether 1,4-cineole while monocyclic aryl derivatives may be represented by compounds like benzaldehyde propylene glycol acetal or 3-phenyl-2-furancarboxaldehyde.
12	Is it heteroaromatic? If YES Q13; If NO Q22	This question separates the aromatic heterocyclics for the purpose of considering whether they are polynuclear (Q14) or unsubstituted (Q13).
13	Does the ring bear any substituents? If YES Q14; If NO Class III	
14	Does the structure contain more than one aromatic ring? If YES Q15; If NO Q22	

15	Is it readily hydrolysed to mononuclear residues? If YES Q22; If NO Q33	If YES, treat the mononuclear heterocyclic residues by Q22 and any carbocyclic residue by Q16.
16	Is it a common terpene -hydrocarbon, -alcohol, -aldehyde or -carboxylic acid (not a ketone)? If YES Class I; If NO Q17	Q16 and Q17 deal with terpenes. A hydrocarbon terpene that is a common terpene and has not already been put in Class I by Q5, would go into Class I by Q16.
17	Is the substance readily hydrolysed to a common terpene, -alcohol, -aldehyde or -carboxylic acid? (If the answer is YES, treat the hydrolysed residues separately and proceed to Q18 for the terpene moiety and to Q19 for any non-terpenoid moiety). If YES Q18; If NO Q19	Since there may be substances that are hydrolysed to two or more residues, one of which is terpene, treat the residues separately from Q18 onward to conclusion.
18	Is the substance one of the following: (a) a vicinal diketone; or a ketone or ketal of a ketone attached to a terminal vinyl group (b) a secondary alcohol or ester of a secondary alcohol attached to a terminal vinyl group (c) allyl alcohol or its acetal, ketal or ester derivative (d) allyl mercaptan, an allyl sulphide, an allyl thioester or allyl amine (e) acrolein, a methacrolein or their acetals (f) acrylic or methacrylic acid (g) an acetylenic compound (h) an acyclic aliphatic ketone, ketal or ketoalcohol with no other functional groups and with four or more carbons on either side of the keto group (i) a substance in which the functional groups (E) are all sterically hindered. If YES Class II; If NO Class I	Q18 examines the terpenes (and later the open-chain and mononuclear substances by reference) to determine whether they contain certain structural features generally thought to be associated with some enhanced toxicity.
19	Is the substance open chain? If YES Q20; If NO Q23 Q19-21 deal with open-chain substances.	
20	Is the structure a linear or simply branched aliphatic compound, containing any one or combination of only the following functional groups: (a) four or less, each, of alcohol, aldehyde, carboxylic acid or esters and/or (b) one each of one or more of the following: acetal, either ketone or ketal but not both, mercaptan, sulphide (mono- or poly-), thioester, polyoxyethylene [(eOCH2CH2e)x with x no greater than 4], or primary or tertiary amine? If YES Q21; If NO Q22	This question should be answered YES if the structure contains one or any possible combination of alcoholic, aldehydic or carboxylic acid or ester groups, provided there are no more than four of any one kind. It should be answered YES if the structure contains in addition to, or instead of, those just listed, any assortment of no more than one each of the following: acetal, either ketone or ketal but not both, mercaptan, monoor polysulphide, thioester, polyoxyethylene, primary or tertiary amine. Answer the question NO if the structure contains more than four of any of the first set of groups, more than

		one of the second set, or any substituent not listed.
21	Does the structure contain three or more different types of functional groups (exclude methoxy and consider acids and esters as one functional type)? If YES Class III; If NO Q18	Aliphatic compounds containing three or more different functional groups (excluding methoxy) are too complex to permit satisfactory prediction of toxicity. They should go therefore, into Class III. However, we do not wish to put into Class III polyesters and similar substances, so these and the methoxy compounds get passed along to Q18.
22	Is the substance a common component of food or structurally closed related to a common component of food? If YES Class II; If NO Q33	This question places in Class II the natural, nature-identical and nearly nature-identical substances not already put into Class I by physiological occurrence or structural criteria. An artificial substance or one not closely related, goes to Q33.
23	Is the substance aromatic? If YES Q27; If NO Q24	Questions 23-26 deal with alicyclic substances.
24	Is the substance monocarbocyclic (excluding cyclopropane or cyclobutane and their derivatives) with ring or aliphatic side chains, unsubstituted or containing only alcohol, aldehyde, side-chain ketone, acid, ester, or Na, K or Ca sulphonate or sulphamate, or acyclic acetal or ketal? If YES Q18; If NO Q25	
25	Is the substance (a) a cyclopropane or cyclobutane with only the substituents mentioned in Q24 or (b) a mono- or bicyclic sulphide or mercaptan? If YES Class II; If NO Q26	
26	Does the structure contain no functional groups other than those listed in Q24 and is either a monocycloalkanone or a bicyclic compound with or without a ring ketone? If YES Class II; If NO Q22	
27	Do(es) the ring(s) have any substituents? If YES Class III; If NO Q28	Questions 27-31 deal with aromatic compounds.
28	Does the structure contain more than one aromatic ring? If YES Q29; If NO Q30	
29	Is it readily hydrolysed to mononuclear residues? (If YES, treat the individual aromatic mononuclear residues by Q30 and any other residue by Q19). If YES Q30; If NO Q33	

30	Disregarding ring hydroxy or methoxy does the ring bear substituents other than 1-5-carbon aliphatic groups, either hydrocarbon or containing alcohol, ketone, aldehyde, carboxyl or simple esters that may be hydrolysed to ring substituents of 5 or less carbons? (If a simple ester that may be hydrolysed, treat the aromatic portion by Q18 and the residue by Q19). If YES Q31; If NO Q18	This should be answered NO if the ring bears only aliphatic groups of 5 carbons or less, which are either hydrocarbon in nature or contain the groups listed. If the ring bears any other substituents than those listed, the question should be answered YES and one should proceed to Q31.
31	Is the substance an acyclic acetal, -ketal or -ester of any of the above substances (see Q30)? If YES Q18; If NO Q32	(If YES, assume hydrolysis and treat the non-aromatic residues by Q19 and the aromatic residue by Q18.) This question is simply designed to see whether the substance would fit within the definition of Q30 if it were not an acetal, a ketal or an ester. In other words, would the substance carry only the groups listed in Q30.
32	Does the substance contain only the functional groups listed in Q30, or their derivatives listed in Q31, but with any or all of the following: (a) a single fused non-aromatic carbocyclic ring, (b) aliphatic substituent chains longer than 5 carbon atoms, or (c) a polyoxyethylene [(eOCH2CH2e)x, with x no greater than 4] chain either on the aromatic ring or on an aliphatic side chain? If YES Class II; If NO Q22	Part (a) is intended to allow simple derivatives of tetralin into Class II while putting polycyclic compounds such as steroids ultimately into Class III except those that may be normal food components. Part (b) allows compounds with permitted functional groups but longer side chains into Class II instead of sending them eventually into Class III. Part (c) puts short-chain polyoxyethylene derivatives of aryl compounds into Class II rather than Class III.
33	Does the substance bear on every major structural component at least one Na, K or Ca sulphonate or sulphamate for every 20 or fewer carbon atoms without any free primary amines except those adjacent to the sulphonate or sulphamate. If YES Class III; If NO Class I	Na, K, Ca sulphonate and sulphamate salts have a strong tendency to decrease toxicity by promoting solubility and rapid excretion. This is particularly noticeable, for example, with some of the food colourings. It is important that the substance bears sufficient sulphonate groups, including one on each major structural fragment into which the original compound might be metabolised. This question serves to steer sulphonated compounds except those with amines non-adjacent to the sulphonate into a presumptively less toxic classification than the compounds would occupy if unsulphonated.

7.2 Specification Sheets

7.2.1 PA/Nylon

NYLON 尼龙.

Xiamen Changsu Industrial Co.,Ltd.
NO.268 Wengjiao Road,Haicang District,Xiamen,Fujian,China.

长塑 CHANGSU

Specification(CSTDS020301-20140530)

Supplier: Xiamen Changsu Industrial Co.,Ltd.

Material: BOPA Film

Film Type: OA1

Description: BOPA (Biaxial Oriented Polyamide) Film is made from the mix of PA-6 chips and additives. It is an advanced food packaging film with superior barrier against gas and odor. BOPA film is nicknamed "King of Films" with its extreme physical performance. It has broad applications in frozen and retort food, fresh vegetables, medicines, chemicals, electronics and etc. The features are as below:

1. Extreme flexibility, anti-impact, anti-grind
2. Total transparency and high gloss
3. Excellent printability
4. Wide range of usage temperature
5. Endurance against acid, alkali, grease and organic solvent. Such properties help extend food shelf life, and specially for perishable food.

Data:

Inspection criterion	Test method	Unit	Nominal	Min	Max
Physical / Chemical Properties (Yield Properties)					
Thickness	ISO 4593	μm	15	14.50	15.30
Density	ASTM D792	g/cm^3 , 23°C	1.14	1.12	1.16
Grammage / Unit weight		g/m^2	17.1	16.24	17.75
Yield	ASTM D4321	m^2/kg	58.48	61.58	56.33
Mechanical Properties					
Tensile strength MD/TD	ASTM D882	MPa	250/286	225/250	280/305
Tensile modulus MD/TD	ASTM D882	MPa	3400/3000	2900/2000	3800/3500
Elongation at break MD/TD	ASTM D882	%	140/115	95/80	160/145
Optical Properties					
Haze	ASTM D 1003	%	2.5	1.8	3.5
Light Transmission Rate	ASTM D 1003	%	91.5	90.5	92.5

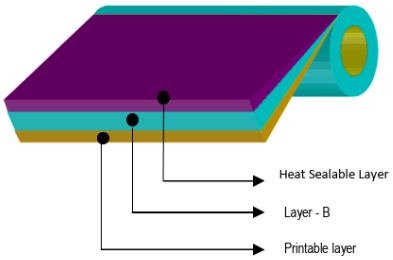
7.2.2 PET

VACOPET™
Transparent Polyester Films by Vacmet

VACOPET HSN

PRODUCT BULLETIN
Revision No-06
Issued on 23rd Feb 2017

VACOPET HSN is a co-extruded three layer transparent heat sealable polyester film suitable for packaging application. One side of this film is specially designed for heat sealing and other can be printed with Vinyl and PU based inks. Selection of inks has to be done by the user carefully in order to get good bonding of inks with the film. This film grade complies with FDA and EC regulations for food packaging.



Product Types:

HSIN –Heat Sealable surface inside, other side printable surface
HSON- Heat Sealable surface outside, other side printable surface

APPLICATION:

- Packaging
- Printing
- Lamination
- Metallization
- FRP applications

Product Data sheet

Properties		Unit	Typical Values						Test Method
Thickness [+/- 2.5%] (Nominal)		**Micron**	**12**	**15**	**19**	**20**	**23**	**30**	INTERNAL
		Gauge	**48**	**60**	**76**	**80**	**92**	**120**	
Yield(Nominal)		m^2/kg	59.7	47.8	37.7	35.8	31.2	23.9	
		in^2/lb	42000	33500	26500	25000	22000	17000	
Tensile Strength (Min)	MD	Kg/cm^2	2000	2000	2000	2000	2000	2000	ASTM D 882
	TD		2000	2000	1900	1900	1900	1900	
	MD	psi	28500	28500	28500	28500	28500	28500	
	TD		28500	28500	28500	28500	27000	27000	
Elongation at Break (Min)	MD	%	100	100	110	110	110	110	
	TD		90	90	100	100	100	100	
Heat Shrinkage (Max) @150°C, 30 minute	MD	%	2.4	2.4	2.4	2.4	2.4	2.4	ASTM D 1204
	TD		1.0	1.0	1.0	1.0	1.0	1.0	
Coefficient of Friction (Max) : Heat Seal to other surface	St	-	0.60	0.60	0.60	0.60	0.60	0.60	ASTM D 1894
	Dy		0.55	0.55	0.55	0.55	0.55	0.55	
Haze(Max)		%	2.5	2.5	3.0	3.0	3.0	3.0	ASTM D 1003
Wetting Tension(Nominal) on both surface [+/- 2]		Dyne/cm	44	44	44	44	44	44	ASTM D 2578
Heat Seal Strength(HS to HS) 140°C/3Kgs/cm2/ 2sec (Avg)		Gm/25 mm	400	400	450	450	500	500	VILS METHOD
Reel Width Tolerance		mm	-0/+4						-

❖ **Next Revision of this datasheet is due latest by Jan. 2018**

Disclaimer

The above information is believed to be reliable and accurate but is presented without guarantee on our part. Vacmet gives no warranty as to the fitness of the above product for any particular purpose and any implied warranty or condition statutory or otherwise. It is recommended to make a trial before any bulk usage.

- For product shelf life and handling & storage instructions of VACOPET products; please refer Material Safety Data sheet.
- Vacopet Material is being sold under terms of General Conditions of Sale of Vacmet India Limited.

7.3 LCMS Data

7.3.1 PET

Charge	Name	Samples	Treatment	Simulants	Change due retorting	retort	Height	Class
Pos	Glycerol monopalmitate	3x EV, 3x EC, 3x EM, 3x EH,	V, C, M, H	Ethanol	Yes	M & H	3,882,564	III
Pos	N,N-bis(2-hydroxyethyl) dodecanamide	1x EV, 2x EC, 5x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	Yes	all	612,887	III
Pos	Tributyl (E)-Aconitate	1x EL,	L	Ethanol	Yes	L	603,296	I
Pos	Caprolactam cyclic Heptamer	4x EL, 2x EM, 3x EH	L, M, H	Ethanol	Yes	All	526,935	I
Pos	Dimantine (Dymanthine)	3x AL, 1x AM,	L	Acetic Acid	Yes	M	385,095	I
Pos	DOF / 2-Ethylhexyl fumarate	6x EL,	L	Ethanol	Yes	L	298,158	I
Pos	Methylester analog of Irganox 1310	6x EL, 1x EM, 2x EH	L, M, H	Ethanol	Yes	All	256,034	III
Pos	2,2,6,6-Tetramethypiperidinol	6x EL,	L	Ethanol	Yes	L	232,090	I
Pos	D-Fructose	1x AH	H	Acetic Acid	Yes	H	210,639	I
Pos	PFTrDA / Perfluorotridecanoic acid	6x EL,	L	Ethanol	Yes	L	196,845	III
Pos	Stearylamine (ODA)	1x AL, 1x AM	L, M	Acetic Acid	Yes	M	193,233	I
Pos	Sucrose	3x EH,	H	Ethanol	Yes	H	141,048	I
Pos	LCV / Leucocrystal violet (Leucomethyl green)	1x EL	L	Ethanol	Yes	L	134,746	III
Pos	DHEPP / Diheptyl phthalate (DHP)	4x EL	L	Ethanol	Yes	L	106,838	III
Pos	Tinuvin 770	1x AL	L	Acetic Acid	Yes	L	105,597	III

Pos	Caprolactam cyclic dimer	6x EL, 1x EH,	L, H	Ethanol	Yes	L	100,656	I
Pos	N,N-bis(2-hydroxyethyl) dodecanamide	5x AL,	V, C, L, M, H	Acetic acid	Yes	L	99,390	III
Pos	PETA / Pentaerythritol triacrylate	2x AL	L	Acetic Acid	Yes	L	82,558	III
Pos	PETA / Pentaerythritol triacrylate	6x EL,	L	Ethanol	Yes	L	79,904	III
Pos	Caprolactam cyclic Heptamer	2x AM,	L, M, H	Acetic Acid	Yes	all	66,688	I
Pos	MNA / m-Nitroaniline (3-Nitroaniline)	1x EL, 1x EM, 2x EH,	L, M, H	Ethanol	Yes	L	64,889	III
Pos	Rhodamine B (C.I. Pigment Violet 1)	4x AL,	L	Acetic Acid	Yes	L	61,705	III
Pos	2,2-Diethoxyacetophenone	3x EV, 3x EC, 6x EL, 2x EM, 3x EH	V, C, L, M, H	Ethanol	No			III
Pos	2,3-Dioctylphenol	1x EV, 3x EC, 1x EM, 3x EH,	V, C, M, H	Ethanol	No			III
Pos	2-Dimethylamino-ethylbenzoate	3x EV, 3x EC, 6x EL, 2x EM, 3x EH	V, C, L, M, H	Ethanol	No			III
Pos	9-Octadecenamide (Oleamide)	2x EV, 1x EC,	V, C	Ethanol	No			III
Pos	9-Octadecenamide (Oleamide)	2x AV, 1x AC,	V, C	Acetic Acid	No			III
Pos	Abietic acid	3x EV, 3x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			III
Pos	Abietic acid	3x AV, 3x AC, 3x AM, 3x AH,	V, C, M, H	Acetic Acid	No			III
Pos	BBOT / 2,5-bis(5-tert-Butyl-2-benzoxazolyl)thiophene	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	Bis 2,4-di-tert-butylphenyl phosphite	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	Bis-HPPP / Bisphenol A bis(2,3-dihydroxypropyl) ether	3x AV,	V	Ethanol	No			III
Pos	Bis-HPPP / Bisphenol A bis(2,3-dihydroxypropyl) ether	3x EV,	V	Acetic Acid	No			III

Pos	DIUP / Diisoundecyl phthalate	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	DMDBA / Bis (3,4-dimethyl-dibenzylidene sorbitol)	3x EV, 1x EM, 3x EH,	V, M, H	Ethanol	No			III
Pos	Dodecanamide	3x EV, 2x EC, 1x EM, 2x EH,	V, C, M, H	Ethanol	No			III
Pos	Dodecanamide	2x AV, 3x AM, 1x AH	V, C, M, H	Acetic Acid	No			III
Pos	Erucamide (Erucic amide)	3x EV, 3x EC, 5x EL, 2x EM, 3x EH	V, C, M, H	Ethanol	No			III
Pos	Irgafos 168 Phosphate	2x EV, 3x EC, 1x EL, 1x EM, 1x EH,	V, C, L, M, H	Ethanol	No			III
Pos	Mono-n-octyl phthalate	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	Monopentyl phthalate	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	N,Nâ€™-Ethylenebis(stearamide)	2x EV, 1x EC, 1x EM, 2x EH,	V, C, M, H	Ethanol	No			III
Pos	N'N-Dibutylformamide	3x EV, 3x EC, 1x EM,	V, C, M	Ethanol	No			III
Pos	Phthalic anhydride	3x EV, 2x EC, 5x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	Stearamide (Octadecanamide)	1x EV, 6x EL, 1x EM, 2x EH,	V, L, M, H	Ethanol	No			III
Pos	Stearamide (Octadecanamide)	2x AV,1x AM,	V, L, M, H	Acetic Acid	No			III
Pos	Tetradecamethylcycloheptasiloxane (D7)	3x EV, 3x EC, 1x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			III
Pos	TPPA / Triphenyl phosphate	3x EV, 3x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			III
Pos	Triester analog of Irganox 1010	3x EV, 3x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			III
Pos	Trimethylolpropane diacrylate 3-(hexamethyleniminyl)propionate	2x EV, 2x EM, 2x EH,	V, M, H	Ethanol	No			III
Pos	12-Hydroxystearic acid	3x EV, 3x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			II

Pos	Irganox 1010	3x EV, 3x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			II
Pos	Isobornyl acrylate	3x EV, 3x EC, 2x EL, 2x EM, 2x EH,	V, C, L, M, H	Ethanol	No			II
Pos	1-Stearoylglycerol (1-Monostearin)	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			I
Pos	2-Ethylhexyl benzoate	3x EV, 3x EC, 6x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			I
Pos	2-Ethylhexyl benzoate	1x AV, 3x AC, 6x AL, 1x AM 3x AH	V, C, L, M, H	Acetic Acid	No			I
Pos	4-Ethoxy-4-isopropyl-methylcyclohexene	2x AV, 3x AM, 1x AH,	V, C, M, H	Acetic Acid	No			I
Pos	4-Ethoxy-4-isopropyl-methylcyclohexene	2x EV, 2x EC, 1x EM, 2x EH,	V, C, M, H	Ethanol	No			I
Pos	4-Methoxybenzoic acid (4-Anisic acid)	1x EL	L	Ethanol	No			I
Pos	ATBC / Tributyl acetylcitrate	3x EV, 6x EL, 1x EM, 3x EH,	V, C, M, H	Ethanol	No			I
Pos	Caprolactam cyclic Trimer	1x AV	V	Acetic Acid	No			I
Pos	DBZP / Dibenzyl phthalate	2x EV, 3x EC,	V, Cl	Ethanol	No			I
Pos	DDP / Didecyl phthalate	3x EV, 2x EC, 1x EM, 2x EH,	V, C, M, H	Ethanol	No			I
Pos	DDP / Didecyl phthalate	1x AC	V, C, M, H	Acetic Acid	No			I
Pos	DEHP / Di(2-ethylhexyl) phthalate	3x EC, 3x EV, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			I
Pos	Dioctyl Decanedioate	3x EV, 1x EC, 1x EL, 2x EM, 3x EH,	V, C, L, M, H	Ethanol	No			I
Pos	Eicosenamide	1x EV, 2x EC,	V, Cl	Ethanol	No			I
Pos	Hexylamine	1x EC	C	Ethanol	No			I
Pos	Icosanol	3x EV, 1x EC, 2x EM, 3x EH	V, C, M, H	Ethanol	No			I
Pos	Linolenic Acid	2x AV, 2x AH,	V, H	Acetic Acid	No			I

Pos	N-Lauryldiethanolamine	3x EV, 1x EC, 2x EM, 3x EH,	V, C, M, H	Ethanol	No			I
Pos	Oleic Acid	1x AC, 5x AL, 2x AM, 2x AH,	V, C, L, M, H	Acetic Acid	No			I
Pos	Oleic Acid	1x EV, 2x EC, 5x EL, 1x EM, 1x EH	V, C, L, M, H	Ethanol	No			I
Pos	Palmitamide (Hexadecanamide)	2x EV, 2x EL, 1x EM, 3x EH,	V, L, M, H	Ethanol	No			I
Pos	Palmitamide (Hexadecanamide)(ISOMER 1)	1x EV, 3x EC, 1x EM	V, C, M	Ethanol	No			I
Pos	Palmitic acid	1x AV, 2x EV, 2x EC,	V, C, M, H	Acetic Acid	No			I
Pos	Palmitic acid	2x EM, 3x EH,	V, C, M, H	Ethanol	No			I
Pos	Triethylene glycol bis(2-ethylhexanoate)	3x EV, 3x EC, 2x EM, 3x EH	V, C, M, H	Ethanol	No			I

7.3.2 PA

Charge	Name	Samples	Temperature	Stimulants	Change due retorting	Retort	Height	Class
Pos	Glycerol monopalmitate	2x EL, 1x EM	L, M	Ethanol	Yes	L & M	4,950,603.13	III
Pos	DHEPP / Diheptyl phthalate (DHP)	6x EL	L	Ethanol	Yes	L	2,957,640.80	III
Pos	DHEPP / Diheptyl phthalate (DHP)	3x AL	L	Acetic acid	Yes	L	2,745,916.00	III
Pos	Phenyl-bis-(2,4,6-trimethylbenzoyl)-phosphine oxide	1x AH	H	Acetic Acid	Yes	H	427,911.47	III
Pos	PFBA / Perfluorobutanoic acid (Heptafluorobutyric acid)	5x EL	L	Ethanol	Yes	L	396,915.60	III
Pos	PFBA / Perfluorobutanoic acid (Heptafluorobutyric acid)	4x AL,	L	Acetic acid	Yes	L	341,070.40	III
Pos	Vinyl caprolactam	1x EL,	L	Ethanol	Yes	L	324,281.60	III
Pos	Cyanox 1791	6x EL	L	Ethanol	Yes	L	297,840.80	III
Pos	Cyanox 1790	3x AL	L	Acetic acid	Yes	L	288,068.80	III
Pos	Irganox 245 (Antioxidant 245)	2x EC, 1x EL, 1x EM, 1x EH	C, L, M, H	Ethanol	Yes	L	278,505.60	III
Pos	Irganox 3114	5x EL	L	Ethanol	Yes	L	265,594.40	III
Pos	Irganox 245 (Antioxidant 245)	\ 4x AL, 2x AM, 2x AH,	C, L, M, H	Acetic acid	Yes	L	263,063.20	III
Pos	Vinyl caprolactam	1x AL,	L	Acetic acid	Yes	L	261,125.20	III
Pos	N,N-bis(2-hydroxyethyl) dodecanamide	1x AC, 3x AL, 3x AM, 2x AH,	C, L, M, H	Acetic Acid	Yes	L	189,778.00	III

Pos	LCV / Leucocrystal violet (Leucomethyl green)	4x AL	L	Acetic Acid	Yes	L	138,580.80	III
Pos	BKF (Cyanox 2246) (2,2â€²-methylene-bis(6-tert-butyl-4-methylphenol))	4x AL,	L	Acetic Acid	Yes	L	124,438.40	III
Pos	Irgacure 1800	1x EL	L	Ethanol	Yes	L	122,553.20	III
Pos	Irgacure 1800	1x AL,	L	Acetic acid	Yes	L	117,211.20	III
Pos	Irganox MD1024	5x EL	L	Ethanol	Yes	L	114,582.40	III
Pos	N-Nitrosopiperidine	2x EL,	L	Ethanol	Yes	L	101,705.20	III
Pos	Methylester analog of Irganox 1310	5x EL	L, M	Ethanol	Yes	L & M	79,947.20	III
Pos	Methylester analog of Irganox 1310	3x AL, 1x AM	L, M	Acetic acid	Yes	L & M	79,268.80	III
Pos	TEHP / Tris(2-ethylhexyl)phosphate	1x AM	M	Acetic Acid	Yes	M	75,742.20	III
Pos	Irgafos 168 (Antioxidant 168)	1x EL	L	Ethanol	Yes	L	72,534.00	III
Pos	N-Nitrosopiperidine	2x AL	L	Acetic acid	Yes	L	66,638.00	III
Pos	Methenamine	2x AL	L	Acetic acid	Yes	L	63,563.20	III
Pos	Crystal Violet (Methyl violet) (Basic Violet 3)	1x AM	M	Acetic Acid	Yes	M	63,076.61	III
Pos	Isopropyl diphenylamine	1xEL	L	Ethanol	Yes	L	61,023.60	III
Pos	Tetradecamethylcycloheptasiloxane (D7)	4x EL	L	Ethanol	Yes	L	59,936.00	III
Pos	Tetradecamethylcycloheptasiloxane (D7)	2x AL,	L	Acetic acid	Yes	L,	54,710.40	III
Pos	Irgafos 168 (Antioxidant 168)	1x AL	L	Acetic acid	Yes	L	50,702.00	III
Pos	Chrysoidine	1x EL	L	Ethanol	Yes	L	50,614.80	III

Neg	Irganox 1081 (Thioalkofen BP)	1x EM	M	Ethanol	Yes	M	22,799.48	III
Neg	Phenol	1x EL	L	Ethanol	Yes	L	22,240.40	III
Pos	Monoester analog of Irganox 1010	2x AL	L	Acetic Acid	Yes	L	81,559.20	II
Neg	Isobornyl acrylate	2x El	L	Ethanol	Yes	L	27,497.60	II
Pos	Caprolactam cyclic Heptamer	3x AH, 2x AL, 2x AM	L, M, H	Acetic acid	Yes	M	17,931,200.00	I
Pos	Caprolactam cyclic Tetramer	3x EL	L	Ethanol	Yes	L	7,610,231.60	I
Pos	Caprolactam cyclic Tetramer	4x AL, 1x AH	L, H	Acetic acid	Yes	L & H	7,001,144.00	I
Pos	DOF / 2-Ethylhexyl fumarate	3x AL	L	Acetic acid	Yes	L	6,512,872.40	I
Pos	DOF / 2-Ethylhexyl fumarate	5x EL,	L	Ethanol	Yes	L	6,356,723.20	I
Pos	Caprolactam cyclic dimer	2x EC, 6x EL	C, L, H	Ethanol	Yes	L	5,522,108.80	I
Pos	Caprolactam cyclic dimer	1x AH, 2x AL	C, L, H	Acetic acid	Yes	L	5,030,130.40	I
Pos	Caprolactam cyclic Hexamer	3x AL, 2x AH,	L, H	Acetic acid	Yes	L &H	912,854.80	I
Pos	Caprolactam cyclic Trimer	2x AC, 2x AM,	C, M	Acetic acid	Yes	M	905,741.20	I
Pos	N-Methyldiethanolamine	5x EL	L	Ethanol	Yes	L	431,919.60	I

Pos	Dimantine (Dymanthine)	2x AM, 2X AH	M, H	Acetic Acid	Yes	H	428,387.56	I
Pos	Pentaethyleneglycol	1x AL	L	Acetic acid	Yes	L	342,146.00	I
Pos	2,4,5-Trimethylaniline	1x EL	L	Ethanol	Yes	L	260,247.60	I
Pos	2,4,5-Trimethylaniline	2x AL,	L	Acetic acid	Yes	L	255,472.00	I
Pos	2-Ethylhexyl benzoate	3x AC, 3x AM, 1x AH,	C, M, H	Acetic Acid	Yes	M	245,863.00	I
Pos	OD PABA / Octyldimethyl PABA (Padimate O)	2x AL	L	Acetic acid	Yes	L	240,701.60	I
Pos	OD PABA / Octyldimethyl PABA (Padimate O)	3x EL,	L	Ethanol	Yes	L	226,604.40	I
Pos	Stearylamine (ODA)	1x AH	L, H	Acetic Acid	Yes	L & H	219,837.98	I
Pos	Hexylamine	2x AC, 3x AM, 2x AH	C, M, H	Acetic acid	Yes	H	186,423.92	I
Neg	2-Ethylhexyl benzoate	4x EL	L	Ethanol	Yes	L	173,597.20	I
Pos	Pentaethyleneglycol	2x EL,	L	Ethanol	Yes	L	93,230.40	I
Pos	Stearylamine (ODA)	1x EL,	L, H	Ethanol	Yes	L & H	80,497.20	I
Pos	PPD / p-Phenylenediamine	4x AL	L	Acetic Acid	Yes	L	73,621.60	I
Pos	TIPA / Triisopropanolamine	4x AL	L	Acetic Acid	Yes	L	65,935.20	I
Neg	Lauryl hydrogen sulfate	4x EL	L	Ethanol	Yes	L	54,653.20	I
Neg	3,5-di-tert-butyl-4-hydroxyacetophenone	2x EL	L	Ethanol	Yes	L	52,449.20	I
Pos	Glycerol (Glycerine)	1x EL	L	Ethanol	Yes	L	52,291.20	I
Neg	Mesitaldehyde	3x EL	L	Ethanol	Yes	L	51,096.80	I

Neg	Lactic acid	3xEL	L	Ethanol	Yes	L	48,403.20	I
Neg	Caprolactam cyclic dimer	4x EL	L	Ethanol	Yes	L	34,192.80	I
Neg	2-Heptenoic acid	1x EL	L	Ethanol	Yes	L	29,700.40	I
Neg	Azelaic Acid	1x EC, 2x EL	C, L	Ethanol	Yes	L	29,289.60	I
Pos	PTBP / 4-tert-Butylphenol		L	Ethanol	Yes	L	50,186.80	
Pos	Irgafos 168 Phosphate	2x EC, 5x EL	L, M	Ethanol	No			III
Pos	Caprolactam	3x AC,1x AL,3x AM, 2x AH	L, C, M, H	Acetic acid	No			III
Pos	Caprolactam	1x EC, 1x EM	C, M	Ethanol	No			III
Pos	Abietic acid	2x EC,1x EM	C, L, M	Ethanol	No			III
Pos	Abietic acid	3x AC, 3x AM, 3x AL	C, L, M	Acetic acid	No			III
Pos	N,Nâ€™-Ethylenebis(stearamide)	2x EC 1x EM,	L, M	Ethanol	No			III
Pos	Isobornyl acrylate	3x EV, 1x EC, 1x EM, 1x EL	C, L	Ethanol	No			II
Pos	12-Hydroxystearic acid	2x EC, 1x EM	V, C, M	Ethanol	No			II
Pos	Isobornyl methacrylate	1x EL, 1x EC	L, C	Ethanol	No			II
Pos	Caprolactam cyclic Heptamer	1x EC,4x EL,	C, L,	Ethanol	No			I
Neg	Caprolactam cyclic Heptamer	4x EL, 3x EC, 1x EM	C, L, M	Ethanol	No			I
Pos	Caprolactam cyclic Pentamer	3x AV, 3x AC, 4x AL, 1x AM, 2x AH	V, C, L, M, H	Acetic acid	No			I
Pos	Oleic Acid	3x AL, 3x AC, 3x AM, 2x AH	C, L, M, H	Acetic Acid	No			I
Pos	Caprolactam cyclic Trimer	1x EC	C,	Ethanol	No			I
Pos	Caprolactam cyclic Hexamer	1x Ec, 1x EL	C, L	Ethanol	NO			I
Pos	Caprolactam cyclic Octamer	4x EL, 1x EC, 1x EM,	C, L, M	Ethanol	No			I
Pos	ATBC / Tributyl acetylcitrate	5x EL, 1x EC,	C, L	Ethanol	No			I
Pos	Palmitic acid	2x EC, 1x EM	M, C	Ethanol	No			I

Pos	Caprolactam cyclic Pentamer	1x EC	C,	Ethanol	No			I
Pos	Caprolactam cyclic Octamer	2x AC, 1x AM	C, M	Acetic acid	No			I
Pos	Sucrose	1x EC	C	Ethanol	No			I
Pos	Bis-HPPP / Bisphenol A bis(2,3-dihydroxypropyl) ether	1x EC	C	Ethanol	No			III
Neg	3,5-di-tert-butyl-4-hydroxybenzaldehyde	2x EL, 1x EC	L	Ethanol	No			

7.3.3 PE

Charge	Name	Samples	Temperature	Stimulants	Change due retorting	Worest Retort	Height	Class
Pos	Palmitamide (Hexadecanamide)	4x EL,	L	Ethanol	Yes	L	1,147,777.60	I
Pos	Tributyl (E)-Aconitate	1x EL	L	Ethanol	Yes	L	646,629.60	I
Pos	Isobornyl acrylate	2x EV, 1x EC, 1x EL, 3x EM, 1x EH,	V, C, L, M, H	Ethanol	Yes	M	608,017.53	II
Pos	Caprolactam cyclic Heptamer	5x EL, 1x EH,	L, H	Ethanol	Yes	L & H	435,592.80	I
Pos	Isobornyl acrylate (Isomer 2)	3x EL,	L	Ethanol	Yes	L	305,496.80	II
Pos	Isobornyl acrylate (Isomer 2)	3x AL,	L	Acetic acid	Yes	L	302,152.40	II
Neg	1,3-Diisopropylbenzene	2x EM	M	Ethanol	Yes	M	268,049.86	I
Pos	N,N-bis(2-hydroxyethyl) dodecanamide	3x EC, 5x EL, 3x EM,1x EH	C, L, M, H	Ethanol	Yes	M &L	255,409.60	III
Pos	Caprolactam cyclic Tetramer	4x EL	L	Ethanol	Yes	L	240,564.40	I
Neg	3,5-di-tert-butyl-4-hydroxyacetophenone	2x EL, 2x EM,	L, M	Ethanol	Yes	M	233,659.80	I
Pos	2,2,6,6-Tetramethypiperidinol	5x EL	L	Ethanol	Yes	L	224,462.00	I
Pos	DOF / 2-Ethylhexyl fumarate	4x EL	L	Ethanol	Yes	L	222,667.20	I
Pos	Dimantine (Dymanthine)	2x EM, 1x EH,	M, H	Ethanol	Yes	M & H	221,162.65	I
Pos	PFTrDA / Perfluorotridecanoic acid	5x EL	L	Ethanol	Yes	L	197,840.00	III
Pos	N,N-bis(2-hydroxyethyl) dodecanamide	1x AC, 4x AL, 1x AH, 3x AM,	C, L, M, H	Acetic acid	Yes	M & L	169,254.00	III

Pos	Sucrose	1x EM	M	Ethanol	Yes	M	162,656.51	I
Neg	Mesitaldehyde	1x EH	H	Ethanol	Yes	H	127,684.82	I
Neg	Bisphenol A ethoxylate	1x EV, 1x EC, 3x EM, 1x EH	V, C, M, H	Ethanol	Yes	M & H	117,776.13	III
Pos	Neopentyl glycol diacrylate	5x EL,	L	Ethanol	Yes	L	116,432.40	I
Neg	Caprolactam cyclic Heptamer	5x EL, 1x EH	L, H	Ethanol	Yes	H	112,052.75	I
Pos	Stearylamine (ODA)	2x EM, 1x EH	M, H	Ethanol	Yes	M & H	107,729.08	I
Pos	Methylester analog of Irganox 1310	1x EC, 3x EM, 5x EL,	C, L, M	Ethanol	Yes	M & L	93,475.29	III
Pos	TPPA / Triphenyl phosphate	3x EV, 3x EC, 3x EM, 1x EH	V, C, L, M, H	Ethanol	yes	H	72,661.01	III
Pos	Caprolactam cyclic dimer	2x EL,	L	Ethanol	Yes	L	65,678.00	I
Pos	Methylester analog of Irganox 1310	2x AL, 2x AM,	C, L, M, H	Acetic acid	Yes	M	60,743.95	III
Neg	1H-Inden-5-ol, 2,3-dihydro-3-(4-hydroxyphenyl)-1,1,3-trimethyl-	2x EM,1x EH	M, H	Ethanol	Yes	M	59,978.62	III
Neg	2-Cyclohexylphenol	2x EM	M	Ethanol	Yes	M	54,768.34	III
Pos	Dimantine (Dymanthine)	1x AM,	M	Acetic acid	Yes	M	54,036.01	I
Neg	PTBP / 4-tert-Butylphenol	4x EL,	L	Ethanol	Yes	L	47,616.40	I
Neg	3,5-di-tert-butyl-4-hydroxybenzaldehyde	2x EL	L	Ethanol	Yes	L	47,160.00	II
Neg	2-Butoxyethyl 4-(dimethylamino)benzoate	6x EL, 3x EM, 1x EH	L, M, H	Ethanol	Yes	M	46,840.74	III
Neg	AZELAIC ACID	1x EC, 1x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	Yes	M & H	36,078.77	I
Neg	Monoester analog of Irganox 1010	1x EC, 1x EM	C,M	Ethanol	Yes	M	34,979.83	II

Neg	Irganox 1081 (Thioalkofen BP)	1x EM	M	Ethanol	Yes	M	29,191.11	III
Neg	6-Methylheptyl methacrylate	1x EH	H	Ethanol	Yes	H	28,368.15	II
Neg	Cyclohexaneacetic acid	2x EC, 1x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	Yes	M & H	23,062.80	I
Neg	BHT-quinone methide (2,6-di-tert-butyl-4-methylene-2,5-cyclohexandienone)	1x EH	H	Ethanol	Yes	H	21,977.95	I
Neg	DBM / Dibutylmaleate	2x EM,	M	Ethanol	Yes	M	21,843.39	I
Pos	2-Butoxyethyl 4-(dimethylamino)benzoate	1x EV, 5x EL, 1x EM, 1x EH	C, L, M, H	Ethanol	No			III
Pos	2-Butoxyethyl 4-(dimethylamino)benzoate	1x AC, 4x AL, 3x AM, 1x AH	C, L, M, H	Acetic acid	No			III
Pos	2,3-Dioctylphenol	1x EC, 2x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	2-Dimethylamino-ethylbenzoate	3x EC,5x EL,3x EM,1x EH	C, L, M, H	Ethanol	No			III
Pos	Abietic Acid	3x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	Abietic Acid	3x AC, 3x AM, 1x AH	C, M, H	Acetic acid	No			III
Pos	BBOT / 2,5-bis(5-tert-Butyl-2-benzoxazolyl)thiophene	3x EC, 5x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III
Pos	Bis 2,4-di-tert-butylphenyl phosphite	3x EC, 5x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III
Neg	Bisphenol TMC	1x EC	C	Ethanol	No			III
Pos	DIUP / Diisoundecyl phthalate	3x EC, 5x EL, 3x EM, 3x EH	C, L, M, H	Ethanol	No			III
Pos	DMDBA / Bis (3,4-dimethyl-dibenzylidene sorbitol)	1x EC	C	Ethanol	No			III
Pos	Dodecanamide	2x EC, 2x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	Erucamide (Erucic amide)	3x EC, 1x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III

Pos	Erucamide (Erucic amide)	4x AL,	L,	Acetic acid	No			III
Pos	Glycerol monopalmitate	3x EC, 6x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III
Pos	Irgafos 168 Phosphate	2x EC, 4x EL, 3x Em, 1x EH	C, L, M, H	Ethanol	No			III
Pos	Mono-n-octyl phthalate	3x EC, 5x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III
Pos	Monopentyl phthalate	3x EC, 5x EL, 3x EM	C, L, M	Ethanol	No			III
Pos	N,Nâ€™-Ethylenebis(stearamide)	1x EC, 2x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	N'N-Dibutylformamide	3x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	Phthalic anhydride	3x EC, 5x EL, 2x EM, 1x EH	C, L, M, H	Ethanol	No			III
Pos	Stearamide (Octadecanamide)	2x EC, 5x EL, 1x EM	C, L, M	Ethanol	No			III
Pos	Tetradecamethylcycloheptasiloxane (D7)	3x EC, 3x EL, 3x EM, 1x EH	C, L, M, H	Ethanol	No			III
Neg	Triester analog of Irganox 1010	1x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	Triester analog of Irganox 1010	3x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			III
Pos	12-Hydroxystearic acid	3x EC, 3x EM, 3x EH	C, M, H	Ethanol	No			II
Pos	2,2-Diethoxyacetophenone	3x EC, 5x EL, 3x EM, 1x EH,	C, L, M, H	Ethanol	No			II
Pos	2,2-Diethoxyacetophenone	3x AC, 2x AM, 1x AH,	C, M, H	Acetic acid	No			II
Pos	Irganox 1010	3x EC, 3x EM, 1x EH,	C, M, H	Ethanol	No			II
Pos	Isobornyl acrylate	2x AC, 2x AM,	C, L, M, H	Acetic acid	No			II
Pos	Isobornyl acrylate (ISOMER 1)	2x EC, 1x EL,	C, L	Ethanol	No			II

Pos	1-Stearoylglycerol (1-Monostearin)	3x EC, 5x EL, 3x EM, 1x EH	C ,L, M, H	Ethanol	No			I
Neg	2-Ethylhexyl benzoate	2x EC, 1x EL, 3x EM, 1x EH,	C ,L, M, H	Ethanol	No			I
Pos	2-Ethylhexyl benzoate	3x EC, 5x EL, 3x EM, 1x EH,	C ,L, M, H	Ethanol	No			I
Pos	2-Ethylhexyl benzoate	3x AC, 3x AM,1x AH,	C, M, H	Acetic acid	No			I
Pos	4-Ethoxy-4-isopropyl-methylcyclohexene	2x EC, 2x EM,1x EH,	C, M, H	Ethanol	No			I
Pos	ATBC / Tributyl acetylcitrate	2x EC, 5x EL, 1x EH,	C ,L, M, H	Ethanol	No			I
Pos	ATBC / Tributyl acetylcitrate	1x AC, 1x AM, 1x AH,	C, M, H	Acetic acid	No			I
Pos	DBZP / Dibenzyl phthalate	3x EC, 3x EM,	C, M	Ethanol	No			I
Pos	DDP / Didecyl phthalate	3x EC, 3x EM, 1x EH,	C, M, H	Ethanol	No			I
Pos	DEHP / Di(2-ethylhexyl) phthalate	3x EC, 2x EM,	C, M	Ethanol	No			I
Pos	Dioctyl Adipate	3x EC, 3x EM,1x EH	C, M, H	Ethanol	No			I
Pos	Dioctyl Decanedioate	4x EL, 3x EM, 1x EH	L, M, H	Ethanol	No			I
Pos	Eicosenamide	1x EC, 1x EM	C, M	Ethanol	No			I
Pos	Hexylamine	1x EC,	C	Ethanol	No			I
Pos	Icosanol	2x EC, 2x EM,	C , M	Ethanol	No			I
Pos	Linolenic Acid	3x EC, 1x EH	C, H	Ethanol	No			I
Pos	N-Lauryldiethanolamine	2x EC, 2x EM,	C, M	Ethanol	No			I
Pos	Palmitamide (Hexadecanamide)(ISOMER 1)	3x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			I

Pos	Palmitic acid	2x EC, 2x EM, 1x EH	C, M, H	Ethanol	No			I
Pos	Propyl 3,4,5-trihydroxybenzoate (Propyl gallate)	1x AC	C	Acetic acid	No			I
Pos	Triethylene glycol bis(2-ethylhexanoate)	3x EC, 3x EM, 1x EH	C, M, H	Ethanol	No			I