



Novel Oxygen Scavenger Systems for Functional Coatings

Mariia Demicheva

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<p>Abstract:</p> <p>This thesis work was aimed at developing a novel oxygen scavenging material suitable for being used in functional coatings. It provided an overview of existing oxygen scavenging systems and technologies, and defined the restriction in using them for food applications. The major objective of this study was creating, optimizing and testing oxygen scavenging substances based on polybutadiene. The study was conducted in October 2014 – January 2015 at Evonik Industries AG situated in Hanau, Germany.</p> <p>The empirical part of this study was conducted at the laboratories of Evonik Industries AG. The recipe for suggested oxygen scavenging material was tested with two polybutadiene types of different isomeric structures and various amounts of additives. The results of the experiments were compared in order to reveal samples with highest oxygen absorption capacity.</p> <p>The experiments resulted in obtaining the material possessing high oxygen scavenging capacity of approximately 26% (mass of oxygen by mass of polybutadiene used), which is relatively close to theoretically suggested maximum. The data obtained during the experiments were not enough to clearly determine the most effective polybutadiene type for oxygen absorption.</p> <p>This thesis suggested the potential oxygen scavenging system based on the obtained material, including possible application methods of the material in functional coatings.</p>	
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Abbreviations, symbols and nomenclature

BHT	butylated hydroxy toluene
°C	degree Celsius
EU	European Union
EVA	ethylene-vinyl acetate
EVOH	ethylene-vinyl alcohol copolymers
MAP	modified atmosphere packaging
PE-LD	low density polyethylene
PVC	polyvinyl chloride
SML	specific migration limits
TBHQ	tert-butylhydroquinone
T _g	glass transition temperature
UV	ultraviolet
A _r	atomic weight

FOREWORD

1 INTRODUCTION

This thesis concerns itself with oxygen scavenging systems for functional coatings. The main focus is on polybutadienes as polymeric materials having good oxygen scavenging potential. First part of the thesis gives a literature review of existing oxygen scavenging technologies and points out those using polybutadiene. It also defines the legal restrictions which apply to using polybutadiene in food applications.

1.1 Background

In the modern world with a tendency to globalization the need for delivering fresh food over long distances while retaining acceptable prices made food preservation technologies very important (Rajeev *et al.* 2011 n.p.). Such means as protective packaging may decrease the amounts of food being lost during processing. In third world countries, where the protective packaging is not used, 30-50% of food is wasted, whereas only 2-3% is lost in developed countries (Fellows 2009 p.770).

Several reasons may cause food spoilage during transportation and storage including microbial growth, chemical interactions in-between the composing elements of the food, action of enzymes that are present in the products, etc. (Tucker 2008 n. p.). Some of those reasons are related to presence of oxygen around the product during storage.

One of the ways to avoid oxygen-related food deterioration reactions, changes in colour, texture and flavour is using modified atmosphere packaging (MAP). In MAP the atmosphere around the food inside the packaging is being changed to a predetermined mixture of gases (Corbo & Bevilacqua 2010 p.196). In this way, the amount of oxygen around the product is being minimized. However, according to Solovyov (2014 p.1), the MAP does not allow to achieve an oxygen content low enough for long storage time of the product. Typically, oxygen contents of 0.1-2% are being obtained, and these values may increase when the food is porous and additional oxygen migrates from within the food into the packaging volume (Vermeiren *et al.* 2003 p.23). Also oxygen tends to penetrate into the package through the packaging material (Byun *et al.* 2011 p.615). Permeability coefficients characterize the amount of oxygen that is able to penetrate through the packaging materials. For instance, in

polymers these coefficients vary from as high as $1.74 \cdot 10^{-12} \text{ m}^3/\text{m}^2 \text{ s Pa}$ for cellulose acetobutyrate to only $5.44 \cdot 10^{-16} \text{ m}^3/\text{m}^2 \text{ s Pa}$ for polyvinyl fluoride (Dominghaus *et al.* 2008).

In order to remove residual and penetrating oxygen from the modified atmosphere package, scavenging materials are being used. They are chemically tying free oxygen, preventing it from causing deteriorative reactions (Solovyov 2014 p.1). Packaging technologies involving both modified atmosphere and oxygen scavengers are classified as active packaging (Siro 2011 p.23). Oxygen scavenging active packaging technologies secure the condition of products (both visual and physical) and prolong their shelf-life (Lagarón 2011 p. 32).

There are several ways of incorporating the scavengers into the packaging system. They can be placed or attached to the inner space as separated sachets or labels, containing the scavenging materials, or can be embodied into the material of the package (Charles *et al.* 2006). Scavengers, incorporated into the material of the package, are seen as being advantageous over sachets, since the latter can be accidentally consumed by people if confused with a part of the product (Akelah 2013 p.330). Various studies describe plastic packaging materials with scavenging components incorporated into the structure. According to Brody *et al.* (2001 p.80), the idea of oxygen scavenging plastics became popular only at the very end of the last century. Since then various technologies were described, such as producing sandwich materials with scavenging layers, pellets with oxygen absorbing properties that can be incorporated into packaging material, ready-to-apply absorbing films and coatings with oxygen scavenging properties (Brody *et al.* 2001; Järnström, 2013). There are not so many technologies invented yet that could be commercially used for food applications due to the sensitivity of the legal regulations in this field.

1.2 Objectives

This thesis aims to develop a new type of oxygen scavenging material based on polybutadiene that can be used in functional coatings and in combination with modified atmosphere packaging. Thereby there are the following objectives to fulfil:

- Create and optimize the recipe of oxygen scavenging material samples, their preparation procedure and amount of additives used;

- Define experimentally the oxygen absorption characteristics of chosen polybutadiene-based samples with predefined amounts of catalysts;
- Suggest the recipe and potential application methods for tested oxygen scavenging substances.

2 LITERATURE REVIEW

2.1 Existing oxygen scavenging systems

Brody *et al.* (2001) define oxygen scavengers as “Materials incorporated into package structures that chemically combine with, and thus effectively remove, oxygen from the inner package environment”. In this paragraph we will consider and describe major oxygen removing systems starting from their early appearance in literature, and classify them.

First publications related to removing the oxygen appeared during the second decade of last century (Brody *et al.* 2001). The reported mechanisms used ferrous sulphate together with moisture absorbers (Brody *et al.* 1995 p.10).

The first patent of the oxygen consuming substance was assigned in Finland already in 1938 and was related to removing the remaining oxygen from metallic packaging (Cruz 2012). However, the early commercial scavenging system became available only in 1970s in Japan with a trading name “Ageless®” (Herman 2014). It was an iron-based system packed into permeable sachets (Herman 2014 p.1, Solovyev 2014 p.5). The components in the sachets were activated in high humidity conditions in the presence of electrolytes such as sodium chloride to accelerate the reaction (Solovyev 2014 p.8). “Ageless®” oxygen scavengers are produced until now by their developer Mitsubishi Gas Chemical Company, along with other types of oxygen scavenging products (MITSUBISHI Gas Chemical America, Inc. 2014).

In 1960s – late 1980s such technologies were invented as blending antioxidants and enzymes into thermoplastics to reduce the gas permeability, embodying sulphites into multilayer packaging materials, ascorbic acid-based oxygen scavengers and singlet oxygen converting and accepting films with photosynthesizing dyes (Brody *et al.* 1995 p.13; Brody *et al.* 2001 pp.35-36).

In 1990s popularity came to the idea of incorporating scavengers into packaging systems as a substitute to sachets, which was released in the forms of films, closure liners, trays, tubes, etc. (Herman 2014 p.2).

Majority of scavenging systems with different chemistries behind have one main challenge - premature activation of the oxygen absorbing reaction. This does not allow systems to be stored for long periods of time before using them for actual products. The way to solve the problem, and therefore a very important parameter for any scavenging system, is the triggering mechanism. It allows the reaction to start when needed and keep the full capacity until required (Yam 2010 p.5). According to Johansson (2013 p.7), there are three mechanisms that are most often used for triggering oxygen scavenging: water activity, UV-light or contact to oxygen itself (special storage conditions are needed to prevent the scavenger from immediate activation).

Another parameter that is inherent to most of the scavenging system is presence of catalyst components, which speeds up the oxygen uptake of the chemicals.

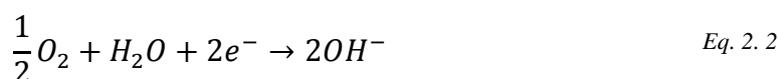
According to Cruz *et al.* (2012 p.25), there are two main types of scavenging systems created by now: metallic-based and non-metallic-based.

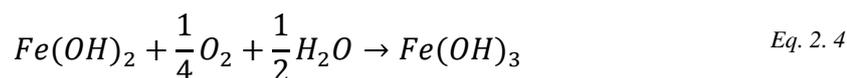
2.1.1 Metallic-based oxygen scavenging systems

Metallic-based compounds are those represented mostly in the sachet technology. The mechanism in them depends on moisture in the sachets because iron needs water as a triggering tool for the reaction (Cruz *et al.* 2012). The main problem with metal-based scavenging systems is activating the metal detectors (Brody *et al.* 2001).

- **Ferrous iron-based systems**

These scavengers comprise the largest segment on the market. They have been used commercially for many years (Herman 2014 p.3). The system uses oxidation of iron oxide to the ferric state, in which the key triggering mechanism is presence of water, or, in other words, humidity (Brody *et al.* 2001 p. 59). The system is normally used in the form of sachets, in which iron powder reacts as following (Cruz *et al.* 2012 p. 25):





According to Brody (2001 pp. 59-60), iron-based systems are the most effective scavenging solutions so far. They allow to achieve as low levels as 0.01% of oxygen content in sealed containers.

- **Other transition metal-based systems**

Other transition metals than iron, such as copper, manganese, titanium and zinc in powder forms are also capable of oxygen reducing reactions (Solovyev 2014). However, due to the environmental considerations, the systems are not commercially used so far.

- **Palladium-based systems**

Palladium-based catalytic oxygen scavengers are characterized by a high reaction speed, when oxygen gas reacts with hydrogen gas resulting in water (Sängerlaub *et al.* 2012). In literature are mentioned such ways of applying palladium-based systems as dispersion on porous aluminium oxide inserted in a sachet form into the sealed package, or same system integrated into the liner of a bottle or jar closure and also a vacuum deposition of palladium layer on a polymer film (Brody *et al.* 2001, Sängeraub *et al.* 2012). Also according to Brody (2001 p. 54), using palladium catalysts it is possible to maintain 0.0001% oxygen level in the package during six month of product shelf life.

2.1.2 Non-metallic-based oxygen scavenging systems

Non-metallic-based scavenging technologies include those in which basic reagent is a non-metal.

- **Sulfites-based systems**

Sulfur compounds that have the oxygen reducing capabilities are sulfites and bisulfites of sodium and potassium (Cavano 2007). Sulfur compounds can be used in the form of sachets, inside gasket liners, bottle closures, in between the layers of flexible material or incorporated into plastic packaging (Cruz *et al.* 2012 p. 32).

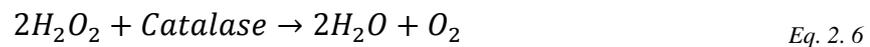
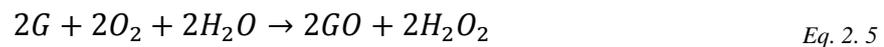
The oxygen-scavenging capacity of bisulfites depends directly on the surface area: the higher the area of exposure to oxygen, the higher the absorption rate. That is why such solutions are

suggested to increase the surface area as integration into carriers with high surface area, as activated carbon, silica gel or multiwall flexible pouch material (Brody *et al.* 2001 p.48).

The biggest concern in using sulfites is that its residuals may cause allergic reactions on some people (Brody *et al.* 2001 p.48).

- **Enzymes-based systems**

Enzymes are the macromolecular substances, accelerating biological transformations (Kulkarni & Deshpande 2007 p.2). It is possible to impart some of the enzymes into the food package structures or place them inside the package as sachets, and then make them function as scavengers by adding an enzyme-specific oxidizable substrate (Solovyev 2014 pp. 23-24). Brody *et al.* (2001 p. 54) describes the idea of removing the oxygen by in-package glucose oxidase – glucose catalase reactions in porous packets. In the presence of water glucose oxidase oxidizes glucose to gluconic acid and hydrogen peroxide, and the latter, since it is highly reactive, then needs to be converted by catalase to water and oxygen (Brody *et al.* 2001). Reaction resulting in oxygen reduction can be seen below (Kaufman *et al.* 2014):



The shown reaction results in reducing oxygen in the package by the grade of two, which leads to zero after a number of reactions (Brody *et al.* 1995 p. 35).

An example of the enzymatic oxygen scavenging system is Enzycoat, reported by the Nordic Innovation Centre “Norden”. Enzycoat system includes glucose oxidase in combination with catalase embedded into latex/TiO₂ dispersion coatings. The system has not been used in commercial applications so far and requires further studies (Antvorskov *et al.* 2008; Järnström 2013).

- **Yeast**

When moist is applied to yeast, it respire scavenging the oxygen and producing alcohol and carbon dioxide (Cruz *et al.* 2012 p.29). Brody *et al.* (2001 p. 59) explain the concept, that implies using yeast in such applications where produced alcohol and carbon dioxide can enter the content of the package without causing any big difference, such as beer.

- **Antioxidants**

According to Halliwell (1995, p. 1341) (as cited in Cirillo & Iemma 2012 p.2), antioxidants are materials that, being added to oxidizable substrates in a small quantities, have an ability to postpone or to stop oxidation.

Antioxidants that are suggested in literature to be used in oxygen scavenging applications are tert-butylhydroquinone (TBHQ), butylated hydroxy toluene (BHT). Incorporated into the structure of the plastic package, these materials are reported to remove the oxygen more effectively than the same materials added to food (Brody *et al.* 2001 p. 46).

Ascorbic acid and ascorbates may also be used in oxygen scavenging applications because they oxidize in air, scavenging molecular oxygen (Solovyev 2014 p.15). The reaction can be accelerated by the use of transition metal catalysts and light.

- **Unsaturated Fatty Acids and Hydrocarbons**

Materials which belong to this group possess ethylenic unsaturation (-CH=CH-) in their structure, and therefore can be used to scavenge oxygen through catalytic autoxidation (Solovyev 2014 p.19). This category includes drying oils, isoprene, butadiene and squalene, and their copolymers with polyolefins and polyesters.

Unsaturated fatty acids and hydrocarbons have an advantage in comparison to most of other types of oxygen scavengers. They do not require moisture as a trigger, which makes them suitable for dry foods (Han 2013 p.115). However, in order to trigger the mechanism of action transition metal salts are required, such as iron, cobalt or nickel (Brody *et al.* 2001 p. 51).

- **Polyamide-based scavengers**

Polyamide-based oxygen scavenging technologies involve using cobalt-catalysed nylon polymers MXD6 blended at 5% with polyethylene terephthalate (Fellows 2009 p.764). The systems based on polyamides are performing more slowly than the absorbers of head oxygen, but they can be effectively used as active barriers for preventing oxygen from penetration into the package (Solovyev 2014 p.21). Advantages of MXD6-based systems are that their capacity allows them to be effective for up to two years (Fellows 2009 p.764).

2.1.3 Existing designs of oxygen scavenging systems

Nowadays, commercial scavenging solutions are available in such formats as (Cruz *et al.* 2012; Rooney 1995):

- Sachets (Freely placed into the package or bonded to its inner space)
- Individual containers
- Incorporated into the packaging material (either low molecular weight ingredients are mixed into plastics or scavenging plastics are used)
 - Plastic films
 - Plastic trays
 - Bottle crowns
 - Plastic bottles
 - Scavengers incorporated into solids being dispersed in the plastics
 - Adhesives
 - Printing inks
 - Lacquers or enamels
- Package inserts
 - Labels
 - Cards
 - Layers coated into the inner package surface

2.1.4 Polymers in oxygen scavenging

Polymers are the most widely used materials in food packaging, and therefore active technologies are being commonly introduced into plastics (Rooney 1995 p.75). However, oxygen scavenging mechanisms were commercialized in sachet forms about 10 years before similar system appeared in plastics (Rooney 1995 p.75).

During 1970s plastic packaging became very popular, which resulted in a need of minimizing its oxygen permeability to maintain shelf life of the food (Brody 2001 p.34). That is why first attempts to protect the products were related to changing the inner plastic package environment by creating vacuum or inert-gas flushing (Brody 2001 p.17).

First work towards producing the oxygen scavenger films was made in 1976 and used reaction of oxygen with hydrogen in presence of palladium (Yam 2012 p. 6).

Nowadays there is a concept of using oxygen scavenging in plastics that involves either using scavenging sachets in packages with low oxygen transmission rates for longer period of time (less than $2.28 \times 10^{-15} \text{ m}^3/\text{m}^2 \text{ s Pa}$), or reinforcing the polymers with higher oxygen transmission rates by incorporating oxygen scavengers in their structure (Abe & Kondoh 1989 as cited in Rooney 1995 pp.77-78).

High permeability plastics, in which oxygen scavenging chemicals can be blended, are plasticised PVC and polyethylene (Rooney 1995 p. 78). Specifics of plastic as a material restricts the number of reactions of the material mixture being incorporated: while small molecules can still diffuse within the plastic layer, larger molecules are being immobilized (Rooney 1995 p.78). There is another possibility of using high permeable plastics in oxygen scavenging. They can be included as layers of the packaging together with the low permeability layer and a scavenging layer to remove, for example, residual oxygen from inner vacuum package space.

Low permeability plastics that are used in scavenging (either as layers or as packaging materials for sachet-based systems) are poly(vinylidene chloride) copolymers, ethylene-vinyl alcohol copolymers (EVOH) and poly(vinyl alcohol) (Rooney 1995 p.78).

Two commercially available products, which are made as described, are Oxbar™ and Amosorb®. Oxbar™ uses cobalt-catalysed nylons impregnated into polyesters to make bottles, and Amosorb® uses polybutadiene as an active ingredient, mixing it with polyester (Brody *et al.* 2001; Herman 2013).

2.2 Oxygen scavenging coatings and films

2.2.1 Properties and types of coatings

Union Guidelines on Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food (2014) defines coating as “a non-self-supporting layer composed of substances applied on an already existing substrate in order to impart special properties or improve technical performances of the finished article”. Ghosh (2006 p.1) gives a shorter definition: “a material (usually a liquid) which is applied onto a surface and appears as either a continuous or discontinuous film after drying”. Based on these two definitions, coatings are the substances that perform their purpose only when applied to another substance. According to Ghosh (2006 p.1), the terms “coating” and “paint” can be used as synonyms. Coatings, or paints, are combined with pigments, such as minerals, in order to correct their printing and optical characteristics, (Johansson 2013 p. 28).

Another definition of coating refers to a process. It is “the process of applying at least one layer of a fluid or melt substance onto the surface of the material (paper, plastic, metal) in the form of films, sheets or shaped structures (i.e., bottles or jars)” (Yam 2010 pp.285-286).

Paints usually consist of the following compounds (Lambourne 1999, as cited in Ghosh 2006):

- Binders – adherent components, forming the films and holding the coating compounds together:
 - polymers,
 - resins.
- Volatile components – solvents that are used for regulating the viscosity of the coatings.
- Pigments.
- Additives:
 - catalysts,
 - driers,
 - flow modifiers.

There are three types of paints (Ghosh 2006):

- solvent-borne – ingredients are dispersed in solvents,
- water-borne – ingredients are dispersed in water,
- solvent-free (or 100% solid) – ingredients dispersed directly in the resin.

Respectively, coatings can be applied to the surface of package in three ways (Johansson 2013, Yam 2010):

- solution – coating dispersed in solvent,
- dispersion – coating materials dispersed in water,
- extrusion – an extruder leads melted thermoplastic through a horizontal die onto the material.

Liquid coatings (solvent-borne and water borne) may be dried by either evaporation or cross-linking. Latter involves curing by oxidation, temperature treatment, ultraviolet light, etc. (Ghosh 2006).

2.2.2 Oxygen scavenging functional coatings

A special group among all the coatings are those called functional. Functional coatings are the coating systems that not only decorate or physically protect the surfaces (barrier and pigment coatings), but also bring some additional functionality to the products they are applied to (Wulf *et al.* 2002). Oxygen scavenging property is one potential additional functionality to the coating.

Scavenging films and coatings have advantages over other technologies, such as sachets, because they do not seem foreign to the packaging (Chanda & Roy 2007 p.7-6). It means that it is harder for the consumers to confuse scavenger in the form of film or coating with part of the food.

2.3 Oxygen scavenging technologies based on polybutadiene

There are various types of polybutadiene with different micro- and macrostructures. Polybutadiene is synthesized from the butadiene monomer. The figure below shows polymerization of polybutadiene from 1,3-butadiene monomer (Li 2010 p. 34):

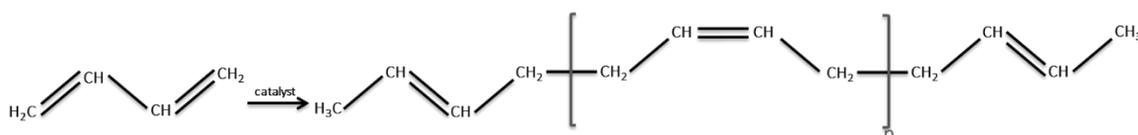


Figure 1. Polymerization of polybutadiene from 1,3-butadiene monomer (Li 2010)

Polybutadiene may contain three isomeric groups: cis-1,4, trans-1,4 and vinyl-1,2, their chemical structure is represented below (Corradini *et al.* 1988, as cited in Crompton 2009 p. 154):

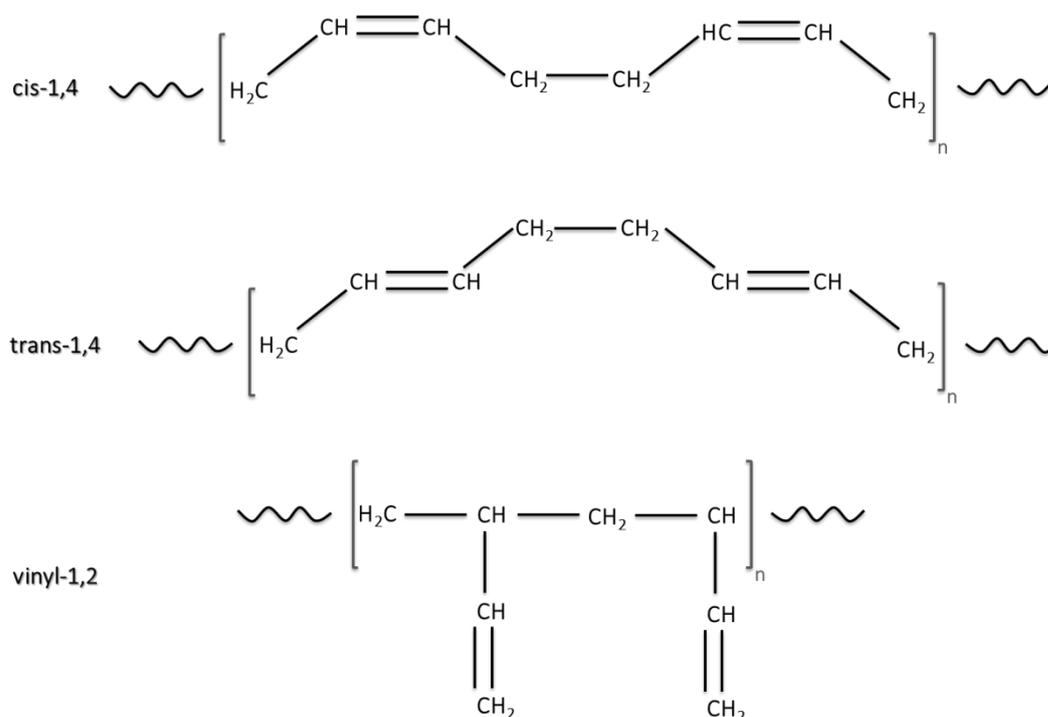


Figure 2. Structure of polybutadiene isomeric units (Crompton 2009)

Polybutadiene samples perform differently, depending on the amount of isomeric units and their tacticities, which, in turn, depend on the initiator of the reaction and polymerisation solvent used (Crompton 2009 p.154). Table 1 below, based on Li (2010 p.34) and Salamone (1996 p. 5657 – 5661), shows the properties of polybutadiene samples depending on the dominating isomeric unit in their structure:

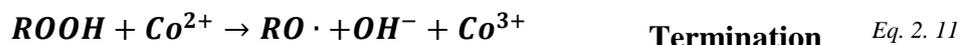
Table 1. Polybutadiene properties depending on the amount of isomers

Polybutadiene type		Distinctive features
High cis-olefin concentration (>90%)		Crystalline, high cut growth resistance; low T _g . high tensile strength. Crystallizes when being stretched
40-85% cis-olefin		Amorphous, intermediate properties
High trans-olefin concentration (>90%)		High crystallinity, high hardness, high thermoplasticity, high melting temperature
High vinyl-olefin concentration	Syndiotactic	High cross-linking, combines properties of plastic and rubber. Mouldable into thin films with high elongation
	Isotactic	High cross-linking, crystallinity
	Atactic (amorphous)	High cross-linking, low hysteresis, good wet resistance

Among all commercial elastomers 1,4-polybutadienes have the lowest glass transition points, except silicone rubbers.

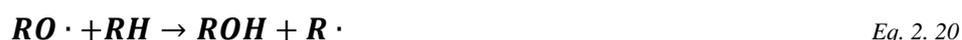
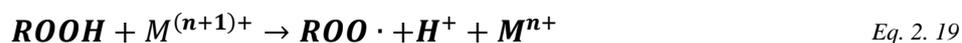
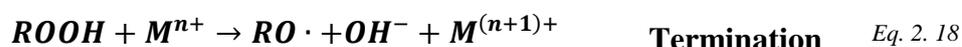
Polybutadiene is considered to be a suitable material for scavenging the oxygen in barrier packaging applications, as mentioned in various patents (Cahill & Chen 2004; Speer & Roberts 1997; Speer & Roberts 1997). Major research studies on scavenging properties of polybutadiene-based materials were conducted by Li (2010), Li *et al.* (2011), Li *et al.* (2012), Tung *et al.* (2012). According to Cruz *et al.* (2014 p. 28), among the functionally terminated unsaturated hydrocarbons, polybutadiene is the most preferable to be incorporated into thermoplastics because of such properties as transparency and similarity to polyethylene in processing behaviour.

In order to accelerate the scavenging action of polybutadiene, transition metal catalysts are used, such as cobalt neodecanoate (Li *et al.* 2012 p. 7138). The oxidation reactions of polybutadiene with cobalt catalysts are believed to proceed as following (Sheldon and Kochi 1981 pp. 33-70, as cited in Li 2010 p. 74; Denisov *et al* 2005 p.596; Ilie & Senetscu 2009 p.6):



RH – section being oxidized

Cobalt catalysts are commonly used for polybutadiene; however, alternative heavy metal catalysts might be used. Reactions below represent general mechanism of heavy metal-oxidation of hydrocarbons (Ilie & Senetscu 2009 p.6; Becker *et al.* 2004 p.206):



RH – section being oxidized

M – metal catalyst

Li (2010 p. 78) suggests explaining the oxidation of polybutadiene as following: first, olefin groups of polybutadiene form peroxy (ROO•) and alkoxy (RO•) free radicals in combination with oxygen, then peroxides and hydroperoxides are formed through free-radical termination reactions, and finally alkoxy free radicals decompose into carbonyl groups (>C=O).

The percentages of cis-, trans- and vinyl-groups influence not only the physical properties of polybutadienes, but also their oxidation (Li 2010 p.61).

The studies mention that often polybutadiene samples intended for commercial use contain antioxidants, and therefore have to be purified before performing best in oxygen scavenging applications (Li *et al.* 2012 p.7138). For removing the antioxidants the authors suggest the following purification measures (Li *et al.* 2012 p.7139):

1. Dissolving 1,4-polybutadiene (50 g) in dry toluene (450 ml)
2. Precipitation of the 1,4-polybutadiene from the solution into methanol (2000 ml) at room temperature
3. Removing the residual solvent in the vacuum oven

Experimentally Li *et al.* (2012) have found that oxygen scavenging efficiency of commercial polybutadiene samples depends on the number of the purification cycles described above and on the time of keeping the samples under vacuum (step 3 of the purification cycle). Among the experiments with 0, 3, 5 and 6 purification cycles, the best result of 15 wt % oxygen absorbed by polybutadiene film was obtained with 5 cycles. And among the experiments with various vacuum storage times, the lowest time of 6 hours gave the highest result in oxygen scavenging (Li *et al.* 2012 p. 7140). The dependency “scavenging efficiency/number of purification cycles” is explained by the amount of antioxidants, remaining in the polymer. The explanation of the dependency “scavenging efficiency/vacuum storage time” is restricted by the fact that the phenomenon is not yet understood (Li *et al.* 2012 p.7140). However, two possible causes are suggested by Li *et al.* (2012 p. 7140). The first possibility is that cross-linking between the polybutadiene double bonds could have happened due to the presence of oxygen radicals that penetrated accidentally during the film making process. The second possible explanation is fluctuation in catalyst activity during the vacuum storage. Li *et al.* (2012 p.7140) assume that catalyst may become less well dispersed as a result of the loss of the mineral oil, formerly dissolving it.

The study by Li *et al.* (2011) revealed that the oxidation of polybutadiene depends on film thickness. Coquillat *et al.* (2007 p.1327) describe the phenomenon of critical thickness L_c of polybutadiene samples being oxidized. Below the L_c polybutadiene films oxidize homogeneously, and above L_c – heterogeneously. Li *et al.* (2011) continued developing this idea and defined a critical thickness of about 28 μm . Oxidized polybutadiene layers become less permeable for oxygen, which additionally complicates the model explaining oxidation of the film.

Oxidation of polybutadiene films is represented schematically on the figure below, where L is a total thickness of the film, L_c is a critical thickness, and L_{no} is a non-oxidized core.

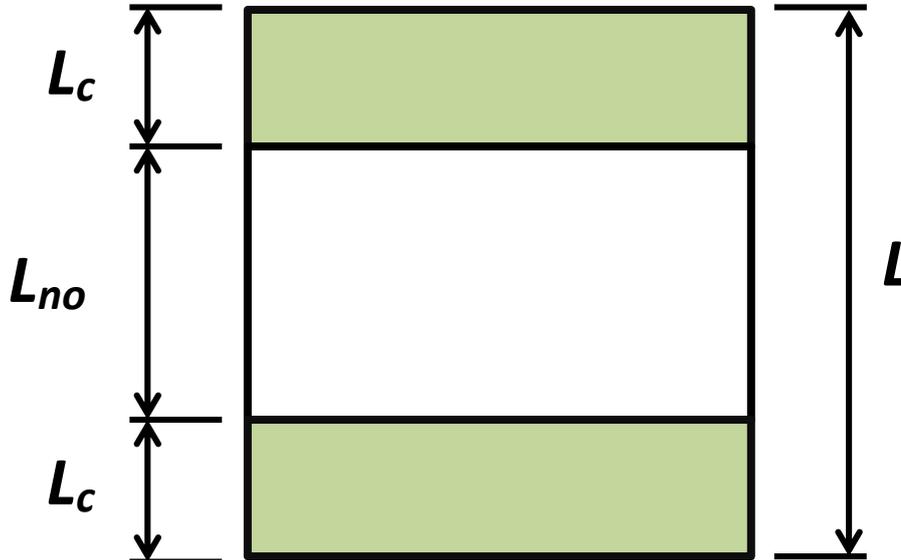


Figure 3. Schematic morphology of an oxidized 1,4-polybutadiene film (Li *et al.* 2011 p.2777)

Simplified model shown on the picture is represented in the following Equation 2.22:

$$m_o = m_{o \max} \frac{2L_c}{L} \quad \text{Eq. 2. 22}$$

In the equation m_o is a maximum oxygen uptake per unit polymer mass and $m_{o \max}$ is the maximum extent of the oxidation of the film oxidized from both sides as represented by the picture (Li *et al.* 2011 p.2778). The value of $m_{o \max}$ is suggested by the authors as about 30 mg of oxygen per 100 mg of polymer.

Li *et al.* (2011) suggested that in polybutadiene one repeating unit reacts with one oxygen atom because the theoretical amount of oxygen mass uptake (of 29.3 wt%) is close to what they observed during the experiments. In 2012 Tung *et al.* gave another number. According to them, theoretically each butadiene unit scavenges 1,1 – 1,3 oxygen atoms on average with cobalt catalyst loadings of 100-800 ppm.

2.4 Legal limitations of using oxygen scavengers for food applications

Nowadays there is a trend in the society towards healthy eating (Weimer 2007; Annunziata & Pascale 2009). More and more people are choosing low-processed foods over highly modified products. Bevilacqua *et al.* (2010 p.1) pointed out a tendency called “green consumerism”, which is determining the current way for prolonging the shelf life of food. It implies choosing natural food preservatives, low temperature treatment processes and technologies with less detrimental consequences for the environment. Oxygen scavengers fit into the described idea, since they are not added to food itself but are a part of the packaging system. However it is necessary that none of the materials used in the package are transported to the food. That is why a very important criterion, which the scavenging packaging has to satisfy, is a limitation of migration of the packaging materials or components thereof into the food.

For health reasons, substances may migrate into the food only for a very limited extent. Concentration of certain substances in food products may not to exceed the predefined amounts. Specific migration limits are stated in the regulations for European Union. Regulation (EC) 450/2009 (2011) covers active and intelligent materials and articles, and regulation (EU) No 10/2011 (2014) describes plastic food contact materials. Depending on the components, oxygen scavenging systems may belong to one of the categories of these regulations or to both of them.

Active substances are defined as those prolonging the shelf-life of the food or improving its condition by releasing or absorbing the substances into or from the package space (Regulation (EC) No 450/2009 2011). Intelligent substances, in turn, are characterised by the ability to monitor the condition of the food or the atmosphere in the packaging (Regulation (EC) No 450/2009 2011). Thus, any scavenging system fits into the category of active substances as long as it absorbs air components from the inner packaging space, and also fits the “intelligent system” criteria when having an ability to display the condition of the food. Additionally, it means that systems designed to decrease the penetrability of the oxygen from outer space into inner by means of scavenging fall into the third category covered by the Regulation (EC) No 450/2009 (2011) – functional barriers. The category includes materials consisting of one or more layers coming into contact with food.

Subjects of the Regulation (EU) No 10/2011 (2014) are plastic intermediate materials and final food contact materials as well as completed plastic components of final food contact material and inner plastic layers. So, the oxygen scavenging systems containing plastics in their structures, belong to this group.

Specific Migration Limits (SMLs) are those established by European Union for individual substances which may be dangerous for human health when present in the food (Regulation (EU) No 10/2011 2014). The SMLs are based on the investigations conducted by EFSA (European Food Safety Authority). For the substances, migration limits of which are not listed in the document, the generic SML is defined of 60 mg/kg (Regulation (EU) No 10/2011 2014). SML for a butadiene monomer is set by European Union regulations; it is 1 mg/kg in final product (Regulation (EU) No 10/2011 2014 p.29).

Critical factor in the food safety is the shelf life of the product. It depends on the oxygen permeability of the packaging and can be calculated using the Equation 2.23 (Fellows 2009 p.719):

$$t_s = \frac{Q_x}{PA\Delta P} \quad \text{Eq. 2. 23}$$

where t_s (s) is a shelf life itself (or, in other words, time to the end of shelf life), Q (mL) is the maximum quantity of oxygen that may penetrate into the package, and ΔP is the difference between the partial pressure of oxygen inside and outside of the container, P – atmospheric pressure and A – area of the package.

The maximum quantity of oxygen that may penetrate into the packaging is individual for different product types. However, according to Solovyev (2014 p.1), oxidative damage and growing of pathogenic microorganisms can occur from oxygen levels in gas mixtures as low as 0.4 vol%, so that value may be taken as a reference point.

In order to commercialise the product, such as oxygen scavenging system, that is intended for a contact with food, specific migration tests have to be conducted. The required tests have to be done using the same foods for which the systems are intended. The conditions for making the tests, such as time, temperature and pressure, have to reproduce the product's shelf life duration and its storage conditions. In this way the test will give the most exact results. The

amounts of products migrated into the food must not exceed the limits to be allowed for commercial use in European Union.

Another measure for the commercialization of the system coming into contact with food is correct labelling. Non-edible parts of the product should be labelled by the warning words such as “Do not eat”. Also, if possible, the symbol “Do not eat” has to be placed on the non-edible parts (EU Guidance to the Commission regulation (EC) No 450/2009 2011).



Figure 4. "Do not eat" symbol (EU Guidance to the Commission regulation (EC) No 450/2009 2011)

3 METHODS

3.1 Experimental

3.1.1 Material

- **Polybutadiene**

Two liquid polybutadiene samples produced by Evonik Industries AG were used in the oxygen scavenging experiments. For the reason of confidentiality, the original brand names and complete structures are not to be revealed. Therefore the polybutadiene samples are to be referred to as “Polybutadiene 1” and “Polybutadiene 2”. Properties of the samples are shown in the table below:

Table 2. Polybutadiene samples used in the experiments

Polybutadiene sample	Properties		Properties, declared by the manufacturer	Applications
Polybutadiene 1 Isomeric structure: <i>High Cis-olefin and moderate Trans-olefin concentration</i>	Mean molar mass	>1500 g/mol	High chemical resistance, high water resistance, high electrical insulation properties, high cold resistance, good solubility in aliphatic, aromatics and ethers	Adhesives and sealants, binders, release agents, etc.
	Density (20 °C)	0.90-0.92 g/cm ³		
	Appearance	Viscous transparent liquid		
Polybutadiene 2 Isomeric structure: <i>High Trans-olefin, moderate Cis-olefin and Vinyl-concentration</i>	Mean molar mass	>1500 g/mol		
	Density (20 °C)	0.90-0.92 g/cm ³		
	Appearance	Viscous transparent liquid		

- **Catalysts**

Metal driers (also called siccatives) were used as catalysts to accelerate the reactions. Driers are organometallic compounds used mostly in alkyd paints for accelerating the drying cross-linking reaction between the double bonds commonly referred as “drying”. They may act as polymerisation or oxidation agents (Gooch 1997 p.121).

Three drier types were used:

- Iron-based primary drier (0.09% iron metal) – Used in coatings drying by oxidation. Recommended amount of the drier, according to the supplier, is 0.5% to 3%. This drier is being positioned by the producer as an alternative to cobalt-based catalysts, as it shows improvements in drying activity.
- Manganese-based secondary oxidative drier (6.9% manganese metal) – Used in combination with primary driers for enhancing better performance. The typical usage of such drier is 0.14% to 0.72%
- Zirconium-based secondary oxidative drier (7.6% zirconium metal) – Recommended amount is 0.05% to 0.3%.

Exact amounts of mentioned driers that show the best performance have to be defined experimentally for each product, based on the recommendations given by the producers. In the further text the names of the driers are coded for the reason of confidentiality and given as Drier 1, Drier 2 and Drier 3.

- **Solvent**

m-Xylene was used as a solvent in the experiments as it has an ability to dissolve polybutadiene.

- **Surface area increasing agent**

An inert agent was used as the agent increasing the surface area of oxygen scavenging substance. The inert substance used has a small particle size in the micrometer range and a high loading capacity.

3.1.2 Materials' preparation methods

As it was already mentioned in the previous chapter, Li *et al.* (2012 p.7138) stated that commercial polybutadiene samples need purification measures to remove the present antioxidants before being used for removing the oxygen. Evonik-produced polybutadiene samples used in the experiments did not require any purification as, according to the producer, they do not contain any antioxidants.

Material preparation consisted of the following steps:

- 1) Polybutadiene sample was dissolved in m-xylene at 20 wt% of polymer;
- 2) Catalysts were added to the solution and well mixed;
- 3) Solution was slowly poured onto the surface area increasing agent while thoroughly stirring to achieve complete absorption and structure's homogeneity. The final mixture had similar appearance to the pure agent, since it absorbed the liquid completely;
- 4) The mixture was stored under vacuum at 60 °C for approximately 14 hours to remove residual solvent;
- 5) After the solvent was removed, the sample was ready for being tested using the set-up described in the chapter below.

Mixing steps were performed inside the fume hood to provide safety as m-xylene and drivers are hazardous substances.

3.1.3 Experiments' set-ups

The installation for testing oxygen scavenging materials used in the experiments can be seen from the figure below.

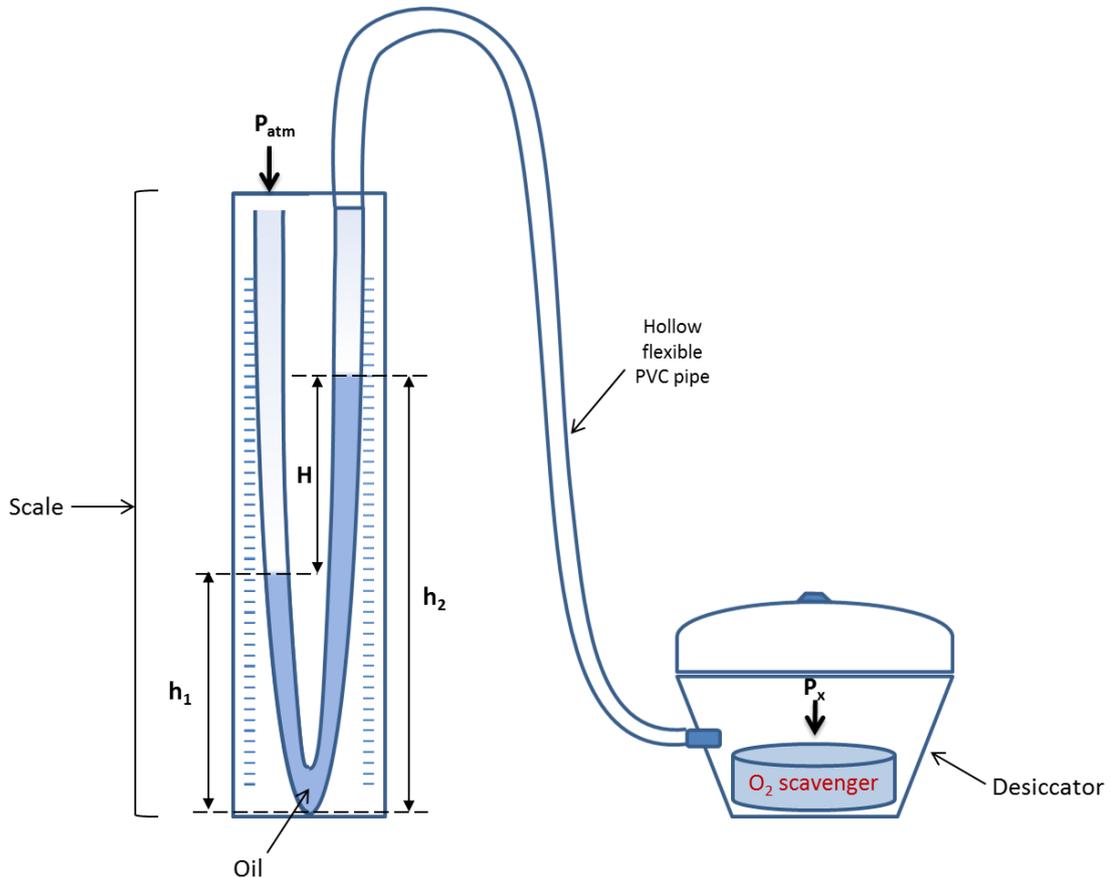


Figure 5. Schematic representation of oxygen-scavenging experiments' set-ups (compiled by author)

Desiccator, schematically represented on the figure, is a thick glass container often used for drying the samples or keeping them away from the ambient atmosphere. Usually desiccators have separate covers and can be sealed with grease (Kenkel *et al.* 2001 p.118; Kenkel *et al.* 2003 p.41). The image of the desiccator can be seen from the Figure 6 below.



Figure 6. Vacuum desiccator. (Photograph Mariia Demicheva. Evonik Industries AG 2014).

Experimental set-up consisted of a sealed desiccator with scavenging material inside and U-shaped pipe attached to a length-measuring scale. As can be seen from Figure 5, one side of the U-pipe was connected to the desiccator, and another was open to the surrounding atmosphere. Liquid oil of known density was poured into the pipe. Oxygen absorption lowered the pressure inside the desiccator. The pressure difference between the outer atmosphere and within the desiccator caused changes in the oil level in the U-pipe. The changes were tracked, and the amount of absorbed oxygen was calculated based on these changes.

3.1.4 Method of calculating the amount of consumed oxygen

The amount of absorbed oxygen was calculated based on several equations, described below.

- **Pressure measurements:**

As it was already mentioned previously, while oxygen is being absorbed by the scavenging material inside the desiccator, pressure there decreases. Thus oil level in the right side of the U-shaped pipe increases (side connected to desiccator), and accordingly the level inside the left (open) side decreases (Figure 5). Developed difference in heights of oil column enables calculating the new pressure value inside the desiccator. For this, the value of hydrostatic

pressure calculated from the oil level column difference has to be subtracted from the original pressure inside the desiccator. Similar principle is used in a U-tube manometer – a special device for defining the fluid pressure by the height of liquid column (Nakayama & Boucher 1998 p.26).

$$p_x = p_{atm} - \rho_{oil}gH \quad \text{Eq. 3. 5}$$

$$H = h_2 - h_1 \quad \text{Eq. 3. 6}$$

$$\text{Thus: } p_x = p_{atm} - \rho_{oil}g(h_2 - h_1) \quad \text{Eq. 3. 7}$$

Where p_x – pressure inside the desiccator;

p_{atm} – atmospheric pressure;

ρ_{oil} – density of the oil;

g – gravitational acceleration;

H – change in heights of oil in the columns of U-tube (Figure 5);

h_1 – height of oil in the left tube;

h_2 – height of oil in the right tube.

- **Ideal gas law:**

When the pressure inside the desiccator is known, it is possible to calculate the number of moles of air inside. The ideal gas law is used (Ambaum 2010 p.8):

$$pV = nRT \quad \text{Eq. 3. 4}$$

$$\text{Thus: } n = \frac{pV}{RT} \quad \text{Eq. 3. 5}$$

Where p – pressure;

V – volume;

n – number of moles;

T – temperature;

$R = 8.314510 \text{ Pa m}^3/\text{mol K}$ – universal gas constant.

By subtracting the amount of moles in the desiccator after the oxygen has been consumed from the number of moles before that, the amount of scavenged oxygen can be found as following (Ambaum 2010 p.2):

$$m = nM$$

Eq. 3.6

Where m – mass;

n – number of moles;

M – molar mass.

Example of oxygen intake calculations with exact numbers for one of the experiments is given below. All the calculations have been done accordingly.

Given:

Experiment 6, Date: 27.11.2014, Time: 13:00.

Table 3. Numerical data for measuring the scavenging activity for the experiment 6 on 27.11.2014

Parameter	Value	Notes
T_{ave}	297.15 K	Average temperature at the laboratory was taken as 24 °C for all the measurements;
ρ_{oil}	905.052 kg/m ³	Measured by mass/volume
V	0.0225 m ³	volume of the desiccator
g	9.80665 m/s ²	Gravitational acceleration (Nakayama & Boucher 1998 p.20)
R	8.314510 Pa m ³ / mol K	universal gas constant (Nakayama & Boucher 1998 p.219)
$A_r(O_2)$	15.9994	atomic weight of oxygen
p_{atm1}^*	101100 Pa	Atmospheric pressure at the beginning of the experiment (Hessian Agency for the Environment and Geology, 2015).
H_1	0	Difference in oil levels at the beginning of the experiment
p_{atm2}	101000 Pa	Atmospheric pressure in 5 hours from starting the experiments (Hessian Agency for the Environment and Geology, 2015).
H_2	0.184 m	Difference in oil levels in 5 hours from starting the experiments

* Atmospheric pressure at the beginning of the experiment corresponds also to initial pressure inside the desiccator

Calculations:

- 1) Pressures p_{x1} and p_{x2} inside the desiccator at the beginning of the experiment and in 5 hours relatively, based on the Equation 3.3, are calculated as following:

$$p_{x1} = p_{atm1} - \rho_{oil}gH_1$$

$$p_{x2} = p_{atm2} - \rho_{oil}gH_2$$

- 2) Numbers of moles of air n_1 and n_2 inside the desiccators at the beginning of the experiment and in 5 hours from starting relatively, based on the equation 3.5:

$$n_1 = \frac{p_{x1}V}{RT} = \frac{(p_{atm1} - \rho_{oil}gH_1)V}{RT}$$

$$n_2 = \frac{p_{x2}V}{RT} = \frac{(p_{atm2} - \rho_{oil}gH_2)V}{RT}$$

- 3) Since only oxygen was scavenged inside the desiccator, n_x – difference between n_1 and n_2 , represents number of moles of scavenged oxygen:

$$n_x = n_1 - n_2 = \frac{(p_{atm1} - \rho_{oil}gH_1)V}{RT} - \frac{(p_{atm2} - \rho_{oil}gH_2)V}{RT} =$$

$$= \frac{(p_{atm1} - \rho_{oil}gH_1 - p_{atm2} + \rho_{oil}gH_2)V}{RT} =$$

$$= \frac{(p_{atm1} - p_{atm2} + \rho_{oil}g(H_2 - H_1))V}{RT}$$

- 4) Knowing the number of moles of oxygen consumed, it is possible to calculate it's mass, using equation 3.6:

$$m = nM$$

$$M(O_2) = 2A_r(O) = 2 * 15.9994 = 31.9988 \frac{g}{mol} = 0.0319988 \frac{kg}{mol}$$

Thus the final equation is:

$$m = \frac{(p_{atm1} - p_{atm2} + \rho_{oil}g(H_2 - H_1))VM}{RT} \quad \text{Eq. 3.7}$$

Inserting the values:

$$m = \frac{\left(101100Pa - 101000Pa + 905.052 \frac{kg}{m^3} * 9.80665 \frac{m}{s^2} * 0.184m\right) 0.0225 m^3 * 0.03199888 \frac{kg}{mol}}{8.314510 \frac{Pa * m^3}{mol * K} * 297.15K} =$$

$$= \frac{\left(100Pa + 1633.097 \frac{kg}{m * s^2}\right) 0.00071997 \frac{m^3 * kg}{mol}}{2470.6566465 \frac{Pa * m^3}{mol}} =$$

$$= \frac{1733.097 Pa * 0.00071997 \frac{m^3 * kg}{mol}}{2470.6566465 \frac{Pa * m^3}{mol}} =$$

$$= \frac{1.24777784709 \frac{Pa * m^3 * kg}{mol}}{2470.6566465 \frac{Pa * m^3}{mol}} = 5.05 * 10^{-4} kg$$

Thus, 0.505 grams of oxygen were absorbed by the tested scavenging substance in 5 hours.

Since various amounts of materials were used in the experiments, the results have been represented as percentage of the mass of consumed oxygen to the mass of polymer used.

All the calculations for the experiments were made using Microsoft Excel sheets, in which the final results were represented as scatter charts. X-scale represented time in hours of the scavenging substance being activated, and Y-scale showed the percentage of scavenged oxygen.

3.1.5 Calculating the theoretical capacity of polybutadiene samples

During the research on scavenging capacity of styrene-butadiene-styrene copolymer films, Tung *et al.* (2012) have experimentally found out that each butadiene unit takes 1.1 – 1.3 oxygen atoms on average with cobalt catalyst loadings of 100-800 ppm.

Based on above mentioned values, theoretical capacity of polybutadiene samples was calculated in percentage to the mass of polybutadiene as shown below when neglecting the end-groups of the polymer chains.

- 1) Molar mass of butadiene unit (C₄H₆) is:

$$M(C_4H_6) = 4 * A_r(C) + 6 * A_r(H) = 4 * 12.0107 + 6 * 1.00794 = 54.09044 g/mol$$

- 2) 1 g of polybutadiene has:

$$\frac{1 g}{54.09044 \frac{g}{mol}} = 0.01849 mol \text{ of butadiene units}$$

- 3) Uptake of 1.1-1.3 oxygen atoms gives:

$$1.1 * 0.01849 mol = 2.0 * 10^{-2} mol$$

$$1.3 * 0.01849 mol = 2.4 * 10^{-2} mol$$

So $2.0 \cdot 10^{-2}$ mol to $2.4 \cdot 10^{-2}$ mol of oxygen atoms can react with butadiene repeating units of 1 g polybutadiene.

4) Molar mass of oxygen atom is:

$$M(O) = A_r(O) = 15.999 \text{ g/mol}$$

$$15.999 \frac{\text{g}}{\text{mol}} * 2.0 * 10^{-2} \text{ mol} = 31 * 10^{-2} \text{ g of } O_2$$

$$15.999 \frac{\text{g}}{\text{mol}} * 2.4 * 10^{-2} \text{ mol} = 38 * 10^{-2} \text{ g of } O_2$$

So 0.31 g to 0.38 g of oxygen (gas) can react with 1 g of polybutadiene.

5) Transferring to mass percent:

$$\frac{31 * 10^{-2} \text{ g}}{1 \text{ g}} * 100\% = 31\%$$

$$\frac{38 * 10^{-2} \text{ g}}{1 \text{ g}} * 100\% = 38\%$$

So, the theoretical value of oxygen uptake (mass of consumed oxygen/mass of polymer) is 31% to 38%.

3.2 Suggested oxygen scavenging system

The project described by this paper included creating and testing an oxygen scavenging substance intended for use in functional coatings. Therefore the following section will include possible applications of the tested mixture.

As the tested scavenging material has an ultimate form of powder, there should be a special way of applying it to the final product. There are two processes that seem to be suitable for applying the material on the surface of the package: extrusion and spray-coating. For both of them the scavenging powder has to be mixed with a suitable polymer that possesses high oxygen permeability and capability of being easily melted. Such polymer can be, for instance, ethylene-vinyl acetate (EVA) copolymer which has a very high oxygen permeability of $4.63 \cdot 10^{-13} \text{ m}^3/\text{m}^2 \text{ s Pa}$ at $23 \text{ }^\circ\text{C}$, or, as an alternative, low density polyethylene (PE-LD) with a relatively high oxygen permeability of $2.31 \cdot 10^{-13} \text{ m}^3/\text{m}^2 \text{ s Pa}$ at $23 \text{ }^\circ\text{C}$ (Domininghaus *et al.* 2008 p.1383). According to Davis (2004 p.53), many polymers can be thermally sprayed on the surface for protection purposes. However, he mentions EVA among those most commonly used for spraying due to its low glass transition temperature.

Extruded or sprayed onto a package of the final product, mixture of scavenging powder and polymer can become one of the packaging layers. Used together with low oxygen permeability layer on the top, e.g., ethylene vinyl alcohol – EVOH (Maul 2005 p.5), and modified atmosphere packaging (reducing the starting amount of oxygen), it would solve two problems: reduce permeability of the package (improve the barrier properties) and scavenge the residual oxygen inside. The schematic illustration of the suggested system can be seen from the Figure 7 below.

The upper part “Exterior of the package” represents the storage atmosphere, containing oxygen. The suggested system implies using MAP technologies, which, according to Vermeiren *et al.* (2003 p.23), enables achieving starting oxygen content of 0.1-2%. The inner layer, represented in green, is intended for protecting the product from migration of scavenging components during storage time. This layer has to possess high oxygen permeability, allowing the migration of residual oxygen inside the package to the scavenging substance. The oxygen scavenging layer (in the middle) contains the scavenging powder mixed with polymer and coated on the inner layer. Both inner layer and scavenging layer can be made using EVA co-

polymer, since, as it is mentioned above, it has high oxygen permeability and is easily processible. The outer layer has to prevent oxygen from migrating into the packaging. It can be made of EVOH, as suggested above.

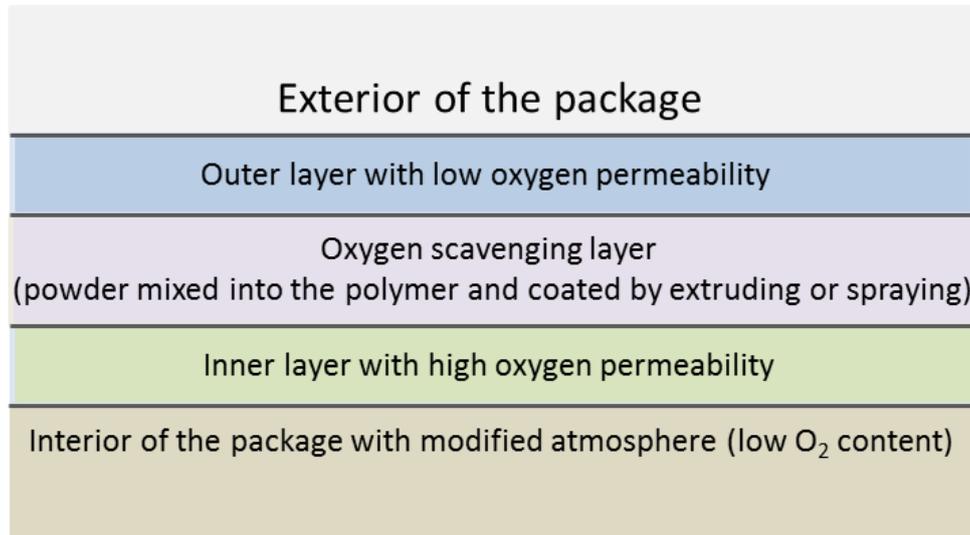


Figure 7. Schematic representation of suggested oxygen scavenging system (compiled by author)

3.3 Results and discussion

As a result of the experiments for this thesis, a novel recipe for oxygen scavenging material is suggested. It includes using polybutadiene with added driers and surface area increasing agent. During the experiments two polybutadiene types were tested with various amounts of additives. The most effective samples were defined based on the observations.

Detailed results of the experiments can be observed from the table in Appendix 1 and from the Figures 8-10. Some of the experiments repeated each other due to uncertainty towards the obtained results. Experiments 15, 16, 22 and 13 have been intentionally conducted for longer time to analyse the stability of scavenging effect.

As can be seen, the best result overall was achieved in the Experiment 16 where “Polybutadiene 1” was used with all 3 driers of twice the recommended amounts. However, it was a long-time experiment, and the effect of 26.48% of scavenged oxygen towards polybutadiene mass was achieved in 427 hours (approximately 18 days) after starting. Experiment 17, being conducted for similarly long time as Experiment 16, showed a very good result as well. However, the value could not be read because the pressure difference was too high and the oil overflowed through the pipe into the desiccator. The results of long experiments demonstrate that the oxidation process occurs stably and for the time enough for storing some products. For the comparison, Li *et al.* (2011 p.2774) report maximum of 19% oxygen uptake in thin polybutadiene films with cobalt catalysts being reached in 5-6 days.

Among those experiments showing high scavenging capacity in shorter period of time, the best results are achieved in the Experiments 6 for Polybutadiene 2 and Experiment 15 for Polybutadiene 1, that absorb 6.40% in 2 hours and 7.07% in 46.5 hours (approximately 2 days) relatively. Scavenging substance for the Experiment 6 contained Polybutadiene 2 with Drier 3 and Drier 1 of the amount twice higher than recommended by the producers. Mixture for the Experiment 15 included Polybutadiene 1 driers of twice the recommended amounts.

Experiment 16 resulted in the highest scavenging capacity of those observed – 26.48%. That value was also the closest to theoretically defined 31% - 38%. With such values the material can be used in the system, suggested in the previous paragraph (Figure 7).

Analysis of all experimentally obtained data indicates that Polybutadiene 2 may possess a higher scavenging capacity at the range of additives used.

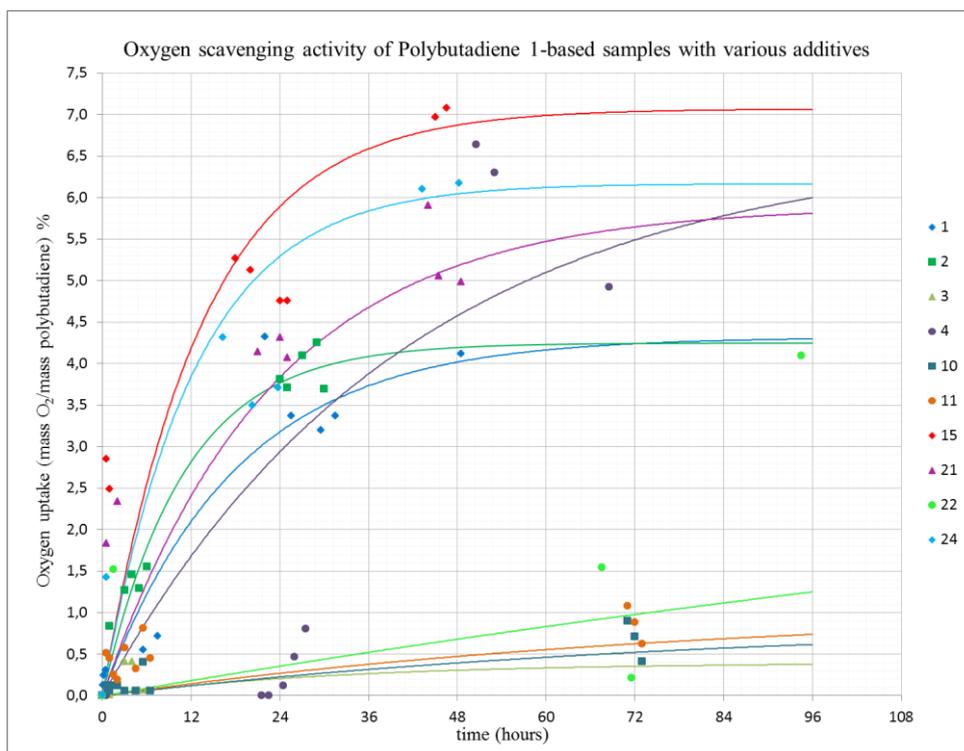


Figure 8. Oxygen uptake of Polybutadiene 1-based scavenging substances with various amounts of catalysts

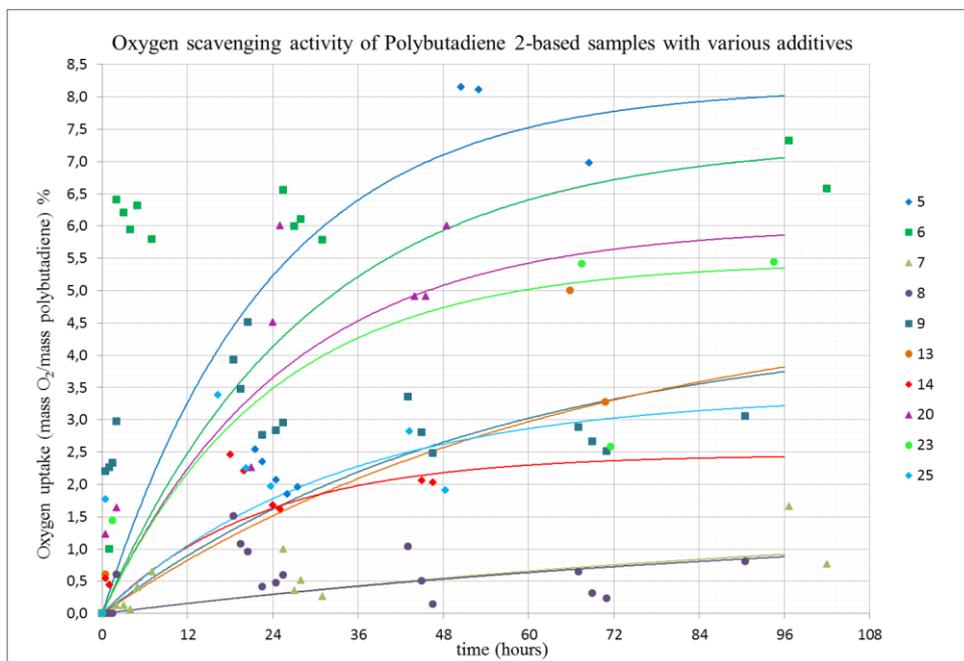


Figure 9. Oxygen uptake of Polybutadiene 2-based scavenging substances with various amounts of catalysts

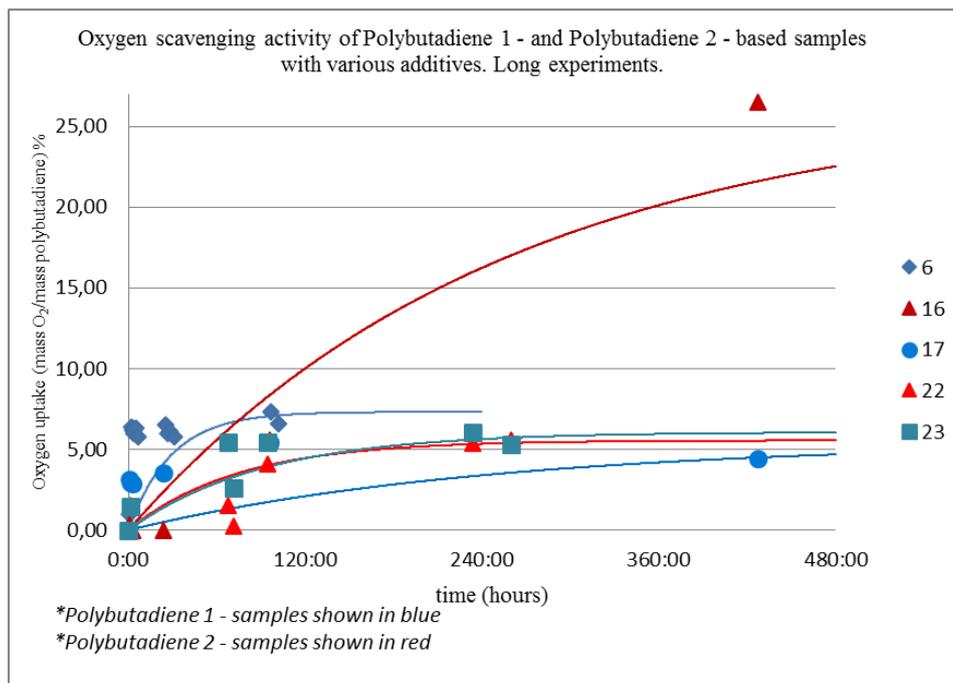


Figure 10. Long experiments on Polybutadiene 1 and Polybutadiene 2-based scavenging substances with various amounts of catalysts

3.3.1 Discussion and suggestions for the following projects

Considering the accuracy of the obtained results, it is necessary to point out a few factors, causing possible errors in the results of the experiments.

First of all, the error occurs already at the early stage of the experiments' – preparation. The materials were prepared and mixed under atmospheric conditions in the laboratory. It means that some of the atmospheric oxygen may have been scavenged even before the materials were placed into the vacuum oven for evaporation of the solvent (between the steps 3 and 4 of preparation), or during transportation from the oven to the set-ups (after the step 5).

Secondly, the set-up itself may have been not completely air-tight. The sealing wax used in the desiccator and the PVC-pipe of the installation (Figure 5) may have allowed some oxygen to migrate into the set-up due to their oxygen permeability.

Also, while the first two mentioned errors may lead to obtaining values that are lower than in reality, there is a third possible error that increases the obtained values. This error is related to the calculations of the amount of oxygen inside the desiccators. Since the ideal gas law was used, the values taken, e.g., constants, are approximate. Also temperatures inside the desicca-

tors were taken as average of 24 °C, and atmospheric pressure values were taken as average for the town, in which the experiments were conducted and could be different for the exact place. To define the error in the calculations, Experiments 18 and 19 were performed on empty desiccators, while the changes of oil levels in the installations caused by the atmospheric pressure changes only were recorded. As results, the values of 0.84% and 0.54% of “scavenged” oxygen were obtained in 24 hours. So, it is necessary to take into account the possible error of 0.54-0.84% on average to each measurement.

There is another possible error, which affects the ability to compare results of the experiments to each other. It is in the preparation of scavenging mixtures. Since, as stated by Li *et al.* (2011 p.2777), the oxidation of polybutadiene depends on the film thickness and, accordingly, on the surface area, the results might have been different from experiment to experiment. Mixing (Step 2 p.32) and the stirring (Step 3 p.32) were performed manually and did not give exactly similarly homogeneous substances every time. The surface area of polybutadiene could vary between the different experiments, which lead to different oxygen consumption values.

Overall, due to restricted duration of the project, there might not be enough of data obtained experimentally for making statistically correct conclusions. Therefore, the recommendation for the following projects is making additional experiments for more accurate conclusions. Also for more accurate oxygen intake measurements in the future projects, using of oxygen sensor, such as OxySence® should be considered (OxySence 2014).

Development of the suggested scavenging systems for functional coatings is suggested for the future projects. The following points have to be taken into account:

- Production steps, involving scavenging material developed during the project of this thesis, have to be made in oxygen-free atmosphere to avoid decreasing of the scavenging capacity of the mixture.
- For the above mentioned reason, storage conditions for the material before its final use on the products have to be oxygen-free.
- As stated in the paragraph 2.4, before commercially using proposed systems, tests to define the Specific Migration Limit have to be performed on them to verify that the food is not being dangerous for health after getting in contact with the material.

Finally, there are concerns nowadays, which cannot be put aside when developing systems as suggested.

It is possible to create the oxygen-free food storage environment, but it should not be forgotten that in such conditions anaerobic microorganisms can grow, causing serious health risks (Lagarón 2011 p. 33).

Also nowadays the expectations towards plastic packaging systems are high. Recyclability is considered an important additional factor. Separating the materials of multi-layered barrier packaging structures might be problematic and can make the end product too expensive for handling (Fellows 2009 p.770).

4 CONCLUSION

Oxygen scavenging properties of polybutadienes were studied during the work on this thesis. The existing investigations on this topic were discussed in the second chapter, including the legal restrictions applicable to polybutadienes.

The oxygen scavenging material's recipe was suggested based on polybutadiene samples produced by Evonik Industries AG with additives alternative to cobalt catalysts, most often used in experiments described by available publications. The suggested polybutadiene-based scavengers have been experimentally proven to function. Results of the experiments show promising oxygen scavenging efficiency of the materials. The highest empirically achieved value is 26.59%, which represents the ratio of mass of oxygen being absorbed to the mass of polybutadiene used in the experiment.

Possible ways of applying the created oxygen scavenging substance to the products were described, including utilization in the functional coatings in combination with modified atmosphere packaging. Further actions to be implemented in future follow-up projects were proposed.

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APPENDIX 1

Clarifications for the table below:

- Amount of area increasing agent is represented by its mass towards polymer mass and is taken based on the absorption value of the material given by the producer.
- Amount of solvent is shown in % to weight of the polymer.
- The amounts of driers given in the table are referred to those recommended values given by the producers. Thus, x2 should be read as “twice the recommended amount”.

Exp. Nr.	Polybutadiene type (1 or 2)	Additives, amount					Time since starting the experiment (hh:mm)	Oxygen uptake (mass of absorbed oxygen/mass of polymer used) (%)	Maximal oxygen uptake for the experiment (%)	Time to achieve maximum
		Drier 1	Drier 2	Drier 3	Solvent (% to polymer weight)	Surface area increasing agent				
1	1	x1	x1	x1	0	0	0:00	0,00	4,32	22:00
							0:02	0,12		
							0:08	0,24		
							0:24	0,30		
							5:30	0,54		
							7:30	0,71		
							22:00	4,32		
							25:30	3,37		
							29:30	3,19		
							31:30	3,37		
						48:30	4,11			
2	1	x10	0	x10	40	0	0:00	0,00	4,25	29:00
							1:00	0,84		
							3:00	1,27		
							4:00	1,46		
							5:00	1,29		
							6:00	1,55		
							24:00	3,82		
							25:00	3,71		
							27:00	4,10		
							29:00	4,25		
							30:00	3,69		
							48:00	0,00		
							69:30	0,00		
							143:00	0,00		
149:00	0,00									

3	1	x10	x10	x10	40	0	0:00	0,00	0,40	3:00
							1:00	0,00		
							3:00	0,40		
							4:00	0,40		
							5:00	0,06		
							6:00	0,06		
							24:00	0,00		
							25:00	0,00		
							27:00	0,00		
							29:00	0,00		
							30:00	0,00		
							48:00	0,00		
							69:30	0,00		
143:00	0,00									
149:00	0,00									
4	1	x1	0	x1	130	60	0:00	0,00	6,64	50:30
							0:30	0,00		
							21:30	0,00		
							22:30	0,00		
							24:30	0,12		
							26:00	0,47		
							27:30	0,81		
							50:30	6,64		
							53:00	6,30		
							68:30	4,93		
5	2	x1	0	x1	165	60	0:00	0,00	8,15	50:30
							0:30	0,00		
							21:30	2,55		
							22:30	2,35		
							24:30	2,07		
							26:00	1,85		
							27:30	1,96		
							50:30	8,15		
							53:00	8,11		
							68:30	6,97		
6	2	x2	0	x2	400	125	0:00	0,00	7,32	96:40
							1:00	0,99		
							2:00	6,40		
							3:00	6,21		
							4:00	5,95		
							5:00	6,31		
							7:00	5,80		
							25:30	6,55		
							27:00	6,00		
							28:00	6,10		
							31:00	5,78		
							96:40	7,32		
							102:00	6,57		

7	2	x2	x2	x2	400	125	0:00	0,00	1,66	96:40
							1:00	0,00		
							2:00	0,12		
							3:00	0,12		
							4:00	0,06		
							5:00	0,40		
							7:00	0,65		
							25:30	1,00		
							27:00	0,35		
							28:00	0,51		
							31:00	0,27		
							96:40	1,66		
102:00	0,77									
8	2	x2	0	x2	400	288	0:00	0,00	1,51	18:30
							0:30	0,00		
							1:00	0,00		
							1:30	0,00		
							2:00	0,61		
							18:30	1,51		
							19:30	1,08		
							20:30	0,96		
							22:30	0,41		
							24:30	0,47		
							25:30	0,59		
							43:00	1,03		
							45:00	0,51		
							46:30	0,14		
							67:00	0,64		
69:00	0,32									
71:00	0,23									
90:30	0,81									
9	2	x2	x2	x2	400	288	0:00	0,00	4,51	20:30
							0:30	2,20		
							1:00	2,26		
							1:30	2,33		
							2:00	2,97		
							18:30	3,93		
							19:30	3,47		
							20:30	4,51		
							22:30	2,76		
							24:30	2,83		
							25:30	2,96		
							43:00	3,36		
							45:00	2,80		
							46:30	2,48		
							67:00	2,88		
69:00	2,66									
71:00	2,51									
90:30	3,06									

10	1	x2	x2	x2	400	288	0:00	0,00	0,90	71:00
							0:30	0,12		
							1:00	0,06		
							1:30	0,12		
							2:00	0,12		
							3:00	0,06		
							4:30	0,06		
							5:30	0,40		
							6:30	0,06		
							71:00	0,90		
							72:00	0,71		
							73:00	0,41		
119:15	0,62									
11	1	x2	0	x2	400	288	0:00	0,00	1,08	71:00
							0:30	0,52		
							1:00	0,45		
							1:30	0,26		
							2:00	0,19		
							3:00	0,58		
							4:30	0,32		
							5:30	0,82		
							6:30	0,45		
							71:00	1,08		
							72:00	0,89		
							73:00	0,63		
119:15	0,59									
12	1	x2	x2	0	400	288	0:00	0,00	0,00	0:00
							0:30	0,00		
							65:50	0,00		
							70:50	0,00		
13	2	x2	x2	0	400	288	0:00	0,00	5,00	65:50
							0:30	0,61		
							65:50	5,00		
							70:50	3,28		
14	2	x2	x2	0	400	288	0:00	0,00	2,46	18:00
							0:30	0,55		
							1:00	0,45		
							18:00	2,46		
							20:00	2,21		
							24:00	1,68		
							25:00	1,62		
							45:00	2,06		
46:30	2,03									
15	1	x2	x2	0	400	288	0:00	0,00	7,07	46:30
							0:30	2,84		
							1:00	2,48		
							18:00	5,26		
							20:00	5,13		
							24:00	4,75		
							25:00	4,75		
							45:00	6,97		
46:30	7,07									

16	1	x2	x2	x2	400	288	0:00	0,00	26,48	427:20
							0:30	0,30		
							1:30	0,00		
							2:50	0,00		
							23:50	0,00		
							95:50	5,58		
							427:20	26,48		
17	2	x2	0	x2	400	288	0:00	0,00	5,47	95:50
							0:30	3,17		
							1:30	2,97		
							2:50	2,87		
							23:50	3,58		
							95:50	5,47		
							427:20	4,44, oil level too high		
18	none, empty desiccator						0:00	0,00	0,83	19:15
							0:40	0,26		
							1:15	0,69		
							19:15	0,83		
							21:15	0,01		
							24:15	0,00		
19	none, empty desiccator						0:00	0,00	0,54	19:15
							0:40	0,00		
							1:15	0,34		
							19:15	0,54		
							21:15	0,26		
							24:15	0,01		
20	2	0	x1	0	400	288	0:00	0,00	6,00	25:00
							0:30	1,23		
							2:00	1,64		
							21:00	2,26		
							24:00	4,51		
							25:00	6,00		
							44:00	4,91		
							45:30	4,91		
							48:30	6,00		
21	1	0	x1	0	400	288	0:00	0,00	5,90	44:00
							0:30	1,83		
							2:00	2,34		
							21:00	4,14		
							24:00	4,31		
							25:00	4,07		
							44:00	5,90		
							45:30	5,05		
							48:30	4,98		
22	1	x1	x1	0	400	288	0:00	0,00	5,56	259:30
							1:30	1,52		
							67:30	1,55		
							71:30	0,22		
							94:30	4,10		
							234:00	5,41		
							259:30	5,56		

23	2	x1	x1	0	400	288	0:00	0,00	6,07	234:00
							1:30	1,43		
							67:30	5,42		
							71:30	2,58		
							94:30	5,44		
							234:00	6,07		
							259:30	5,30		
24	1	x2	x2	0	400	288	0:00	0,00	6,17	48:15
							0:30	1,42		
							16:15	4,31		
							20:15	3,49		
							23:45	3,70		
							43:15	6,10		
48:15	6,17									
25	1	x2	0	x2	400	288	0:00	0,00	3,39	16:15
							0:30	1,77		
							16:15	3,39		
							20:15	2,25		
							23:45	1,97		
							43:15	2,82		
48:15	1,91									