

# Degradation of Low Density Polyethylene During Extrusion. IV. Off-Flavor Compounds in Extruded Films of Stabilized LDPE

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**ABSTRACT:** This study was aimed at finding a correlation between the experienced off-flavor in packed foods and the presence of specific degradation products in LDPE packaging films. The possibility to trap degradation products by chemical reactions with scavengers, i.e., a zeolite additive or antioxidants, was investigated. This would prevent degradation products from migrating to the polymer film surface and further into food in contact with the film. It was found that off-flavor noted in water packed in LDPE films depended on extrusion temperature and exposure time for the melt to oxygen, that is, the parameters that influence the contents of oxidation products that are able to migrate from the polymer film. It was also found that adsorption of oxidative degradation products in a zeolite additive or protection of LDPE by using antioxidants could prevent off-flavor

in the packed product (water). However, the antioxidant should be selected with regard to extrusion temperature because thermal instability in the additive might jeopardize the intended effect. Multifunctional antioxidants seem to provide improved protection, the most effective one evaluated in this work being Irganox E201, i.e., vitamin E. Concentrations of oxidized degradation products are well correlated to the perceived off-flavor in the packed water. The highest correlation between off-flavor and oxidized components was found for ketones in the range of C<sub>7</sub> to C<sub>9</sub> and aldehydes in the range of C<sub>6</sub> to C<sub>9</sub>. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 583–595, 2005

**Key words:** polyethylene; degradation; degradation products; extrusion; stabilizers; antioxidants

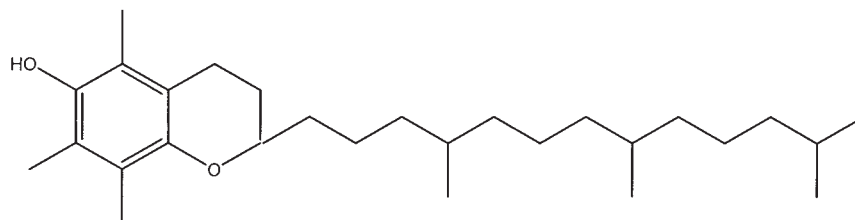
## INTRODUCTION

In all societies the demand for quality increases all the time. In this respect, packaging in general, and more specifically food packaging, is increasingly in focus. The concept of quality is a very subjective one and depends on time, place, occasion, and the habits of the consumers. Considering the consumers' demands, the main quality parameters are appearance, color, texture, and flavor of the food. These parameters are classified as sensorial attributes and cannot directly be evaluated by physical–chemical analyses. More subjective methods have to be used, employing trained sensory panels and specific methodology. The perceived taste of food itself depends on the original taste of the food as well as contaminants released by the package that the food is distributed in. However, analytical instruments and procedures are continuously developed, and lower and lower concentrations of flavor components as well as contaminants can be

detected. This fact provides us with increased possibilities for evaluating and understanding the interaction between perceived off-flavor and chemical components present in the food.

Polyethylene (PE) is the most important polymer used in food packaging. Ethylene polymers degrade during processing and the contribution from the degraded PE to taste and odor has been investigated and reported in several papers.<sup>1–11</sup> Because of the increased quality demands there is an increasing interest in finding correlations between quality factors and marker substances, i.e., off-flavor. Storm van Leeuwen et al.<sup>8,10</sup> have discussed the relation between the presence of aldehydes, ketones, and acids in extrusion coated polyethylene film samples, and the off-taste generated in food packed in these films. They also reported a synergistic behavior of aldehydes, ketones, and acids giving off-flavor sensations even though the different components were below their threshold concentrations. Based on our previous work regarding degradation products found in extruder smoke<sup>1</sup> and in extruded PE films,<sup>12</sup> we extended our study with attempts to understand what types of components cause off-flavor in water being packed in LDPE. The aim of this study was to find a correlation between the

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**Scheme 1** The structure of Irganox E201.

experienced off-flavor and PE degradation products present in extruded film.<sup>13</sup> The present article deals with the effects of different antioxidants and their concentrations in a LDPE material aimed for extrusion coating on the degradation products and their relation to the perceived off-flavor.

## EXPERIMENTAL

### Materials

#### Low density polyethylene

The LDPE grade used in the study was CA 8200, Borealis AS, Norway, with a density of 918 kg/m<sup>3</sup>, and a melt flow index of 7.5 g/10 min.<sup>14</sup>

#### Adsorbent

One inorganic zeolite type adsorbent, Abscent 3000, 89,768–2042000364, from UOP, Des Plains, IL (USA), designated Zeolite, was used in the investigation. This adsorbent has a hydrophilic structure and has affinity for oxidized degradation products.

#### Irganox E201

Irganox E201 is a hindered phenol antioxidant (Ciba Speciality Chemicals, Basel, Switzerland) based on

$\alpha$ -tocopherol (vitamin E). The structure is given in Scheme 1. According to the producer the additive has high compatibility with polyolefins and low migration.<sup>15</sup>

#### Irgafos 12

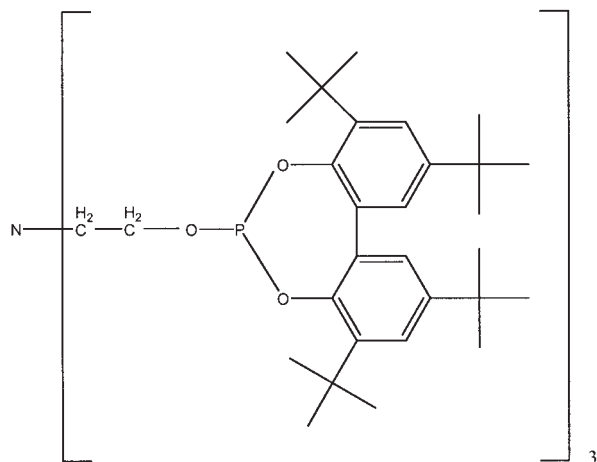
Irgafos 12 is trivalent phosphorus based peroxide decomposer (Ciba Speciality Chemicals, Basel, Switzerland). The additive is claimed to have high hydrolytic stability. The structure is given in Scheme 2.<sup>15</sup>

#### Irganox HP 136

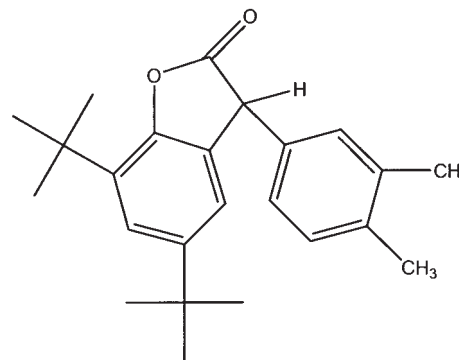
Irganox HP 136 is a lactone-based antioxidant (Ciba Speciality Chemicals, Basel, Switzerland). According to the manufacturer the additive has the structure given in Scheme 3, and it is able to trap both carbon-centered and the peroxy radicals with high efficiency.<sup>15,16</sup>

#### Material preparation

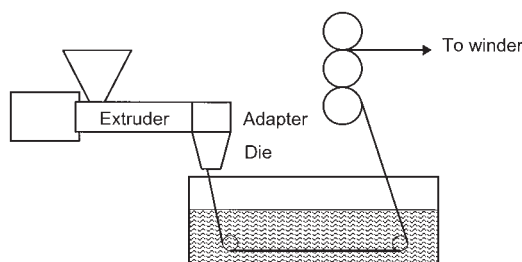
Six different material samples were prepared. As a reference sample pure LDPE was used as delivered in polyethylene bags. Blends of LDPE and 1,000 mg/kg Zeolite, 300 and 600 mg/kg Irgafos 12, 100 mg/kg Irganox E201, and 200 mg/kg Irganox HP 136, respectively, were prepared. For the preparation of the blends the desired amounts of LDPE and the additive were accurately weighed in a polyethylene bag and dry blended. The bag was agitated until a uniform mix



**Scheme 2** The structure of Irgafos 12.



**Scheme 3** The structure of Irganox HP 136.



**Figure 1** Film extrusion set-up. The exposure distance for oxygen was adjusted by the water level in the water bath. The exposure distances were 20, 50, and 80 mm.

was obtained and then supplied directly to the extruder and extruded without segregation.

### Process equipment

Film extrusion was carried out with a laboratory extruder, Rheocord 90 (HAAKE, Karlsruhe, Germany), having a 19 mm screw diameter (L : D of 24 : 1, compression ratio of 4 : 1) and equipped with a Mad-doc shear module. The equipment used horizontal extrusion through a die turned 90° to a vertical position above a water bath (Fig. 1), which was used to control the exposure time to atmospheric oxygen. After the water bath a take-off unit wound up the film. With this set-up, film samples were prepared. Adjusting the distances between the die and the water surface regulated the melt exposure time to atmospheric oxygen. Exposure distances of 20, 50, and 80 mm were used. The take-off unit was set at constant speed of 5.0 m/min and the extruder screw speed at 60 rpm, which gave a suitable film width, thickness, and surface area. The exposure time for the molten film in contact with air was estimated at approximately 1.9 s for the 80 mm air gap. The used extrusion temperature profiles (Table I) gave polymer melt temperatures of approximately 280, 300, and 320°C.

### Film sampling

The film extrusion was run at least 45 min for equilibration at every new temperature profile before sampling, which was done in two ways. For the identification of degradation products the film samples were

cut out at the winder stand without winding the film. The samples were placed into loosely wound coils wrapped in grease-free 18  $\mu$ m aluminum foil (Plus Pack AS, Odense, Denmark). Samples for off-flavor evaluation were taken as bundles of film sheets, without separation, by cutting the film coil and wrapping in aluminum foil. This procedure protected the sample from contamination and evaporation of low molecular weight material.

### Off-flavor evaluation

#### Sample preparation

Water was used for sensory evaluation due to neutral taste and simple detection of flavors.<sup>17</sup> Water used in the evaluation of off-flavor was activated carbon-filtered municipal tap water, which had been flushed for 4 h prior to collection in 1-L glass bottles. The water was recognized as extremely good by the sensory group and was referred to as having no taste of its own. Approximately 3.50 g each of the extruded film samples were put into glass bottles prior to filling with 1,000 mL water. This is approximately the same amount of polymer film as the food contact layer in a 1-L carton package. Three bottles were prepared per sample, and they were left for 24 h at room temperature (23°C). From each bottle 700 mL was used for the sensorial evaluation and the remaining 300 mL from the bottles was combined and used for chemical analysis.

#### Evaluation procedure

Four different evaluation sessions were performed. Each session consisted of six different samples. Each set of samples was judged from an off-flavor intensity point of view. The samples were served to the panelists in well-ventilated polypropylene cups covered by a polypropylene lid. Random codes, which were different from one analysis to another, identified the samples. A panel of trained panelists consisting of 16 persons carried out the sensory evaluations of the water sample. The panel routinely tests packaging material off-flavor in water, using an unstructured 120-mm linear scale according to the ISO 6564-1985 9.1.3. To facilitate the further handling of data, the

**TABLE I**  
Extruder Temperature Settings<sup>a</sup>

Profile	Zone 1 (°C)	Zone 2 (°C)	Zone 3 (°C)	Zone 4 (°C)	Zone 5 (°C)	Zone 6 (°C)	Melt temperature (°C)
280	230	255	280	280	274	274	280
300	230	270	300	300	290	290	300
320	255	285	320	320	310	310	320

<sup>a</sup> Extruder screw: zone 1-3; adapter: zone 4; die: zone 5-6. The melt temperature is measured at the melt inlet in the die.

120-mm scale was rescaled to intensity scores 0–100 by dividing the ratings by 1.2.

To compare the results obtained in previous work,<sup>18</sup> in which the ISO 4120–1983 B3 scale was used, the intensity score scale was divided into six equal intervals. Intensity scores 0–17 then equal to “No off-flavor,” 18–33 to “Very weak off-flavor,” 34–49 to “Weak off-flavor,” 50–67 to “Average off-flavor,” 68–83 to “Strong off-flavor,” and 84–100 to “Very strong off-flavor.”

### Identification of oxidation products

#### Sample preparation

*Film.* A small piece of film was cut out from a film sample with clean scissors. The film sample was picked from one of the layers situated in the middle of the coil. The weight of the sample was adjusted to 80 mg and accurately weighed using a Mettler AT 250 balance (Mettler Toledo, Greifensee, Switzerland). The film sample was wound around a glass-rod and put into a desorption glass tube. The tube was then placed in the sample rack of the thermo desorption autosampler.<sup>12</sup>

*Water.* An internal standard was prepared by weighing  $100.0 \pm 1.0$  mg of 1,4-dibromobenzene (CAS 106–37-6, 99%, Acros Organics, Geel, Belgium) into a vial and diluting it with 10.0 mL dichloromethane (Enviroscan 99.9%, Lab-scan, Stillorgan, Dublin, Ireland). Of this solution 10  $\mu$ L was added to 10.0 mL of methanol (Pestiscan 99.9%, Lab-scan).

Stripper vials with a side injection port (volume 100 mL) were cleaned with 3% solution of a detergent (Extran MA02 neutral, Merck, Darmstadt, Germany) and rinsed at least five times with ultrapure water filtered through a Milli-RQ 6 PLUS with Millipore Purification Pak (Millipore SA, Molsheim, France) and stored in an oven at 150°C. The vials were loaded with 100.0 g of water samples used in the sensory evaluation as described above. Of the internal standard solution, 10.0  $\mu$ L was introduced to the stripper vials below the liquid level.

Dynamic headspace analysis was used for identification of volatile organic compounds in the water phase. Helium gas (scientific helium 6.0, Air Liquide Gas AB, Malmö, Sweden) was bubbled through the aqueous samples by means of a Dynamic Thermal Stripper (Model 1000, Dynatherm Analytical Instruments, Inc., Kelton, PA, USA). The volatile compounds passed together with the gas and adsorbent, Carbotrap 300 (200 mg Carbotrap B and 300 mg Carbotrap C) from Supelco (Supelco Park, Bellefonte, PA, USA). The adsorbents were preconditioned in reverse purge flow in a tube conditioner Model 60 Six (Tube Conditioner, Dynatherm Analytical Instruments, Inc. Oxford, PA, USA) at 265°C for 44 min with a 9-min

cooling time prior to testing. The dynamic headspace analysis was run with a purge flow of 100 mL/min and a preheat time of 15 min. To strip the volatiles from the water, a 25-min bubble time followed by an adsorbent drying time of 10 min was used. The temperature settings were 140, 70, and 65°C for the block, the oven, and the tube, respectively. After trapping, the absorbent tube was transferred to a thermal desorption system.

#### Analysis

*Film.* The analytical set-up consisted of a thermodesorption unit (TDS-2) equipped with a thermodesorption autosampler (TDS-A) from Gerstel (Gerstel GmbH and Co. KG, Mülheim an der Ruhr, Germany). Through the desorption chamber a flow of 50 mL/min of He was passed. After equilibration at 20°C the sample tube (Gerstel, o.d. 6.0 mm/i.d. 3.9 mm, length 178 mm), was inserted. The temperature was held at 20°C for 1 min for flushing the system free from oxygen before increasing the temperature to 100°C at 60°C/min. The temperature was then held at 100°C for 20 min. The flow from the thermodesorption unit was passed through a deactivated capillary transfer line (o.d. 0.70 mm/i.d. 0.53 mm and length 145 mm), held at 275°C, to the cooled injection system (CIS-3, Gerstel) in the gas chromatograph. During desorption the He flow (50 mL/min) thorough the desorption chamber passed the cooled injection system, which was held at –70°C to trap the desorbed compounds. After the desorption step the injector was put in splitless position for 1 min. The flow through the injector and the column was then approximately 1 mL/min. The temperature was initially kept at –70°C for 0.5 min and then rapidly increased to 300°C at 12°C/s. The temperature was then held at 300°C for 10 min for cleaning the injector.

A Gas Chromatograph HP5890 Series II (Hewlett-Packard, Palo Alto, CA, USA) equipped with Mass Selective Detector MSD 5971 Series (Agilent Technologies, Palo Alto, CA, USA) was used. The column was HP-1 (crosslinked methyl siloxane) 60 m  $\times$  0.32 mm, with 1.0  $\mu$ m film thickness. The flow was pressure regulated with a head pressure of 9 p.s.i., which gave a column flow of 1.0 to 1.5 mL/min. The oven temperature was initially held at 20°C for 0.5 min and then was increased to 260°C at 5°C/min. The temperature was held at 260°C for 4 min. The transfer line to the mass selective detector was kept at 280°C. Electron impact mode was used at 70 eV. Scanning was performed between  $m/z$  30 and 350. The resulting electron multiplication voltage was used in the standard spectra autotuning mode. Solvent delay was 5 min. Software used was Chemstation G1701AA Version A.03.00 from Agilent Technologies.

Every film sample was evaluated in triplicate and, between every two samples (six desorption runs), a blank consisting of an empty desorption glass tube including the glass rod was run to ensure the cleanliness of the column.

*Water.* Identification of oxidation products was done with GC/MS. The set-up consisted of a thermodesorption unit TDS-2 equipped with a thermodesorption autosampler TDS-A from Gerstel (Gerstel GmbH and Co. KG, Mülheim an der Ruhr, Germany). After equilibration of the desorption chamber at a flow of He of 50 mL/min and 30°C, the sample tube (Gerstel, o.d. 6.0 mm/i.d. 3.9 mm, length 178 mm) was inserted. The temperature was held at 30°C for 1 min for flushing the system of oxygen before increasing the temperature to 265°C with 60°C/min. The following analytical procedure was identical to the film procedure as above.

*Identification of oxidized volatile components.* Organic acids (acetic acid to dodecanoic acid) were analyzed by integrating the ion-chromatograms at  $m/z = 60$ ,<sup>19</sup> except for propanoic acid. Propanoic acid was not included because it does not give rise to the  $m/z = 60$  peak as all other organic acids do.

Aldehydes (butanal to dodecanal) were analyzed by integrating the ion-chromatograms at  $m/z = 44$ .<sup>19</sup>

Ketones, preferable methyl-ones, were analyzed by integrating the ion-chromatograms at  $m/z = 58$ <sup>19</sup> and at  $m/z = 85$ .<sup>19</sup>

All peaks were integrated in the Total Ion Count mode (TIC) at the identified retention time to obtain representative amounts of each component.

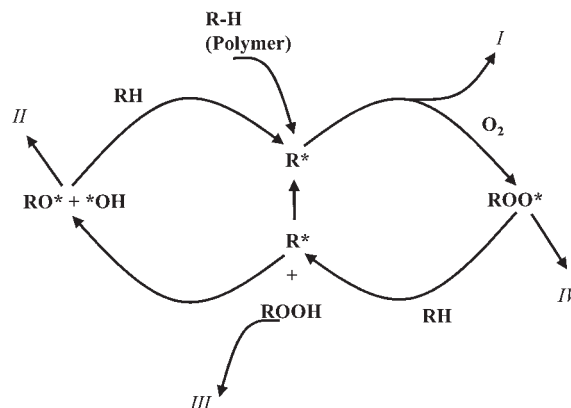
### Correlations between off-flavor and oxidation compounds

To identify which components are most likely to cause off-flavor in the water samples, Simca P-8 software (Umetrics AB, Umeå, Sweden) for Principal Component Analysis<sup>13,20</sup> was used. To simplify the statistical evaluation the TIC chromatograms were recalculated with a time resolution of 0.04 min. The data sets were analyzed with the Partial Least Squares Projection to Latent Structures model (PLS) by the Simca P-8 software with the TIC per retention time as the predictor according to their contributions to off-flavor as the dependent.<sup>20,21</sup> By this technique compounds contributing most to the off-flavor variation could be identified.

To evaluate which of the volatile compounds that correlates to the off-flavor ranking, the Simca-P8 software program for Principal Component Discriminate Analysis<sup>20,21</sup> (PLSDA) was used.

## RESULTS AND DISCUSSION

In our previous work<sup>1,12,13</sup> we have discussed polyethylene degradation during extrusion coating, which



**Scheme 4** Autooxidation cycle of polyolefins. R- is the polymer residual molecule and the Roman numbers I-IV denote different reaction possibilities for the antioxidant.

types of degradation products are formed, and from which step in the process they originate. Other studies reported in the literature,<sup>9,10,18,19,22</sup> although conducted at lower temperatures, have shown similar degradation product patterns. Alcohols and esters seem to be more abundant at lower temperatures. We have also investigated the possibility of trapping radicals and degradation products by chemical reaction with scavengers to prevent degradation products from migrating from the polymer film into food that is in contact with the film. The off-flavor generated in water, which had been in contact with the various polyethylene films, was evaluated by a trained sensory panel.<sup>18</sup> Encouraged by the results in that investigation our aim in the present work was to minimize the degradation-related off-flavor that was induced in water.

In previous studies,<sup>12,23</sup> we have reported that the volatile oxidative degradation products remained the same when a primary antioxidant was added to the LDPE. From this finding it was concluded that the migration of degradation products and the corresponding off-flavor would be independent of the radicals formed in the extruder barrel at high or low concentrations of antioxidants. The oxidative degradation was found to mainly depend on the temperature of the melt and the contact time to oxygen in the air gap, which is in line with other reports.<sup>9,10</sup> At the film surface reactions between primary carbon-centered radicals and the surrounding oxygen in air will generate a high concentration of oxygen-centered radicals. These radicals will enter into the autooxidation reaction cycle (Scheme 4) and rapidly generate substantial amounts of oxidized degradation products, which might generate off-flavor in packed food. Consequently, the effects of secondary and combined primary and secondary antioxidants on degradation products and off-flavor were investigated.

In the present study one LDPE grade that was designed for extrusion coating was selected. Virgin

TABLE II  
Design Matrix with Responses for All 26 Experiments<sup>a</sup>

Experiment no.	$x_1$ Extrusion temperature		$x_2$ Air gap		$x_3$ Additive concentration (mg/kg)	$x_4$ Type of additive	Y Off-flavor scores
	280°C	320°C	20 mm	80 mm			
7-01		+	+		1,000	Zeolite	61
7-02	+			+	1,000	Zeolite	2
7-03	+		+		600	Irgafos 12	8
7-04		+		+	600	Irgafos 12	74
7-05	+		+		100	Irganox E201	23
7-06		+		+	100	Irganox E201	72
7-07		+	+		100	Irganox E201	59
7-08	+			+	200	HP136	37
7-09	+		+		200	HP136	17
7-10		+	+		200	HP136	66
7-11		300°C		50 mm	300	Irgafos 12	48
7-12	+		+		0	No additive	18
7-13	+			+	0	No additive	33
7-14		+		+	0	No additive	70
7-15		+	+		0	No additive	66
7-16	+		+		100	Irganox E201	8
7-17	+			+	1,000	Zeolite	22
7-18	+		+		1,000	Zeolite	8
7-19		300°C		50 mm	300	Irgafos 12	58

<sup>a</sup> 7-02 and 7-05 were omitted from the model evaluation (see text).

LDPE was compared to the same LDPE grade containing a zeolite adsorbent, a secondary antioxidant (Irgafos 12), and two multifunctional antioxidants (Irganox E201 and Irganox HP 136), respectively. A multifunctional antioxidant behaves as primary and secondary antioxidants in combination. Primary antioxidants stabilize the initial radicals during the thermomechanical treatment in the extruder, by that reducing the radical concentration in the film exiting the die orifice. Secondary antioxidants would stabilize oxyradicals formed at the polymer melt surface in the air gap. A decreased radical concentration in the melt would lower the amounts of oxidized degradation products in the film, thus decreasing the off-flavor intensity in the packed product (water). Antioxidants that are both primary and secondary radical stabilizers would thus be the most effective ones with respect to decreasing the off-flavor intensity.

Another interesting issue is how effective adsorbing the oxidized degradation products in an adsorbent would be relative to using an antioxidant. Degradation products formed from the antioxidant itself at high temperatures might influence the off-flavor intensity and thus be related to the thermal stability of the antioxidants.

The effects on off-taste of the selected additives in water being in contact with the extruded films were evaluated through a reduced multifactorial experimental design, as seen in Table II. This design was created by the Modde 6.0 software<sup>20</sup> and reduced to predict synergistic effects at a two-factor level in accordance with eq. (1).<sup>21</sup>

$$Y = \beta_0 + \sum_{i=1}^n \beta_i x_i + \sum_{i=1}^{n-1} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

$$(i < j; 1 \leq j \leq n)$$

Factors used ( $x_i$ ,  $x_j$ ) were extrusion temperature, exposure time in air gap, additive type, and concentration of additive. The off-flavor intensities ( $Y$ ), ranked by the sensory panel, were fitted into the multilinear regression model given in eq. (1). The parameters  $\beta_{0-4}$  are fitting constants and  $\varepsilon$  is the residual response variation not described by the model. The used maximum concentrations of respective additive in the extruded films were based on recommendations given by the antioxidant producer. The concentration of adsorbent was based on previous work.<sup>18</sup> In the present study one-tenth of that concentration was selected based on the good effect the zeolite had shown earlier.

Off-flavor intensity was rated by the sensory panel in accordance with previous work.<sup>18</sup> The sensory evaluation results were clear and uniform in the ranking of off-flavor between the tested samples as seen in Table II. Applying eq. (1) to experiments 7-01 to 7-19 (Table II) indicated that experiment 7-02 and 7-05 had unexpected off-flavor intensities. By further statistical calculation on these experiments it was concluded that these samples (7-02 and 7-05) were outliers.

Sample number 7-19 was a replicate of sample 7-11. The off-flavor score noted for 7-25 was higher than that noted for 7-14. However, the higher score value can be explained by the fact that 7-19 was the only high off-flavor sample present in the new series (sample 7-16 to

**TABLE III**  
Quality Parameters Obtained for the Multilinear Regression Model Used

Parameter	Value	Critical value
Goodness of fit ( $R^2$ )	0.97	$0 < R^2 < 1$ (perfect model)
Goodness of prediction ( $Q^2$ )	0.91	$-\infty < Q^2 \leq 1$ (perfect model)
Regression $p$ value	0.00	$p < 0.05$
Lack of fit $p$ value	0.67	$p > 0.05$
Condition number	3.3 <sup>a</sup>	

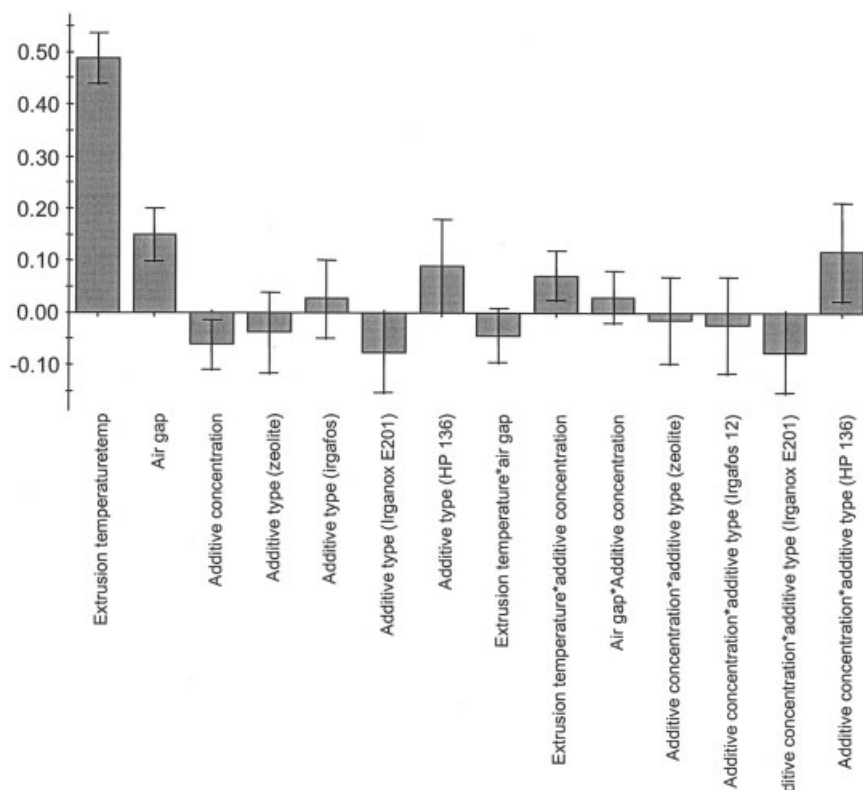
<sup>a</sup> Implies good design considering that it contains quality variables.

7–19). It is known that the panelists tend to overestimate a score for a sample with odd intensity in a series.<sup>18</sup>

In the further evaluation, samples 7–02 and 7–05 were excluded and multilinear regression (MLR) was applied to the remaining samples. Comparing the quality parameters as seen in Table III, the model showed good fit to the data. Considering that the model contains qualitative variables, the Condition Number of 3.3 points to a good design.<sup>21</sup>

The regression coefficients for the investigated variables, i.e., [extrusion temperature], [air gap], [additive concentration], and [type of additive] (Table II) are plotted in Figure 2. A positive regression coefficient implies that an increase of the variable generates an off-flavor intensity increase. It can thus be concluded

that the variable [extrusion temperature] is the most important one for the experienced off-flavor intensity, which has also been discussed by others.<sup>9,11</sup> Other significant variables with positive regression coefficients leading to increased off-flavor intensity were [air gap] and [HP 136 additive], together with the two-factorial interactions [temperature  $\times$  additive concentration] and [HP 136 additive  $\times$  additive concentration]. Significantly negative regression coefficients were generated by the variables [additive concentration] and [Irganox E201 additive], implying that the off-flavor intensity decreases with increasing variable level. No other variables and two-factorial interactions significantly contributed to the perceived off-flavor intensity.



**Figure 2** Coefficient plot generated by the statistical model created from the reduced multifactorial experimental design (Table II).

TABLE IV  
Sensory Evaluation of LDPE Films Extruded at Different Temperatures and Air Gaps and Using Different Additives<sup>a</sup>

Extrusion		Off-flavor ratings				
Temperature (°C)	Air gap (mm)	Irgafos 12	Irganox E201	HP 136	Zeolite	LDPE (reference)
280	20	0	0	1	0	1
280	50		0			
280	80		0	2	1 [0]	2 [1]
300	50	3				
320	20		3–4	4	3	3–4
320	80	4	4		4 [2]	4 [4]

<sup>a</sup> The scale used is, no off-flavor (0), very weak off-flavor (1), weak off-flavor (2), average off-flavor (3), strong off-flavor (4), and very strong off-flavor (5). The values in brackets are results reported previously.<sup>18</sup>

### Off-flavor

Given the results from the reduced factorial experiment the effects of different additive types on the off-flavor were considered. It can be concluded from the regression coefficient plot in Figure 2 that the off-flavor intensities for all additives were clearly dependent on the extrusion temperature and the exposure time of the melt to air prior to quenching. The effects of each type of additive, i.e., adsorbents, primary antioxidants, and secondary antioxidants, respectively, are discussed in detail below. It can be noted that the off-flavor ratings were similar to those previously reported.<sup>18</sup>

### Zeolite

In the present study a zeolite concentration of 1,000 mg/kg was evaluated, which is only one-tenth of the concentration evaluated for off-flavor in our previous work.<sup>18</sup> Despite the lower additive concentration the results obtained in the present study did correlate well to those reported earlier<sup>18</sup> (Table IV). At 280°C extrusion temperature no difference at all between the studies was detected (“No off-flavor”). At the high extrusion temperature (320°C), however, a difference was noticed. In the present study an off-flavor rating equal to “Strong off-flavor” was obtained rather than “Weak off-flavor.” This is explained by the fact that a higher adsorbent concentration has a larger adsorption capacity and, consequently, less oxidized polyethylene degradation products can migrate into the water, causing off-flavor. The model based on eq. (1), as seen in Figure 2, also shows this. The regression coefficients of variable [zeolite additive] and the two-factorial variable [additive concentration × zeolite additive] indicate a negative response, however it is not significant. It is also clear from Figure 2 that the general parameter [additive concentration] gave a significant negative coefficient. In Figures 3 and 4, the predicted off-flavor responses according to the model for the

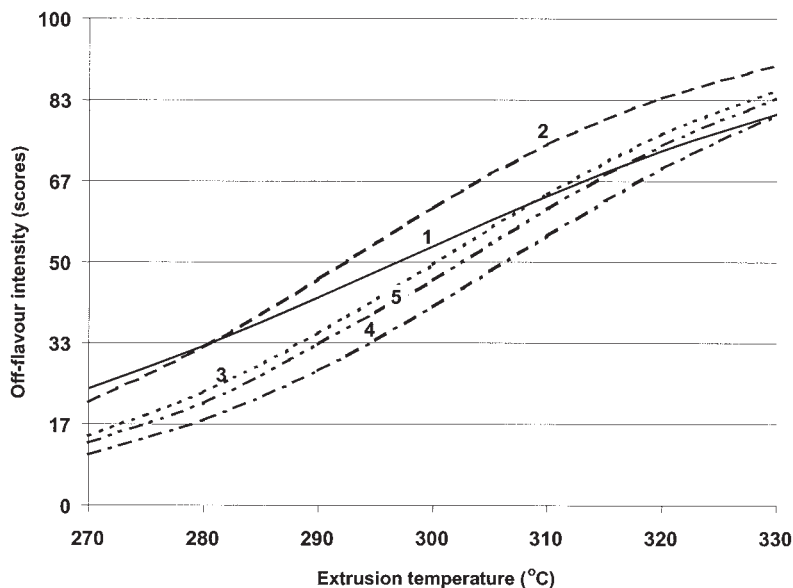
extrusion temperature interval 270–330°C are plotted. From these plots it can be concluded that the zeolite adsorbent additive should decrease the flavor scores in the water throughout the whole temperature range, in comparison to the nonmodified LDPE. It can also be concluded that the sensitivity for melt exposure to oxygen (air) is less important than for pure LDPE. The model thus predicts that adsorption of the oxidized degradation products at the inorganic zeolite improves the taste of the product (water) in the temperature range 270–330°C.

### Secondary antioxidants

One material containing a secondary antioxidant,<sup>24,25</sup> Irgafos 12, was evaluated. According to the manufacturer Irgafos 12 contains phenolic phosphite ester groups attached to nitrogen. Generally phosphites react as hydroperoxide decomposers (Scheme 4 III) in the autocatalytic degradation cycle, where hydroperoxides and peroxy radicals transform into inactive products and phenoxy radicals of lower reactivity (Scheme 5).<sup>24,25</sup>

The phosphite antioxidant seems to be most active at extrusion temperatures lower than 300°C, but at 320°C an instability of the antioxidant itself seems to create more off-flavor than noted for the reference LDPE (Table II). Increasing concentrations of the additive decrease the off-flavor ratings as discussed above for the general concentration variable in Figure 2. Furthermore, the two-factorial response interaction of [additive concentration × Irgafos 12 additive] in Figure 2 was negative. However, it was found that the variable [Irgafos 12 additive] had a positive effect, which means that the obtained off-flavor scores increased relative to LDPE. This effect was not significant. The off-flavor response prediction by eq. (1) in the interval 270–330°C is given in Figures 3 and 4, and it is clear from the figures that the curves representing Irgafos 12 have a steeper increase with temperature



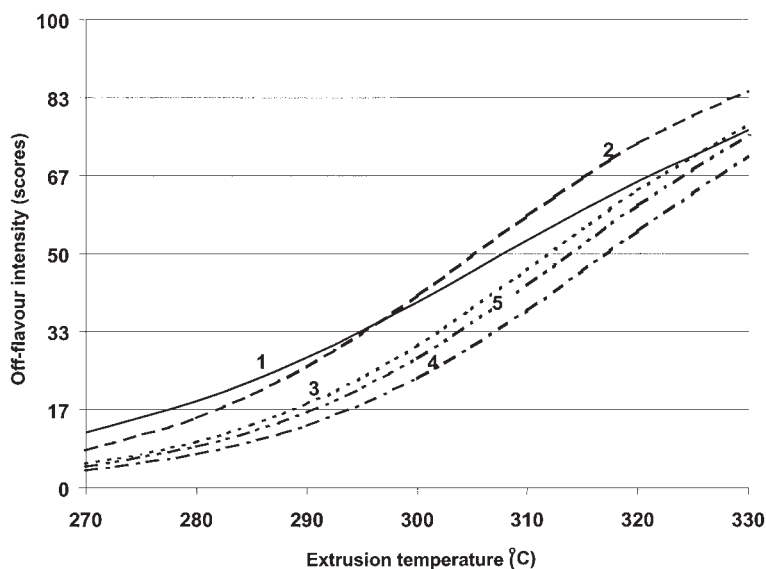


**Figure 3** Off-flavor scores as a function of extrusion temperature for different films extruded with an air gap of 80 mm, as predicted by the statistical model created from the reduced multifactorial experimental design; 1, LDPE film; 2, LDPE film with HP 136 (200 mg/kg); 3, LDPE film with Irgafos 12 (600 mg/kg); 4, LDPE film with Irganox E201 (100 mg/kg); and 5, LDPE film with Abscent 3000 (1,000 mg/kg).

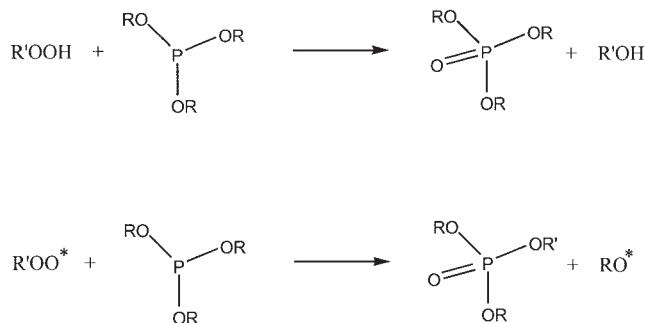
and cross the additive-free reference LDPE film at 310–320°C. This effect might be a result of high amounts of oxyradicals produced at these high extrusion temperatures. It can be observed that the predicted off-flavor ratings at different air gaps (exposure times) cross the LDPE curves at similar temperatures, which implies that Irgafos 12 might be unstable at extrusion temperatures above 300°C and thus loses its radical scavenging effect.

#### Multifunctional antioxidants

Irganox HP 136 is a lactone (Scheme 6) antioxidant that has the possibility of trapping both oxygen and carbon-centered radicals due to the weak C–H bond at the carbon bridging the two aromatic rings. The radicals formed are highly resonance stabilized by the two aromatic rings.<sup>24,25</sup> This highly stabilized radical would be able to terminate a second radical attack.



**Figure 4** Off-flavor scores as a function of extrusion temperature for different films extruded with an air gap of 20 mm, as predicted by the statistical model created from the reduced multifactorial experimental design; 1, LDPE film; 2, LDPE film with HP 136 (200 mg/kg); 3, LDPE film with Irgafos 12 (600 mg/kg); 4, LDPE film with Irganox E201 (100 mg/kg); and 5, LDPE film with Abscent 3000 (1,000 mg/kg).



Scheme 5

The lactone reacts with carbon-centered radicals in the autooxidation cycle (Scheme 4 I), and also yields inactive products with oxygen-centered radicals (Scheme 4 II).

The off-flavor panel rated films stabilized with HP 136 almost equal to the reference LDPE at 280°C, while at 320°C HP 136 had higher ratings than the reference. This fact implies that the lactone itself might be unstable at the high temperatures common to extrusion-coating processes. This could also be concluded from the regression coefficient plot (Fig. 2) where the coefficients for [HP 136 additive] and two-factorial coefficient [HP 136 additive  $\times$  additive concentration] were significantly positive, thus indicating an increase in the off-flavor scores relative to LDPE. The predicted off-flavor intensities in Figures 3 and 4 for HP 136-containing films correlate well with the reference LDPE film. It may be concluded that the lactone stabilizer might not be active at the high extrusion temperatures used. Generally lactone antioxidants are used together with other antioxidants that have long-term stabilization effects, i.e., phenols and phosphites.<sup>24</sup>

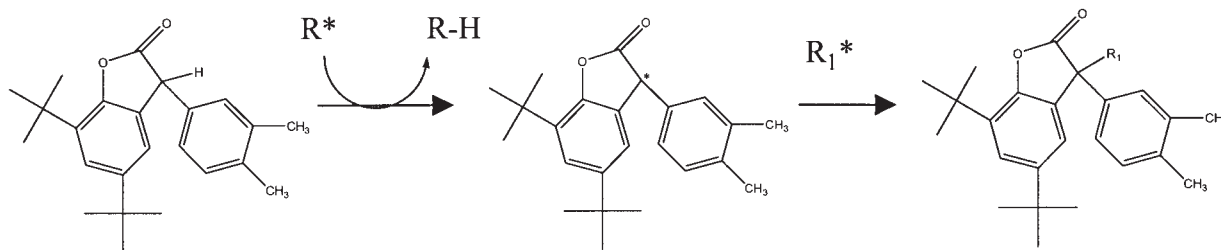
Irganox E201 is a hindered phenol type antioxidant based on  $\alpha$ -tocopherol, i.e., vitamin E (Scheme 7). The  $\alpha$ -tocopherol is a well-known antioxidant used in many different applications, for example, in foods, cosmetics, medical implants, and food packaging.<sup>15,10,26,27</sup>

The radical stabilization mechanism<sup>28</sup> and the reactivity of the additive in the autooxidation cycle leads

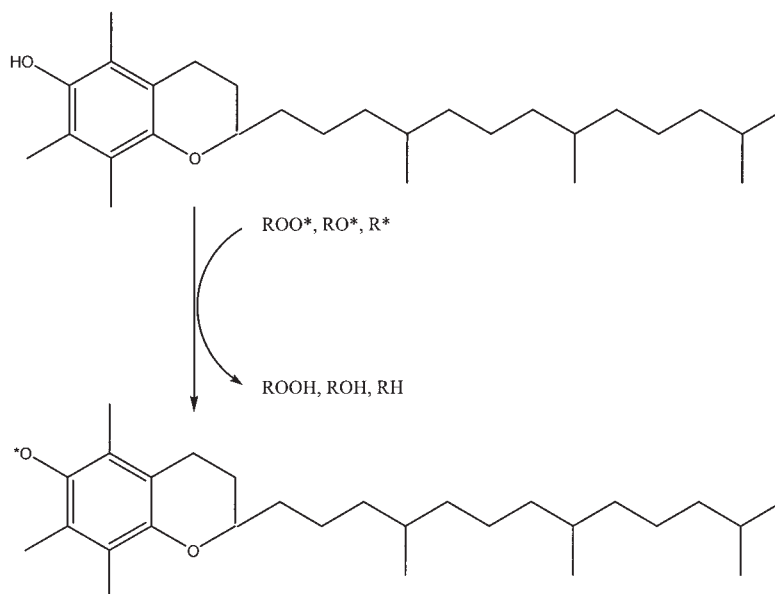
to high efficiency as an antioxidant.  $\alpha$ -Tocopherol reacts with carbon-centered radicals, which slows down the oxidative degradation (Scheme 4 I). In the secondary stage of autooxidation the  $\alpha$ -tocopherol may react with oxygen-centered free radicals to yield inactive products such as alcohols and water (Scheme 4 II).<sup>29</sup> Furthermore, the oxidative degradation would be hindered by the  $\alpha$ -tocopherol and different configurations of the tocopheroxyl radical could react with oxygen-centered radicals (Schemes 4 IV and 7). Radicals derived from  $\alpha$ -tocopherol are stabilized due to the great number of different possible molecular rearrangements and optional reaction possibilities.<sup>28</sup> The reaction rate constant is about 150 times larger for  $\alpha$ -tocopherol than for common hindered phenolic antioxidants.<sup>29</sup>

For films stabilized by  $\alpha$ -tocopherol the off-flavor response was clearly dependent on the extrusion temperature and the time the melt was in contact with air prior to the quenching (Table IV). In Figure 2 the predicted off-flavor ratings according to the statistical model [Eq. (1)] are plotted. The off-flavor scores are illustrated for concentrations of 100 mg/kg Irganox E201. Irganox E201 was the only additive type that had a significantly negative regression coefficient, which implies that the off-flavor scores were lower than the reference LDPE scores in the whole temperature interval examined. The two-factorial [additive concentration  $\times$  Irganox E201 additive] had also a negative regression coefficient; however, it was not significant. The antioxidant seems to be most effective at large air gaps. This could be an effect of the high reaction rates for radical reactions, which prevents the radical concentration from exceeding critical concentrations for forming oxidized degradation products.

The surface oxidation of LDPE is highly increased by the exposure time, as observed previously.<sup>12,23</sup> In the statistical model this fact is evident in the coefficient plot (Fig. 2) from the large positive regression coefficients for the variables [extrusion temperature] and [air gap].  $\alpha$ -Tocopherol gives decreased off-flavor scores relative to LDPE throughout the whole temperature interval, even at the highest temperatures studied (Figs. 3 and 4). This can be explained by the additive having a high temperature stability and a



Scheme 6



Scheme 7

high reaction rate constant.<sup>29</sup> A higher concentration of  $\alpha$ -tocopherol in the polymer might lower the off-flavor ratings due to oxidative degradation, but it should be kept in mind that the additive itself could contribute to the perceived off-flavor, as discussed above.

#### Comparing the different additives

Comparing how the different additives influence the off-flavor intensities it can be concluded that  $\alpha$ -tocopherol (Irganox E201) seems to be the most effective within the whole extrusion temperature interval studied (Figs. 3 and 4). This finding is also in line with results presented by Storm van Leeuwen et al.<sup>10</sup> The phosphite-based antioxidant (Irgafos 12) and the zeolite behaved similarly but were predicted to give higher off-flavors compared with the  $\alpha$ -tocopherol. This difference was probably a result of not optimizing additive concentrations with respect to off-flavor scores. It can be concluded from Figure 2 that the concentration has a significant influence on the off-

flavor. All additives lowered the off-flavor scores at low temperatures, while at extrusion temperatures above 290–295°C the lactone-based additive (HP 136) created more off flavor than the reference LDPE. This can be concluded from Figure 2 where this additive gives a significant positive coefficient for both the variable [HP 136] and the two-factorial parameter [concentration  $\times$  additive type HP 136].

#### Comparing model predictions with experiments

To evaluate the model predictability of off-flavor intensities some new test films were produced. The materials and processing conditions are given in Table V. These films were evaluated and their off-flavor intensity rated in accordance with the methodology described above. The results from these experiments is listed in Table V, and it can be concluded that the off-flavor intensities predicted by the statistical model correlated well with those obtained in the evaluation.

TABLE V  
Test of Model Prediction Accuracy for Off-Flavor

Extrusion temperature (°C)	Air gap (mm)	Additive concentration (mg/kg)	Predicted off-flavor scores	Obtained off-flavor scores	Obtained/predicted ratio
320	80	Zeolite 1,000	73	69	0.95
300	50	Irgafos 12 300	45	51	1.13
320	80	No additive 0	72	70	0.96
280	80	Irganox E201 100	14	12	0.86
280	50	Irganox E201 100	10	10	1.00

TABLE VI  
Compounds Found To Correlate Most to the Perceived Off-Flavor in Water<sup>a</sup>

Rank	Alcohol	Aldehyde	Ketone
1			5-Nonanone
2			2-Nonanone
3			3-Heptanone
4			2-Octanone
5		Octanal	
6		Hexanal	
7		Heptanal	
8			3-Octanone
9			4-Octanone
10	5-Nonanol		
11	1-Decanol		
12			2-Heptanone
13	Nonanol		
14			3-Nonanone
15	2,4-Dimethyl-4-heptanol		
16		2-methylpropanal	
17		Nonanal	
18	3-Nonanol		

<sup>a</sup> No acids were found, as discussed in text.

### Correlations between off-flavor and oxidized products

To find out which components are most likely to cause off-flavor in the packed water, Simca-P8 software<sup>13</sup> for PLS was applied. The TIC chromatographic data as predictors were tested against the perceived off-flavor data as dependents. The PLS approach, which was discussed in the previous work,<sup>18</sup> identified the most off-flavor-giving compounds as ketones (as nonanones, heptanones, and octanones), together with aldehydes (hexanal, heptanal, octanal, and nonanal) and alcohols (as primary, secondary and tertial alcohols) (Table VI). These findings are in line with the results found in previous work.<sup>10,18</sup>

Other researchers have reported<sup>8,9</sup> that the presence of carboxylic acids is needed to produce off-flavor from aldehydes and ketones present in the water at very low concentrations, probably by synergism. The effect on off-flavor from the carboxylic acids in the present system is an unsolved issue and will be further investigated. The acids were present in the extruded films but could not be found in water exposed to the films. They should, however, most likely be present in the water but because of the analytical technique used they were not detected, as discussed in previous work.<sup>18</sup>

### CONCLUSIONS

From this work it was concluded that the off-flavor noted in water packed in LDPE film depended on extrusion temperature and exposure time for the melt to oxygen, that is, the parameters that influence the contents of oxidation products able to migrate from

the polymer film. It was also concluded that adsorption of oxidative degradation products in a zeolite or protecting the LDPE by using antioxidants could prevent off-flavor in the packed product (water). However, the antioxidant should be selected with regard to extrusion temperature because thermal instability in the additive might jeopardize the aimed effect. Multifunctional antioxidants seem to provide improved protection, the most effective one evaluated in this work being the Irganox E201 (vitamin E). Concentrations of oxidized degradation products are well correlated to the perceived off-flavor in the packed water. The highest correlation between off-flavor and oxidized components were found for the ketones in the range of C<sub>7</sub> to C<sub>9</sub> and aldehydes in the range of C<sub>6</sub> to C<sub>9</sub>.

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