Arabian Journal of Chemistry (2017) **10**, S1938–S1954

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Characterization of plastic packaging additives: Food contact, stability and toxicity

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Received 31 May 2012; accepted 18 July 2013
Available online 24 July 2013

KEYWORDS

Antioxidants;
Endocrine disruptors;
Heavy metals;
Phtalates;
Spectrometry;
NIAS

Abstract Plastic additives are analyzed by spectrometric (FTIR, ICP-AES) and chromatographic (GC/MS, HPLC) methods in order to define their stability, purity and toxicity. All findings relate to the compounds identified in our packaging and their effect on human health. We wanted to show that some additives contain heavy metals (lead, cobalt, nickel, copper, etc.), highly toxic phtalates (Dibutyl phtalate or DBP) and contaminants (Non-intentionally added substances: NIAS, degradation products). Some additives used are even carcinogenic or tumorigenic.
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1. Introduction

Eighty percent of plastics in the world are thermoplastics. The most commonly used ones in food packaging industry are usually polystyrene, polyethylene, polyvinyl chloride, etc. (Reyne, 1991). Additives are introduced in polymers in order to improve the physical (mechanical, thermal, etc.) and chemical properties of the packaging (Reyne, 1991; Galotto et al., 2011a): plasticizers are used **[3]** (Saint-Laurent and Rhainds, 2004), antioxidants (Bart, 2001; PIRA, 2003; Arias et al., 2009; Garrido-Lopez and Tena, 2005; Zhou et al., 1999; Garrido-Lopez et al., 2007), anti-UV (Garrido-Lopez and Tena, 2005), etc.

However, it has been reported that these adjuvants may contain compounds with adverse effects on human health and environment (Grosclaude, 1999; Lacaze, 1993).

In this context and after an initial identification of our packaging and additives by Fourier transform infrared spectroscopy (FTIR), we proceed to the preliminary determination of heavy metals in these additives by Inductively coupled plasma-Atomic emission spectrometry (ICP-AES). This technique is concurrent with the atomic absorption (AAS), the element mass spectrometry (ICP-MS) (Rouessac and Rouessac, 2009; Mendham et al., 2006), etc. Then, to estimate the composition of organic substances in packaging, a full range of commercial additives and packaging extracts are characterized by Gas chromatography coupled with mass spectrometry (GC/MS). Studies describe several thermal methods for introducing polymers in the chromatographic column: thermal desorption, thermogravimetry (TGA), degradation in a tubular oven, pyrolysis (PY) (Bart, 2001; Mortaigne, 1996), etc.

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2013.07.022
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Table 1 Plastic samples used for the spectrometric and chromatographic analyses.

Manufacture (Entse) and manufactured products	Sample	Type
Entse A: various food packaging	Ech 1	LDPE granules used in the manufacture of flexible plugs
	Ech 2	PP granules used in the manufacture of *chamia* (=almond and nougat paste) packaging
Entse B: food bags	Ech 3	LDPE granules used in the manufacture of meat and fish bags
Entse C:	Ech 4	Transparent polystyrene box meals
various food packaging	Ech 5	White polystyrene box meals
Entse D: polystyrene food packaging	Ech 6	White polystyrene tray
Entse E:	Ech 7	White polystyrene plate for dessert
polystyrene food packaging	Ech 8	White polystyrene cup
Entse F: various food packaging	Ech 9	HDPE yoghurt pot
Entse G: polypropylene food packaging	Ech 10	PP granules used in the manufacture of oil packaging
	Ech 11	Chips from the production of oil packaging: recycled into non-food products (cleaning products, etc.)
Entse H:	Ech 12	HDPE plug
HDPE caps: injected and blown	Ech 13	HDPE plug
Entse I: HDPE and LDPE bags: extrusion/blow	Ech 14	Bag for meat
Entse J: yoghurt pot	Ech 15	Yoghurt pot
Entse K: yoghurt pot	Ech 16	Yoghurt pot
Entse L: plastic packaging films	Ech 17	Film for tea
Entse M: plastic packaging films	Ech 18	Film for couscous
Entse N:	Ech 19	PSE tray for meat
PSE trays	Ech 20	PSE tray for meat

These techniques have many advantages: high sensitivity, no risk of contamination (little handling), no interference from the solvent and respect of the environment (no solvent) (Bart, 2001).

However, they may also be quite costly and sometimes require a fairly laborious work (ex: the tube oven). So we choose solvent extraction that allows an easy analysis of the extracted products and a good separation of polymers and additives. Many GC/MS protocols are described in the literature to identify antioxidants, UV stabilizers, plasticizers and other plastic additives (Sanches Silva et al., 2006; Coulier et al., 2007; Burman et al., 2005; Espert et al., 2005). In our case, the analysis reveals the presence of a phosphite antioxidant "*Irgafos 168*" in several plastic packaging. Furthermore, ICP results show levels of Copper and Nickel important for this additive. So we quantify this additive in plastic packaging by High-performance liquid chromatography (HPLC) using an internal standard.

2. Materials

Plastic packagings studied are shown in Table 1. The additives subjected to analysis are phenolic antioxidants (*Hostanox O3 P, Hostanox O10 P, Hostanox O16*), phosphite antioxidants (*Hostanox PAR 24*), mixtures of antioxidant (*Hostanox Blend*), UV stabilizer or "*anti-UV*" (*Hostavin N20P*) and antistatic agents (*Hostastat FA38P*, *Hostastat FE2P*) (see Table 2). Some antioxidants, anti-UV and antistatic molecules are given in Figs. 1 and 2.

3. Method

3.1. Experimental protocols

3.1.1. Identification of packaging and commercial additives by infrared spectrometry

FTIR spectrometry (**AVATAR**, **OMNI-SEMPLER 360**) is used to identify packaging and commercial additives.

The plastics are directly cut in the package and then analyzed. The spectra obtained are compared to a specialized database (Postaire, 1991).

In general, the percentage of additives added to plastics is very low and often under 3% (DGCCRF, 2009). They almost do not interfere in the infrared profile of polymers. The spectrum obtained is similar to that of pure resin (Postaire, 1991).

Commercial additive powder is homogenized in a mortar with 1% KBr for spectrometry (similar to the inks additives procedure (Vila et al., 2007; Silverstein et al., 2004)).

3.1.2. Extraction of additives from plastic packaging for GC/MS analysis

The additives are extracted from the packaging in the liquid phase by dissolution and re-precipitation of the polymer (Bart, 2001) using the appropriate solvent: toluene/methanol (1:1) for polyolefin and chloroform/methanol (1:1) for polystyrene. As recommended by Mortaigne (1996), we use a solvent which

Table 2 List of additives used in the analyzes.

Sample	Trade name et CAS number	Formula	Type	Melting range (MR) or solidification point (SP) (°C)
Add 1	Hostanox O3 P CAS No. 32509-66-3 (powder)	Bis[3,3-bis-(4′-hydroxy-3′-tert-butyl-phenyl) butanoicacid] glycol ester	Phenolic antioxidant	167–171 (MR)
Add 2	Hostanox PAR 24 P (ou Irgafos 168) CAS No. 31570-04-4 (powder)	Tris(2,4-di-tert-butylphenyl) phosphate	Phosphite antioxidant	181–187 (MR)
Add 3	Hostanox PAR 24 FF CAS No. 31570-04-4 (poudre)	Tris(2,4-di-tert-butylphenyl) phosphate	Phosphite antioxidant	183–187 (MR)
Add 4	Hostanox 016 P (ou Irganox 1076) CAS No. 2082-79-3 (powder)	Octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate	Phenolic antioxidant	50–52 (MR)
Add 5	Hostanox 03 Pills CAS No. 32509-66-3	Bis[3,3-bis-(4′-hydroxy-3′-tert-butyl-phenyl) butanoicacid] glycol ester	Phenolic antioxidant	167–171 (MR)
Add 6[a]	Hostanox SE 10 GR CAS No. 2500-88-1	Distearyl-disulfide	Antioxidant: sulphur containing co-stabilizer	58–59 (MR)
Add 7	Hostanox Blend M 101 P = Hostanox PAR 24 P (Add 2) + Hostanox 010 P (Add 10)	See Add 2 and Add 10 formula	See Add 2 and Add 10	
Add 8	Hostanox SE 4 FL CAS No. 693-36-7	Distearyl-3,3′-thiodipropionate	Antioxidant: sulphur containing co-stabilizer	63–68 (MR)
Add 9[a]	Hostanox OSP 1 MicroPills CAS No. 36339-47-6	Tris [2-tert-butyl-4-thio (2′-methyl-4′-hydroxy-5′-tert-butyl)-phenyl-5- methyl] phenylphosphite	Phosphite antioxidant	> 105 (MR)
Add 10	Hostanox 010 P CAS No. 6683-19-8 (poudre)	Tetrakis [methylene(3,5-di-tert-butyl-4 -Hydroxyhydrocin-namate)] methan	Phenolic antioxidant	110–125 (MR)
Add 11	Hostanox 010 FF CAS No. 6683-19-8	Tetrakis-(methylene-(3,5-di-(tert) butyl-4-hydrocinnamate))methane	Phenolic antioxidant	110–125 (MR)
Add 12	Hostanox 016 FF (ou Irganox 1076) CAS No. 2082-79-3 (poudre)	Octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate	Phenolic antioxidant	49–54 (MR)
Add 13[a]	Hostavin N24 liq (HALS: Hindered amine) CAS No. 85099-51-0 + 85099-50-9 (mélange)	Mixture of 2,2,4,4-tetramethyl-20-(ß-myristyl-oxycarbonyl)-ethyl-7-oxa-3,20-diaza-dispiro-[5.1.11.2] -heneicosanon-21 and 2,2,4,4-tetramethyl-20-(ß-lauryl-oxycarbonyl)-ethyl-7-oxa-3,20-diaza-dispiro-(5,1,11,2)-heneicosanon-21	Anti-UV	16 (SP)
Add 14	Hostavin Aro 8P CAS No. 1843-05-6	2-Hydroxy-4-noctyoxybenzophenone	Anti-UV	48 (MR)
Add 15	Hostavin Aro 8 GR CAS No. 1843-05-6	2-Hydroxy-4-noctyoxybenzophenone	Anti-UV	48 (MR)
Add 16[a]	Hostavin N20 P CAS No. 64338-16-5	2,2,4,4-Tetramethyl-7-oxa-3,20-diaza-dispiro-[5.1.11.2]-heneicosan-21-o	Anti-UV	230 (MR)
Add 17	Hostastat FE 2P CAS No. 31566-31-1	Glycerol monostearate	Antistatic	60 (MR)
Add 18	Hostastat FE 20 liq CAS No. 85029-63-6	Fatty acid ester	Antistatic	19 (SP)
Add 19	Hostastat FA 38 P (powder) CAS No. 61791-44-4 and 1592-23-0 (mixture)	Mixture of N,N-bis-(2-hydroxy-ethyl)-alkyl-(C14-C18)-amines (56%) and Calcium Stearate (44%)	Antistatic	97 (MR)
Add 20	Hostastat FA 14 liq CAS No. 99241-69-7	Ethoxylated alkylamine	Antistatic	⩽5 (SP)

[a] Additive not approved for food contact.

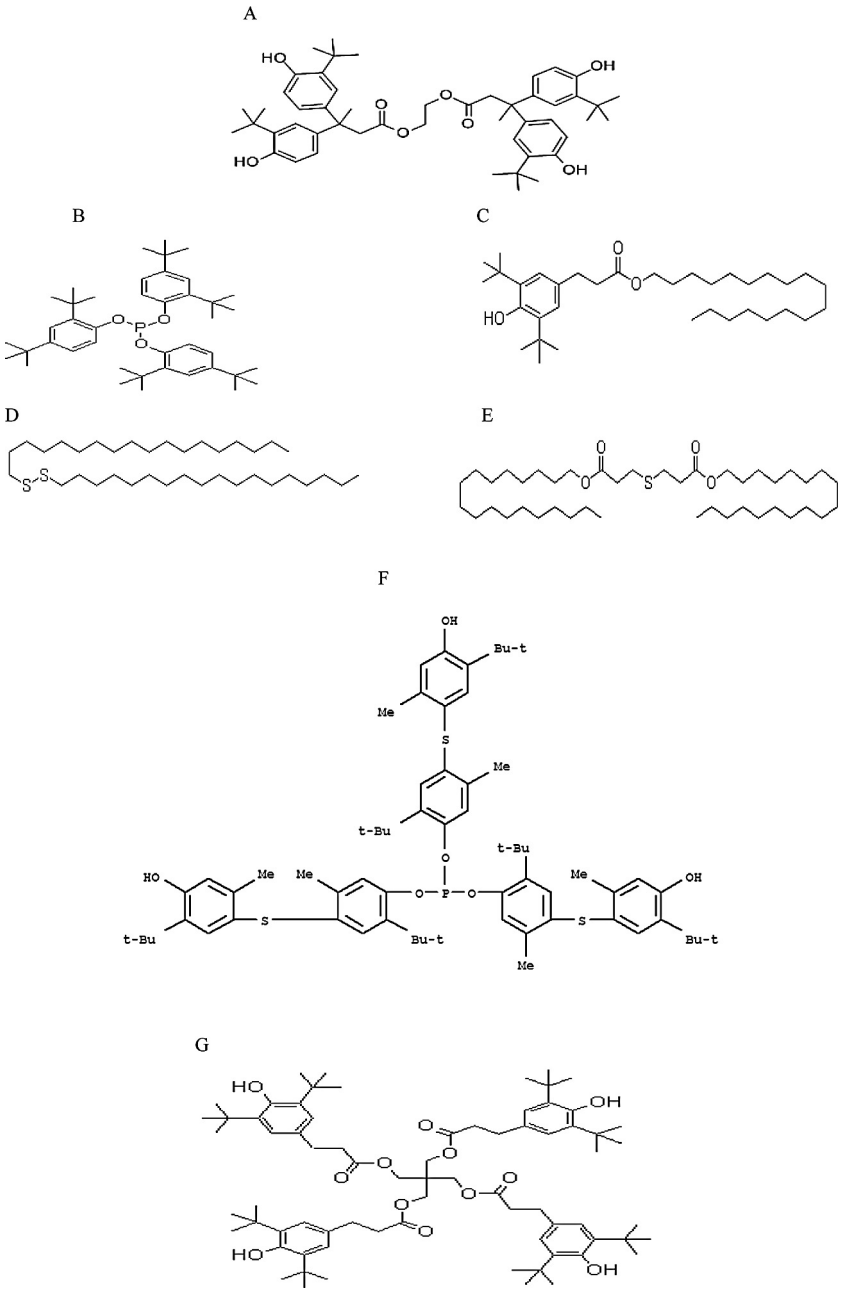


Figure 1 Antioxidant molecule. (A) Add 1 (Hostanox O3 P). (B) Add 2 (Hostanox PAR 24). (C) Add 4 (Hostanox 016). (D) Add 6 (Hostanox SE 10). (E) Add 8 (Hostanox SE 4). (F) Add 9 (Hostanox OSP 1). (G) Add 10 (Hostanox 010).

allows a significant swelling of macromolecules. The extract is then filtered and concentrated on a rotary evaporator (70–80 °C at 150 tr/min). Additives are then injected into the GC/MS column.

3.1.3. Mineralization of commercial additives for ICP analysis

It takes 0.5 grams of solid additive. We add 5 ml of HNO_3. The solution remains 24 hours at rest and is evaporated by adding 5 ml of HNO_3. This step is repeated twice. Finally the whole is transferred in a 50 ml flask which is completed with distilled water.

3.2. Analytical methods

3.2.1. The heavy metals content of additives

The heavy metals content of plastics extracts is given by a **JY ULTIMA** atomic emission spectrometer (ICP-AES) **[120–800 nm]**. The operating conditions are presented in Table 3.

3.2.2. The additives identification by GC–MS

Gas chromatography **(Agilent 6890)** coupled with a mass spectrometer type quadrupole **(Agilent 5973)** identifies certain commercial additives (in methanol) and those present in the

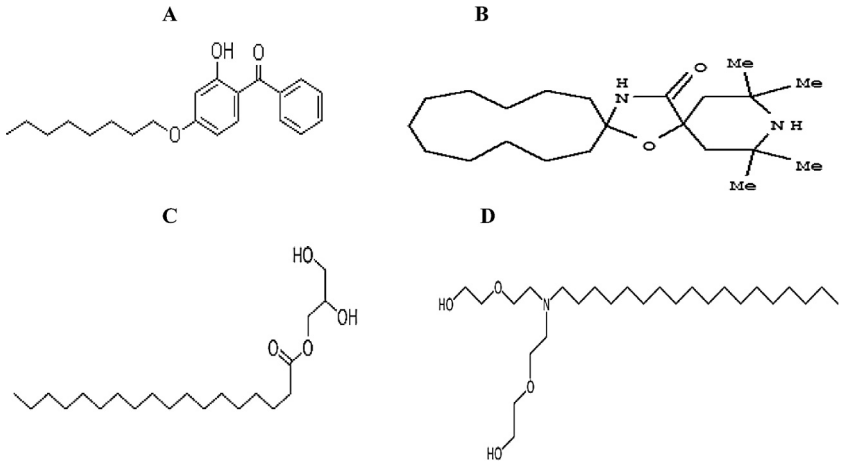


Figure 2 Anti-UV and antistatic molecule. (A) Add 14 (Hostavin Aro 8). (B) Add 16 (Hostavin N20). (C) Add 17 (Hostastat FE 2). (D) Add 20 (Hostastat FA 14).

Table 3 ICP-AES analysis protocol.

Plasma observation	Radial
Frequency	40.68 MHz
Control of the gas flow rates	Computer
Control of the peristaltic pump (sample and drain)	Computer
Cooling	Air
Plasma gas flow	12 l/min
Auxiliary gas flow	0 l/min
Sheath gas flow	0.2 l/min
Nebulization gas flow	0.9 l/min
Nebulization gas pressure	2.8 bars
Sample flow	1 ml/min

extracts obtained. The column used is of type HP 5 MS (copolymer of 5% diphenyl and 95% dimethyl siloxane) with dimensions 30×0.25 mm and 0.25 μm particle size. Two oven temperature programs are implemented in Table 4.

3.2.3. Quantitative analysis by HPLC of Irgafos 168 in packaging

We have quantified the antioxidant *Irgafos 168* in four plastic packaging using an internal standard (PIRA, 2003; Lindsay, 1992; Rosset et al., 1991) which is often a counterpart of analyte (Rosset et al., 1991). In our case, we have used the antioxidant *Irganox 1040* (*Hostanox 010 P*).

There are several techniques for extracting the additive from its matrix. Examples include the Soxhlet and ultrasonic extractions. There are also those by supercritical fluid (SFE) (Arias et al., 2009; Zhou et al., 1999; Pinto, 1997), fluid or pressurized liquid (PFE or PLE) (Garrido-Lopez and Tena, 2005; Garrido-Lopez et al., 2007), or microwave-assisted extraction (MAE) (Arias et al., 2009).

In our study, the antioxidant is extracted from its support (polyolefin or polystyrene) by total dissolution of the polymer in toluene (case of polyolefins) or in chloroform (case of polystyrene) and by precipitating it with methanol. We have followed a traditional reflux protocol (PIRA, 2003; Arias et al., 2009). Arias et al. (2009) have shown that the extraction of

Table 4 Temperature program protocols for GC/MS analyzes.

Samples	Protocol 1	Protocol 2
	Commercial additives	Extract
Injector temperature	300 °C	300 °C
Injection volume	1 μl	1 μl
Flow rate of carrier gas (helium)	1.5 mL min^{-1}	1.5 mL min^{-1}
Initial temperature	80 °C; (1 min)	150 °C; (3 min)
Final temperature	290 °C; Compensate for 10 min at 290 °C	320 °C; Compensate for 20 min at 320 °C
Ramp	10 °C/min	10 °C/min
Time analysis	32 min	40 min

Table 5 The standard range used for the HPLC quantitative analysis of *Irgafos 168*.

Standard solution No.	0	1	2	3	4	5
Internal standard volume ($V_{010\ P}$ en ml)	0.1	0.1	0.1	0.1	0.1	0.1
Additive solution volume (Vi en μl)	0	50	100	500	1000	1500
Sample final concentration (Cf en mg/l)	0	2.5	5	25	50	75

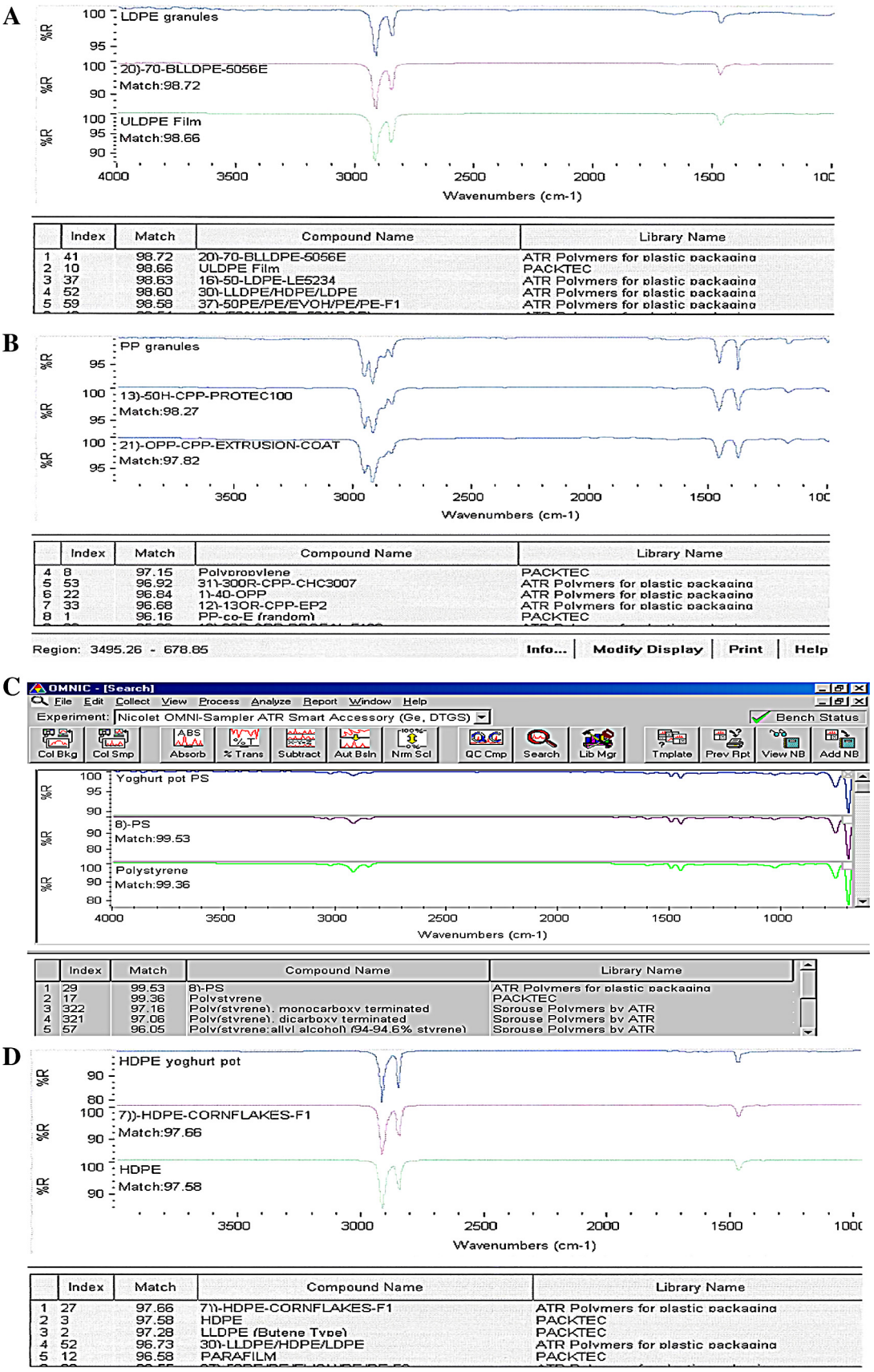


Figure 3 The infrared identification of polymers samples. (A) ech 1 (LDPE). (B) ech 2 (PP). (C) ech 3 (PS). (D) ech 9 (HDPE).

Table 6 The results obtained after the identification of additives by infrared spectrometry FTIR.

Sample	Trade name	FTIR identification
Add 1	Hostanox O3 P CAS No. 32509-66-3 (powder)	Agerite superlite[b] (mixture of polybutylated bisphenol A)
Add 2	Hostanox PAR 24 P (Irgafos 168)	Irgafos 168[a]
Add 3	Hostanox PAR 24 FF (Irgafos 168) CAS No. 31570-04-4 (powder)	Irgafos 168[a]
Add 4	Hostanox 016 P CAS No. 2082-79-3 (powder)	UCAR cyracure UVR – 6110[c] (cycloaliphatic epoxy resin)
Add 5	Hostanox 03 Pills	Parlon S-125[c] (elastomer chlorinated)
Add 6	Hostanox SE 10 GR (fat)	Conoco 736 wax (paraffin wax)[c]
Add 7	Hostanox Blend M 101 P (ou Irganox B215)	Irganox B215[a]
Add 8	Hostanox SE 4 FL	Poly(vinyl)stearate (a wax-like polymer of vinyl stearate)[c]
Add 9	Hostanox OSP 1 MicroPills	Hostanox VP OSP1[a] (antioxidant)
Add 10	Hostanox 010 P (Irganox 1010) CAS No. 6683-19-8 (poudre)	Irganox 1010[a]
Add 11	Hostanox 010 FF (Irganox 1010)	Irganox 1010[a]
Add 12	Hostanox 016 FF CAS No. 2082-79-3 (powder)	Poly(lauryl acrylate) ou octadecyl acrylate homopolymer[c]
Add 13	Hostavin N24 liq (liquid)	Pentalyn 261 ou refined tall oil (monomer natural oil = rosin oil)[c]
Add 14	Hostavin Aro 8P (Cyasorb UV-531)	Cyasorb UV-531[a] (ou Hostavin Aro 8, Octabenzone): additive stabilizer
Add 15	Hostavin Aro 8 GR (Cyasorb UV-531)	Cyasorb UV-531[a] (ou Hostavin Aro 8, Octabenzone): additive stabilizer
Add 16[d]	Hostavin N20 P	Cyasorb UV-3604[b] (Hindered amine light stabilizer)
Add 17[d]	Hostastat FE 2P (glycerol monostearate)	Kessco ethylene glycol monostearate[b] (glycol stearate): additive plasticizer
Add 19	Hostastat FA 38 P (powder)	Conoco 736 wax (paraffin wax)[c]

[a] Molecule similar to the commercial molecule.
[b] Molecule close to the commercial molecule (same type but little different structure).
[c] Molecule completely different from the commercial molecule and not in the positive list.
[d] Additive not approved for food contact.

Irgafos 168 by toluene/methanol (volume ratio; 1:1) was more appropriate than by xylene/methanol (volume ratio; 1:1).

So we have first prepared solutions of *Irgafos 168* "*IRG 168*" (1000 mg/l), internal standard *Hostanox 010 P* "*010 P*" (500 mg/l) and standards (Table 5). The internal standard "*O10 P*" has been added during the plastic dissolution. The methanol (20 ml) has been then used to precipitate the plastic and to maintain only the additives in solution. The supernatant containing the additives has been filtered and injected into the column.

3.3. Results and discussions

3.3.1. The polymers and additives identification by FTIR

Most packages analyzed are based on polyolefin (polyethylene, polypropylene) and polystyrene. Infrared spectra of some samples are shown in Fig. 3. The FTIR characterization of commercial additives is given in Table 6. Some spectra of the molecules identified are shown in Fig. 4. Most additives identified have a structure similar to that indicated by the supplier (Ex: *Add 7: Irganox B215* (**Ciba® IRGANOX® B 215**)). Others have structures close to the commercial molecule (*Add 1, 16, 17*). For example, the FTIR analysis of *Add 1* identifies a molecule close to the *Hostanox O3P* (commercial molecule): these two molecules belong to the same family of the phenolic antioxidant. The molecule identified is an Agerite superlite (mixture of polybutylated bisphenol A). It is often used as a stabilizer in plastic packaging (regulatory: *FDA 21 CFR 175.105, 177.2600*) (Ash, 2004). But it is not in the positive list **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**.

Some additives only (*Add 4, 5, 6, 8, 12, 13*) give results far from commercial data. It appears that in this case the FTIR spectrum is more that of a resin (*Add 4*), wax (*Add 6, 8, 19*), oil (*Add 13*), elastomer (*Add 5*) or homopolymer (*Add 12*) to which the additive is mixed. The commercial product is not always pure. The additives in the form of a fatty or liquid product are usually mixed with oils or waxes based on paraffin or rosin (*Add 6, 13, 19*). It should be noted that none of these waxes or resins appear in the positive list for food contact **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**.

3.3.2. The additives heavy metals content

Table 7 presents the commercial additives heavy metals content.

3.3.2.1. The antioxidants. 3.3.2.1.1. The phenolic antioxidants. ***Hostanox O16FF*** (*Add 12*) is the additive that has the highest levels of lead and copper. Although antioxidants have been used and studied for over 50 years, we pay attention to stabilizers loaded with heavy metals, particularly lead. The gradual replacement of lead with cadmium-zinc is strongly encouraged (Houtmeyers, 2006). The blend stabilizer responds to this feature. Its lead content is very low and its Cadmium and Zinc content is much stronger than the other additives studied.

Hostanox O10 P and ***O10FF*** (*Add 10* et *Add 11*) have a significant cobalt content (0.78 ppm for the *O10P* and 0.79 ppm for the *O10FF*), especially if the specific migration of this metal is limited to 0.1 ppm.

The additives *Hostanox O 10* and *Hostanox O 16* have the labels *R 53* "*May cause long-term adverse effects in the aquatic*

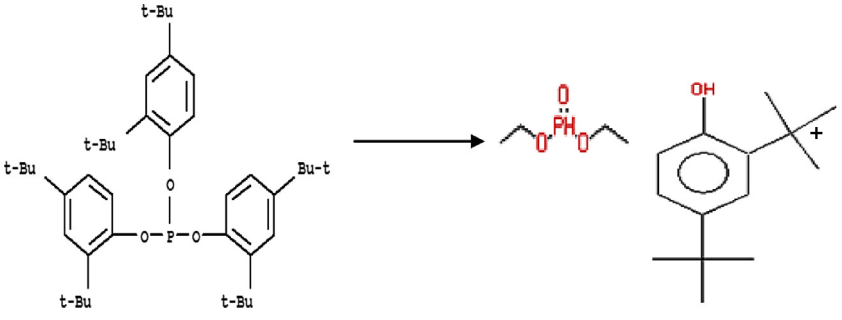
environment" and *S 61* "*Avoid release to the environment*" (Pigments & Additives Division - Clariant, 2006). *53 "May cause long-term adverse effects in the aquatic environment"* and *S 61 "Avoid release to the environment"*.

The *Hostanox O3 P* (*Add 1*) does not require labeling (Pigments & Additives Division – Clariant, 2006). However, its Cobalt content remains relatively high. This stabilizer is used for specific applications (Pigments & Additives Division – Clariant, 2006).

3.3.2.1.2. The phosphite antioxidant: Hostanox 24FF (Add 3). This is the additive studied that contains the least of toxic metals (lead, cobalt, cadmium) and less toxic metals (zinc, iron, manganese). However, its significant levels of nickel and copper can explain the label assigned to it: R 52 "*Harmful to aquatic organism*", R 53 "*May cause long-term adverse effects in the aquatic environment*" and S 61 "*Avoid release to the environment*" (Pigments & Additives Division – Clariant, 2006).

3.3.2.1.3. The antioxidant "Blend": Hostanox Blend M 101P (Add 7). This stabilizer has high levels of Nobalt (highly toxic), and nickel. Its zinc concentration is also very high compared to other additives tested. But zinc is not very toxic, provided it is below the migration limit.

3.3.2.2. The anti-UV (Hostavin N 20). ***Hostavin N 20*** requires no warning label against risks (Polymer additives for the plastics industry, Overview – Clariant, 2010). This additive is also the least loaded with Nickel, Copper and Chromium and its lead content is quite low. However, it has not been approved for food contact packaging (Polymer additives for the plastics industry, Overview – Clariant, 2010). This may be due to its significant concentrations of cadmium and cobalt.



Add 3 (*Hostanox PAR 24 FF* **ou** *Irgafos 168*)

Degradation products

3.3.2.3. The antistic agents: Hostastat FE 2 (Add 17) and Hostastat FA 38 (Add 19). ***Hostastat FE 2*** does not have high levels of heavy metals. It is also not a hazardous substance (Pigments & Additives Division – Clariant, 2006).

However, ***Hostastat FA 38*** is the most highly concentrated in nickel, manganese, chromium and iron. Furthermore, the concentration of cobalt is the most important of the list and the cadmium content is quite high. Its labels are R38 "*Irritating to skin*" and R41 "*Risk of serious damage to eyes*" (Antistatic agents – Clariant, 2010).

3.3.3. The additive identification by GC/MS

The mass spectra of the Octabenzone molecule is shown in Fig. 5.

3.3.3.1. The commercial additives. The commercial additives identified by GC/MS are listed in Table 8. Among the eight samples analyzed, only two molecules correspond to the commercial molecules (supplier data). These are the anti-UV *Add 14* and *Add 16*. One of them is based on *benzophenone*. These compounds are fairly stable. Six other samples have structures deriving from the commercial molecule: the antioxidants *Add 1*, *3*, *7*, *10*, *12* and the antistatic *Add 17*. Carette (1993) have shown that they are usually degradation products obtained by chain scission. It is always reported that antioxidants are highly sensitive to hydrolysis, heat, etc. An example of degradation products identified by GC/MS is presented below:

Note that substances deriving from the commercial molecule, are not all permitted for food contact (not all in the positive list) (see notes ***a*** and ***b*** of Table 8).

Finally, some GC/MS results have revealed new molecules, quite different from those provided by the supplier. These include for example the *Octabenzone* (or *Cyassorb UV 531*, *Hostavin Aro 8*, etc.) and the *Metilox* (or *Irganox 1300*) present in additives *Add 7, 10, 16, 17*. They are either additives added to the commercial molecule to stabilize the polymer (case of *Octabenzone*) or intermediates for the synthesis of additives (such as the *Metilox* used in the synthesis of phenolic antioxidants (Pitteloud and Dubs, 1994)). Note that *Octabenzone* must have a risk assessment and authorization prior to use **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**.

The *Metilox* is of low toxicity in acute toxicity tests, with an oral LD50 value higher than 5000 mg/kg (SIDS Initial Assessment Report for 13th SIAM, 2001).

3.3.3.2. The packaging extracts. The GC/MS results of extracts analysis are presented in Table 9. The compounds detected are:

3.3.3.2.1. lubricants. Most samples analyzed contain polymeric lubricants. The most commonly used is the Methylpalmitate. Even if it does not appear in the positive list, it is found mainly in polystyrene packagings. The lubricants improve the

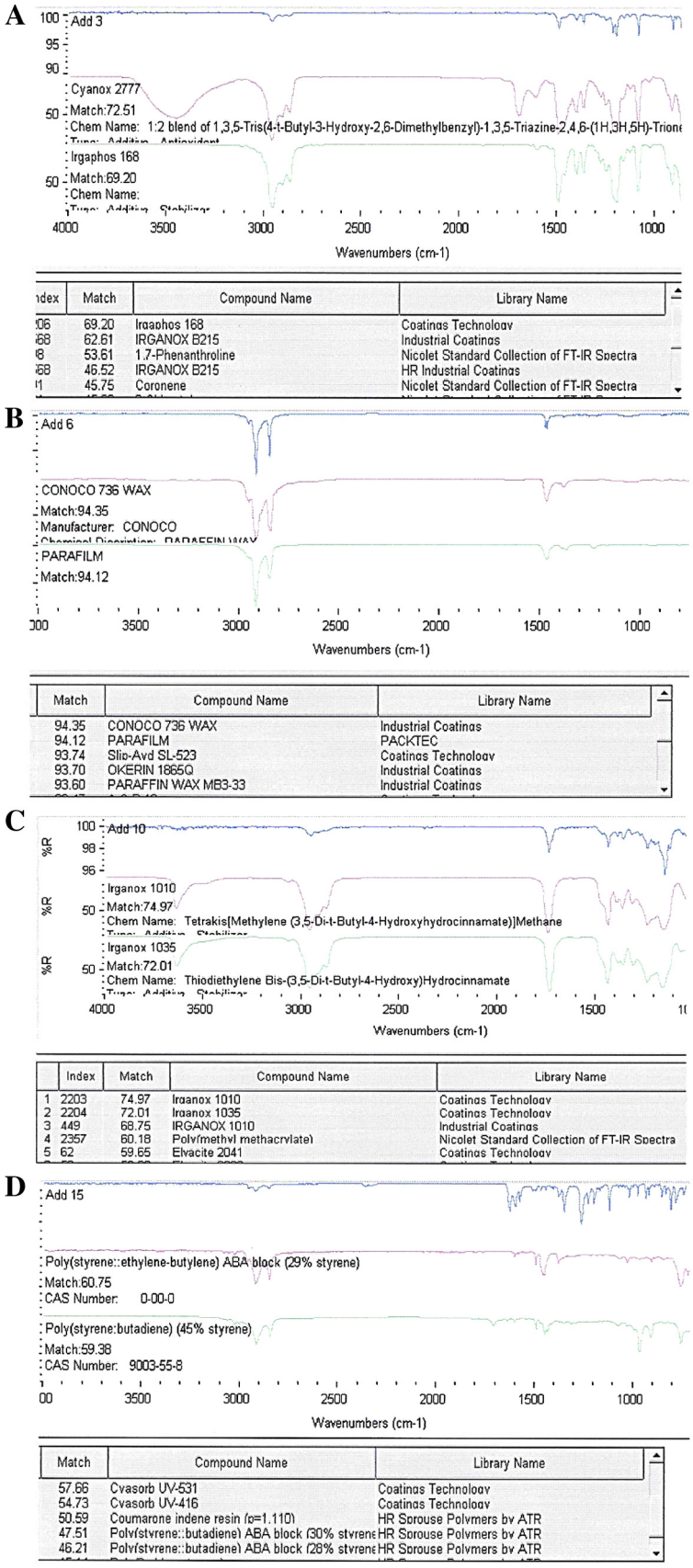


Figure 4 The infrared identification of commercial additives. (A) Add 3. (B) Add 6. (C) Add 10. (D) Add 15.

Table 7 Heavy metal content of commercial additives given by ICP-AES.

Elément (ppm)	Additifs clariant								
	Phenolic antioxidants				Phosphite anti-oxidant	Anti-oxidant *Blend*[a]	Anti-UV	Antistatics	
	Add 1	Add 10	Add 11	Add 12	Add 3	Add 7	Add 16	Add 17	Add 19
Ni	5.43	2.08	4.32	6	3	7.3	1.46	2.29	16.42
Cd	0.53	0.57	0.60	< 0.05	< 0.05	0.81	0.46	0.56	0.57
Co	0.85	0.78	0.79	< 0.1	< 0.1	0.87	0.70	0.68	0.83
Cu	0.33	0.49	1.02	13	8	0.95	0.26	0.77	1.35
Pb	< 0.10	< 0.10	< 0.10	3	< 0.1	< 0.10	< 0.10	< 0.10	< 0.10
Mn	2.00	1.65	2.04	0.87	0.89	2.01	1.02	1.69	5.61
Cr	5.20	1.43	5.39	2	2	3.56	1.83	2.61	24.68
Zn	70.72	71.08	84.80	48	17	102.45	67.58	83.44	73.48
Fe	67.83	42.25	65.68	10	13	58.47	28.10	57.23	93.15

[a] *Add 7* is a mixture of phenolic and phosphite antioxidants: Hostanox 010 and Hostanox PAR 24 (1:1).

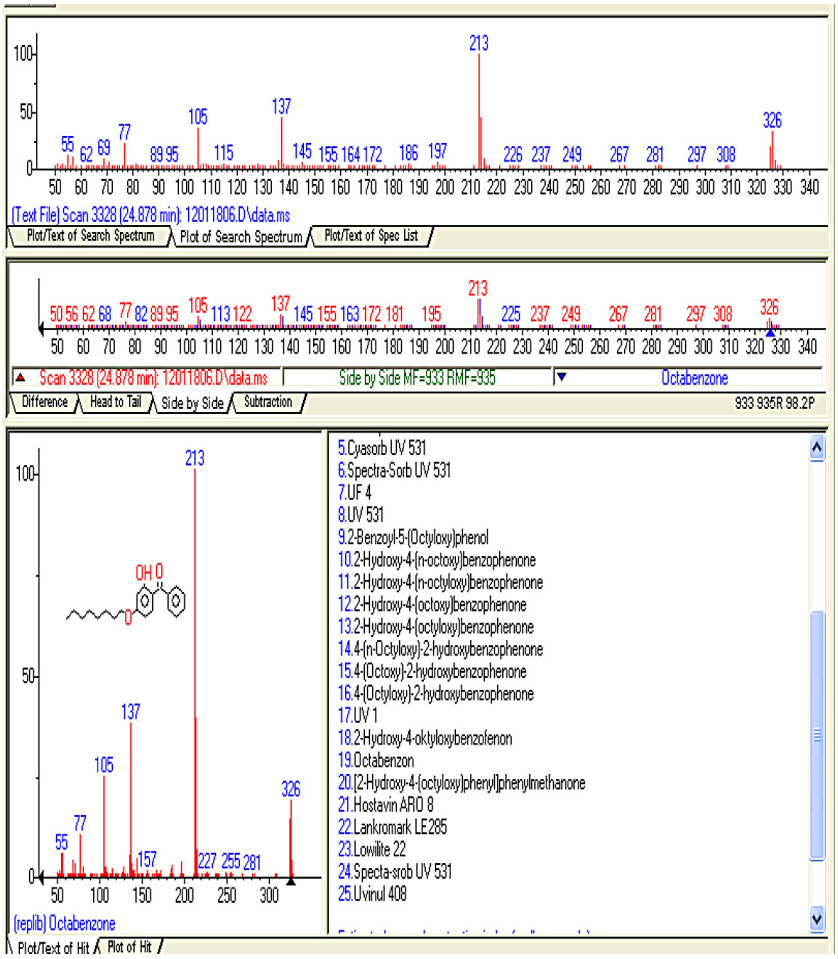


Figure 5 Mass spectra of the Octabenzone identified by GC/MS.

mechanical strength of PS. They can change the rheology of the polymer melt. They are applied either in bulk or in surface to reduce friction with the thermoforming equipment and increase the flexibility of PS (http://www.chemicalland21.com). Some PP or LDPE samples contain this additive or its derivative (Benzaldehyde 3,4-dimethyl-Methylpalmitate). There is also Methylstearate (Octadecanoic acid, methyl ester) in polypropylene and polystyrene packaging. But this additive is not in the positive list and according to Lewis (2008), it has tumorigenic effects.

Erucamide is a lubricant more rarely used (present only in the LDPE sample *Ech 3*). This is a fatty acid amide slip agent (Zweifel et al., 2009). It is integrated by the manufacturer of polymers in an extruder pellet or by the processor through

Table 8 List of commercial additives identified by GC/MS.

Sample	Trade name	GC/MS identification
Add 1	Hostanox O3 P CAS No. 32509-66-3 (powder) = Bis[3,3-bis-(4′-hydroxy-3′-tert-butyl-phenyl) butanoicacid] glycol ester[a] (LMS = 6 mg/kg)	2,6-Di-tert-butyl-4-(2,4-dimethylbenzyl)phenol[b] CAS No. 203786-39-4
Add 3	Hostanox PAR 24 FF [a] (ou Irgafos 168) CAS No. 31570-04-4 (powder) = Tris(2,4-di-tert-butylphenyl) phosphite	Diethyl phosphate[b] CAS No. 598-02-7 Phenol, 2,4-bis(1,1-dimethylethyl)-[b] CAS No. 96-76-4 Phenol, 2,4,6-tris(1,1-dimethylethyl)-[b] CAS No. 732-26-3
Add 7	Hostanox Blend M 101 P = Mixture of Add 2 (Hostanox PAR 24 P [a] or Irgafos 168) and Add 10 (Hostanox 010 P [a] or Irganox 1010)	Phenol, 2,4,6-tris(1,1-dimethylethyl)-(Alkofen B)[b] CAS No. 732-26-3 Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester (Metilox ou Irganox 1300: structure very close to that of Irganox 1076)[b] CAS No. 6386-38-5 Octabenzone[a]
Add 10	Hostanox 010 P (Irganox 1010) CAS No. 6683-19-8 = Tetrakis [methylene(3,5-di-tert-butyl-4-Hydroxyhydrocin-namate)] methane [a]	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, octadecyl ester (Irganox 1076)[a] CAS No. 2082-79-3 Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester[b] Phenol, 2,4,6-tris(1,1-dimethylethyl)-(ou Alkofen B)[b] CAS No. 732-26-3
Add 12	Hostanox 016 FF (or Irganox 1076) CAS No. 2082-79-3 (powder) = Octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate [a]	Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, methyl ester[b] CAS No. 6386-38-5
Add 14	Hostavin Aro 8P CAS No. 1843-05-6 = 2-Hydroxy-4-noctyoxybenzophenone (Octabenzone)[a]	Octabenzone[a] CAS No. 1843-05-6
Add 16[c]	Hostavin N20 P CAS No. 64338-16-5 = 2,2,4,4-Tetramethyl-7-oxa-3,20-diaza-dispiro-[5.1.11.2]-heneicosan-21-o[b]	Octabenzone[a] 2,2,4,4-Tetramethyl-3,20-diaza-7-oxadispiro[5.1.11.2]heneicosan-21-one[b] CAS No. 64338-16-5
Add 17[c]	Hostastat FE 2P CAS No. 31566-31-1 = Glycerol monostearate [b]	Hexadecanoic acid, methyl ester (Methylpalmitate)[b] CAS No. 112-39-0Methylstearate CAS No. 112-61-8 Octabenzone [a]

[a] In the positive list.
[b] Not in the positive list.
[c] Commercial additive not approved for food contact.

masterbatches (Zweifel et al., 2009). The *European Regulation No. 10/2011* authorizes the use of Erucamide for the manufacture of packaging for food contact **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. No migration limit has been prescribed for this additive. However, it has been shown that it tends to migrate into the food (Bart, 2006). Recently, several volatile compounds have been found in water from PET bottles exposed to sunlight. Bach et al. (2012) have shown that they come from the photooxidation of Erucamide present in bottle closures. Unfortunately, the closing equipment has not been analyzed and this hypothesis could not be confirmed.

Table 9 List of plastic extracts compounds identified by GC/MS.

Manufacture	Sample	Polymer type	GC/MS identification
A	Ech 1	Pebd	Methylpalmitate isomer
	Ech 2	PP	Methylpalmitate
			Irgafos 168 oxidized form
B	Ech 3	Pebd	Benzaldehyde dimethyl acetal
			Methylpalmitate
			Erucamide
C	Ech 4	PS	Methylpalmitate
			Polysiloxanne
	Ech 5	PS	Methylpalmitate
			Phtalic acid, 2-methoxyethyl tetradecyl ester
			Methadone N-oxide
D	Ech 6	PS	Benzene 1,1′-(1,2-cyclobutanediyl) bis-cis-
			Methyl palmitate
			Octadecanoic acid, methyl ester
E	Ech 7	PS	Benzene 1,1′-(1,2-cyclobutanediyl) bis-trans
			Methylpalmitate
			Octadecanoic acid, methyl ester
	Ech 8	PS	Benzene1,1′-(1,2-cyclobutanediyl) bis-cis
			Octadecanoic acid, methyl ester
F	Ech 9	Pehd	Irgafos 168
G	Ech 10	PP	Benzaldehyde dimethyl acetal
			Benzaldehyde 3,4-dimethyl-Methylpalmitate
			Octadecanoic acid, methyl ester
			Methylpalmitate isomer
			Bumetrizole
	Ech 11	PP recycled	Benzaldehyde dimethyl acetal
			Benzaldehyde 3,4-dimethyl-Methylpalmitate
			Octadecanoic acid, methyl ester
			Irgafos 168 oxidized
			Bumetrizole
H	Ech 12	PP	Benzoic acid, 4-ethoxy-, ethyl ester
			Propanoic acid, 2-methyl-(1, 1-dimethylethyl)-2-methyl-1,3-propanediyl ester
			Dodecanoic acid, 1-methylethyl ester (isopropyl laurate)
			Benzyl Benzoate: ascabin, ascabiol
	Ech 13	PP	Unox 4206: Chissonox 206
			Propanoic acid, 2-methyl-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester
			Isopropyl laurate
			Benzyl Benzoate: ascabin, ascabiol
I	Ech 14	PEhd	DL-2,3-butanediol (6982-25-8)
			Structure close to: propanoic acid, 2-methyl-, butyl ester (97-87-0)
			Benzoic acid, 4-ethoxy-, ethyl ester (23676-09-7)
			I-propyl dodecanoate
			Structure close to: glutamide (1121-89-7)
			Benzyl Benzoate: ascabin, ascabiol
			Irganox 1076 1,3–Dioxolane, 2-methyl-2-(1-methylethyl)-(4405-16-7)
			Structure close to: Valeric anhydride (2082-59-9)
			DIOP: Diisooctyl phtalate (27554-26-3)
J	Ech 15	PS	Benzyl Benzoate: ascabin, ascabiol
			Irganox 1076
			Methadone N-oxide
K	Ech 16	PS	Propanoic acid, butyl ester: UN 1914
			Benzyl Benzoate: ascabin, ascabiol Irganox 1076
			Methadone N-oxide
L	Ech 17	PP	Benzoic acid, 4-ethoxy-, ethyl ester (23676-09-7)
			Carbamodithioic acid, diethyl, ethyl ester
			I-propyl dodecanoate
			Benzyl Benzoate: ascabin, ascabiol
			3,6,9,12,15-oxabicyclo(15,3)heneicosa-1(21),17,19-triene-2,16-dione
			Irganox 1076
			Caradate 30: diphenylmethane diisocyanate
			MEHP: 1,2 benzenedicarboxylic acid, mono 2-(ethylhexyl ester)

Table 9 List of plastic extracts compounds identified by GC/MS.

Manufacture	Sample	Polymer type	GC/MS identification
M	Ech 18	PP	Propanoic acid,2-methyl-, butyl ester: butyl isobutyrate Benzoic acid, 4-ethoxy-, ethyl ester (23676-09-7) Benzyl Benzoate: ascabin, ascabiol 1,4 benzenedicarboxylic acid, bis (2-hydroxyethyl)ester: bis (2-hydroxyethyl) terephtalate Irganox 1076 Caradate 30: diphenylmethane diisocyanate Citroflex A: Tributyl acetylcitrate DIOP: Diisooctyl phtalate (27554-26-3)
N	Ech 19	PSE	Benzyl Benzoate: ascabin, ascabiol Irganox 1076 DIBP: Phtalic acid, diisobutyl ester DIOP: Diisooctyl phtalate (27554-26-3) Methadone N-oxide
	Ech 20	PSE	Benzoic acid, methyl ester: niobe oil (93-58-3) Benzyl benzoate: ascabiol (120-51-4) Irganox 1076 DBP: Dibutyl phtalate (84-74-2) Decanedioic acid, dibutyl ester: Polycizer DBS (109-43-3) Methadone N-oxide

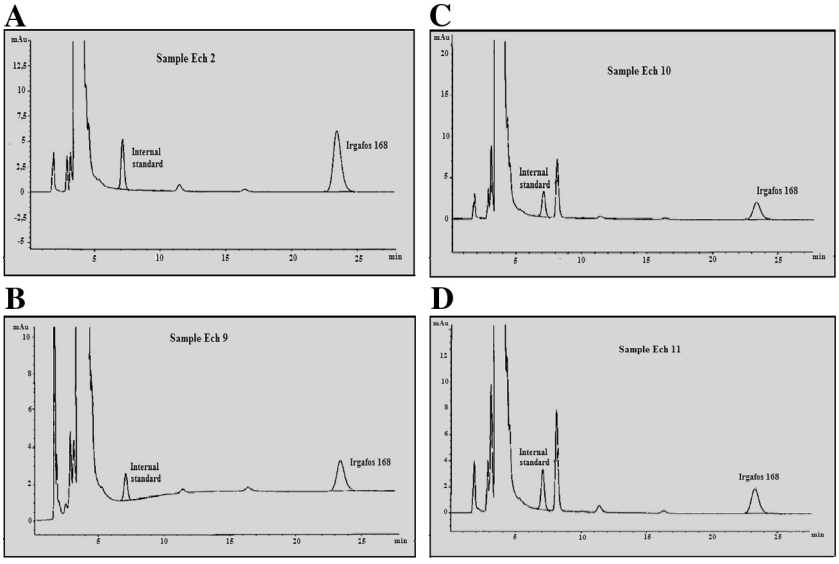


Figure 6 Chromatograms of *Irgafos 168* molecules quantified by HPLC. (A) Ech 2. (B) Ech 9. (C) Ech 10. (D) Ech 11.

Table 10 *Irgafos 168* content given by the HPLC study of plastic packaging.

Plastic sample	Final product	Area ratio (IRG/SI) *y*	Concentration ratio (IRG/SI) *x*	$Conc_{Irg\ 168}$[a] (ppm ou mg/kg)	*m* (g)[b]	% $_{Irg\ 168}$[c]
Ech 2	*Chamia* packaging	3.0741688	1.7110975	4.2777	20	0.043
Ech 9	Yoghurt pots	2.6435581	1.4927794	3.7319	8.75	0.037
Ech 10	Oil packaging	1.5885023	0.9578697	2.3947	257	0.024
Ech 11	Chips from the production of oil packaging	1.4532048	0.8892743	2.2232	10	0.022

[a] Concentration of Irgafos 168.
[b] Mass of the packaging.
[c] Percentage of Irgafos 168.

The Niobe oil identified in a PSE sample (*Ech 20*) is also a lubricant permitted by the **European Regulation No. 10/2011**. Typical lubricants are fatty alcohols (C_{12}–C_{22}) or fatty acids (C_{14}–C_{18}) (Piringer and Baner, 2008). The *isopropyl laurate* ($C_{15}H_{30}O_2$) identified in the *Ech 12* of PP is probably a lubricant but is not in the positive list. The molecules of *butyl isobutyrate* and *propyl laurate* (*I-propyl dodecanoate*) are probably deriving from lubricant agents ($C_xH_yO_z$).

3.3.3.2.2. The plasticizers. Much of the packaging analyzed are composed of *benzyl benzoate* (*Ascabiol*). It is a plasticizer (Simonds et al., 1944) but it is not reported as an additive or auxiliary polymer production in the positive list **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011).** It seems to have a low degree of toxicity (McEvoy, 1993) and it does not appear to cause mutagenic effects (Dollery, 1991). There is no much documentation about it on pregnancy and reproduction. However, it is not recommended for pregnant women (Ascabiol package insert; Ascabiol data sheet; McEvoy, 1993; Dollery, 1991; Koren, 1990).

Then we have found mainly phtalates in PSE packaging and sometimes in HDPE (*Ech 14*) and PP (*Ech 17* and *18*). We have identified *DIBP*, *DIOP*, *DBP* and *MEHP*.

DIBP is not reported as an additive or auxiliary polymer production in the positive list **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. However, it is found quite frequently in plastic packaging (Shen, 2005). The phtalic acid ester is a plasticizer (Di Bella et al., 2010; Whelan, 1994) that tends to migrate to fatty foods such as olive oil (Di Bella et al., 2010; Nanni et al., 2011). Toxicological studies in mice have also shown that *DIBP* had effects on the reproductive system (testis) (Shinshi and Kogo, 1980). For economic reasons, the *DIOP* is a plasticizer (with eight carbon atoms) which is most widely traded (Whelan, 1994; Brydson, 1999). It is compatible with the polystyrene (Whelan, 1994). It is approved by the *FDA* as constituting food packaging materials that come in contact with aqueous foods, but not with fatty foods (Gooch, 2011).

DBP can be used as an additive or auxiliary production of polymers with a *0.3 mg/kg LMS*. Strict rules are defined for this additive **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. It should be used as a plasticizer in materials and articles contacting with food grease. And it may be a processing aid in polyolefin in concentrations up to 0.05% in the final product **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. This is an endocrine disruptor (Zimmer, 2008) and according to Zimmer (2008) and to the Council Regulation (EEC) No. 793/93 (1993), it is classified among the three most toxic phtalates to reproduction (with DEHP and BBP).

MEHP is not in the positive list and studies have shown that it decreases testicular testosterone in mice (Papadopoulos, 2007). For Harris and Sumpter (2001), MEHP is the most toxic metabolite of DEHP. Articles are increasingly interested in food packaging plasticizers based on phtalate: one speaks repeatedly of ''endocrine disruptors'', (Muncke, 2009). In addition to phtalates, we have noticed the presence of plasticizers to lower toxicity in the samples *Ech 20* and *Ech 18*: *dibutyl sebacate* (*DBS*) and *acetyl tributyl citrate* (*ATBC* or *Citroflex A*).

The *DBS* is an aliphatic acid ester used as a substitute to *phtalates*. Because of their high cost compared to phtalate, *sebacate* derivatives are used for targeted applications (Marcilla et al., 2004.). The *DBS* can be used as an additive or auxiliary production of polymers but strict rules are defined for this additive **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. It is found as a plasticizer for polystyrene (Senichev and Tereshatov, 2004). This is one of the most effective plasticizers of the *sebacate* type. It is non toxic, and is suitable for use in food packaging (Gooch, 2011).

ATBC is a *citrate* plasticizer that is mainly found in PVC plastic (Fankhauser-Noti and Grob, 2006; Marcilla et al., 2008). Fankhauser-Noti and Grob (2006) showed the ability of this additive to migrate into fatty foods used as an additive or auxiliary polymer production but with very specific restrictions **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. It has low toxicity by ingestion according to the *Handbook of green chemicals* (Muncke, 2009).

And, the expanded polystyrene contains more plasticizers than other polystyrenes plastics. They are added to increase flexibility, workability or distensibility of expanded plastic (Craver and Carraher, 2000).

3.3.3.2.3. antioxidants. Antioxidants found in our samples are often *Irganox 1076* (or derivatives: *Propanoic acid, 2-methyl-(1,1-dimethylethyl)-2-methyl-1,3-propanediyl ester*) and *Irgafos 168* (or its oxidized forms). Phenolic antioxidant *Irganox 1076* (*Hostanox 016*) is present in both polystyrene (PS, PSE) and polyolefin (PP and HDPE). Several studies use it as a model to describe the specific migration of the additive from plastic into food (Galotto et al., 2011a, 2011b; Sanches Silva et al., 2006). Its ability to migrate is well known. It can certainly be used as an additive or auxiliary polymer production (*LMS* = 6 mg/kg) **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)** but with labels *R 53* and *S 61* (Pigments & Additives Division – Clariant, 2006). The ICP analyses also have shown that the *Hostanox 016* contains a high lead content compared to other tested stabilizers.

Then, the phosphite antioxidant *Irgafos 168* (*Hostanox PAR 24*) appears mainly in PP and HDPE samples, not in polystyrene (PS and PSE). This additive is authorized for food contact (*LMS* undefined in the positive list) [F]. It does not have a high content of heavy metals, except copper (see *ICP* results). Other phosphite antioxidants are considered toxic: *arylsubstituted phosphites* (Lefaus, 1968), *triphenyl phosphite* (highly toxic), etc. Lau and Wong (2000) examined that trisubstituted derivatives are much more toxic than the mono and the disubstituted one.

It is important to note that all PP packaging analyzed contain antioxidants (including *Irganox 1076* and *Irgafos 168*). The presence of antioxidant is necessary in PP packaging. Indeed, the polypropylene is highly branched. Its viscosity decreases rapidly in processing machine because of many chain scissions. Knowing that the polyolefin oxidation depends on their branching degree, the polypropylene (highly branched) is very sensitive to oxidation (Carette, 1993).

The phosphite antioxidant reduces the polypropylene coloration during thermal aging. But these antioxidants are very sensitive to hydrolysis; their effectiveness may decrease during storage (Carette, 1993). Polypropylene also contains *Bumetrizole* (*2(3′-tert-butyl-2′-hydroxy-5′-methylphenyl)-2H-5-chlorobenzotriazole*). It is generally used to slow the oxidation process of the polymer exposed to UV light. It preferentially degrades itself and helps in this way to stabilize the polymer (Lau and Wong, 2000).

Benzotriazole derivatives do not have high toxicity. However, they are still tested for possible genetic effects. Their use as antioxidants in the packaging materials is allowed but not for fatty food contact (Lau and Wong, 2000). However, the GC/MS results indicate its presence in a container used for an olive oil packaging.

Finally, we have noted the absence of antioxidants in LDPE packaging. The degree of branching of LDPE is quite low, split strings are few and branching reactions are numerous. The LDPE viscosity in processing machine decreases less rapidly than that of polypropylene (Carette, 1993). This phenomenon can be attributed to the presence of vinylidene groups in LDPE:

$$\mathbf{R} + \mathbf{H_2C} = \mathbf{CH} - \mathbf{R'} \rightarrow \mathbf{R} - \mathbf{CH_2} - \mathbf{C^{\cdot}H} - \mathbf{R'} \text{ (branching reaction of LDPE)}$$

LDPE is not very sensitive to oxidation (related to the branching degree). However, it can be stabilized by phenolic antioxidants of low molecular weight at low concentrations (less than 0.05%), associated with phosphites (Carette, 1993).

3.3.3.2.4. The other stabilizers. Benzoic acid, 4-ethoxy-, ethyl ester (*Cas No. 23676–09-7*) is identified in HDPE and PP packaging. It can be used as an additive or auxiliary polymer production (LMS = 3.6 mg/kg) **(Regulation (EU) No. 10/2011 of the Commission of 14 January 2011)**. It is typically found in water bottles made of PET with a significant ability to migrate (Lilya, 2001).

Polypropylenes also contain *Chissonox 206* (*Vinyl cyclohexene diepoxide*) and *Caradate 30* (*Methylenebis (phenyl isocyanate), MDI*). The *Chissonox 206* is generally used as a monomer in the production of epoxy resins for coatings and adhesives, as a chemical intermediate and as a reactive diluent in some epoxy resins deriving from *bisphenol A* and *epichlorohydrin* (Pohanish, 2012; Report on Carcinogens, 2011). It seems to have a carcinogenic effect in humans (Report on Carcinogens, 2011; ICSC, 1998 **validated;** IARC, 1987; IARC, 1994). However, no specific regulations are reported to reduce exposure to this substance (Report on Carcinogens, 2011). The *Caradate 30* is generally used in the production of polyurethane foams and in plastics, polyurethane coatings, elastomers and thermoplastic resins (Pohanish, 2012). *LMS* is not reported for this product but according to *Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens* (Pohanish, 2012), its ingestion can cause abdominal cramps and vomiting.

3.3.3.2.5. Other compounds: NIAS (NIAS = substances not intentionally added). Other molecules have been identified in the samples but few studies link them to plastic packaging. For example, polystyrene contains the *Methadone N-oxide* and *Propanoic acid, butyl ester* (*UN 1914*). Low density polyethylene and polypropylene contain the *Benzaldehyde dimethyl acetal*. High-density polyethylene contains *1,3-dioxolane, 2-methyl-2-(1-methylethyl-*, *DL-2,3-butanediol*, *glutamide* (*Cas No. 1121-89-7*) and *Valeric anhydride*. These compounds can be considered as "*not intentionally added*" (*NIAS*) ones. They are produced by initial reactants or additives authorized (Bach et al., 2012) and they can be considered as contaminants in food packaging (Lau and Wong, 2000).

3.3.4. Quantitative analysis of Irgafos 168 (Add 2) in packaging

The calibration curve gives the area ratio of *Irgafos 168* and the internal standard versus the ratio of concentrations for these two substances.

The calibration curve equation is: $y = 1.9724x - 0.3008$

The concentration of *Irgafos 168* ($\boldsymbol{Conc_{Irgafos168}}$) is given by the following equation:

$\boldsymbol{Conc_{Irgafos168} = 2.5x\ (ppm)}$, avec $\boldsymbol{Conc_{SI} = 2.5\ ppm}$

The chromatograms of the analyzed samples are shown in Fig. 6.

Table 10 presents the concentration ($\mathbf{Conc_{Irg\ 168}}$) and the percentage of *Irgafos 168* ($\mathbf{\%_{Irg\ 168}}$) in the packaging analyzed.

Knowing for example that the mass of a small pot of yogurt is 8.75 g, we have 32 mg of Irgafos 168 in this pot ($8.75.10^{-3} \times 3.7519$ mg), corresponding to 0.037%.

It has been found that the antioxidant content is variable in the polyolefin but always under 0.05%. The highest is that of polypropylene *Ech 2* (chamia box). Next is the High Density Polyethylene *Ech 9* (yoghurt) and polypropylene *Ech 10* (oil container). This percentage decreases even more when the polymer is reground for other uses (such as the polypropylene *Ech 11* for detergent container). Samples *Ech 10* and *Ech 11* have an *Irgafos 168* lower rate than other packages but they are constituted of other stabilizers such as *Bumetrizole* (see Table 9). Plastic packaging producers use the parameters of quantity and variety of additives to stabilize their product.

4. Conclusion

Based on the analyses performed on several additives, we have observed that these additives sometimes contain compounds harmful to human health and environment. First, the additives are not always pure products. They are often mixed with resins and waxes (*rosin*), oils (*paraffin*), etc., which do not appear in the positive list for food contact. These substances are often found when the additives are fat or liquid form (see FTIR results).

Moreover, the GC/MS results have shown additives structures quite different from the commercial structure: it corresponds to degradation products, etc. For example, this has been observed in the antioxidants analysis. They are not very stable and they are highly sensitive to hydrolysis and heat.

We have also detected new molecules (*Octabenzone*, *Metilox*), entirely absent from the additive data sheets. They are either other additives to stabilize the polymer (*synergistic effect*), or intermediates for the adjuvants synthesis. Some of these molecules are not very toxic (ex: *Metilox*) but most of them are not mentioned in the positive list.

Then, some adjuvants contain significant levels of heavy metals. This is the case for lead in the phenolic antioxidant *Hostanox O16FF*, cobalt in *Hostanox O10 P*, *O10FF* and *O3P*, or nickel and copper in the phosphite antioxidant *Hostanox 24FF*. These levels explain their labels (*R53* or *S61*). Lead tends to be increasingly replaced by cadmium-zinc. This is the case of some antioxidants "*blend*" as *Hostanox Blend M 101P*. Antistatic agents are often not approved for food contact. Moreover, the GC/MS results show that they are absent from food packaging. Their Nickel, Manganese, Chromium and iron concentrations are sometimes quite high (case of *Hostastat FA 38*).

Moreover, even if the additive concentration in packaging remains quite low (see HPLC results performed on *Irgafos 168*), we have counted a large variety of them (see GC/MS results of plastic extracts). The most common are lubricant agents, particularly *Methylpalmitate* and *Methylstearate*. However they are not in the positive list and the second one is "*tumorigenic*". Other lubricants authorized for food contact,

are rarely used (ex: *Erucamide* and *Niobe oil*). Then, one plasticizer usually identified is the *benzyl benzoate* (*Ascabiol*). Even if its toxicity level is low, some studies do not recommend it for pregnant women. There are also many phtalates: *DIBP*, *DIOP*, *DBP* and *MEHP*. Most of them are not in the positive list (*DIBP*, *MEHP*) or are not allowed to make contact with fatty foods. However we find them in meat packaging (ex: *DIOP* in Ech *14* and Ech *19*, *DBP* in *Ech 20*). Some of them are even highly toxic. This is the case for *DBP*, which is still allowed with a *LMS* = 0.3 mg/kg. Phtalates are in general harmful to the reproductive system: they are characterized as "*endocrine disruptors*". Some plasticizers, less toxic, are substitutes for phtalates (ex: *DBS*, *ATBC*). But they are used for specific applications due to their high cost.

Then, antioxidants found in our samples are often phenolic (*Irganox 1076*) or phosphite (*Irgafos 168*). Many studies describe their migration into food. They are sometimes highly charged in Pb (case of *Irganox 1076*). But other antioxidants are considered more toxic (*phosphites arylsubstituted*, *Triphenylphosphites*, etc.). There are also *benzotriazole derivatives* such as *Bumetrizole*. They do not have high toxicity but they do not allow for contact with fatty foods. However, we have identified *bumetrizole* in packaging of olive oil.

Packagings contain other stabilizers such as *Chissonox 206*, *Caradate 30* and *Benzoic acid, 4-ethoxy-, ethyl ester*. The first one presents a carcinogenic effect on humans and the second can cause abdominal cramps and vomiting. No migration limit or other restrictions are reported for these two substances. The *Benzoic acid, 4-ethoxy-, ethyl ester* are allowed with *LMS* 3.6 mg/kg. Other compounds are found in our plastic packaging: The *Methadone N-oxide*, *Propanoic acid, butyl ester (UN 1914)*, *benzaldehyde dimethyl acetal*, *1,3-Dioxolane*, *2-methyl-2-(1-methylethyl)-*, *DL-2,3-butanediol*, *glutamide* and *Valeric anhydride*. These are probably not intentionally added substances (*NIAS*). Even if they come from initial reactants or additives allowed, they can be considered as contaminants in food. It is necessary to combine chemical and toxicological data and determine the origin (impurities, byproducts, etc.) and the content of these compounds.

In conclusion, we have noted that packaging manufacturers do not generally exceed the additive authorized levels. However they allow the use of compounds harmful to consumer health (phtalates, etc.). It is therefore imperative to educate people on the contents of the packages they use daily. We must develop communication about the purpose and applications of these packaging: containers not authorized for fatty food contact should not contain meat!

Finally, it is necessary to encourage the use of substitutes for harmful additives. In the case of plasticizers for example, phtalates may be replaced by *sebacate* or *citrate* molecules.

References

Antistatic agents – Product leaflet – Clariant; DA 3217 E_10/10, pp. 1–18.

Arias, M., Penichet, I., Ysambertt, F., Bauza, R., Zougagh, M., Rios, A., 2009. Fast supercritical fluid extraction of low-and high-density polyethylene additives: comparison with conventional reflux and automatic Soxhlet extraction. J. Supercrit. Fluids 50, 22–28.

Ascabiol data sheet (Rhone-Poulenc Rorer—UK), Rec 8/93.

Ascabiol package insert (May and Baker, Rhone-Poulenc—UK), Rev 7/90, Rec 8/93.

Ash, I., 2004. Handbook of Green Chemicals, second ed. Synapse Information Resources, Inc., New York.

Bach, C., Dauchy, X., Chagnon, M.C., Etienne, S., 2012. Chemical compounds and toxicological assessments of drinking water stored in polyethylene terephthalate (PET) bottles: a source of controversy reviewed. Water Res. 46, 571–583.

Bart, J.C.J., 2001. Direct solid sampling methods for gas chromatographic analysis of polymer/additive formulations. Polym. Test. 20, 729–740.

Bart, J.C.J., 2006. Polymer additive analytics: industrial practice and case studies. In: Quality of Food Contact Polymer, first ed. Firenze University Press, Firenze, Italy, pp. 249–316.

Brydson, J.A., 1999. Plastics materials. In: Plasticisers, seventh ed. Butterworth-Heinmann, Oxford, pp. 330–336.

Burman, L., Albertsson, A.C., Hoglund, A., 2005. Solid-phase microextraction for qualitative and quantitative determination of migrated degradation products of antioxidants in an organic aqueous solution. J. Chromatogr. A 1080, 107–116.

Carette, L., 1993. Plastiques et Composites – Généralités sur les Adjuvants, Vol. AM2. Techniques de l'ingénieur, Paris, Chapter A3230.

Ciba® IRGANOX® B 215. Synergistic Processing and Long-Term Thermal Stabilizer System. Ciba Specialty Chemicals, Inc.

Coulier, L., Orbons, Hub G.M., Rijk, R., 2007. Analytical protocol to study the food safety of (multiple-) recycled high-density polyethylene (HDPE) and polypropylene (PP) crates: influence of recycling on the migration and formation of degradation products. Polym. Degrad. Stab. 92, 2016–2025.

Council Regulation (EEC) No. 793/93 of 23 March 1993 on the Evaluation and Control of the Risks of Existing Substances (OJ L 84, 5 April 1993), European Union, Brussels, 1993.

Craver, C.D., Carraher Jr., C.E., 2000. Plasticizers – Applied Polymer Science: 21st Century, first ed. Elsevier Science Ltd., Oxford, UK, pp. 157–175.

Direction Generale de la Concurrence, de la Consommation et de la Repression des Fraudes (DGCCRF), Plastiques (liste des additifs) - Liste des additifs de matière plastique pour contact alimentaire, visés par l'article 4 de l'arrêté du 2 janvier 2003. Ministère de l'économie et des finances de la République Française (portail), 2009.

Di Bella, G., La Pera, L., Lo Turco, V., Pollicino, D., Dugo, G., 2010. Olives and olive oil in health and disease prevention. In: Preedy, V.R., Watson, R.R. (Eds.), Plasticizer in Olive Oils, first ed. Elsevier Inc., London, pp. 481–488.

Dollery, C. (Ed.), 1991. Therapeutic Drugs, Edinburgh, pp. 53–54.

Espert, A., De las Heras, L.A., Karlsson, S., 2005. Emission of possible odourous low molecular weight compounds in recycled biofibre/polypropylene composites monitored by head-space SPME-GC–MS. Polym. Degrad. Stab. 90, 555–562.

Fankhauser-Noti, A., Grob, K., 2006. Migration of plasticizers from PVC gaskets of lids for glass jars into oily foods: amount of gasket material in food contact, proportion of plasticizer migrating into food and compliance testing by simulation. Trends Food Sci. Technol. 17, 105–112.

Galotto, M.J., Torres, A., Guarda, A., Moraga, N., Romero, J., 2011a. Experimental and theoretical study of LDPE versus different concentrations of Irganox 1076 and different thickness. Food Res. Int. 44, 566–574.

Galotto, M.J., Torres, A., Guarda, A., Moraga, N., Romero, J., 2011b. Experimental and theoretical study of LDPE: evaluation of different food stimulants and temperatures. Food Res. Int. 44, 3072–3078.

Garrido-Lopez, A., Tena, M.T., 2005. Experimental design approach for the optimisation of pressurised fluid extraction of additives from polyethylene films. J. Chromatogr. 1099, 75–83.

Garrido-Lopez, A., Sancet, I., Montano, P., Gonzalez, R., Tena, M.T., 2007. Micro-wave assisted oxidation of phosphite-type antioxidant

additives in polyethylene film extracts. J. Chromatogr. 1175, 154–161.
Gooch, J.W., 2011. Encyclopedic Dictionary of Polymers, second ed. Springer Reference.
Grosclaude, G., 1999. L'eau, Milieu naturel et maîtrise (Tome 1). INRA Edition, Paris.
Harris, C.A., Sumpter, J.P., 2001. Endocrine disruptors part I – the handbook of environmental chemistry. In: Metzler, M. (Ed.), The Endocrine Disrupting Potential of Phthalates. Springer, Berlin, Heidelberg, pp. 169–202.
Houtmeyers, J., 2006. Livre Blanc du Chlore. Plastifiants et Stabilisants. Belgochlore, Bruxelles, pp. 3.6.6–3.6.7.
IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 1987. Overall evaluations of carcinogenicity: an updating of IARC monographs, IARC monographs on the evaluation of carcinogenic risks to humans, Vol 1–42, Suppl. 7. International Agency for Research on Cancer, Lyon.
IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 1994. Some industrial chemicals. IARC Monographs on the Evaluation of Carcinogenic Risks, vol. 60. International Agency for Research on Cancer, Lyon.
ICSC: International Chemical Safety Cards No. 0820, 1998 validated. National Institute for occupational Safety and Health.
Koren, G. (Ed.), 1990. Maternal-fetal toxicology. A clinicians' guide, New York, p 59.
Lacaze, J.C., 1993. La dégradation de l'environnement côtier-conséquences écologiques. Ed Masson, Paris.
Lau, O.W., Wong, S.K., 2000. Contamination in food from packaging material. J. Chromatogr. A 882, 255–270.
Lefaus, R., 1968. Practical Toxicology of Plastics. Iliffe, London.
Lewis Sr., R.J., 2008. Hazardous Chemicals Desk Reference, sixth ed. John Wiley & Sons, Inc., New Jersey.
Lilya, D., 2001. Society for Risk Analysis 2001 Annual Meeting, Environmental Engineering Program (Abstract of Meeting Paper), University of Idaho.
Lindsay, S., 1992. High Performance Liquid Chromatography, second ed. John Wiley & Sons Ltd., Chichester, England.
Marcilla, A., Garcia, J.C., Beltran, A., 2004. Handbook of plasticizers. In: Wypych, G. (Ed.), Plasticizers in Various Industrial Products – Substitutes to Phtalates. Chemtec Laboratories, Toronto, Canada, pp. 389–471.
Marcilla, A., Garcia, S., Garcia-Quesada, J.C., 2008. Migrability of PVC plasticizers. Polym. Test. 27, 221–233.
McEvoy, 1993. AHFS Drug Information. MD: American Society of Hospital Pharmacists, Bethesda, p. 2199.
Mendham, Denney, Barnes, Thomas, 2006. Analyse Chimique Quantitative de Vogel, Traduction de la sixième édition Anglaise. Edition De Boeck Université, Bruxelles.
Mortaigne, B., 1996. Techniques d'analyse. Caractérisation des polymères par couplage GC/SM. Ed. Techniques de l'ingénieur, Paris, pp. 3768–3769.
Muncke, J., 2009. Exposure to endocrine disrupting compounds via the food chain: is packaging a relevant source? Sci. Total Environ. 407, 4549–4559.
Nanni, N., Fiselier, K., Grob, K., Di Pasquale, M., Fabrizi, L., Aureli, P., Coni, E., 2011. Contamination of vegetable oils marketed in Italy by phthalic acid esters. Food Control 22, 209–214.
Papadopoulos, V., 2007. The Leydig cell in health and disease. In: Payne, A.H., Hardy, M.P. (Eds.), Environmental Factors that Disrupt Leydig Cell Steroidogenesis. Humana Press, Totowa, NJ, pp. 393–415.
Pigments & Additives Division - Plastic Business – Antioxidants: Sandostab, Hostanox – Antioxidants for the stabilization of polymers; Clariant; DA 3195 E_01/06, pp. 1–4.
Pinto, A.M., 1997. Quantitative Analysis of Antioxidants from High Density Polyethylene (HDPE) by off-line Supercritical Fluid Extraction Coupled High Performance Liquid Chromatography Thesis submitted to the Faculty of the Virginia Polytechnic Institute and State University in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.
PIRA, 2003. Determination of Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenol)propionate (« Irganox 1076 ») and Tris(2,4-di-tert-butylphenyl)phosphite (« Irgafos 168 ») in polyolefins – EU Project – Specific migration – Method No. 19, Revision 3.
Piringer, O.G., Baner, A.L., 2008. Plastic Packaging. Interactions with Food and Pharmaceuticals, second ed. Wiley-VCH, Weinheim, Germany.
Pitteloud, R., Dubs, P., 1994. Antioxidants for industrial applications. Chimia 48, 417–419.
Pohanish, R.P., 2012. M-Sittig's Handbook of Toxic and Hazardous Chemicals and Carcinogens, sixth ed. Elsevier Inc., Oxford, UK, pp 1636–1893.
Polymer additives for the plastics industry, Overview – Clariant; DA 3100 E_10/10, pp. 1–16.
Postaire, E., 1991. Les matières Plastiques à usage Pharmaceutique – Propriétés Générales et Biotechniques, second ed. Editions Médicales Internationales, Cachan, France.
Regulation (EU) No. 10/2011 of the Commission of 14 January 2011 concerning plastics materials which enter in contact with foodstuff.
Report on Carcinogens, twelfth ed., 2011. Research Triangle Park, NC: US Department of Health and Human Services, Public Health Service, National Toxicology Program.
Reyne, M., 1991. Les Plastiques dans l'emballage. Hermès, Paris.
Rosset, R., Caude, M., Jardy, A., 1991. Chromatographies en Phases Liquides et Supercritiques, first ed. Masson, Paris.
Rouessac, F., Rouessac, A., 2009. Analyse Chimique – Méthodes et Techniques Expérimentales Modernes, 7ème édition. Dunod, Paris.
Saint-Laurent, L., Rhainds, M., 2004. Les phtalates: Etats des Connaissances sur la Toxicité et l'exposition de la Population Générale. Communiqué de veille Toxicologique. Institut National de santé Publique, pp. 1–9.
Sanches Silva, A., Sendon Garcia, R., Cooper, I., Franz, R., Paseiro Losada, P., 2006. Compilation of analytical methods and guidelines for the determination of selected model migrants from plastic packaging. Trends Food Sci. Technol. 17, 535–546.
Senichev, V.Y., Tereshatov, V.V., 2004. Handbook of plasticizers. In: Wypych, G. (Ed.), Influence of Plasticizers on the Glass Transition Temperature of Polymers. Chemtec Laboratories, Toronto, Canada, pp. 218–227.
Shen, H.Y., 2005. Simultaneous screening and determination eight phthalates in plastic products for food use by sonication-assisted extraction/GC–MS methods. Talanta 66, 734–739.
Shinshi, O., Kogo, H., 1980. Effect of phthalic acid esters on mouse testes. Toxicol. Lett. 5, 413–416.
SIDS Initial Assessment Report for 13th SIAM, 2001 – UNEP Publications, Bern, 6–9 November 2001.
Silverstein, R.M., Basler, G.C., Morill, T.C., 2004. Identification Spectrométrique de Composés Organiques, Traduction of the fifth ed.. De Boeck Supérieur, Bruxelles, pp. 91–164.
Simonds, H.R., Ellis, C., Bigelow, M.H., 1944. Handbook of Plastics. D. Van Nostrand, New York.
Vila, A., Ferrer, N., Garcia, J.F., 2007. Chemical composition of contemporary black printing inks based on infrared spectroscopy: basic information for the characterization and discrimination of artistic prints. Anal. Chim. Acta 591, 97–105.
Whelan, T., 1994. Polymer Technology Dictionary, first ed. Chapman & Hall, London.
Zhou, L.Y., Ashraf-Khorassani, M., Taylor, L.T., 1999. Comparison of methods for quantitative analysis of additives in low-density polyethylene using supercritical fluid and enhanced solvent extraction. J. Chromatogr. 858, 209–218.
Zimmer, A.C., 2008. Polluants Chimiques: Enfants en Danger. Editions de l'atelier, Paris.
Zweifel, H., Maier, R.D., Schiller, M., 2009. Plastics Additives Handbook, sixth ed. Hanser Verlag, Munich.