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EXTRACTION AND QUANTITATION OF POLYOLEFIN ADDITIVES

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ABSTRACT

The extraction and subsequent separation and quantitation of polymer additives in polyolefins has proven to be a challenge for the analytical chemist. There have been several workers over the years who have investigated the separation of additives in polyolefins (1-7), but the extraction and recovery (at >90%) in reasonable times has been most difficult. The Soxhlet extraction technique has been used for many years, but suffers in that it takes over twelve hours to extract most of the additives used in polyolefin formulations. Some workers have used the ultrasonic bath (7), but not very much work has been done with the microwave oven. We have investigated some ways to extract the additives from polyolefins, namely, microwave oven and ultrasonic bath techniques for high density polyethylene (HDPE), low density polyethylene (LDPE), and polypropylene. We have concentrated on identifying and quantitating recoveries for typical polyolefin antioxidants, such as Irganox 1010, Irgafos 168, and Cyasorb UV 531. The extraction times are typically 20 minutes for the microwave oven and 30-60 minutes for the ultrasonic bath with 90+ % recoveries being obtained. Both normal phase isocratic (used when phosphites are present) and reverse phase gradient LC techniques are discussed. We have also extracted the slip agent, erucamide, from LDPE, using reverse phase, at 200nm.

INTRODUCTION

The additive packages used for polyolefins can be quite complicated, containing several antioxidants, both primary (such as hindered phenols) and secondary (also called "synergistic") antioxidants, as well as antistats, slips, pigments, etc. It is very important to the processing and longevity of the fabricated product that the correct amount of each

additive is present. Failure to choose the correct additive package may result in degradation during processing or premature oxidation/aging and early failure in the field. For this reason it is very important for the chemist/engineer to be assured that the correct amount of the desired additive(s) is present.

Slip agents are usually long chain aliphatic amides, such as oleamide and erucamide. These compounds can be extracted out with methylene chloride/cyclohexane mixtures and are soluble in warm acetonitrile. They can be detected by UV at 200nm (using conventional water/acetonitrile reverse phase gradients over a 4u C₁₈ column). For this discussion, we will concentrate on the extraction and subsequent chromatographic separation of common antioxidants. We will also mention some recent work that has been completed on recovery of erucamide in LDPE. Table I lists the antioxidants (and slip agents) that we have extracted and chromatographed successfully.

EXPERIMENTAL

Instrumentation - A Waters Model 600 Powerline Gradient Controller was used for the HPLC separations. This consisted of a Model 600 gradient pumping system, with an M490 variable wavelength UV detector, and a Waters 712 WISP autosampler. Also used was a Waters Model 990 photodiode array detector. The columns used for the separations consisted of a Waters Nova-Pak C₁₈ (4u) reverse phase column and Waters Nova-Pak (4u) and Resolve (5u) SiO₂ normal phase columns (all measuring 3.9mm i.d. x 15cm). The data system consisted of a Waters Model 860 VAX system with ExpertEase software (Waters Chromatography Division, Millipore Corp., Milford, MA). The microwave oven used for the extractions was a CEM (CEM Corp., Indian Trail, North Carolina) Model MDS-81. The ultrasonic bath used was a Branson (Branson Cleaning Equipment Co., Shelton, Connecticut) B-52 (240W) unit. The Wiley Mill (VWR Sci. Co., Westwood, Mass.) used for the grinding procedure was Model #3383-L10.

RESULTS AND DISCUSSION

This paper is organized into 3 sections: A) HDPE will deal with the extraction and chromatographic analysis of 3 antioxidants compounded into a high density polyethylene; B) POLYPROPYLENE will discuss the extraction and chromatographic analysis of antioxidants compounded into 5 different polypropylene resins; and C) LDPE will present some recent results on low density polyethylene recoveries.

A) HDPE

We obtained a sample of high density polyethylene (HDPE) in pellet form to which had been compounded 500 ppm each of BHT (butylated hydroxytoluene), Irganox 1010 and Irganox 1076. Four separate extraction solvents were utilized, the first being a 9:1 mixture of cyclohexane and isopropyl alcohol (IPA). The second choice (which proved to be more efficient) was a 50:50 mixture of the same two solvents. The third choice was a

TABLE I

POLYOLEFIN ANTIOXIDANTS

ADDITIVE	CHEMICAL NAME	MANUFACTURER*
BHT	Butylated hydroxytoluene	Many
BHEB	Butylated hydroxyethylbenzene	Many
Irgafos 168	Tris (2,4-di-t-butylphenyl) phosphite	Ciba-Geigy
Irganox 1010	Tetrakis methylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate) methane	Ciba-Geigy
Irganox 1076 Ultranox 276	Octadecyl-3,5-di-t-butyl-4-hydroxyhydrocinnamate	Ciba-Geigy Borg-Warner
Irganox 1330 Goodrite 1330	1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxy-benzyl)-benzene	Ciba-Geigy B.F. Goodrich
Irganox 3114	1,3,5-tris (3,5-di-t-butyl-4-hydroxybenzyl)-s-triazine-2,4,6-(1H,3H,5H)-trione	Ciba-Geigy
Tinuvin 328	2-(2'-hydroxy-3',5'-di-t-amylphenyl) benzotriazole	Ciba-Geigy
Cyasorb UV 531	2-hydroxy-4-n-octabenzophenone	American Cyanamid
Ultranox 626	Bis (2,4-di-t-butylphenyl) pentaerythritol diphosphite	Borg Warner
AM 340	Hindered phenol	Ferro
Erucamide	Same (long chain amide)	Many
Oleamide	Same (long chain amide)	Many

*Note: There are other manufacturers not listed who also provide many of the above stabilizers. We have also chromatographed other antioxidants, such as Pep-Q and Tinuvin P, which will be shown in the attached chromatograms, but are not necessarily part of the extraction studies. Also, many of the additives mentioned by trade name have registered trademarks owned by the manufacturer.

75:25 mixture of methylene chloride (MeCl_2) and cyclohexane; and the fourth choice being a 98:2 methylene chloride/IPA mixture. Using the first solvent mixture, 3 different methods of extraction were tried; i.e., Soxhlet, ultrasonic (conventional laboratory sonic bath), and microwave oven (high powered, programmable, laboratory microwave oven). Only the ultrasonic and microwave methods were used with the 50:50, 75:25 and 98:2 mixtures as the Soxhlet method proved to be too long and tedious.

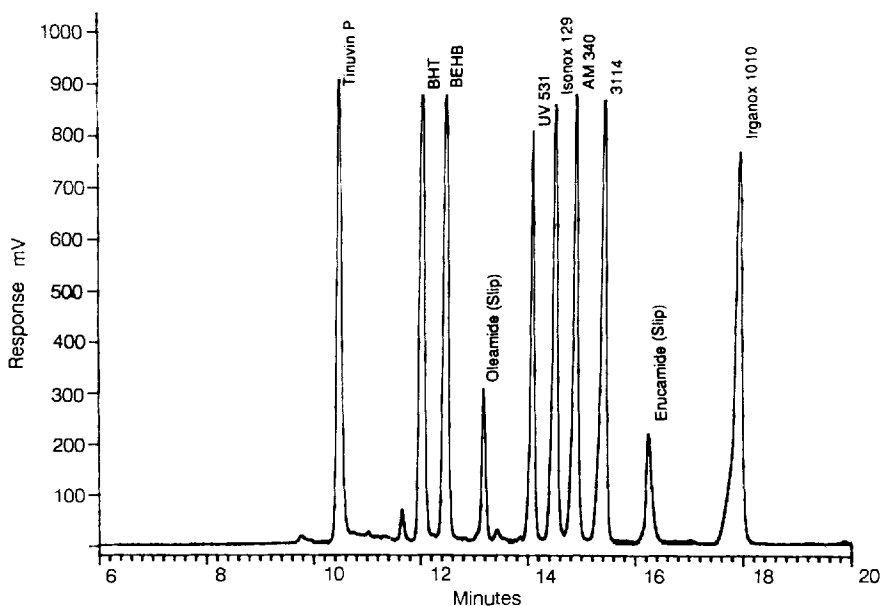


FIGURE 1. Chromatogram of common polyolefin additive standards with a Nova-Pak C18 column, maintained at 50°C. Reverse phase gradient separation with 3:2 water/acetonitrile to 100% acetonitrile (linear gradient to five minutes). Flow rate is 1.50 ml/minute. Detection with UV at 200nm.

The HDPE (for all extraction methods) was ground, using the Wiley Mill, to 20 mesh, with 5 grams \pm 0.10 mg being added to exactly 50 mls of the solvent mixture. It should be noted that care has to be taken during the grinding procedure to prevent excessive heating of the resin, as volatile antioxidants such as BHT may be lost. We have used liquid nitrogen cooling during the grinding procedure and it worked quite well. After the desired extraction time period, the HDPE is removed by filtration and the solvent mixture is allowed to evaporate to dryness without any heat applied. The additives are resolubilized with acetonitrile and brought to mark in a volumetric flask. If time is a major concern, the extraction solution (at a known volume) may be injected directly into the chromatograph before complete evaporation. If the extraction solvent has any UV absorption, it will be observed as a peak eluting near the void volume. Solvents such as cyclohexane and IPA will show little to no absorption above 220nm. The LC analysis consists of a reverse phase gradient with 3:2 water/acetonitrile to 100% acetonitrile (5 minute linear gradient) with a Nova-Pak C₁₈ column (15cm).

Figure 1 shows a typical chromatogram of antioxidant and slip agent standard using the reverse phase gradient at 200nm. It should be noted that Irganox 1330 elutes after 1010

TABLE II

MICROWAVE EXTRACTION RESULTS - HDPE

ADDITIVE	Concentration (ppm) 1:1 Cyclohexane/IPA	Concentration (ppm) 98:2 MeCl ₂ /IPA
BHT	451 (90%)	455 (91%)
1010	454 (91%)	459 (92%)
1076	480 (96%)	474 (95%)

The above data correspond to an R.S.D. of $\sim 1.8\%$ for the 3 additives over 6 separate extractions.

at ~ 18.3 minutes, and Irganox 1076 elutes at ~ 21 minutes, all baseline resolved. This gradient procedure at 200nm allows for separation of 12 of the more common antioxidants and slip agents. Five grams of the ground HDPE resin were extracted by both the ultrasonic bath and the microwave oven using a 50:50 mixture of the cyclohexane and 2-propanol. It was found that only a 20 minute heating of the solution in the microwave oven at 50% power (and stirring every 5 minutes) was required to extract the additives. The HDPE was ground to 20 mesh with the Wiley Mill for this experiment as well. The 98:2 MeCl₂/IPA mixture was also used for the microwave oven method (20 minutes at 25% power with stirring every 5 minutes). Six different extractions were performed with the resin with the average results for the microwave extraction shown in Table II. Concentrations are in ppm and the percentages represent the % recovery (out of 500 ppm initial concentration).

The 50:50 cyclohexane/IPA and 75:25 MeCl₂/cyclohexane mixtures proved to work extremely well with the ultrasonic method of extraction. The ground HDPE was extracted for one hour in the ultrasonic bath, with the solution being stirred for at least 30 seconds every 10 minutes. The extraction was carried out for only 30 minutes using the MeCl₂/cyclohexane mixture (again stirring every 10 minutes). Table III illustrates the recoveries in ppm and percent recoveries obtained for each additive.

In all cases, the separations were carried out using a 15cm Nova-Pak C₁₈ column, with a gradient of 60:40 water/acetonitrile to 100% CH₃CN (5 minute linear gradient). The column temperature should be held above room temperature, such as 40-55°C. This helps to improve peak shapes. Also, after every 8-10 injections, it is a good idea to allow THF to flow through the column (at 50°C or less) for 5 minutes to dissolve any low molecular weight waxes that may have adsorbed onto the column. We also used a 7.5cm Nova-Pak column which will bring the 1010 and 1076 retention times down significantly. The shorter column can be used when the additive package is relatively simple (3 components or less, for example), with the same water/acetonitrile gradient. If the additive package is much more complicated (i.e., contains several additives that elute very closely), then the 15cm Nova-Pak should be used.

TABLE III

ULTRASONIC EXTRACTION RESULTS - HDPE

ADDITIVE	Concentration (ppm) 1:1 Cyclohexane/IPA (60 Min)	Concentration (ppm) 75:25 MeCl ₂ /Cyclohexane (30 Min)
BHT	454 (91%)	449 (90%)
1010	457 (91%)	458 (92%)
1076	475 (95%)	481 (96%)

The above data represent an R.S.D. of ~1.9%, again over 6 separate extractions as was done in the microwave extractions.

In summary, the 50:50 cyclohexane/IPA mixture works very well with both the ultrasonic bath extraction method (1 hour with stirring every 10 minutes) and with the microwave oven method (only 20 minutes at 50% power, stirring every 5 minutes). The stirring is very important, as agitation will facilitate the extraction of the additives out of the polymer matrix. The small amount of IPA added to the MeCl₂ mixture for the microwave extraction is necessary as MeCl₂ alone heats up very slowly in the microwave, and the IPA (because of the polar OH group) heats up very quickly. The addition of only 2% was enough to heat up the solution and extract the additives successfully. The 75:25 MeCl₂/cyclohexane mixture used with the ultrasonic bath also worked very well. Any of these three methods may be used to efficiently extract out the additive package from HDPE. An advantage of using the methylene chloride solvent mixtures is that the extraction temperatures do not exceed 50°C; this is desirable when volatiles or easily degradable antioxidants such as BHT and phosphite esters are extracted. After 6 separate extractions/injections were performed, it was found that the relative standard deviation was approximately 2%.

B) POLYPROPYLENE

We investigated the ultrasonic and microwave extraction procedures and determined recoveries for polypropylene. Several polypropylene resins were examined that contained a variety of additive packages. The additives were present at various levels, with the precision of the compounding being ± 35 ppm. The polypropylene formulations consisted of antistats, pigments, fillers, slip agents, and antioxidants/UV degradants.

For the purpose of this work, we will concentrate on the extraction, identification and quantitation of the antioxidants, including the phosphite esters. Each of the resins was said to possibly contain an unknown (but low) amount of Irganox 1076 which was compounded into the resin initially. The 1076 can be sometimes observed in some of the chromatograms for the resins. In addition to the usual hindered phenolic type antioxidants such as Irganox 1010, 1076 and 3114, many of the resins contained phosphite esters such as Irgafos 168 and

Ultrinox 626. These phosphite esters are referred to as secondary antioxidants, or synergistic antioxidants. One of their primary functions is to react with the hydroperoxide (-OOH) group which forms as the last step prior to chain scission. Where reverse phase separation techniques require water as part of the gradient elution scheme, the phosphite esters are prone to hydrolysis. We therefore examined normal phase chromatographic techniques, using a Resolve and also a Nova-Pak silica column when the phosphites were present. Several solvent combinations were tried, as well as many gradient and isocratic methods. One chromatographic system that worked quite well was a 70:30 mixture of *n*-butyl chloride/methylene chloride. The same methylene chloride/IPA, methylene chloride/cyclohexane and cyclohexane/IPA solvent mixtures that were used for the HDPE extractions were also investigated for the polypropylene resins. Both the variable wavelength UV detector (at 225nm) and the photodiode array detector were used for the analysis. The following additives were chromatographed as part of the normal phase separation study:

AM 340	Irganox 1076
BHT	Irganox 3114
Cyasorb UV 531	Irganox 1330
Irgafos 168 (phosphite)	Tinuvin 328
Irganox 1010	Ultrinox 626 (phosphite)

The Irgafos 168, Irganox 1010, 1076 and 3114 can all be separated in under 7 minutes at a 1.5 ml/min flow rate. The first extraction consisted of a microwave oven procedure, heating 5 grams (\pm .10 mg) of resin that were previously ground in the Wiley Mill to 20 mesh in 50mls of a 98:2 methylene chloride/2-propanol mixture. The IPA is added to allow for heating of the mixture in the microwave. The resins were extracted in the microwave oven for 20 minutes at 25% power, with stirring every 5 minutes. After the extraction period, the solutions were allowed to cool and then filtered and rinsed with methylene chloride. The solvent temperature (48°C) was above the boiling point of methylene chloride (40°C) in the sealed sample containers. The additive solutions were then brought to mark in a volumetric flask (10 or 25ml depending on the amount of additives present in the resin), then chromatographed by the normal phase, isocratic separation procedure. The normal phase separation is recommended only when a phosphite ester is present in the formulation, or if the formulation is relatively simple. A complicated formulation containing several antioxidants (but no phosphite) or one of the slip agents would best be separated by reverse phase techniques, which will be discussed below.

Figure 2 shows the normal phase isocratic separation of four antioxidant standards: Irgafos 168, Irganox 1076, Irganox 3114, and Irganox 1010. Table IV lists the recoveries obtained for four of the resins, two of which contain a phosphite ester, using the microwave oven and the 98:2 methylene chloride/isopropanol mixture (20 minutes).

The recoveries are excellent for all of the additives except the Irganox 3114, which was recovered at only 79%. There is a minor peak present that elutes very close to where Irganox 1076 elutes and, upon examining the spectra with the photodiode array detector, it was found to be a hindered phenol (such as 1076). Some of the resins were reported to

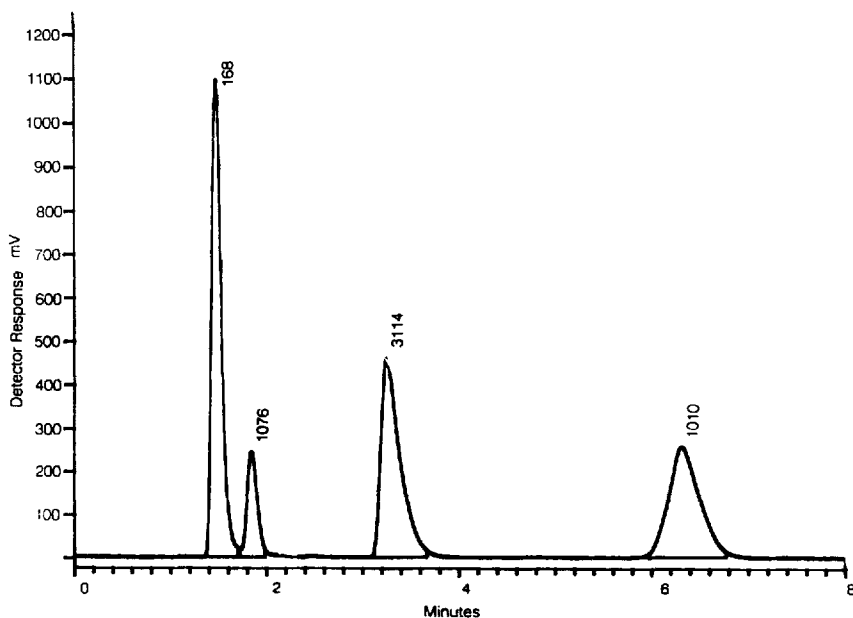


FIGURE 2. Chromatogram of common polyolefin additive standards with a Resolve silica column maintained at 30°C. Normal phase isocratic separation with 70:30 n-butyl chloride/methylene chloride. Flow rate is 1.50 ml/minute. Detection with UV at 225nm.

contain an unknown amount of 1076. The 1010 was recovered in the two resins at better than 92%. This is one of the more difficult antioxidants to recover, and the resin must be ground in the Wiley Mill for extraction to be successful. During the grinding procedure, one must be careful not to force the resin through the 20 mesh screen too quickly as the heat buildup may cause the polymer to melt, which will cause loss of the more volatile antioxidants and plug the screen. Addition of carbon dioxide or liquid nitrogen will prevent this from happening. Some of the resins were extracted "as is" (pellets, not ground) and recoveries were excellent using the microwave technique, except for 1010 which could be extracted at no better than ~50% recovery without grinding. The next step was to microwave extract the "E" resin and perform the chromatographic separation 6 times in order to determine the reproducibility of the technique. Table V shows the results.

This results in a value of 496 ± 16 ppm, or 3.3% for Irgafos 168, and a value of 995 ± 26 ppm, or 2.6% for the Irganox 1010. We would expect the Irgafos (phosphite) to not be quite as good as far as precision is concerned, as this material has a tendency to degrade more easily, and the peak height/area variance from run to run was greater than for the 1010.

TABLE IV

**MICROWAVE EXTRACTION RESULTS - POLYPROPYLENE
98:2 METHYLENE CHLORIDE/ISOPROPANOL**

ADDITIVE	Amount Recovered (ppm)	Amount Present (ppm) ± 35	% Recovery
RESIN "D" *			
Irganox 3114	565	600	94
Cyasorb UV 531	442	500	88
RESIN "E"			
Irgafos 168	521	500	100+
Irganox 1010	986	1000	99
RESIN "G"			
Ultranox 626	709	800	89
Irganox 3114	635	800	79
RESIN "I"			
BHT	513	500	100+
Irganox 1010	931	1000	93

***Note:** The "D" resin also contained 2,000 ppm of AM 340, but the normal phase separation results were not as good as for the reverse phase analysis to be discussed later on.

TABLE V

"E" RESIN EXTRACTION REPRODUCIBILITY STUDY

Extraction #	Conc. Irg.168 (ppm)	Conc. Irg.1010 (ppm)
1	521	986
2	485	1034
3	509	981
4	476	1019
5	489	978
6	496	970
	[R.S.D. = 3.3%]	[R.S.D. = 2.6%]

TABLE VI

ULTRASONIC EXTRACTIONS - 75:25 MeCl₂/CYCLOHEXANE

ADDITIVE	Conc. (ppm) 30 min.	Conc. (ppm) 60 min.
Irg.168-1	522/500	492/500
Irg.168-2	494/500	516/500
Irg.168-3	513/500	503/500
1010-1	929/1,000	982/1,000
1010-2	882/1,000	998/1,000
1010-3	921/1,000	980/1,000

The next procedure consisted of an ultrasonic extraction of the "E" resin (again ground with the Wiley Mill) using a 75:25 MeCl₂/cyclohexane solvent mixture. The first extraction was done for 30 minutes, as the table below indicates. An additional 30 minutes (or 1 hour total) was required to extract out the 1010 at 98+ % recovery. Each extraction was done in triplicate, with the results shown in Table VI.

Table VI indicates that all of the Irgafos 168 is extracted in only 30 minutes, with ~88% (worst case) of the 1010 being extracted. We can "squeeze out" a little more of the 1010 if we choose to extract in the ultrasonic bath for a full hour. Figure 3 shows the chromatogram for the ultrasonic bath extract from the "E" polypropylene resin. The small peak just under 2 minutes was not quantitated as 1076, as we did not know how much 1076, if any, was present in this resin (as discussed previously).

All of the above chromatography for the polypropylene extractions was carried out using the normal phase isocratic separation with the 15cm Resolve SiO₂ column and the 70:30 BuCl₂/MeCl₂ mixture. This procedure proved to be excellent for several of the resins that contained the phosphite esters, with no evidence of any hydrolysis or other severe degradation of the phosphites having taken place.

We have recently investigated flow programming using a Nova-Pak Silica column and an isocratic mixture of 80:20 n-butyl chloride/methylene chloride. The flow program starts at 0.75 ml/min, then increases to 1 ml/min after 1 minute, then to 1.5 ml/min at 2.5 minutes, then to 2.5 ml/min after 5 minutes. These flow steps are all linear. Figure 4 shows the chromatogram using flow programming for Irgafos 168, Pep-Q (both phosphite esters), Irganox 1076, Tinuvin P, Irganox 3114, and 1010. The separation is not as selective as for the reverse phase, but one can separate phosphite antioxidants from each other and some of the phenolic antioxidants in under 6 minutes. The reverse phase separations afford much better selectivity than do the normal phase separations, but the retention times are longer. Three resins (not containing a phosphite) were extracted in both the microwave oven and in the ultrasonic bath methods using a 50:50 mixture of cyclohexane

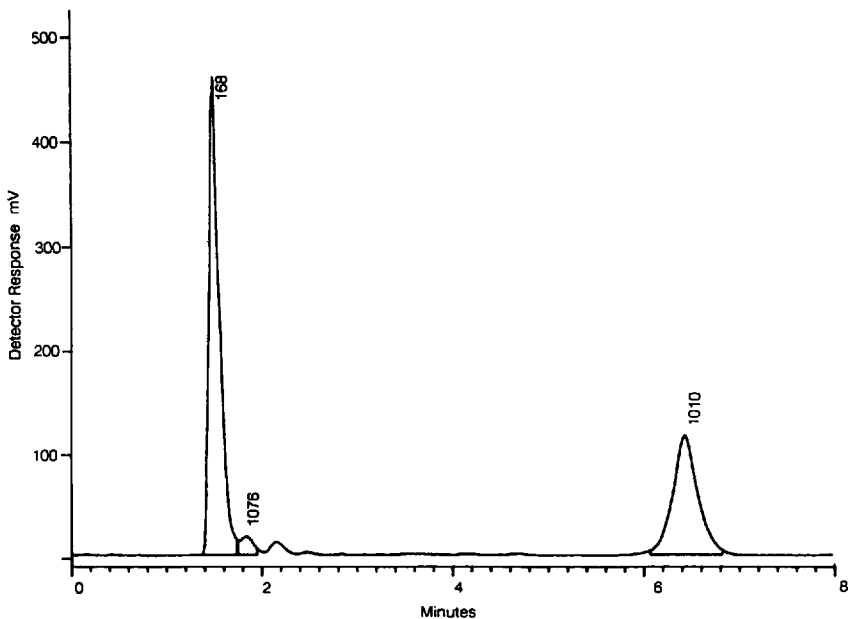


FIGURE 3. Chromatogram of ultrasonic bath extract from polypropylene resin "E", with a Resolve silica column. Normal phase isocratic separation as in FIGURE 2.

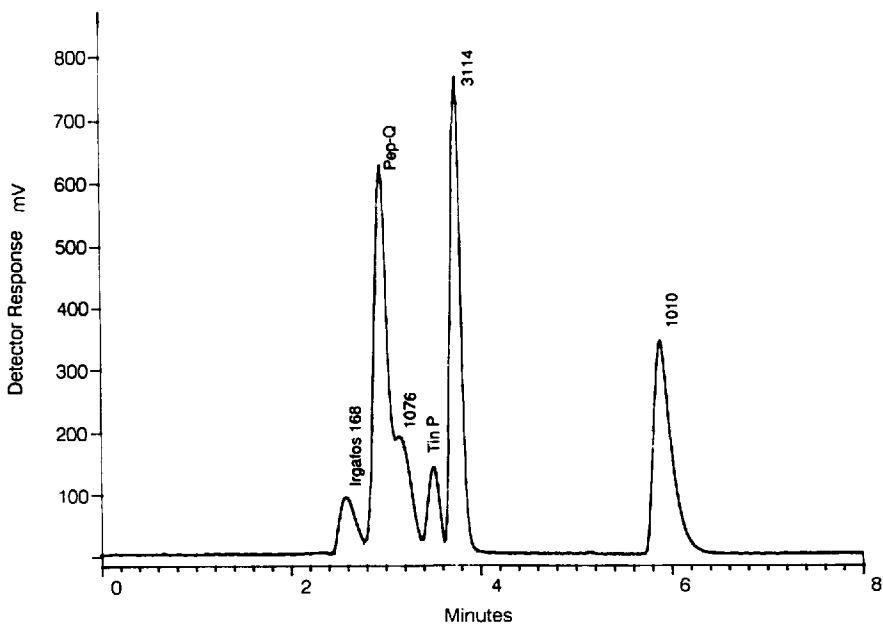


FIGURE 4. Chromatogram of additive standards with a Nova-Pak silica column, maintained at 35°C. Normal phase isocratic separation with flow programming as described in the text. Eluent is 80:20 n-butyl chloride/methylene chloride. Detection with UV at 230nm.

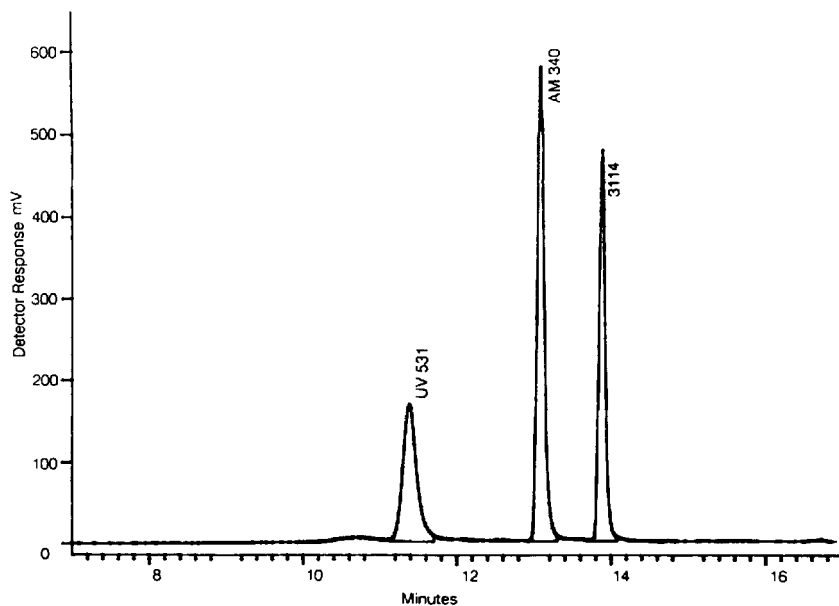


FIGURE 5. Chromatogram of microwave oven extract from polypropylene resin "D", with a Nova-Pak C18 column. Reverse phase gradient separation as in FIGURE 1. UV detection at 225nm.

and 2-propanol. The microwave extraction was carried out for just 20 minutes at 25% power, with stirring for 30 seconds at 5 minute intervals. The ultrasonic extraction was carried out for 1 hour with stirring every 15 minutes. The 5 grams of polypropylene resin was ground as usual on the Wiley Mill. Figure 5 shows the reverse phase gradient chromatogram for the "D" resin. Just as an experiment, the "E" resin was also extracted, but the Irgafos 168 could not be detected. The 1010 was recovered, however. The recovery results (average of triplicate extractions) in ppm and percent are shown in Tables VII and VIII.

The microwave oven provides a very fast means of extracting the additives from the ground resin. This technique can be performed on unground resins as well, depending upon the components present in the formulation. If 1010 is present, for example, the resin must be ground, otherwise the 1010 will not be recovered at better than 50%. The ultrasonic bath provides an inexpensive and relatively fast way of extracting the additives. The Soxhlet method of extraction was not tried with these polypropylene resins, as we would assume that it would take at least 7 hours to extract out the majority of the additives, and perhaps as much as 16 hours to recover 1010, for example.

TABLE VII

**MICROWAVE EXTRACTIONS; REVERSE PHASE LC
50:50 CYCLOHEXANE/ISOPROPANOL - 20 MIN.**

ADDITIVE	Amount Recovered/Present (ppm)
	RESIN "D"
Irganox 3114	604/600 (100%)
Cyasorb UV 531	511/500 (100%)
AM 340	1770/2000 (89%)
	RESIN "E"
Irgafos 168	Not Detected
Irganox 1010	986/1000 (99%)
	RESIN "I"
BHT	484/500 (97%)
1010	947/1000 (95%)
	RESIN "K"
BHT	1274/1400 (91%)
1010	961/1000 (96%)

TABLE VIII

**ULTRASONIC EXTRACTION RECOVERIES 50:50
CYCLOHEXANE/ISOPROPANOL - 60 MIN.**

	RESIN "D"
Irganox 3114	583/600 (97%)
Cyasorb UV 531	491/500 (98%)
AM 340	1788/2000 (89%)
	RESIN "E"
Irgafos 168	Not detected
Irganox 1010	977/1000 (98%)
	RESIN "I"
BHT	469/500 (94%)
1010	953/1000 (95%)
	RESIN "K"
BHT	1242/1400 (89%)
1010	938/1000 (94%)

TABLE IX
MICROWAVE EXTRACTION RECOVERIES
(98:2 METHYLENE CHLORIDE/IPA)

RESIN	BHT	BHEB	ISONOX 129	IRG. 1010	IRG. 1076
A-1	238	244	239	232	240
A-2	241	248	244	221	229
A-3	231	237	238	228	232
B-1	881	882	928	917	943
B-2	920	896	944	903	926
B-3	904	871	907	895	935

TABLE X
ULTRASONIC BATH RECOVERIES
(75:25 MeCl₂/CYCLOHEXANE)

RESIN	BHT	BHEB	ISONOX 129	IRG. 1010	IRG. 1076
A-1	236	237	220	222	225
A-2	231	233	238	208	219
A-3	233	223	228	219	234
B-1	908	896	933	891	901
B-2	896	901	915	920	922
B-3	893	894	926	907	911

C) LDPE

The last group of resins extracted was four low density polyethylenes (LDPE), labelled A through D. Resin A contained 250 ppm each of BHT, BHEB, Isonox 129, Irganox 1010, and Irganox 1076. Resin B contained 1,000 ppm of each antioxidant. Resin C contained 500 ppm of the erucamide slip agent, and Resin D had 1,500 ppm of the erucamide. The microwave oven was used to extract each of the ground (20 mesh again, under liquid nitrogen) resins with 98:2 methylene chloride/isopropanol for 20 minutes (same procedures as for the previous polyolefins).

The recovery results (3 different extractions on 3 different days) are summarized in Table IX.

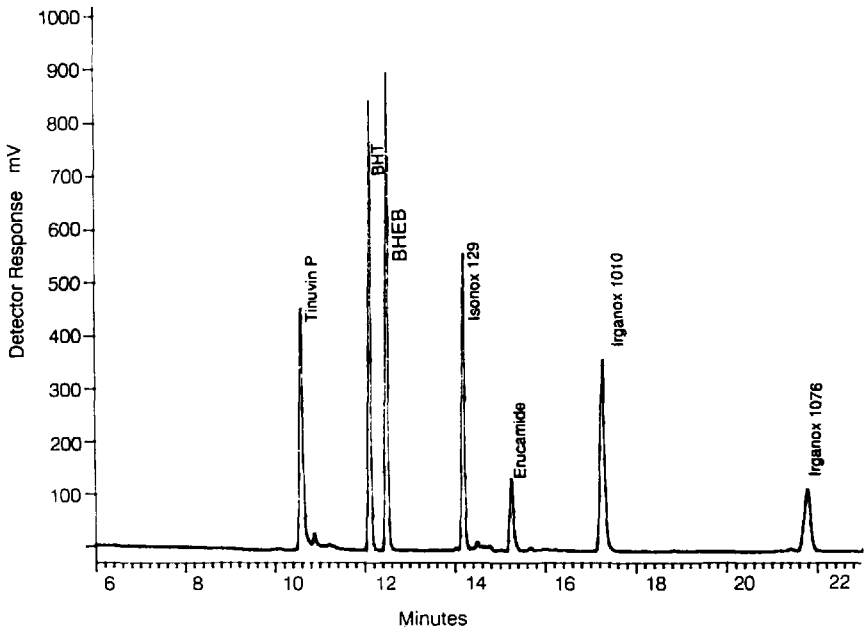


FIGURE 6. Chromatogram of microwave oven extract from LDPE resin "B", with a Nova-Pak C18 column. Reverse phase gradient separation as for FIGURES 1 and 5. UV detection at 225nm.

TABLE XI

MICROWAVE OVEN EXTRACTION RECOVERIES
(98:2 METHYLENE CHLORIDE/IPA)

RESIN	Erucamide Recovered	% Recovery
C-1	457/500	91
C-2	452/500	90
C-3	473/500	95
D-1	1329/1500	89
D-2	1364/1500	91
D-3	1343/1500	90

TABLE XII

**ULTRASONIC BATH EXTRACTION RECOVERIES
(75:25 METHYLENE CHLORIDE/CYCLOHEXANE)**

RESIN	Erucamide Recovered	% Recovery
C-1	465/500	93
C-2	471/500	94
C-3	457/500	91
D-1	1334/1500	89
D-2	1338/1500	89
D-3	1352/1500	90

Table X shows the recoveries for Resins A and B using the ultrasonic bath with the 75:25 methylene chloride/cyclohexane mixture (30 minutes).

The microwave oven was a little more successful in extracting out the 1010. When the ultrasonic bath time is increased to 1 hour, the 1010 recoveries increase to >90%. Figure 6 shows the reverse phase chromatogram for the microwave oven extracted LDPE Resin B. Resins C and D (containing 500 and 1500 ppm erucamide, respectively) were next extracted using the same extraction solutions. Again, exactly 5 grams of the 20 mesh ground resin were extracted in 50mls of the extraction solvents. Tables XI and XII show the recovery results for the erucamide slip.

The recoveries for the erucamide are basically the same for the 2 extraction techniques, and both are very good.

CONCLUSIONS

There are other means of extraction of polyolefin additives, such as "super heating" a solvent mixture in a sealed vial to as much as 30°C above the boiling point. Also, in situ boiling (such as with toluene or IPA, for example) is also used, but takes 3-4 times longer than the microwave oven and 2-3 times longer than the ultrasonic bath. We have demonstrated two quick ways to extract and quantitate the levels of typical antioxidants present in high and low density polyethylene, as well as polypropylene. Most analytical laboratories have at their disposal an ultrasonic bath cleaner that will work very well at extracting out the antioxidants. The only other materials required are 250ml beakers and watch glasses. The microwave oven allows the extractions to be done more quickly, but at a much higher initial cost. Up to 12 samples can be extracted at once in the oven, and sample handling is quite easy. Both techniques afford a great time savings when compared to conventional Soxhlet extraction. It is difficult to set up more than four Soxhlet condensers in a hood, so the sample throughput is obviously much less than for the other two techniques.

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