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Determination of Cyasorb UV 1084 and its degradation products in low-density polyethylene film by high-performance liquid chromatography

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ABSTRACT

A reversed-phase high-performance liquid chromatographic (HPLC) method utilizing a photodiode-array detector was developed that is capable of identifying and quantifying Cyasorb UV 1084, a UV light stabilizer, and some of its UV and thermal decomposition products in low-density polyethylene (LDPE) resins in the presence of common antioxidants and UV stabilizers. Isopropanol extracts Cyasorb UV 1084 from the LDPE concentrate at greater than 95% efficiency. The overall precision of the method is very good, the relative standard deviation being less than 4%. This HPLC method was used to determine Cyasorb UV 1084 in concentrates and manufactured films. It was found that the level of Cyasorb UV 1084 in concentrates was as expected and had not degraded. However, lower than specified levels of Cyasorb UV 1084 were found in the manufactured film and clear evidence for thermal decomposition products was observed. This loss of Cyasorb UV 1084 apparently caused a shorter film life.

INTRODUCTION

UV light stabilizers and antioxidants are added to polyethylene to protect it from thermal and oxidative degradation at the elevated processing temperatures and oxidative degradation caused by exposure to the UV radiation from sunlight [1].

Cyasorb UV 1084, [2,2′-thiobis(4-*tert*.-octylphenolato)]-*n*-butylaminenickel(II), is used in low-, medium- and high-density polyethylene and in polypropylene as a UV light absorber, an antioxidant and a dye acceptor. The phenolic portion of the compound makes it a good heat stabilizer, and it is used as a stabilizer against UV light because of its light-absorbing capability.

Low-density polethylene (LDPE), used in agricultural mulches, greenhouse films or packaging that will be exposed to the outdoors, contains Cyasorb UV 1084 to protect it against high temperatures and UV radiation from the sun. Studies have demonstrated that film containing Cyasorb UV 1084 is stable for 12 months in Florida, whereas the film without stabilizer will last only about 2.5 months before it becomes brittle [2].

In our tests, commercially available co-extruded cast film was used. This film has a black layer and a white layer. The white layer contains about 2% Cyasorb UV 1084. Certain films contained a dark streaking due to die drool and were judged to be a problem owing to discoloration at high temperatures and deterioration when exposed to the Florida sun. The streaks were analyzed by X-ray diffraction and found to be nickel sulfide, one of the thermal decomposition product of Cyasorb UV 1084. Atomic absorption spectrometric (AAS) and UV analysis implied that the Cyasorb UV 1084 was present at the level expected. Mass spectrometric analysis indicated no significant differences between good and problem films, each giving similar decomposition products of the Cyasorb UV 1084 on heating in the probe. Fig. 1 shows the structures of Cyasorb UV 1084 and other thermal decomposition

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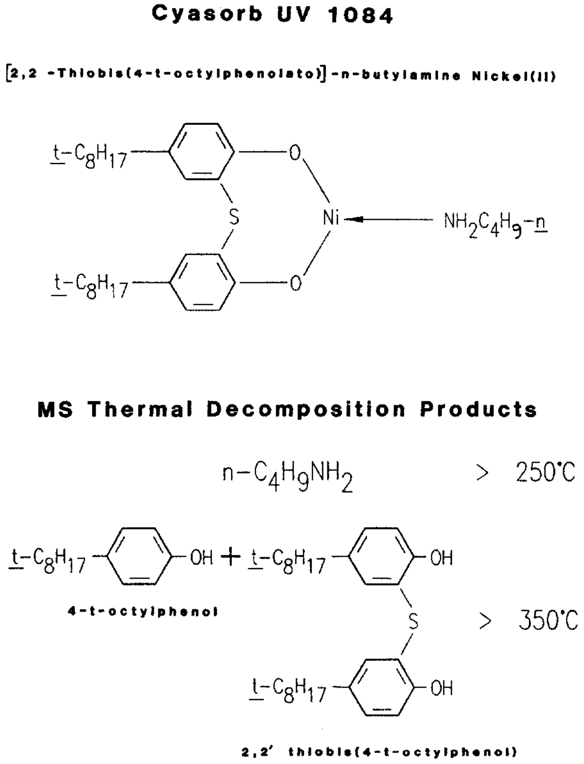

Fig. 1. Cyasorb UV 1084 and its thermal decomposition products identified by mass spectrometry. t = *tert*.

products determined by mass spectrometry. To understand what is occurring in the film, a high-performance liquid chromatographic (HPLC) method was developed to analyze for Cyasorb UV 1084 and its possible decomposition products in films and in concentrates, which comprise 20% of the white layer of the film.

EXPERIMENTAL

Chromatographic apparatus

The HPLC system used consists of a Model 712 WISP autosampler, a Model 600E gradient system with a column heater thermostated at 40°C, a Model 990 photodiode-array detector and an NEC Power Mate 2 data gathering station (Waters Assoc.). A Perkin-Elmer 3 × 3 C_{18} (3-μm particles) 3 cm × 4.6 mm I.D column was used. The mobile phase was either isopropanol–water–acetic acid (94.5:5.0:0.5) with isocratic elution at 2.0 ml/min, or a 2-min linear gradient at 1.0 ml/min from isopropanol–water–acetic acid (65:34.5:0.5) to isopropanol–acetic acid (99.5:0.5).

Chemicals

Cyasorb UV 1084 and 2,2-thiobis(4-*tert.*-octylphenol) were obtained from American Cyanamid (Wayne, NJ, USA), 4-*tert.*-octylphenol from Aldrich (Milwaukee, WI, USA), isopropanol (OmniSolv) obtained from EM Science (Gibbstown, NJ, USA) and glacial acetic acid from Ashland Chemical (Columbus, OH, USA). Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA).

Preparation of standard solutions

The standard solutions consisted of Cyasorb UV 1084, 2,2-thiobis(4-*tert.*-octylphenol) and 4-*tert.*-octylphenol dissolved in isopropanol. To dissolve the material completely, the solutions must be heated to about 40°C or placed in an ultrasonic bath.

Sample preparation

LDPE concentrate pellets or manufactured film were ground to 40 mesh using a Wiley mill. For those grinding experiments where liquid nitrogen was used to keep the samples from overheating, the sample pelets and film were ground in a liquid nitrogen-cooled Spex mill for 10 min. A 3-g sample of ground film or a 0.5-g sample of ground concentrate was refluxed with 100 ml of isopropanol for 1 h in a 250-ml flat-bottommed flask with a water-cooled condenser. For film samples, after cooling, the extract was filtered through a 0.2-μm filter. For concentrate samples, after cooling, the extract was diluted 1:10 with isopropanol before filtering to keep the Cyasorb UV 1084 signal in the linear calibration range.

Quantitative evaluation

Calibration graphs were constructed for each analyte in the concentration range 10–500 mg/l. A linear regression curve of concentration *versus* peak area was calculated. Eight complete replicate analyses were performed on two LDPE concentrates for the extraction recovery study for Cyasorb UV 1084 shown in Table I.

TABLE I

CYASORB UV 1084 RECOVERY STUDY

Extraction from an LDPE concentrate by refluxing with isopropanol for 1 h.

Concentrate	Parameter	Value
A	Mean Cyasorb UV 1084 (%)	9.69
	Standard deviation (%)	0.07
	Relative standard deviation (%)	0.72
	95% confidence limit for average (%)	9.69 ± 0.05
	n	8
B	Mean Cyasorb UV 1084 (%)	9.58
	Standard deviation (%)	0.38
	Relative standard deviation (%)	3.97
	95% confidence limit for average (%)	9.58 ± 0.33
	n	8

RESULTS AND DISCUSSION

Chromatographic separations

Cyasorb UV 1084 historically has been measured in polymers by determining nickel by AAS after ashing the polymer [3]. This method is fairly accurate and has the required sensitivity but lacks selectivity. Thus, all nickel-containing compounds in the polymer will be detected. This method, however, is not capable of determining the thermal decomposition products, 4-*tert.*-octylphenol and 2,2′-thiobis (4-*tert.*-octylphenol).

In 1977, an HPLC method was developed for the determination of Cyasorb UV 1084 [4]. A 1-g amount of powdered polyethylene sample was extracted for 6 h with 50 ml of chloroform. The extract was evaporated at low pressure and then dissolved in the mobile phase. It was separated on a Merkosorb Si 60 silica HPLC column using heptane–methylene chloride (2:1) as the mobile phase and a refractive index detector. A shorter extraction time and an improved separation of Cyasorb UV 1084 from interfering components were required to make the method practical for our purposes.

To improve the separation of Cyasorb UV 1084 from interfering antioxidants and its degradation products, a separation on a Perkin-Elmer 3 × 3 C_{18} column using isopropanol–water–acetic acid (94.5:5:0.5) at 2.0 ml/min as the mobile phase was developed. Acetate as acetic acid is added to sharpen any acid or phenolic components present in the sample. All components were detected at 226 nm, which is the absorbance maximum for Cyasorb UV 1084 in isopropanol. Using these isocratic conditions, Cyasorb UV 1084 produces a symmetrical but broad peak at 2.8 min.

Different separation conditions were needed to cause the 2,2′-thiobis(4-*tert.*-octylphenol) and 4-*tert.*-octylphenol peaks to be retained longer on the HPLC column and move them away from the solvent front. Using a Perkin-Elmer 3 × 3 C_{18} column, a 2-minute linear gradient at 1 ml/min provided the needed separation. The initial conditions were isopropanol–water–acetic acid (65:34.5:0.5) and the final conditions isopropanol–acetic acid (99.5:0.5). Fig. 2 is a chromatogram of a standard solution showing the separation of Cyasorb UV 1084, 2,2′-thiobis(4-*tert.*-octylphenol) and 4-*tert.*-octylphenol. Fig. 3 is a chromatogram of an extract from film 1 where 2,2′-thiobis(4-*tert.*-octylphenol) and Cyasorb UV 1084 can be seen. The first peak is the solvent front. The second peak is an unknown component, but is not 4-*tert.*-octylphenol. There are also a number of minor peaks that could possibly be impurities or other degradation products of the Cyasorb UV 1084. Using this gradient a number of common antioxidants and UV stabilizers can also be analyzed. Table II lists some common additives and their retention times. Early-eluting additives such as Irganox MD1024, Tinuvin P and Santanox R require a different gradient with initial conditions that are weaker than this gradient to produce retention on the column.

Using this gradient system, the baseline increases at wavelengths below 290 nm owing to increasing isopropanol absorption. Also, the Cyasorb UV

TABLE II

RETENTION TIMES (t_R) FOR COMMON POLYMER ADDITIVES

Additive	t_R (min)	Additive	t_R (min)
BHT	1.7	Irganox 1010	6.7
BHEB	2.0	Ethyl 330	7.0
Isonox 129	2.2	Irganox 1076	7.3
UV 531	4.0	Irgafos 168	7.7
Cyanox 1790	4.1	TNPP	8.8

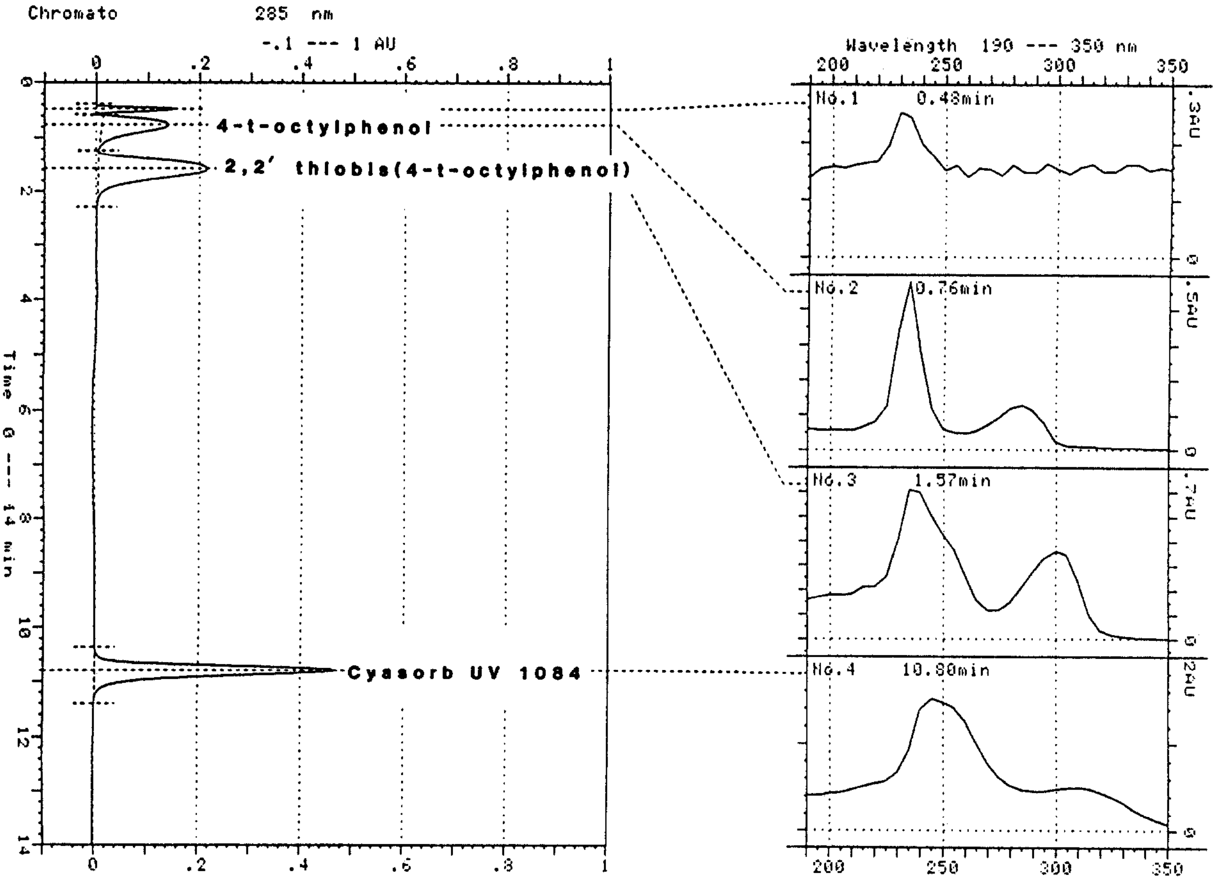

Fig. 2. Gradient separation of Cyasorb UV 1084 and two thermal decomposition products.

1084 signal drops significantly at wavelengths above 265 nm. A wavelength of 255 nm provides an acceptable compromise between background interference and component signal size. When using peak area to determine concentration, we found that peaks measured at 255 nm give the same results as those measured at 226 nm using the isocratic system. Hence, 255 nm was the wavelength chosen for determining Cyasorb UV 1084 and decomposition levels in a LDPE polymer.

Extraction

Various solvents were investigated for extracting Cyasorb UV 1084 from concentrates and films. Optimum extraction is achieved with a solvent that dissolves the component of interest and partially swells the polymer, enabling trapped component to be released. All extractions were carried out by reflux heating of sample ground to 40 mesh. Cyasorb UV 1084 is very soluble in polar chlorinated hydrocarbons such as methylene chloride and chloroform and non-polar hydrocarbons such as heptane and toluene. Methylene chloride was selected as one of the first solvents to try. Even after extended extraction times of up to 2 h, methylene chloride was found to be a poor extraction solvent. Also, solvent exchange was required before it could be injected onto the reversed-phase HPLC column owing to solvent immiscibility. Toluene, isopropanol, ethanol, methanol and acetonitrile were also investigated. Shaking with toluene at room temperature was found to extract about 90% of the Cyasorb UV 1084 from the colored concentrate but required solvent exchange before injection onto the reversed-

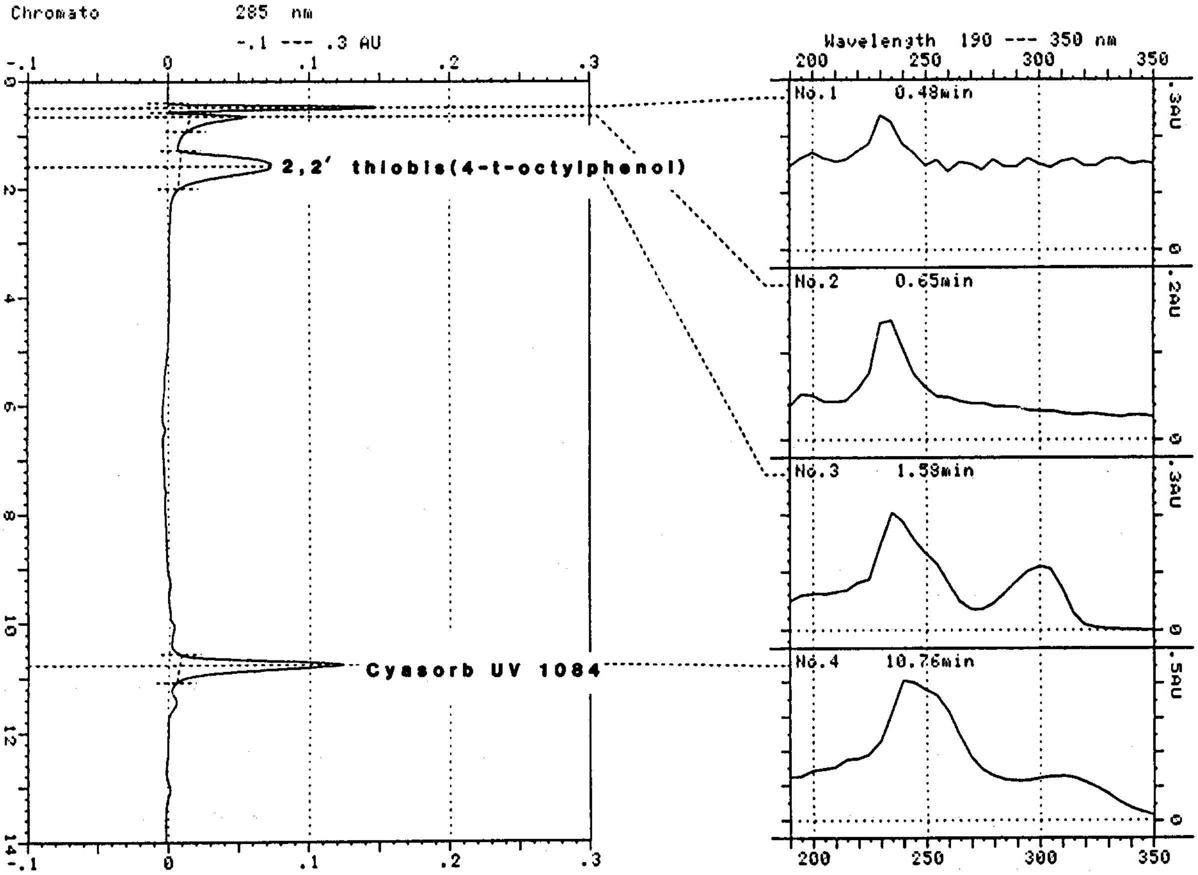

Fig. 3. Gradient separation of components in film 1 extract.

phase column. Typically, toluene can be diluted with a polar solvent such as methanol to cause the solution to be miscible with the mobile phase. In this instance the large solvent peak masks the two breakdown products even with weaker initial conditions of the gradient. Refluxing of LDPE with isopropanol for 1 h extracted 95% of the expected Cyasorb UV 1084 from the concentrate. A 2-h reflux failed to extract additional additive. To assure complete extraction, after refluxing the ground polymer was filtered from the extract, rinsed with fresh solvent, dried and refluxed a second time with fresh isopropanol. Table I shows the results for a single extraction of two concentrate samples, each containing about 10% of Cyasorb UV 1084. These data indicate that a single extraction is sufficient for the analysis. Previously extracted polymer samples were analyzed by AAS and IR spectrometry and verified that no Cyasorb UV 1084 remained after extraction. Acetonitrile and the other alcohols were found to have poorer extraction efficiencies than isopropanol. Therefore, isopropanol was chosen as the extraction solvent for Cyasorb UV 1084 in LDPE.

The co-extruded films were expected to contain 0.7–0.9% of Cyasorb UV 1084. All of the above solvents were tested using extraction times extended to 2 h owing to low recoveries. Using a 1-h isopropanol extraction only 0.44% of Cyasorb UV 1084 was found in film 1, which had not been exposed to weathering (Table III). Also, less than 10% of the expected Cyasorb UV 1084 was found in brittle weathered film 2. Film 3, the white layer of co-extruded film 1, was expected to contain about 1.8–

TABLE III

EXTRACTION RECOVERIES FOR AND AAS ANALYSIS OF THE FILM SAMPLES BEFORE AND AFTER EXTRACTION

Sample	Expected Cyasorb UV 1084 (%)	After extraction		Before extraction		
		Ni content found by AAS (ppm)	Cyasorb UV 1084 content based on Ni determination (%)	Ni content found by AAS (ppm)	Cyasorb UV 1084 content based on Ni determination (%)	Cyasorb UV 1084 found by HPLC (%)
Film 1	0.7–0.9	120	0.117	1001	0.974	0.440
Film 2	0.7–0.9	746	0.726	780	0.759	0.020
Film 3	1.8–2.0	180	1.75	1950	1.897	1.38

2.0% of Cyasorb UV 1084. This film was selected for analysis to determine if the carbon black or some other component in the black layer was impairing the extraction. Less than 50% of the expected amount was found as in the co-extruded films. Hence the components in the black layer do not appear to be the cause of the low recoveries of Cyasorb UV 1084. These results indicated either a poor extraction efficiency or possible degradation

Degradation of UV 1084

Film samples before and after extraction were submitted to nickel determination by AAS to determine the Cyasorb UV 1084 extraction efficiency. The results are given in Table III. All film samples before extraction had about the expected level of nickel. New film samples, 1 and 3, after extraction retained 9–12% of the original nickel. The weathered sample, film 2, still retained 95% of its original nickel. To determine if this residual nickel is due to the Cyasorb UV 1084, film 2 samples, before and after extraction, were analyzed by Fourier transform IR spectrometry. The extracted sample had no sharp band at 1600 cm^{-1} characteristic of Cyasorb UV 1084. Hence the nickel remaining in the film after extraction was not due to Cyasorb UV 1084 or its two decomposition products, 4-*tert.*-octylphenol and 2,2′-thiobis(4-*tert.*-octylphenol), as all would have a sharp aromatic band at 1600 cm^{-1}. As nickel sulfide was found in the films by X-ray diffraction, it is the most likely form of nickel in the films after extraction.

Two degradation products of Cyasorb UV 1084, 4-*tert.*-octylphenol and 2,2′-thiobis(4-*tert.*-octylphenol), were run on the isocratic HPLC system. When the spectrum of the early-eluting peak found in film extracts is superimposed on the spectrum of the two known degradation products there is a very good match of the unknown components and 2,2′-thiobis(4-*tert.*-octylphenol). This early-eluting peak was confirmed by mass spectrymetry to be 2,2′-thiobis(4-*tert.*-octylphenol).

In an attempt to degrade Cyasorb UV 1084, a solution of Cyasorb UV 1084 in isopropanol was placed in a quartz tube and irradiated with UV light for 48 h. No degradation was seen. The solution was then placed in a sunlit window, and within 4 weeks the Cyasorb UV 1084 had degraded. A chromatogram of this solution shows that the major component by retention time appears to be 2,2′-thiobis(4-*tert.*octylphenol) (Fig. 4). A normalized spectrum overlay of this component and 2,2′-thiobis(4-*tert.*-octylphenol) confirms its identity (Fig. 5). Mass spectrometric analysis also identified the major component in this solution as 2,2′-thiobis(4-*tert.*-octylphenol).

To be confident about our results, it was essential to know where the Cyasorb UV 1084 was breaking down: in the concentrate, in the film or during the analysis process. The various steps in the analysis where degradation could occur were examined. One possible cause fo the loss of the Cyasorb UV 1084 in the analysis is the milling step. During milling, the polymer can heat up, causing degradation and loss of certain additives. Samples were ground with and without liquid nitrogen cooling to determine whether the milling step was causing a breakdown of Cyasorb UV 1084. No significant difference was found between samples milled with or without liquid nitrogen. Another step where Cyasorb UV 1084 could

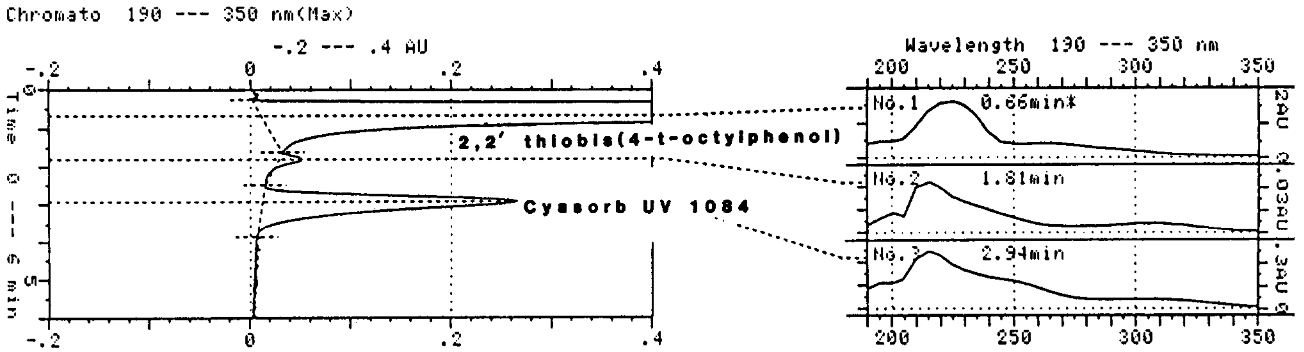

Fig. 4. Isocratic separation of the UV breakdown product of Cyasorb UV 1084.

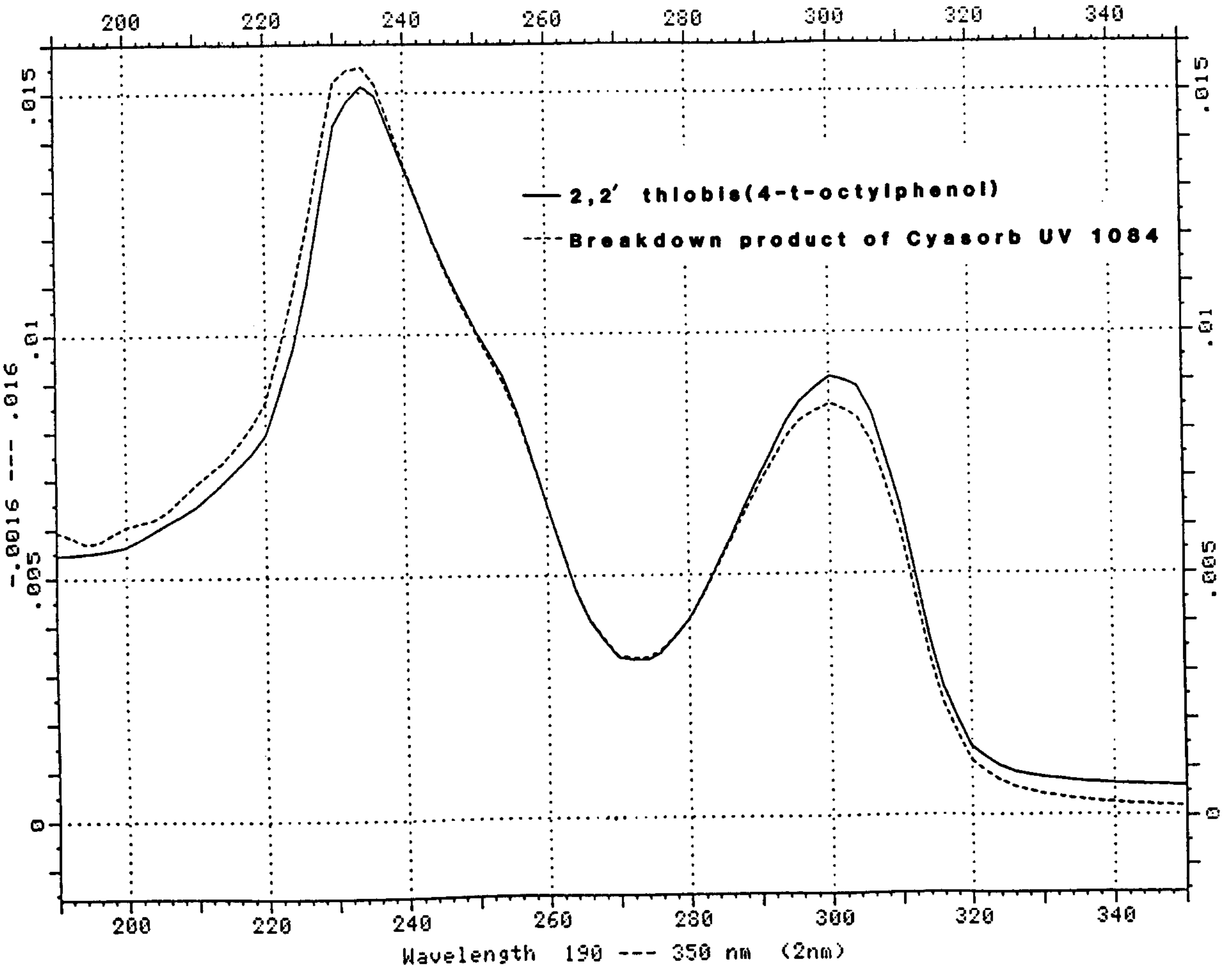

Fig. 5. Normalized overlay of the degradation product of Cyasorb UV 1084 and 2,2′-thiobis(4-*tert.*-octylphenol).

TABLE IV

CYASORB UV 1084 PRESENT IN NEW FILM DETERMINED BY AAS AND HPLC

All values in ppm.

Sample	AAS		HPLC	
	Ni level	Cyasorb UV 1084	Thiobis[a]	Cyasorb UV 1084
Film 4	847	8250	6870	110
Film 5	861	8390	3910	2280
Film 6	914	8900	4080	2250

break down is during the extraction. To check this, two experiments were run. Cyasorb UV 1084 was refluxed for 1 h in isopropanol and barefoot resin was refluxed for 1 h in an isopropanol solution containing Cyasorb UV 1084. No decrease in the Cyasorb UV 1084 signal or formation of degradation products was seen.We therefore found no evidence for Cyasorb UV 1084 degradation caused by the analytical procedure.

Solving the degradation problem

Using this HPLC method, we found no degradation in any of the concentrates used to make the films, but significant degradation was evident in film samples, including those not placed in sunlight. Hence we concluded that some of the Cyasorb UV 1084 degraded during the manufacture of the films. This resulted in lower than expected levels in the film, possibly causing early degradation of the films placed in sunlight. Table IV shows a comparison of the amount of Cyasorb UV 1084 in three new film samples based on their nickel contents determined by AAS and HPLC. Film 4 contains only 110 ppm of Cyasorb UV 1084 by HPLC or 1.3% of the original amount based on nickel results obtained by AAS; 83% degraded to 2,2′-thiobis(4-*tert.*-octylphenol) with the remaining 15.7% most likely being in an inorganic form such as nickel sulfide. Films 5 and 6 had 25–27% of the Cyasorb UV 1084 unchanged with 46–47% degrading to 2,2′-thiobis(4-*tert.*-octylphenol) and the remainder probably being present in an inorganic form.

CONCLUSIONS

Reversed-phase HPLC with photodiode-array detection is capable of separating, identifying and determining Cyasorb UV 1084 and its decomposition products, 4-*tert.*-octylphenol and 2,2′-thiobis (4-*tert.*-octylphenol). The extraction efficiency of Cyasorb UV 1084 from LDPE concentrates using isopropanol is greater than 95% with a relative standard deviation of less than 4%. This method is also capable of complete extraction of the Cyasorb UV 1084 and two of its major decomposition products in films.

Using this method, it was determined that the Cyasorb UV 1084 was unaltered and at the expected level in the concentrates. However, it had partially degraded to 2,2′-thiobis(4-*tert.*-octylphenol) during production of the film, which resulted in faster deterioration of the films when exposed to sunlight.

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