

## Determination of a Polymeric Light Stabiliser (Chimassorb 944\*) in Polypropylene

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### Bestimmung eines polymeren Lichtschutzmittels (Chimassorb 944\*) in Polypropylen

**Zusammenfassung.** Eine Methode zur Gehaltsbestimmung des polymeren Lichtschutzmittels Chimassorb 944 in Polypropylen wird vorgestellt. Die Polymermatrix wird in heißem Dekalin gelöst und durch Abkühlen ausgefällt. Chimassorb 944 wird aus der Suspension mit verdünnter Schwefelsäure extrahiert und dadurch von anderen störenden Additiven abgetrennt. Die Quantifizierung erfolgt UV-spektrophotometrisch. Je nach Lösungsmittel zum Lösen und Fällen des Polypropylen wird ein unterschiedliches Ausmaß an Mitfällung beobachtet. Durch 16stündige Soxhletextraktion mit Chloroform wird Chimassorb 944, wie für seine technische Anwendung gewünscht, nur in geringem Maße extrahiert.

**Summary.** A method is described for the quantitative determination of the polymeric light stabiliser Chimassorb 944 in polypropylene. The polymer matrix is dissolved in hot decalin and precipitated by cooling. Extracting Chimassorb 944 from the suspension with diluted sulphuric acid effects a separation from other interfering additives. Chimassorb 944 is then quantitatively determined by UV spectroscopy. Depending on the solvent for dissolving and precipitating of the polypropylene matrix, different degrees of coprecipitation are found. By Soxhlet extraction during 16 h with chloroform, Chimassorb 944 is only slightly extracted. This is an advantage in view of its technical application.

### Introduction

Polypropylene, as well as other polyolefins, is frequently stabilised against the detrimental action of heat and light by the addition of antioxidants and light stabilisers. Normally, these additives have a monomeric structure; the specific analysis of their content in plastics is in most instances carried out by high-pressure liquid chromatography [1–4] or gas chromatography [5]. Applied to the recently developed polymeric light stabilisers, e.g. Chimassorb 944 (Fig. 1), both methods meet with difficulties because its volatility is too low for gas chromatography, and the polymeric composition leads, in our experience, to unsatisfactory HPLC chromatograms. Considering the chemical stability of the structure, decomposition to uniform monomers, e.g. hydrolysis, is not very promising.

Compression moulding to films and subsequent quantitative determination of the triazine absorption by IR spectroscopy proved to be a fast method but sometimes failed with formulations in actual practice because of interference with other additives or partly degraded polyolefin matrix. The same holds true for the determination via the total nitrogen content in the presence of nitrogen-containing pigments or lubricants. NMR spectroscopy [6] offers one possibility of determining polymeric stabilisers but requires large-scale equipment.

This paper describes a method consisting of dissolving the polypropylene in an appropriate solvent; after precipitation of the plastic, the stabiliser is extracted from the suspension by sulphuric acid. This extraction step is essential, as interfering additives remain in the organic layer. Quantification is performed non-specifically by UV spectroscopy. Varying the solvent for the polypropylene, coprecipitation of Chimassorb 944 with the plastic can be studied and minimised for quantitative analysis.

### Experimental

UV spectra were recorded with a Perkin Elmer 552 spectrophotometer between 200 and 350 nm using a 1 cm quartz cell and 1 N sulphuric acid in the reference beam; absorbance range: 0 to 2. A calibration solution was prepared with 1.00 mg of Chimassorb 944 in 100.0 ml of 1 N sulphuric acid containing 0.5% diethanolamine. The Lambert-Beer law is fulfilled up to more than 2 mg per 100 ml. All solvents were of analytical grade and used without further purification. Old samples of decalin proved to be partly oxidised and led to irregular results. Freshly opened bottles of decalin, Merck No. 803101, were suitable.

0.3% (w/w) Chimassorb 944 was incorporated into polypropylene powder by extrusion. The content was verified by the determination of total nitrogen (expected content, see Table 1).

*Analysis after Dissolution of the Polymer.* 1.00 g of the polypropylene pellets was dissolved in 100 ml of solvent (see Table 1) at 150°C bath temperature during max. 40 min with stirring. When decalin was used, 100 mg of tetrakis [methylene-3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)-propionate]methane (Irganox 1010\*) was added before heating to prevent autoxidation of decalin. This would otherwise cause interfering UV absorptions. The hot solution was allowed to cool down to room temperature without stirring, whereupon the polypropylene precipitated. The resulting suspension was treated with ultrasound for 5 min, then

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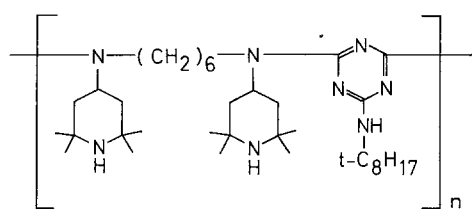


Fig. 1. Chimassorb 944

Table 1. Recovery of 0.3% Chimassorb 944 in polypropylene after dissolving/precipitating in various solvents

Solvent	Chimassorb 944 found, % of expected content
Decalin	96 (RSD = 1.4% for $N = 9$ )
n-Decane	83
1,1,2,2-Tetrachloroethane	39
Toluene	91
Toluene, precipitation with methanol	93
Soxhlet extraction with chloroform	22

quantitatively transferred to a separatory funnel and extracted with 100.0 ml of sulphuric acid containing 0.5% diethanolamine. The addition of diethanolamine proved to be useful in avoiding the absorption of small quantities of Chimassorb 944 on the glass walls. Phase separation took several hours. With all solvents except decalin and decane, the aqueous layer was washed with hexane to remove UV absorbing solvent rests. Chimassorb 944 was quantified in the aqueous layer by recording the UV spectrum (see Fig. 2) and comparison of the maximum absorbance at 245 nm with that of the calibration solution.

*Analysis after Soxhlet Extraction.* 5.00 g of the polypropylene pellets was extracted in a Soxhlet extractor with chloroform during 16 h. The chloroform solution was concentrated to 10 ml, mixed with 40 ml hexane and extracted as described above.

## Results and Discussion

As shown in Table 1, the best results are obtained with decalin as a solvent. The insufficient recovery with decane and tetrachloroethane is attributed to coprecipitation with polypropylene. For confirmation of this hypothesis, the precipitated polymer was filtered off from the tetrachloroethane solution and again submitted to analysis: 30% of the calculated residual content was found; this recovery lies within the expected order of magnitude (see Table 1).

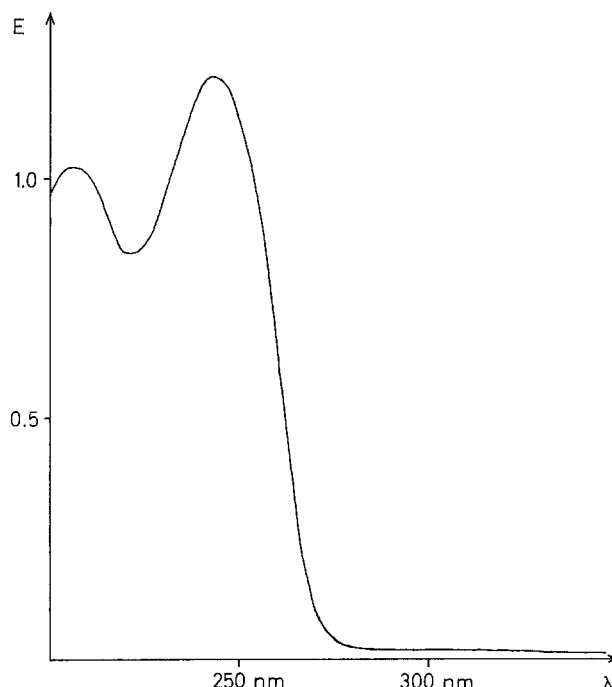


Fig. 2. UV spectrum of Chimassorb 944 after isolation from polypropylene, containing 0.3% Chimassorb 944, with decalin (see experimental section)

Using decalin as a solvent, less than 0.01% Chimassorb 944 in polypropylene is detectable. UV absorbers and phenolic antioxidants in usual application concentrations (0.05–0.5%) do not interfere as they are separated off during the extraction step.

The analysis of polypropylene multifilaments yielded reliable results only if the fibres were washed with water before analysis; a negative influence of the spinning finish is suspected.

Though successfully used for the extraction of monomeric additives from polypropylene, Soxhlet extraction with chloroform leads to a minor recovery of Chimassorb 944 (see Table 1). The tendency both, towards coprecipitation and low extractability, can be explained by the polymeric nature of this additive. The low extractability is of advantage in view of the technical application of this product, e.g. when used for the stabilisation of polypropylene fibres which may be dry-cleaned.

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