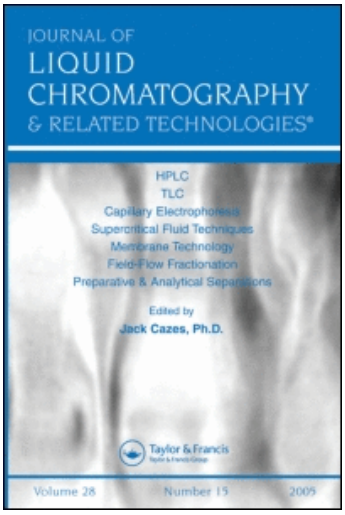

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CHROMATOGRAPHIC DETERMINATION OF UV ABSORBERS IN CAR PAINTS

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ABSTRACT

Car paints not only must be stable to sunlight effects but also must protect paint sub-layers. For this purpose, the transparent melaminic/acrylic paints of recent formulation contain added stabilisers (UV-As) which are able to absorb UV radiation.

The present work presents a chromatographic method that can be easily applied in industrial laboratories for the separation and determination of three hydroxybenzotiazoles, commercially known as Tinuvin 900, Tinuvin 328, and Tinuvin 1130, widely used as UV absorbers. The method, that involves the extraction process from the polymeric matrix and the RP-HPLC determination, is validated with respect to a lab prepared model paint and applied to commercial samples of known and unknown composition.

INTRODUCTION

The continuously growing competition in car markets forces the firms to also pay increasing attention to the external aspect of the car; this mostly depends on the quality of the paints. Paint coatings are required to exert a daily protection (possibly for the whole car life) to mechanical, chemical, and weathering (light, temperature, hail, humidity, oxygen…) stresses. Car bodies are generally painted by the "two-coat" technique: a transparent layer (clear-coat), usually constituted by reticulated melamine-acrylic resin, is added to the pigmenting layer.

The major drawback of these polymers is their photochemical degradation induced by radical reactions started by high frequency radiation of solar spectra. To improve the photochemical resistance, the polymeric substrate is made up of stabilisers, the UV Absorbers UV-As. These products show the maximum of absorbance in the range 290-350 nm and avoid the radiation penetrating into the substrate, it being absorbed and quickly dissipating into vibrational and rotational energy. This process must be faster than the corresponding substrate reaction and neither UV-As nor polymers must be damaged in the energy conversion process.

UV-As are characterized by different structures, such as: hydroxyphenyl-s-triazines, oxanilides, hydroxybenzophenones, hydroxyphenylpirimidines, salicylic acid derivatives, cyanoacylates and hydroxyphenylbenzotriazoles, the last ones being the most commonly used.

The qualitative and quantitative analysis of UV-As in polymeric matrices presents great interest for UV-As producers, both in developing quality control processes and in analysing formulations by concurrent firms.

Coupled supercritical-fluid extraction/supercritical-fluid chromatography (SFE-SFC) with flame ionisation detection (FID) technique is widely used for the quantitative analysis of polymeric additives,[1] in particular, polypropylene[2] and unplasticized poly(vinylchloride).[3] Capillary SFC with stopped-flow FTIR detection has also been used to determinate Tinuvin P[4]. Determination of UV stabilizers (including Tinuvin P and Tinuvin 327) in polyethylene terephthalate (PET) bottles has been performed by Size Exclusion Chromatography (SEC) after extraction of the analytes in CH_2Cl_2 (6 hours) and ultrasonication process (1 hour).[5] SEC combined with HPLC was used for analysis of Tinuvin P in cellulose acetate polymer,[6] UV-As, and antioxidants in polymers.[7]

Analysis of UV-As, after solvent extraction (2 hours) of the polymeric matrix has been performed by GC/FID[8] and by HPLC.[9] After Soxhlet extraction (7 hours) of the polymer in $CHCl_3$ the identification of the additives by UV spectrophotometry and NMR[10] was been performed. Mixtures of polymeric additives have been analysed by high energy MS and tandem MS with different ionization techniques (MALDI, EI, CI, liquid SIMS, and FD).[11] MS has also

been used for in situ determination of polymeric additives desorbed and photoionised by laser emission.[12] Hyroxybenzophenones and hydroxyphenylbenzotriazoles in propylene have been analysed, after acetylation, by normal phase HPLC on silica gel column.[13] UV stabilizers in PV, after derivatizations with dabsyl chloride, have been also determined by RP-HPLC with Raman detection.[14]

The major part of literature methods involves time-consuming (hours) extraction and derivatization procedures or else makes use of quite expensive equipment. Moreover, to our knowledge, the literature does not report any method for the analysis of the hydroxyphenylbenzotriazoles in melaminic/acrylic transparent paints.

The present paper presents an analytical method for the determination of the UV-As hydroxybenzotiazoles Tinuvin 900, Tinuvin 328 and Tinuvin 1130 in polymeric transparent paints, developed in co-operation with the Research Centre of a car-paint firm (PPG Industries Italia in Quattordio, Alessandria, Italy). The molecular structures of the compounds are represented in Figure 1.

Since a method that must be used in industry laboratories must be simple, fast, and economic, a procedure based on a solvent extraction process and the use of the RP-HPLC-UV technique was developed.

EXPERIMENTAL

Apparatus

The analyses were carried out by a LaChrom-HPLC Merck Hitachi (Darmstadt, Germany) with a Pump Module L-7100, interfaced with Module D-7000, and with two detectors: the UV Detector module L-7400 and the Diode Array Detector Module L-7450; the data were analyzed by the D-7000 Multi HPLC System Manager Software.

A UV-Vis Unicam spectrophotometer series 8700 was used for the spectrophotometric determinations.

Reagents

The standards of the UV absorbers Tinuvin 328 (2-(2-hydroxy-3,5-di-ter-amyl- phenyl)benzotriazole), Tinuvin 900 ((2-(2-hydroxy-3,5-dimethyl-benzyl) phenyl) benzotriazole) and Tinuvin 1130 (2-(2-hydroxy-3-terbutyl-5-methyl-propionate)-benzotriazole) were purchased from Ciba Geigy (Basel, Switzerland). Tinuvin 1130 contains two minor impurities.

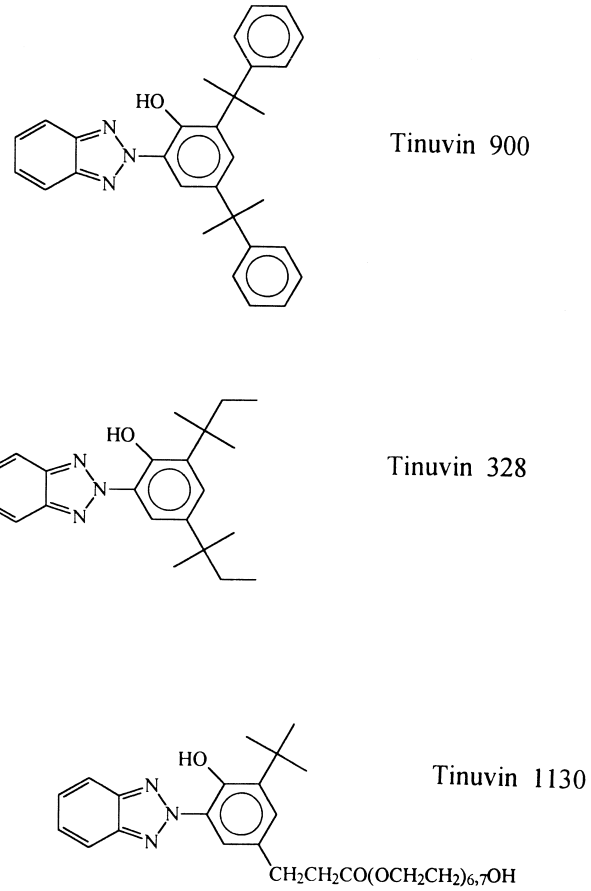

Figure 1. Molecular structures of the analytes.

Acetonitrile and tetrahydrofurane were HPLC-gradient grade Merck chemicals (Darmstadt, Germany). Acetonitrile, tetrahydrofurane, and *n*-hexane used in the extraction process were analytical grade chemicals by Carlo Erba (Milano, Italy). Ultrapure water from a Millipore Milli-Q system (Milford, MA) was used for mobile phase and standard solution preparation.

Chromatographic Conditions

The stationary phase was a Chrompack C_{18} column (150.0 × 4.6 mm, 5 µm) used together with a Chrompack C_{18} (3 mm i.d. x 5.0 mm, 5µm) guard pre-

column. An H_2O-ACN mixture was used as the mobile phase, in gradient elution mode with ACN concentration increasing from 10% to 100% in 12 min, at elution flow-rate of 1.0 mL/min.

The absorbance spectra were recorded in the range 200-400 nm and the wavelength of 343 nm was chosen as a compromise between the highest absorbance of the analytes and the lowest matrix interference. It must be observed that at 343 nm the chromatogram of Tinuvin 1130 presents a second lower intensity peak due to a declared impurity contained in the standard.

Standard Preparation

The standard solutions were prepared by dissolving the analytes in THF and subsequent dilutions with CH_3CN.

Model samples of transparent paints containing known concentrations of the studied UV-As were prepared in the laboratory and used for the development method. An acrylic/melaminic resin was used, free from the investigated additives and containing 64.5% in dry resin, as evaluated by drying samples of about 2.0 g of resin at 105°C for 3 hours (and weighing before and after drying). The prepared paints (six samples) contained the three UV-As at concentrations of about 1% (three samples) and 2% (three samples), as those generally employed in transparent commercial paints.

Extraction Procedure

To 1.0 g sample 25 mL of *n*-hexane are slowly (about 1mL/min) added under magnetic stirring. After a decantation process (about 5 min), the surfactant is transferred to a 50 mL flask and the solid phase separated and washed. The surfactant solution is diluted 1/5 v/v and filtered (0.2 μm). 2 mL of the filtered solution are evaporated to dryness and the residue collected with ACN to volumes of 10 mL (the procedure is necessary because of the poor mixibility between ACN and *n*-hexane).

RESULTS

Chromatographic Method Development

As mentioned, reversed-phase HPLC technique was used with a ACN-water mixture as the mobile phase. To achieve the separation of the three UV-As investigated, it was necessary to employ gradient elution with ACN concentration increasing from 10% to 100% in 12 min (flow rate = 1.0 mL/min).

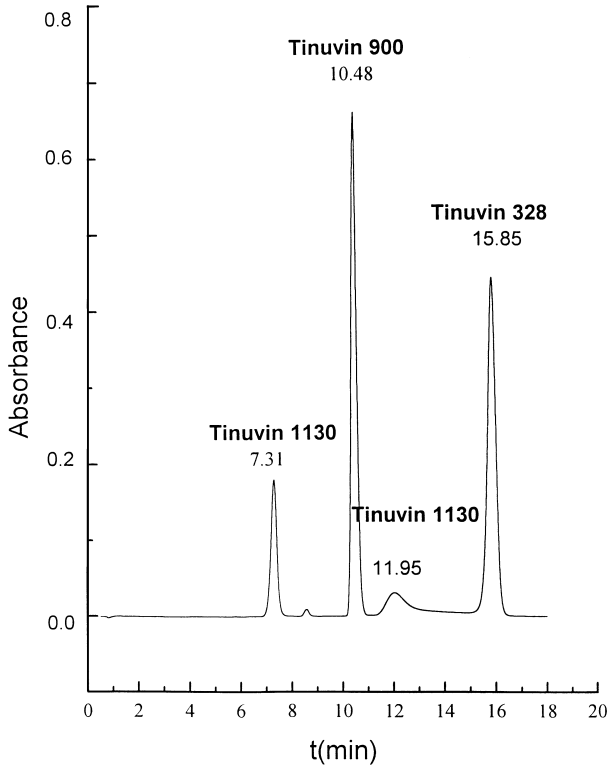

Figure 2. Chromatogram of a mixture of Tinuvin 1130, Tinuvin 900, and Tinuvin 328 (20 mg/L each). Stationary phase: Chrompack C_{18} column (150.0 x 4.6 mm, 5.0 µm) with a Chrompack C_{18} guard column (3.0 mm i.d. x 5.0 mm, 5.0 µm). Mobile phase: H_2O-ACN in gradient elution mode: ACN increasing from 10% to 100% in 12 min. Flow rate 1.0 mL/min. UV detection (343 nm). Injection volume: 100 µL.

Figure 2 shows the separation of the analytes (at aconcentration of 20 mg/L each). The retention time repeatability for subsequent injections was always within 1% and the reproducibility within 4%. Analyses carried out for the three analytes in the range from 1.00 to 50.00 mg/L permitted the verification of the linear response between signal (peak area) and concentration and to build the calibration plots. The correlation coefficients R^2 were always greater than 0.98.

The detection limits evaluated by sensitivity (peak area for 1.00 mg/L, as given by the slope of the calibration plot) and a signal to noise ratio =3 resulted in the three analytes always being lower than 0.5 mg/L.

Some experiments were also performed to evaluate the ruggedness of the method; of particular importance for a method that must be used in industry laboratories. As known, the ruggedness of a method is its ability to give the expected results even in the presence of small changes of the experimental conditions. The changes are casual, not intentional, and can not be avoided in normal laboratory practice, due to variability of instruments, reagents, operator, atmospheric conditions, etc. To evaluate ruggedness, robustness tests are employed which are able to evaluate the effect on the results of known variations intentionally induced to the system and of the same order of those that can naturally occur.

In this work, variations of ± 10% were imposed with respect to the nominal conditions, *i.e.* to the % concentration of ACN in the mobile phase, to the gradient program time, and to the flow-rate. Even if retention is affected by these variations, resolution and sensitivity are always maintained and indicate the robustness of the method.

Paint Sample Analysis

Extraction Process

A crucial point is the development of a pre-treatment procedure able to separate in a transparent paint sample the UV-As from the polymeric matrix. On the lab-prepared model samples of the acrylic-melaminic resin containing the three UV-As, experiments were performed to find out the solvent able to solubilise at maximum extent the analytes and at minimum the resin matrix. The use of acetone, THF, ACN and *n*-hexane was compared: in acetone, THF and ACN both the UV-As and the resin are soluble. The best solvent proved to be *n*-hexane in which the resin is practically insoluble, while Tinuvin 900, Tinuvin 328, and, at lower extent, Tinuvin 1130 are soluble. Preliminary experiments performed by adding, under electromagnetic stirring, *n*-hexane to different amounts of the model sample, filtering the solution (0.2 μm), and weighing the filter, showed that about 1 g of the resin requires 20 mL of *n*-hexane. Aliquots of 10 mL of surfactant were then dried, weighed, and the percent of the residual dry resin was calculated. The data collected for six samples show good reproducibility and indicate that only about 10% of the acrylic resin is extracted by *n*-hexane. Experiments performed in Gel-Permeation Chromatography (GPC) on filtered extracts of the resin, respectively obtained in *n*-hexane and tetrahydrophurane (THF) (volumes of 25 mL for 1g resin), indicate that while the extracts by THF show MM >6400 Dalton, the *n*-hexane extracts show molecular size lower than 1200 Dalton.

With *n*-hexane, model samples at known concentrations of UVAs underwent extraction and analysis. Results are reported in Table 1a, 1b, and 1c. Recovery of Tinuvins 900 & 328 is around 67%, while Tinuvin 1130, recovery is only 22.0 % and does not increase for addition of small volumes of THF.

Table 1

Percent Recovery Yield for Tinuvin 900, Tinuvin 328, and Tinuvin 1130 for Model Samples at Known Concentrations

a) Tinuvin 900

Exp.	mg Sample	mg UVA Present	mg UVA Found	% Recovery Yield
1	1066.7	10.0	6.6	66.0
2	1162.3	10.9	8.4	77.1
3	1121.0	10.5	7.2	68.6
4	1075.2	10.1	7.9	78.1
5	970.7	9.1	6.6	72.2
6	1224.2	11.5	8.3	72.0
7	1006.4	17.8	12.3	69.0
8	1034.2	18.3	11.8	64.2
9	1037.6	18.4	12.2	66.5
10	1066.3	18.9	12.0	63.3
Average	**1076.5**	**13.6**	**9.3**	**69.7**

b) Tinuvin 328

1	1363.9	14.6	9.5	64.9
2	1070.1	11.5	7.9	68.8
3	1082.9	11.6	7.6	65.7
4	1026.6	11.0	7.4	67.6
5	1023.2	11.0	6.8	62.3
6	1031.0	19.7	12.2	62.2
7	1168.7	22.3	16.0	71.8
8	1025.3	19.6	10.9	55.8
9	1049.1	20.0	12.0	59.8
10	1002.7	19.2	14.3	74.7
Average	**1084.4**	**16.0**	**10.5**	**65.4**

c) Tinuvin 1130

1	1104.8	23.1	4.9	21.3
2	1251.3	26.1	5.6	21.5
3	977.3	20.4	4.1	19.8
4	1531.3	32.0	5.2	16.3
5	1304.4	27.3	6.2	22.8
6	1377.8	14.9	3.8	25.2
7	1507.2	31.5	7.7	24.7
8	1204.6	25.2	6.2	24.5
Average	**1282.3**	**25.1**	**5.5**	**22.0**

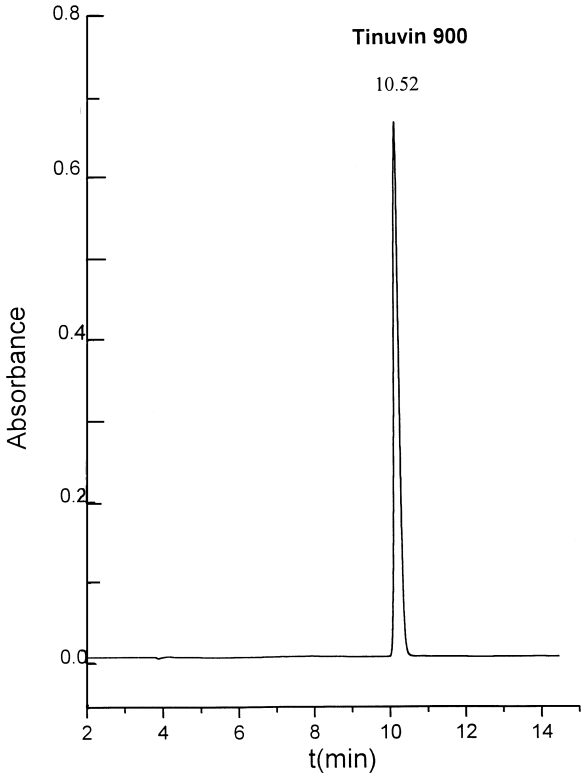

Figure 3. Chromatogram of a commercial transparent paint with a 0.6% nominal content of Tinuvin 900. Conditions as in Figure 2.

Real Sample Analysis

The analysis performed for a sample of transparent acrylic-melaminic resin produced by the PGC laboratories and characterised by a nominal content of Tinuvin 900 of 0.65% gave a content of 0.52%, calculated by the calibration plot and confirmed (0.58%) by the standard addition method, that also indicated the absence of important matrix effect.

The chromatogram (Figure 3) of a commercial acrylic/melaminic transparent paint containing a 0.6% nominal content of Tinuvin 900 indicates the presence of the analyte at per cent concentration (evaluated by standard addition method) as 0.66%.

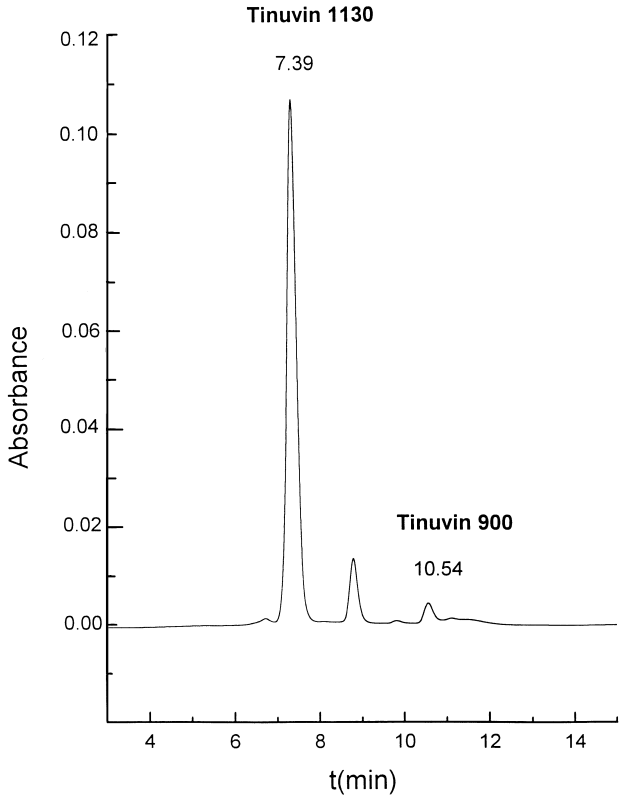

Figure 4. Chromatogram of a commercial sample. Conditions as in Figure 2.

The analysis of a commercial paint sample of unknown composition (Figure 4) gave a per cent concentration of 0.97% of Tinuvin 1130 and of 0.11% of Tinuvin 900; this concentration is very lower than the concentrations generally added in commercial products and it is likely due to impurities contained in the commercial Tinuvin 1130.

In conclusion Tinuvin 1130, Tinuvin 900 and Tinuvin 328 in transparent car paints can be determined by a simple, fast, economic, and robust RP-HPLC procedure in total analysis time of lower than 17 minutes.

Detection limits for the three analytes is always lower than 0.5 mg/L, which is much lower than that which is generally added to the commercial paints.

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