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## Note

### Simple rapid thin-layer chromatographic method for the detection of optical brighteners in polymers

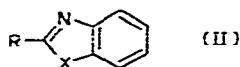
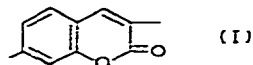
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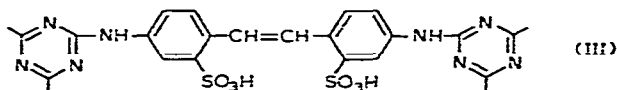
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Optical brighteners are key products in a wide range of industries. They are in regular use not only in plastics but also in textiles, detergents, papers and organic coatings<sup>1</sup>. These substances improve the whiteness and impart excellent brightness to plastics. Recently, they have also been used as thin-layer chromatography (TLC) detection reagents<sup>2</sup>.

Chemical compounds used as optical brighteners for plastics are mainly coumarin (I), benzazole (II) and stilbene (III) derivatives<sup>1</sup>.



R = organic radical    X = NH, O or S



Anionic stilbene derivatives are usually recommended for exhaust applications from aqueous systems<sup>1</sup>, although Leucopur<sup>®</sup> PAM (Sandoz, Basle, Switzerland) is designed for incorporation in the polyamide mass prior to spinning. Non-ionic coumarin and benzazole derivatives are designed for the mass fluorescent whitening of plastics<sup>1</sup>. They can be added during polymerization or at a later point in the melt extrusion process. Effective amounts of these additives in plastics are usually in the range of 0.001–1.0% (w/w).

This laboratory is required to determine the presence of small amounts of optical brighteners in polymers and plastics. TLC has been extensively applied to the determination of additives in polymer extracts<sup>3,4</sup>. A fast and simplified TLC method has been developed which eliminates the extraction process and allows the direct determination and separation of optical brighteners from the host polymer.

## EXPERIMENTAL

*Materials*

All TLC was carried out on plastic backed, precoated silica gel 1B2 plates (J. T. Baker, Phillipsburg, NJ, U.S.A.). Commercial polymers and optical brighteners as well as reagent grade solvents were used throughout this study.

TABLE I  
CHROMATOGRAPHIC BEHAVIOR OF SOME OPTICAL BRIGHTENER/SYNTHETIC POLYMER SYSTEMS

<i>Polymer/solvent</i>	<i>Optical brightener</i>	$R_F(\text{Polymer})$	$R_F(\text{Brightener})$
Polyesterurethane/DMF Estane 58134 (B. F. Goodrich, Kitchener, Canada)	Uvitex OB; benzazole type (Ciba-Geigy, Basle, Switzerland)	0	0.60
	Blankophor KU; coumarin type (Bayer, Leverkusen, G. F. R.)	0	0.16
	Leucopur EGM; coumarin type (Sandoz, Basle, Switzerland)	0	0.70
	Leucopur PAM: anionic stilbene type (Sandoz)	0	0.75*
	Blank experiment**	0	—
Polyurethane/DMF Texin 985A (Bayer)	Uvitex OB	0	0.60
	Leucopur EGM	0	0.60
Dimer fatty acid-based polyamide***/chloroform Unirez 2209 (Unioncamp Corp., Jacksonville, FL, U.S.A.)	Uvitex OB	0 <sup>‡</sup>	0.65
	Leucopur PAM	0	0.77*
Polycaprolactam/formic acid Durethan B-56 (Bayer)	Leucopur PAM	0	0.77*
	Leucopur EGM	0.95 <sup>††</sup>	0.60
Polystyrene/toluene Amoco Grade R3 (Amoco Chemicals, Chicago, IL, U.S.A.)	Leucopur EGM	0.95 <sup>††</sup>	0.60
	Leucopur EGM	0.95 <sup>††</sup>	0.60
Polypropylene/toluene A-Fax 500 (Hercules, Crowley, LA, U.S.A.)	Leucopur EGM	0.95 <sup>††</sup>	0.60
	Leucopur EGM	0.95 <sup>††</sup>	0.60
Polyester <sup>†††</sup> /trifluoroacetic acid-chloroform (1:9) (Atlantic Chemical Corp., Nutley, NJ, U.S.A.)	Atlantic whitener EBA; non-ionic type	0	0.50
	Atlantic whitener EBA; non-ionic type	0	0.50

\* With anionic stilbene derivatives, a second weakly fluorescent spot<sup>5</sup> appears in the chromatogram ( $R_F = 0.54$ ). When chloroform was used as a developer, the optical brightener remained at the starting level ( $R_F = 0$ ).

\*\* In all cases, the  $R_F$  of the polymer in the blank experiment was identical to that in the sample experiment.

\*\*\* Sample already fluoresces before adding the brightener.

† Examination of the plate (after elution) under UV light revealed two glowing spots. The first spot ( $R_F = 0$ ) assigned to the inherently fluorescent polymer and the second ( $R_F = 0.65$ ) due to the added optical brightener.

†† The plates were sprayed with 20%  $H_2SO_4$  aqueous solutions and charred at 120°C to develop the polymer spots. Precoated glass plates were used for these experiments.

††† This sample consists of polyester fibres that have been optically brightened by the manufacturer.

### *Samples preparation*

Stock solution of optical brighteners were prepared containing 0.001 mg of brightener per ml of solvent. Chloroform was used for non-ionic benzazole and coumarin derivatives and dimethylformamide (DMF) was used for anionic stilbene derivatives. A 1-ml volume of brightener solution was added to 100 mg of the polymer dissolved in a suitable solvent (see Table I). The sample solutions were taken to dryness at 110°C to give a transparent plastic film.

### *Chromatographic procedure*

The plastic films (100 mg) were dissolved in 2 ml of solvent (see Table I). With the aid of a disposable Pasteur pipette, one drop (1–2  $\mu$ l) of polymer solution was directly applied to the thin layer. The plates were dried in a 110°C oven and developed in a cylindrical tank for a distance of 10 cm past the origin. Chloroform was used as developer for non-ionic brighteners. Anionic stilbene derivatives were eluted with the solvent system<sup>5</sup> pyridine-*n*-butanol-ethanol-ammonia (sp. gr. 0.88) (30:40:10:20). After elution and drying, the optical brighteners were located under long-wave (365 nm) UV light. Blank polymer solutions (free of optical brighteners) were also prepared and chromatographed.

## RESULTS AND DISCUSSION

Using the direct application procedure described above, the separation of the brightener from the host polymer as a discrete spot was achieved in all cases. The chromatographic behavior of the optical brightener/polymer systems investigated is summarized in Table I. Under the experimental conditions used, polymers containing polar functional groups (polyurethanes, polyamides and polyesters) remained immobile at the starting spot. Polystyrene and polypropylene migrated up to the solvent front and did not interfere with the optical brightener. The visual sensitivity of detection was determined by analyzing decreasing concentrations of optical brighteners and was found to be as low as 0.001 % (w/w) of the polymer. Furthermore, this method makes it possible to determine whether a polymer is inherently fluorescent when examined under a UV lamp (e.g.: dimer fatty acid-based polyamides) and/or contains an optical brightener.

The applicability of this method can be extended to the separation of other additives from their host polymer. For instance, using fluorescent indicator-containing layers, the presence in polymers of small amounts of a UV light-absorbing antioxidant could be directly determined.

## REFERENCES

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