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APPLICATION OF CAPILLARY GAS CHROMATOGRAPHY IN THE STABILITY CONTROL OF PHTHALATE-ESTER-TYPE POLY(VINYL CHLORIDE) PLASTICISERS TREATED WITH LIGHT AND PLASMA

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SUMMARY

By means of high-resolution capillary gas chromatography we followed the change in composition of poly(vinyl chloride) plasticisers during treatment with light of a wide range of wavelengths and with plasma. The composition is not significantly altered by either treatment, therefore the plasticisers would not appear to be responsible for the ageing of soft poly(vinyl chloride).

INTRODUCTION

In the production of soft poly(vinyl chloride) (PVC), greater amounts of plasticisers are used than any other additive. Their role is to improve the processing ability of PVC and to increase its flexibility and elasticity. Plasticisers must therefore meet the following requirements: adequate efficiency; compatibility with the polymers; low volatility; resistance to chemicals and solvents; good autostability; colourlessness; odourlessness; flavourlessness; colourfastness; inexpensive.

Because of the great importance of the plasticisers and their stability, we investigate the treastment of PVC sheets, containing different plasticisers, with light of a wide range of wavelengths and also with plasma irradiation. The treatment with light simulated the everyday exposure of the plasticisers during use and plasma treatment is used during the manufacture of PVC to confer advantageous properties on the polymer itself.

Some previous reports[1–5] have dealt with special analytical problems of phthalate-ester-type plasticisers, but these did not cover ageing processes.

EXPERIMENTAL

Treatment of the PVC sheets with light was carried out under the following conditions: sample space temperature, 45°C; black-body temperature, 65°C; relative humidity, 0.16 w/w; wavelength, 295–835 nm; apparatus, Xenotest 1200.

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The conditions for plasma treatment were as follows: method, air-to-air method; line speed, 10 m/min; vacuum attained, less than $30 \cdot 10^{-3}$ Torr.

After extraction with diethyl ether, the plasticisers were analysed by capillary gas chromatography (GC), under the following conditions: Pyrex glass column, 20 m × 0.2 mm I.D.; stationary phase, SE-52; temperature, 80–300°C; programme rate, 15°C/min; carrier-gas and flow-rate, argon at 1 ml/min; detector, flame ionisation detector; sample amount, 2–3 μl; split ratio, 1:100; apparatus, Carlo-Erba Model 2300; data system, Spectra Physics SP-4000.

RESULTS AND DISCUSSION

Light treatment

Figs. 1–3 show the chromatograms of three frequently used plasticisers before and after a light treatment of 5000 h. Eviplast 6-10, Eviplast 7-9 and Eviplast 81 (United Chemical Works, Budapest, Hungary) (for composition, see Table I) are wide-boiling-range, middle-boiling-range and narrow-boiling-range plasticisers, respectively. The mean individual peaks were identified by a combination of GC and mass spectrometry.

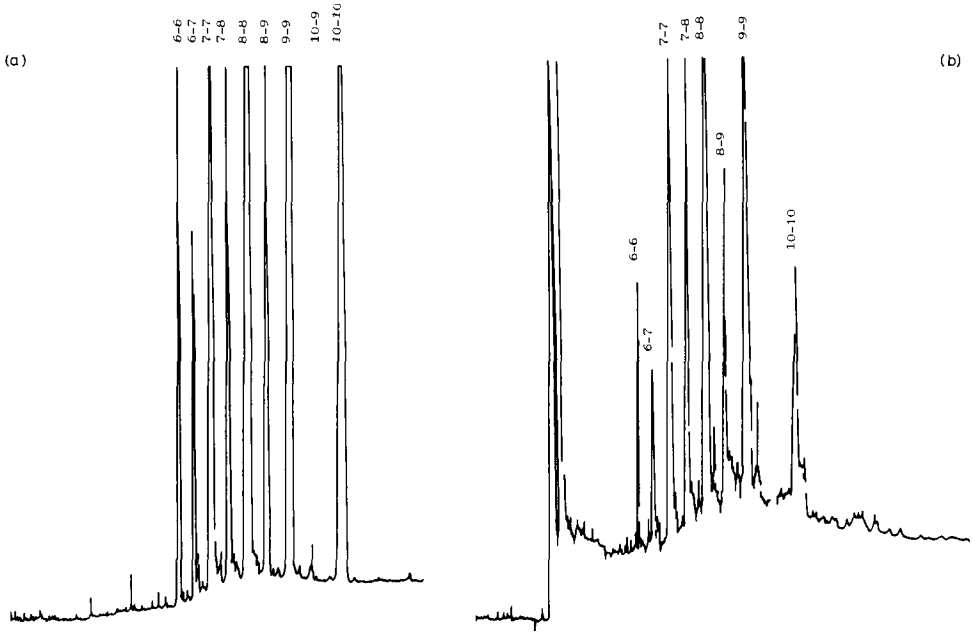

Fig. 1. GC fingerprints of Eviplast 6-10 before UV ageing (a) and after UV ageing of 5000 h (b).

Table I summarises the numerical data of the compositions of the plasticisers analysed. The numbers in the first column represent the carbon numbers of ester chains connected to the phthalic acid ring.

The chromatograms show no significant change up to 1000 h. Decomposition increases significantly after 5000 h, especially in case of the most homogeneous sample, Eviplast 81, which contains diethylhexylphthalate as the main component.

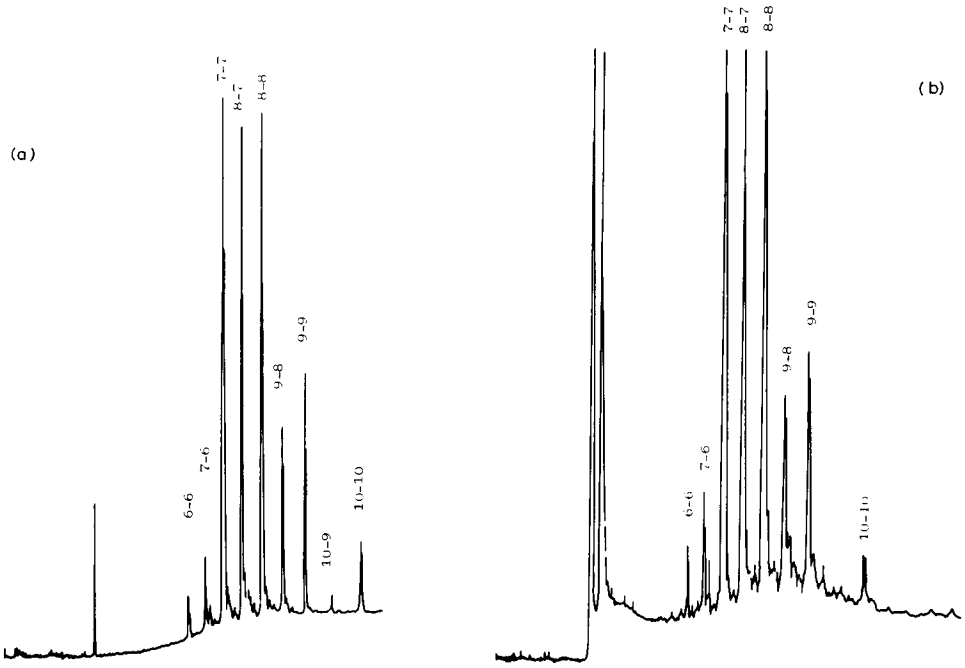

Fig. 2. GC fingerprints of Eviplast 7-9 before UV ageing (a) and after UV ageing of 5000 h (b).

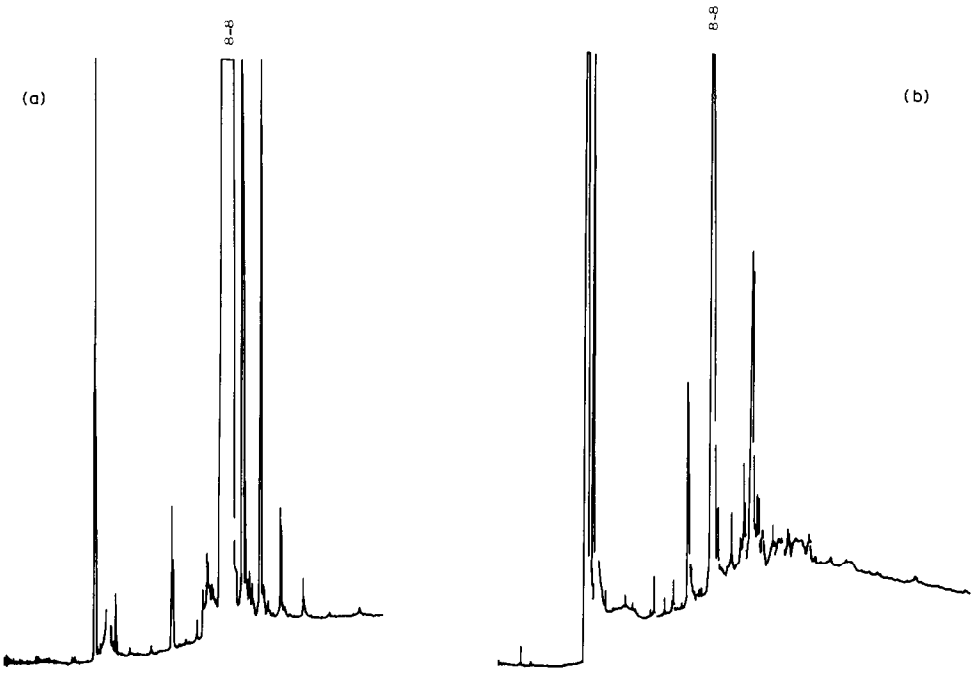

Fig. 3. GC fingerprints of Eviplast 81 before UV ageing (a) and after UV ageing of 5000 h (b).

TABLE I

CHANGE OF COMPOSITION OF PLASTICISERS AFTER LIGHT TREATMENT

Carbon number of n-alkyl ester chains	*Time of treatment (h)*				
	0	*100*	*500*	*1000*	*5000*
Eviplast 6-10					
6-6	2.12	1.99	2.13	1.73	1.60
6-7	1.46	1.31	1.50	1.48	1.64
7-7	16.77	16.60	16.39	15.44	14.48
7-8	6.04	6.05	6.15	6.35	7.25
8-8	32.18	33.06	31.53	28.02	23.57
8-9	3.60	3.48	3.61	4.18	4.32
9-9	27.33	28.23	26.70	23.71	16.01
10-9	0.19	0.19	0.20	0.48	0.50
10-10	8.68	8.66	8.83	7.91	3.40
	98.37	99.57	97.04	89.30	72.77
Eviplast 7-9					
6-6	1.35	0.95	1.26	1.01	1.38
6-7	2.76	2.28	2.60	2.20	2.93
7-7	21.49	17.83	19.18	16.73	23.31
7-8	19.98	18.34	18.42	16.54	16.48
8-8	23.54	22.79	22.63	21.71	19.76
8-9	8.73	9.15	8.88	8.93	6.91
9-9	10.87	11.87	10.71	12.02	8.59
10-9	0.54	0.67	0.59	0.19	0.03
10-10	3.70	4.54	3.82	4.52	2.05
	92.96	88.42	88.09	83.85	81.44
Eviplast 81					
8-8 Diethylhexylphthalate	95.74	93.91	93.36	91.52	55.40

TABLE II

COMPOSITION OF PLASTICISERS BEFORE AND AFTER PLASMA TREATMENT

Carbon number of n-alkyl ester chains	*Eviplast 6-10**		*Eviplast 7-9**	
	Before	*After*	*Before*	*After*
7-6	1.35	1.42	2.11	2.15
7-7	38.04	40.90	23.87	23.74
8-7	21.81	24.70	19.50	18.51
8-8	14.56	17.07	18.63	18.51
9-8	4.78	4.77	7.66	7.56
9-9	4.78	4.77	5.85	5.71
10-10	1.47	1.35	2.24	2.17
	86.79	94.98	79.86	79.18

* These samples were obtained from different industrial sources than those Table I, therefore they had different chemical compositions.

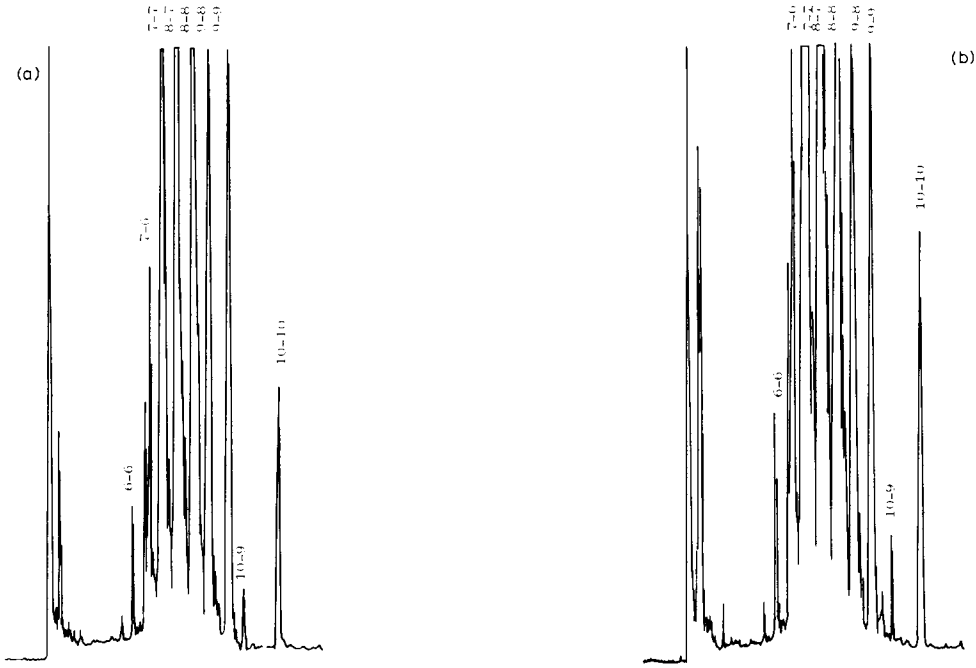

Fig. 4. GC fingerprints of Eviplast 7-9 before plasma treatment (a) and after plasma treatment (b).

Plasma treatment

Fig. 4 shows the chromatograms of Eviplast 7-9 plasticiser extracted from PVC sheets before and after plasma treatment. The identical fingerprints of the chromatograms and the unchanged sum of the *n*-alkylphthalate concentration values (Table II) prove the chemical stability of plasticisers.

Table II lists the compositions of two different samples extracted from PVC sheets before and after plasma treatment.

CONCLUSIONS

Capillary GC is a very efficient tool for obtaining detailed information about the composition of phthalate-ester-type PVC plasticisers before and after different treatments.

We have established that during prolonged and drastic light treatment the composition of the plasticisers remains the same, even after 1000 h, although the PVC itself is chemically and mechanically totally decomposed during this time.

In the case of plasma treatment, which modifies beneficially the physical properties of PVC, the composition of the phthalic-ester-type plasticisers remains constant.

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