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Investigation of an Odour Problem on Cigarette Packets*

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INTRODUCTION

Certain packets from a batch of filter cigarettes, manufactured from a standard tobacco blend, were found, via quality control procedures, to have a "sickly, rancid" odour. The packaging components were all of a normal stock which had been used to pack other cigarettes with no noticeable off-notes. Not all the packets in the batch were affected, although the same packaging had apparently been used throughout.
The odour was apparent as soon as the tearstrip was removed. Although the odour was noticeable in all parts of the cigarette, it appeared to be concentrated in the filter tip. A slightly rancid off-note could still be detected in the filter tips after prolonged ventilation of the packets. The odour was also noticed when the cigarettes were smoked.

EXPERIMENTAL

Instrumentation

Hewlett-Packard 5880 gas chromatograph with a flame ionisation detector and a split/splitless capillary injection system. Column: 15 m SE−52 (0.25 mm inside diameter) glass capillary. Odour appraisal of the individual compounds eluted from the GC was carried out by connecting the column to a piece of glass capillary which vented outside the oven, using shrink polytetrafluoroethylene tubing. The column temperature program was from 40 °C to 200 °C at 5 °/minute. Carrier gas was hydrogen at a linear velocity of 50 cm/second. Injector and detector temperatures were 250 °C and 300 °C respectively.
Vacuum Generators Micromass 70−70F mass spectrometer** coupled to a Hewlett-Packard 5710A gas chromatograph with a 15 m SE-52 glass capillary column.
Perkin-Elmer 283 infra-red spectrometer connected to a Perkin-Elmer data station. The samples were run as transparent films or cast from solution onto sodium chloride plates.

Extraction of the Odour

Tips and tobacco were extracted with pentane (Fisons, HPLC grade) using a Soxhlet extraction apparatus. The pentane extract was run through a silica gel column (5 g, Machery-Nagel, 0.2−0.5 mm, activated at 120 °C) and the column washed with a further 50 ml pentane. The odorous material was eluted with 10 % ether in pentane, the fraction between 25−35 ml being collected. This fraction was reduced to a low volume under nitrogen, then transferred to a 1 ml Reactivial (Pierce) and the volume reduced to approx. 50 µl. Care was taken not to remove all the solvent, otherwise the lower-boiling components could be lost.
The overwrap plasticizers were extracted by shaking with a small amount of acetone for 5−10 minutes, which was then decanted and taken to a low volume under nitrogen.

Synthesis of Dioxaspiro Compounds

Dioxaspiro compounds were synthesized from 1/10 equimolar amounts of cyclohexanone and the appropriate alcohol by refluxing in toluene with 0.5 g toluene-*p*-sulphonic acid (2). A Dean and Stark water separator removed the water produced during the reaction and refluxing continued until the calculated amount of water had been collected.
No attempt was made to purify the compounds produced as the toluene solution was sufficiently pure for the required analysis.

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Figure 2. Mass spectrum of compound A.

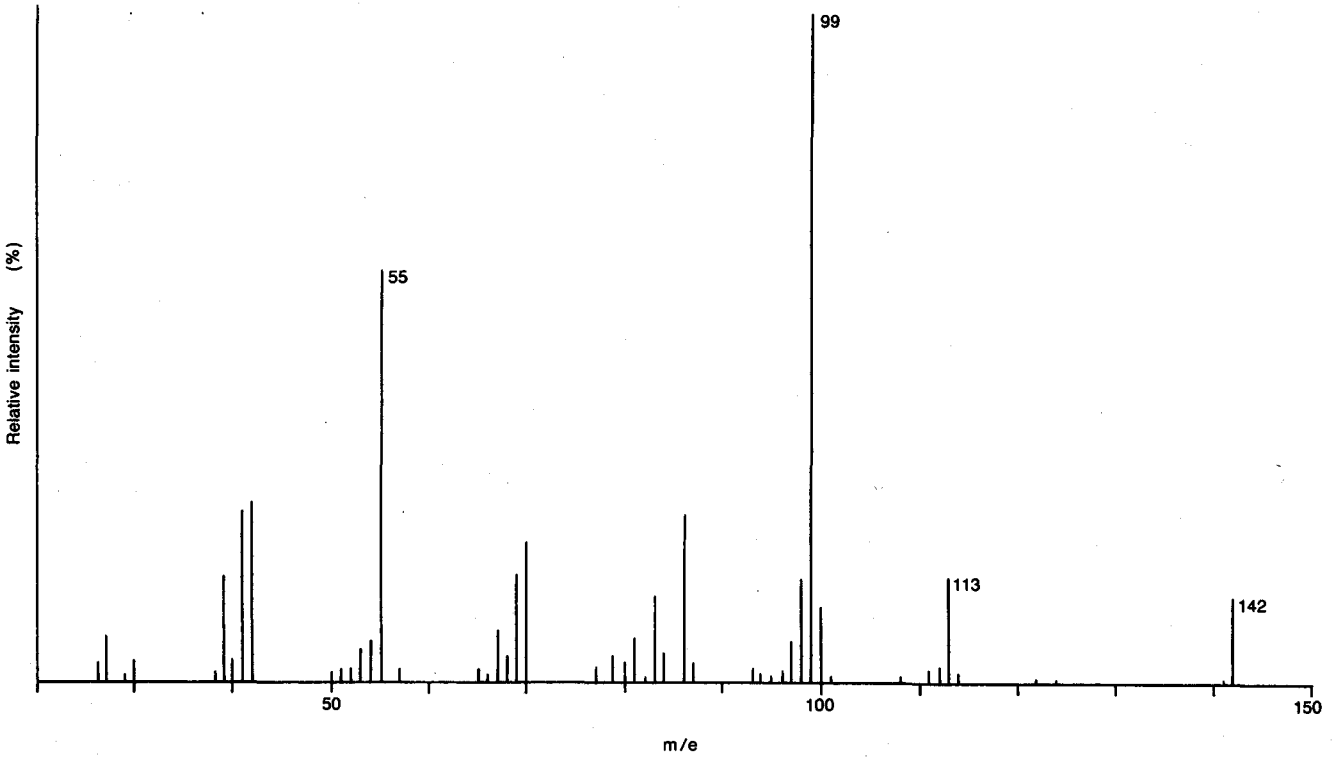


Figure 3. Mass spectrum of compound B.

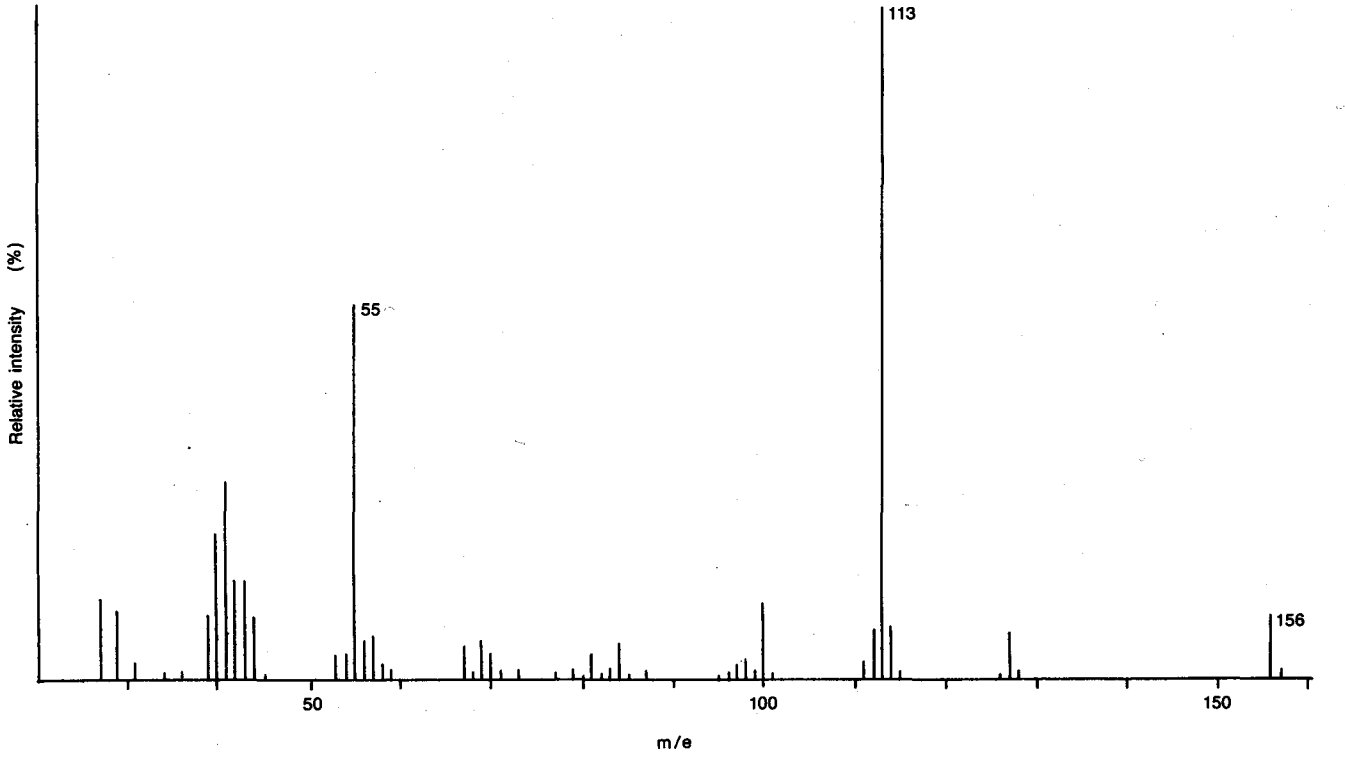
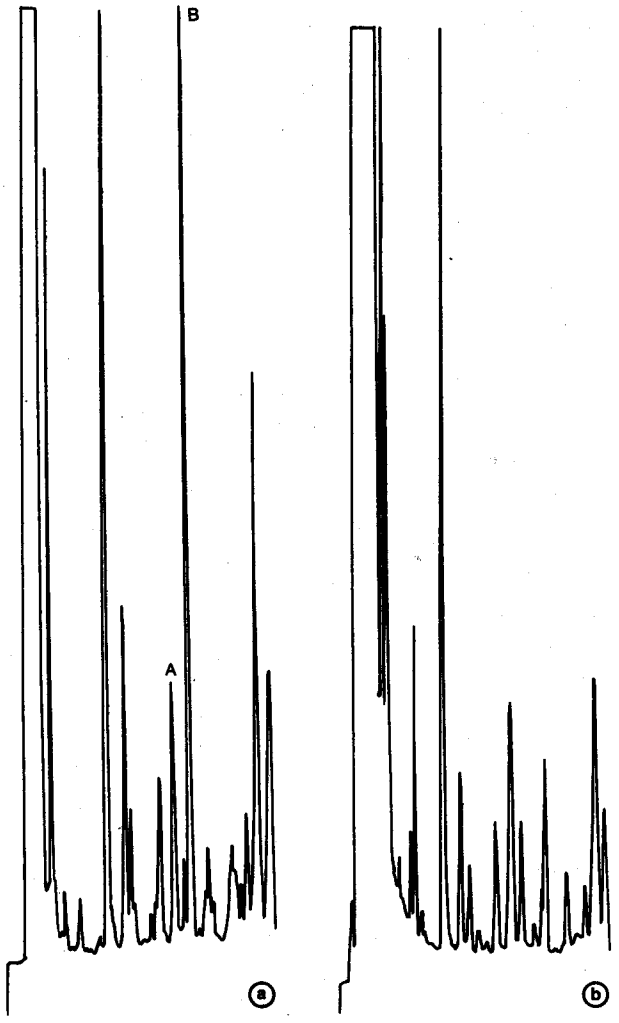


Figure 1. Comparison of gas chromatograms of odorous (a) and non-odorous (b) tip extracts showing peaks due to compounds A and B.

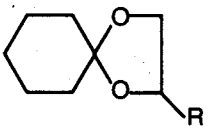


DISCUSSION

Identification of the Odorous Compounds

On receipt of the tainted samples, the odour was initially located in the filter tips, and was extracted with pentane. The odorous tip extract was separated by gas chromatography on a capillary column giving a chromatogram (partially reproduced in Figure 1) which was extremely complex, but showed two peaks (A and B) which were not present in a similar fraction isolated from the filter tips of control cigarettes. Human nasal assessment confirmed that these two peaks were responsible for the odour with compound B making the major contribution. Further examination of the tobacco, cigarette packets and overwraps showed that the main area of contamination, apart from the filter tips, was the overwrap, especially in the region of the tearstrip. This suggested that the odour may have originated on the tearstrip and migrated to the filter tips, and to a lesser extent the tobacco, after packing.

Figure 4. Structure of dioxaspiro compound.



The mass spectra of compounds A and B (Figures 2 and 3) indicated that the two compounds were obviously closely related chemically, a difference of 14 mass units suggesting that compound B might be a methyl analogue of A. Accurate mass measurement was used to assign empirical formulae of $C_8H_{14}O_2$ and $C_9H_{16}O_2$ for A and B, respectively.

In an examination of reference mass spectra (1), the closest match for A was found to be 1,4-dioxaspiro-(4,5)decane (Figure 4) but a match for B was not found. If B was a methyl analogue of A then the mass spectrum indicated that the methyl group was attached to the five-membered ring and B would therefore be 2-methyl-1,4-dioxaspiro(4,5)decane (Figure 4).

Ethers are not normally especially odorous, however a recent paper (2) suggested that 1,3-dioxolanes had interesting but not unpleasant odours. These compounds had been formed as artifacts in a commercial beef flavour by the condensation of propane-1,2-diol (a commonly used solvent for commercial flavours) with carbonyl compounds present in the flavour (Figure 5).

Figure 5. Synthesis of 1,3-dioxolanes.

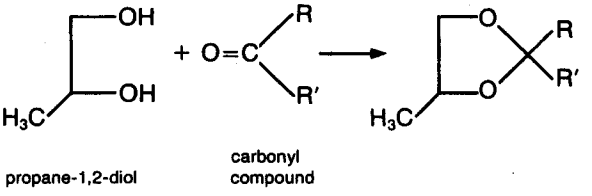
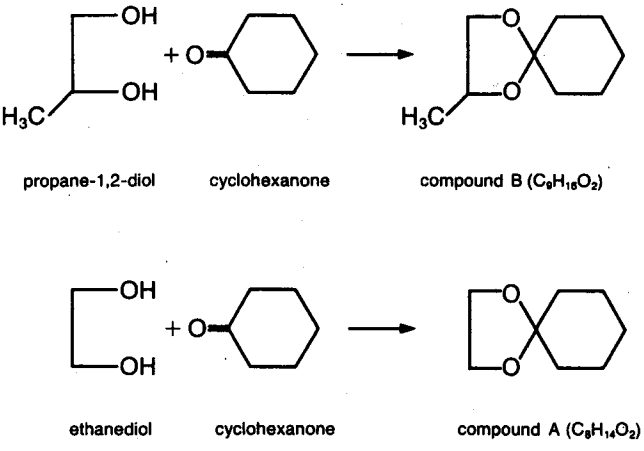


Figure 6. Reaction of cyclohexanone with ethanediols and propanediols.



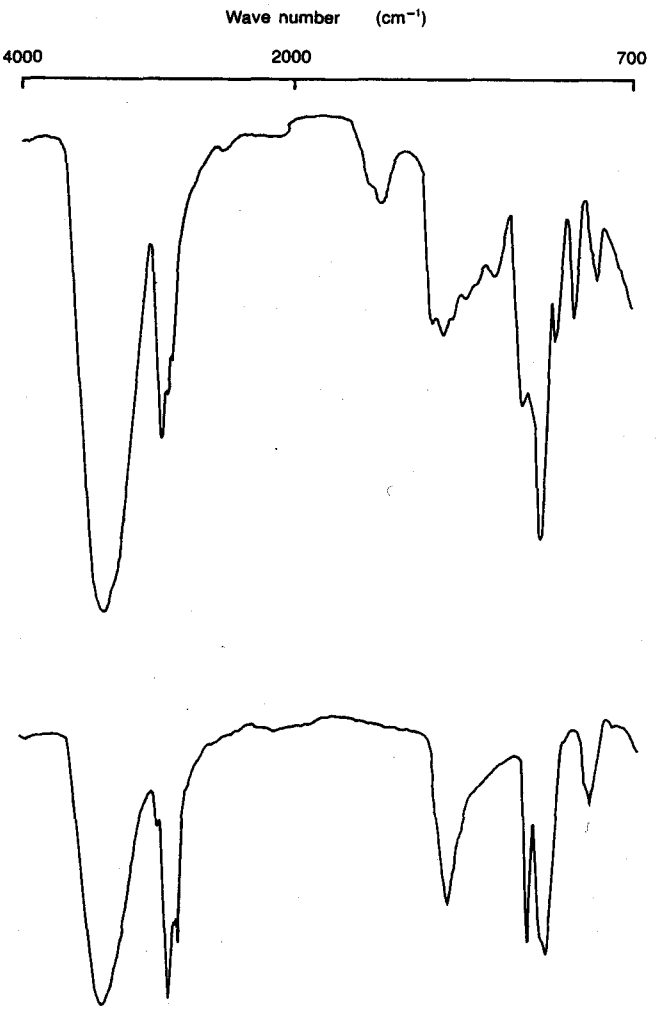
The formation of similar spiro compounds by the reaction of cyclohexanone with propane-1,2-diol and ethane-1,2-diol (Figure 6) was the likely source of the odour. These two spiro compounds were synthesized and the retention times on gas chromatography were identical with those of A and B and their mass spectra also matched, proving conclusively that these spiro compounds were responsible for the odour. Furthermore, the readiness by which these compounds were synthesized from cyclohexanone and the glycols suggested that this was their mode of formation on the tearstrips.

Source of the Odorous Compounds

Having identified the odour as being due to the presence of 1,4-dioxaspiro(4,5)decane and its 2-methyl analogue, it was essential to understand why they had been formed and why only certain cigarette packets were affected.

The source of cyclohexanone, one of the precursors, was readily apparent as it was one of the components of the tearstrip solvent which explained why the main area of odour contamination had been found near the tearstrip.

Figure 7. Infra-red spectra of odorous (a) and non-odorous (b) overwrap extracts.



However, the source of the diols was less obvious. Examination of the 20's overwraps from both the non-odorous and odorous packets of cigarettes showed that they were made from a regenerated cellulose layer coated with a vinylidene chloride - nitrile co-polymer but there were slight differences in the infra-red spectra. A difference between the two overwraps was confirmed by infra-red examination of their acetone extracts, which showed that different alcohols had been used as plasticizers (Figure 7). Examination of the extracts by GC and GC/MS showed that the non-odorous overwraps contained diethylene glycol but the overwraps from the odorous packets had been plasticized with a mixture of glycerol and propane-1,2-diol. A small amount of ethane-1,2-diol was also found and was probably present as an impurity in the propane-1,2-diol.

It was evident that cyclohexanone in the tearstrip solvent had reacted with propane-1,2-diol and ethane-1,2-diol in the overwrap to produce the odorous compounds. The dioxaspiro compound from cyclohexanone and glycerol was prepared but it was not found in the odorous packets. The overwrap plasticized with diethylene glycol did not give a problem as the reaction of cyclohexanone with diethylene glycol (a 1,5-diol) would be unlikely since this would involve the formation of an eight-membered ring.

The packet overwrap is normally plasticized with diethylene glycol. Unfortunately the overwrap on certain packets contained non-specified propane-1,2-diol and ethane-1,2-diol as plasticizers and the reaction of these with cyclohexanone from the tearstrip solvent was the cause of the problem.

SUMMARY

The cause of an odour in certain packets of a batch of cigarettes has been investigated. Two compounds identified as being responsible for the odour were 1,4-dioxaspiro(4,5)decane and 2-methyl-1,4-dioxaspiro(4,5)decane which were formed from the reaction of cyclohexanone, a component of the tearstrip solvent, with ethane-1,2-diol and propane-1,2-diol. These diols had been found as plasticizers in the film used for some packet overwraps but no odour was produced when diethylene glycol, the usual plasticizer, was used in the film.

ZUSAMMENFASSUNG

Es wurde untersucht, worauf ein gewisser, nur einigen Packungen einer Partie von Zigaretten anhaftender Geruch zurückzuführen ist. Als Ursache der Geruchsbildung wurden die beiden Verbindungen 1,4-Dioxaspiro(4,5)decan und 2-Methyl-1,4-dioxaspiro(4,5)decan identifiziert, welche bei der Reaktion von Cyclohexanon, einem Lösungsmittelbestandteil des Aufreißfadens, mit

Ethan-1,2-diol und Propan-1,2-diol entstehen. Es zeigte sich, daß diese Diole im Klarsichtfolieneinschlag einiger Packungen als Weichmacher enthalten waren und daß sich kein Geruch bildete, wenn – wie normalerweise üblich – als Weichmacher Diethylenglykol verwendet worden war.

RÉSUMÉ

On a cherché l'origine de l'odeur constatée sur certains paquets d'un lot de cigarettes, ce qui permit d'identifier deux composés qui en étaient cause, à savoir: 1,4-dioxaspiro(4,5)décane et 2-méthyl-1,4-dioxaspiro(4,5)décane. Ces derniers résultaient de la réaction du cyclohexanone (l'un des constituants de la bandelette d'arrachage) sur l'éthane-1,2-diol et le propane-1,2-diol. On constata en effet que ces dioles avaient été utilisés comme plastifiants dans le film de surenveloppement et qu'il n'y avait aucune odeur lorsque l'on recourait, comme d'habitude, au diéthylène glycol en tant que plastifiant.

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