

CHROM. 12,546

CALCIUM COMPLEX GREASE AS A LOW-POLARITY STATIONARY PHASE

J. K. HAKEN and D. SRISUKH

Department of Polymer Science, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033 (Australia)

and

F. VERNON

Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancashire M5 4WT (Great Britain)

(Received November 20th, 1979)

SUMMARY

Considerable and unexpected thermal stability has been found with a calcium complex hydrocarbon grease proposed as a non-polar stationary phase. Although the polarity is unsatisfactory, improved stability has been achieved by the addition of an antioxidant. The use of an antioxidant increased significantly the thermal stability of low-polarity hydrogenated Apiezon M, which has been reported as an acceptable non-polar basic stationary phase for use at high temperatures.

INTRODUCTION

The use of a calcium complex grease as a non-polar stationary phase suitable at temperatures up to 250° has been reported^{1,2}. The material was recommended as a replacement for low-polarity stationary phases, including Apiezon L, dimethyl-polysiloxane, DC-550 [methyl (75%) phenyl (25%) polysiloxane].

Recent interest has concerned the development of thermally stable materials for use as non-polar basic stationary phases in the Rohrschneider-McReynolds-type classifications.

Squalane, which is an established non-polar standard, possesses an extremely low temperature limit above which excessive bleeding and oxidation occur, with an accompanying increase in polarity. The low operating temperature requires that stationary phases be selected on the basis of their low-temperature behaviour in order to effect separations at much higher operating temperatures and, conversely, materials potentially suitable for use at high temperatures cannot be characterized within the Rohrschneider-McReynolds scheme owing to their physical condition at these lower temperatures.

Huber and Kováts³ studied the requirements of hydrocarbons for use at high temperatures, and indicated that a molecular weight in excess of 1100 would allow

operation at 300°. 24,24-Diethyl-19,29-dioctadecylheptatetracontane ($C_{87}H_{176}$), molecular weight 1222, was synthesized by Riedo *et al.*⁴, and prolonged use at 180° without any significant increase in the phase constants or deterioration in the peak shape was demonstrated by Haken and Ho⁵. As this hydrocarbon is very expensive, alternatives have been considered, and an exhaustively hydrogenated Apiezon M was prepared by Vernon and Ogundipe⁶ that exhibits essentially identical polarity. As some reluctance by workers to use a processed industrial material might be expected, Haken and Vernon⁷ examined a series of samples of exhaustively hydrogenated Apiezon M and showed that a reproducible material can be obtained with this refined, inexpensive material and that it offers an attractive alternative to the expensive synthetic hydrocarbon, with essentially identical column constants and thermal stability.

While calcium complex grease is obviously unsatisfactory as a low-polarity basic stationary phase, in this work we have examined the thermal stability of the grease, particularly as earlier studies⁸ had shown that simple greases exhibited poor thermal stability. The introduction of carbonyl material, *i.e.*, soaps, provided a site for rapid oxidation. The enhanced stability of the calcium complex grease has been shown to be due to the inclusion of antioxidants. An improved thermal stability of hydrogenated Apiezon M on the addition of an antioxidant has been demonstrated by prolonged use at 220° without any significant increase in the phase constants.

EXPERIMENTAL

The analyses were carried out using 10% of the stationary phases on Chromosorb W AW DMCS. Aluminium and stainless-steel columns of O.D. 1/8 and 1/4 in. were employed, there being no variation in the retention indices of test compounds on squalane with either column material, provided that the support is inactive. Determinations were carried out at 120° and 220°.

To increase the speed and accuracy of the determination of retention data, a Hewlett-Packard 5750 research gas chromatograph was interfaced with a 16 K PDP 11/40 digital computer. The chromatograph employed a splitter and individually operated detectors with injection by a Hewlett-Packard 7670A automatic sampler. Calculations of dead time and retention indices were conducted mathematically within the system.

RESULTS AND DISCUSSION

Various hydrocarbons, many in the form of greases, have been reported as stationary phases since the inception of gas chromatography and the effect of varying polar character was demonstrated in 1956⁹. Simple greases contain calcium, sodium or lithium soaps and have poor thermal stability, which can be improved by complexing the soaps with various inorganic salts. Aliphatic acids with chain lengths varying from C_2 (acetate) to C_{14} (myristate) or mixtures thereof are usually used¹⁰.

The retention indices of calcium complex grease are shown in Table I together with values for squalane and other low-polarity materials, and Rohrschneider constants of the grease used by Badoni and Bhagat^{1,2} and of Apiezon. It is evident that the grease used in this work has a higher polarity than those reported by the earlier

TABLE I

RETENTION INDICES OF McREYNOLDS SOULTES AND ROHRSCHEIDER CONSTANTS OF CALCIUM COMPLEX GREASE AND OTHER STATIONARY PHASES

<i>Material</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i>	<i>S</i>
Calcium complex grease	692	654	667	678	763
Apiezon MH	671	599	632	667	726
C ₈₇ H ₁₇₆	674	600	630	664	724
Apiezon M	686	627	651	698	767
Squalane	653	590	627	652	699
	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i>	<i>s</i>
Calcium complex grease ²	0.29	0.18	0.30	0.22	0.58
Apiezon ²	0.32	0.39	0.25	0.48	0.55

workers, which generally have lower retention indices than Apiezon whereas the present material has higher values. The higher polarity is due to an increased soap concentration and/or more unsaturation, each of which provide sites for oxidation and consequently a poorer performance.

The calcium complex grease column was operated continuously at 180° and, after 10 days, the retention indices were essentially unaltered and the material was surprisingly comparable (in thermal stability) to the essentially saturated Apiezon MH and the C₈₇H₁₇₆ hydrocarbon. The stability of hydrogenated Apiezon L has recently been reported by Onuska¹¹ and considerable stability at 200° is indicated. The calcium complex grease was further studied at 220° and only slight increases in the retention indices were evident after 30 days, as shown in Table II. The performance of grease samples⁵ was extremely poor, and was worse than values reported for squalane⁵. The deterioration of squalane is apparently variable, as different rates of deterioration have been reported^{5,12,13}.

TABLE II

McREYNOLDS CONSTANTS OF CALCIUM COMPLEX GREASE DETERMINED AT 120° AFTER CONTINUOUS USE AT 220°

<i>Day</i>	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i>	<i>S</i>
1	692	654	667	678	763
3	692	654	667	678	763
4	692	654	667	678	765
10	691	654	667	679	764
12	692	660	667	678	765
15	692	660	666	678	768
17	691	665	670	679	765
18	691	664	670	679	768
20	691	665	671	680	772
21	687	670	670	679	773
22	688	673	674	680	773
25	688	673	680	679	775
26	688	673	686	678	778
29	689	672	685	679	778
30	689	672	685	679	779

As the high stability of the calcium complex grease was difficult to explain simply on the basis of the constituent soap, the material was examined and the presence of an antioxidant confirmed; this was found to be 0.4% (w/w) of a mixture of *tert.*-butylphenols. The antioxidant Ethyl 735 produced by the Ethyl Corp. (Baton Rouge, La., U.S.A.) is a mixture consisting of approximately 85% of 2,6-di-*tert.*-butylphenol, 8% of 2,4-di-*tert.*-butylphenol, 11% of 2,4,6-tri-*tert.*-butylphenol and 1% of other substituted phenols.

The effect of antioxidants in reversed-phase gas chromatography with olefinic stationary phases has recently been reported by Evans and Newton^{14,15}, and the inhibition achieved was explained in terms of the present knowledge of antioxidant action. With olefinic materials, hydroperoxide formation from an α -methylene hydrogen atom is accompanied by the formation of peroxide groups to yield products that lead to chain scission via a free-radical reaction. Antioxidants either interrupt the propagation reaction or decompose the hydroperoxides into fragments that do not initiate the free-radical reaction. Evans and Newton^{14,15} demonstrated a general increase in retention, as shown by an increased polarity of the stationary phase, due to the oxygenated species produced, followed by rapid deterioration corresponding to the onset of autocatalysis. The use of antioxidants introduces an induction period, where little change is evident, followed by normal oxidation on depletion of the additive, which may be a phenolic or amino compound¹⁶. The compounds used by Evans and Newton¹⁵ were 0.05% of 2,6-di-*tert.*-butyl-4-methylphenol, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine and cadmium di-*n*-butylthiocarbonate, all materials commonly used in industrial processing and produced by ICI (London, Great Britain). The inhibitor used in the calcium complex grease is chemically similar to 2,6-di-*tert.*-butyl-4-methylphenol, the most significant difference being in the increased concentration used.

The obvious efficiency of the stabilizers suggests that the thermally stable low-polarity phases introduced in recent years, *viz.*, C₈₇H₁₇₆ and hydrogenated Apiezon MH, might be further stabilized by means of chemical additives, thus allowing a longer life or higher operating temperatures to be employed. The effect on the polarity of the stationary phase was determined by the addition of 0.4% of Ethyl 735 to Apiezon MH and determination of the retention indices for the test

TABLE III

INCREASE IN McREYNOLDS CONSTANTS OF APIEZON MH AT 220° ON ADDITION OF ANTIOXIDANT

Day	Apiezon MH					Apiezon MH + antioxidant				
	X	Y	Z	U	S	X	Y	Z	U	S
1	—	—	—	—	—	—	—	—	—	—
2	—	1	—	1	1	—	1	—	—	—
3	2	3	1	2	4	1	—	—	—	—
4	3	8	3	6	4	—	2	2	—	—
6	5	16	9	14	16	—	2	2	1	2
8	9	25	15	22	17	1	2	3	3	3
10	9	27	17	29	25	1	5	4	5	4
12	11	29	20	31	26	2	5	4	6	4
14	11	31	21	32	27	2	6	4	6	5

solutes. At this level no increased retention was observed, as shown by the initial values in Table III. As Apiezon MH has been shown to be unaffected by continuous use at 180° for 10 days, a higher temperature (240°) was selected, which was higher than that used with lipids when examined on a simple Apiezon column. The retention indices on Apiezon MH columns with and without addition of antioxidant are shown in Table III, where it is evident that both materials have a substantial service life, deterioration of the unstabilized hydrocarbon commencing after 3 days whereas with the antioxidant deterioration commenced after 8 days.

The results show the practicability of stabilizing hydrocarbon stationary phases without increasing the polarity as indicated by use of McReynolds solutes. The antioxidant level used is higher than that employed by Evans and Newton¹⁵, whose aim was to achieve polymer stabilization and who employed levels appropriate to the polymer industry. In the present application the cost of the antioxidant is negligible compared with the cost of the column, whereas in a polymer application costs of additives are very significant and accordingly higher loadings are possible in chromatography.

We have not attempted to correlate the antioxidant level with stability or endeavoured to determine the optimal level. It is probable that more effective antioxidants are available.

In conclusion, the efficiency of stabilization of hydrocarbon stationary phases has been clearly demonstrated and it is possible that the stability of other chemical classes might also be improved by specific antioxidants. The deterioration of polyester phases in lipid studies is well known, the effect on the retention of new and aged polyester columns having been demonstrated over 15 years ago¹⁷.

REFERENCES

- 1 R. P. Badoni and S. D. Bhagat, *Indian J. Chem.*, 14A (1976) 905.
- 2 R. P. Badoni and S. D. Bhagat, *Indian J. Chem.*, 16B (1978) 640.
- 3 G. A. Huber and E. sz. Kováts, *Anal. Chem.*, 45 (1973) 1155.
- 4 F. Riedo, D. Fritz, G. Tarján and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 63.
- 5 J. K. Haken and D. K. M. Ho, *J. Chromatogr.*, 142 (1977) 203.
- 6 F. Vernon and C. O. E. Ogundipe, *J. Chromatogr.*, 132 (1977) 181.
- 7 J. K. Haken and F. Vernon, *J. Chromatogr.*, 186 (1979) 89
- 8 J. K. Haken, unpublished results.
- 9 A. T. James and A. J. P. Martin, *J. Appl. Chem.*, 6 (1956) 105.
- 10 S. Dawtrey, in G. D. Hobson (Editor), *Modern Petroleum Technology*, Applied Science Publ., Barking, 4th ed., 1970, p. 763.
- 11 F. I. Onuska, *J. Chromatogr.*, 186 (1979) 259.
- 12 M. B. Evans and J. F. Smith, *J. Chromatogr.*, 28 (1967) 277.
- 13 J. A. G. Dominquez, E. F. Sanchez, J. G. Munoz and M. J. Molera, *J. Chromatogr. Sci.*, 17 (1979) 281.
- 14 M. B. Evans and R. Newton, *Chromatographia*, 11 (1978) 311.
- 15 M. B. Evans and R. Newton, *Chromatographia*, 12 (1979) 83.
- 16 G. Scott, *Atmospheric Oxidation and Antioxidants*, Elsevier, Amsterdam, 1965.
- 17 P. Magidman, S. F. Herb, R. A. Barford and R. W. Riemenschneider, *J. Amer. Oil Chem. Soc.*, 39 (1962) 137.