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## GAS CHROMATOGRAPHIC PROCEDURE FOR THE QUALITATIVE ANALYSIS OF SILICONE POLYESTER RESINS AFTER ALKALINE FUSION

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### SUMMARY

The qualitative analysis of linear silicone polyester resins after alkali fusion is described. The identification of all fragments of the resins *i.e.* polyol, carboxylic acid, silicate, methane and benzene is achieved by gas chromatography. Polyol, carboxylic acid and silicate fragments are separated simultaneously as their trimethylsilyl derivatives.

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### INTRODUCTION

A wide variety of polyester resins are available commercially and have formed the backbone of the coating industry. While the development and acceptance of a seemingly endless number of new resinous polymers have reduced the overall importance of the polyester materials, the tonnage consumption remains high and the products have even found expanding usage in several areas. Silicone polyester resins are among the most versatile materials with extensive commercial application in coil coating and related metal finishing.

Since the advent of gas chromatography, a number of analytical methods of applying this technique to coating analysis have appeared. Analytical procedures employing fusion reactions preliminary to gas chromatography have been reported for polyamides<sup>1-7</sup>, polymeric esters<sup>8</sup>, polyurethanes<sup>9-15</sup>, and silicone polyester resins<sup>16,17</sup>. Either alkali or acid fusion reactions were used to cleave the polymer into fragments, and then each fragment was converted to its appropriate derivative to allow examination by gas chromatography.

Simultaneous determination of phthalic anhydride and polyols in alkyds has been reported<sup>18</sup>. Ethanolysis is used preliminary to gas chromatography. Such a method is limited to the identification of phthalic anhydride and other readily hydrolysible alkyds, polyesters containing substantial amounts of iso- or terephthalic acid esters being resistant to simple solution hydrolysis. However acid- and alkali-fusion reactions prior to gas chromatography have been used successfully for the cleavage of polyesters with substantial hydrolysis resistance and for the simultaneous

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identification of various polyols and carboxylic acids from a series of silicone-polyester resins<sup>19</sup>.

The silicon content of such resins has been determined as silica by ignition, although such a procedure is not applicable to pigmented samples. Trimethylsilylation of acidified sodium silicate solutions has been described with minerals by Lentz<sup>20</sup> who used hexamethyldisilazane (HMDS). Wu *et al.*<sup>21</sup>, using the same procedure, identified the reaction products by mass spectrometry. Gotz and Masson<sup>22</sup> followed substantially the same procedure but with a mixture of HMDS and trimethylchlorosilane (TMCS) while Garzó *et al.*<sup>23</sup> preferred HMDS.

Verzele and co-workers<sup>24-26</sup> have reported the hydrolysis of the silica gel matrix of HPLC column materials with potassium hydroxide and the use of trimethylsilylation with trimethylsilylimidazole (TMSI). A spectrophotometric method has also been reported<sup>27</sup> for the determination of silicon in silicone-containing samples. Alkali fusion was employed to produce silicates suitable for spectrophotometric analysis by the reduced heteropoly blue complex method.

The analysis of silicone-modified polyesters has not been extensively studied. The determination of polyols in silicone polyesters has been reported<sup>28</sup>. The method used involved saponification with tetramethylammonium hydroxide at 100°C for 20 min, followed by derivatisation of the polyol to the trimethylsilyl ethers and subsequent gas chromatography. The organic moieties in the polysiloxane have been estimated as the corresponding hydrocarbons: methane from dimethylpolysiloxanes by Schleuter and Siggia<sup>29</sup> and benzene from phenylsiloxanes by Vimalasiri *et al.*<sup>9</sup>. Alkali fusion procedures were used in each case. Acid-fusion reactions have also recently been shown to liberate hydrocarbons corresponding to the alkyl or aryl substituents in polysiloxanes<sup>16,17</sup>.

Our present work describes the analysis of linear silicone polyester resins by alkali fusion preliminary to gas chromatography. Polyols, dicarboxylic acids and silicon fragments are identified simultaneously as their trimethylsilyl derivatives, and the organic pendant groups of the condensed siloxane intermediate are also examined by gas solid chromatography on a Porapak Q column. The analysis of the organic compounds and of the silica from the siloxane moiety have not previously been reported simultaneously with resinous materials.

## EXPERIMENTAL

### *Samples*

The samples examined were a series of polyester resins, modified with silicone intermediate SY-231, from Wacker-Chemie GMBH, *i.e.* a methoxy functional methyl phenyl polysiloxane. They were prepared by simple condensation according to the formulations shown in Table I.

### *Alkali fusion*

The alkali fusion reaction was carried out on 200 mg of polymer sample with 13 g of potassium hydroxide-sodium acetate prepared according to the procedure previously reported<sup>16</sup>. The reaction was achieved by heating the polymer reagent mixture in a stainless-steel tube at 250°C for 1 h. The gases trapped in the tube were used for the analysis of the organic pendant groups of the condensed siloxane intermediate by injecting about 0.5 ml of gas, collected onto a Porapak® Q column.

TABLE I  
FORMULATION OF SILICONE POLYESTER RESINS

Ingredient	Weight (%)		
	Sample 1	Sample 2	Sample 3
Silicone intermediate SY231	32.9	48.2	48.2
Trimethylolpropane (TMP)	41.7	49.9	16.7
Trimethylolethane (TME)	—	—	28.8
Neopentylglycol (NPG)	—	8.9	8.9
Isophthalic acid (IPA)	25.4	29.6	29.6
Adipic acid (AA)	11.2	24.0	24.0

For further analysis, the tube was allowed to cool to room temperature. The tube was then opened and the contents were partly transferred to a beaker. This was followed by the addition of a dilute hydrochloric acid to liberate the carboxylic acids. After evaporation to dryness on a water-bath, an excess of TMCS and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) reagent (1:1, v/v) was added for silylation by refluxing the mixture in a round-bottom flask at 80°C for 0.5 h. The trimethylsilyl derivatives were recovered by extraction with using chloroform and after drying the extract was concentrated under reduced pressure prior to analysis.

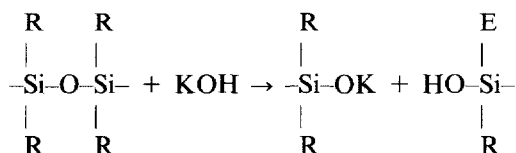
#### Gas chromatography

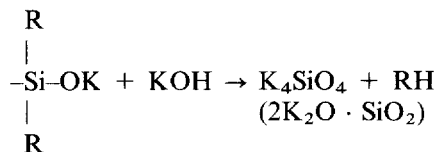
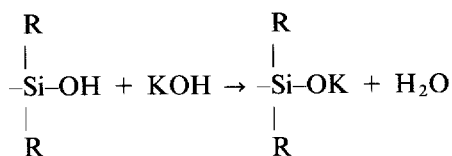
Gas chromatography was carried out on a Hewlett-Packard 5750 Research model gas chromatograph with flame-ionization detection and helium as carrier gas.

The trimethylsilyl derivatives were separated on an aluminium column (4 ft. × 1/4 in. O.D.), packed with 6% (w/w) SE-30 on Gas Chrom Q. The column was temperature programmed between 100 and 195°C at 10°C/min. The separation of methane and benzene was carried out on a 6 ft. × 1/8 in. O.D. stainless-steel column, packed with Porapak Q. The column was operated according to the previous work<sup>16,17</sup>, *i.e.* isothermally at 76°C for 1 min, then temperature-programmed at 40°C/min to 240°C and held for 2 min for the headspace analysis after alkali fusion.

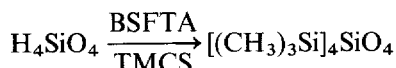
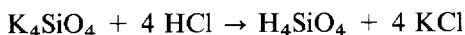
#### RESULTS AND DISCUSSION

The silicone polyesters examined were successfully cleaved into the corresponding polyols, carboxylic acids, silicate, methane, and benzene by using alkali-fusion reaction as follows:





The trimethylsilylation of the liberated silicates occurs by reaction of the silicic acid formed with (BSTFA).



The addition of TMCS increases the reaction rate. The trisilyl ether derivatives of the dicarboxylic acids and polyols are formed simultaneously.

Separations of the reaction products from sample 2 (Table I) with five components is shown in Fig. 1 while a comparable separation of sample 3 with the

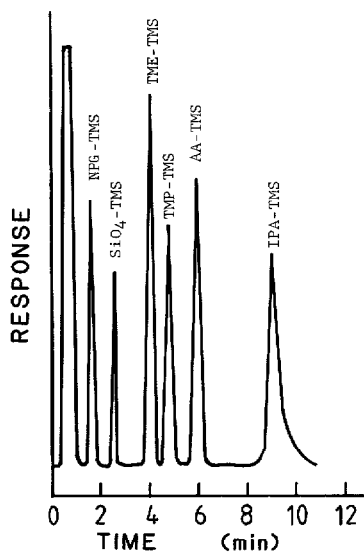


Fig. 1. Gas chromatogram showing simultaneous separation of polyol, dicarboxylic acid and silicate trimethylsilyl (TMS) derivatives from sample 2. Compound abbreviations given in Table I.

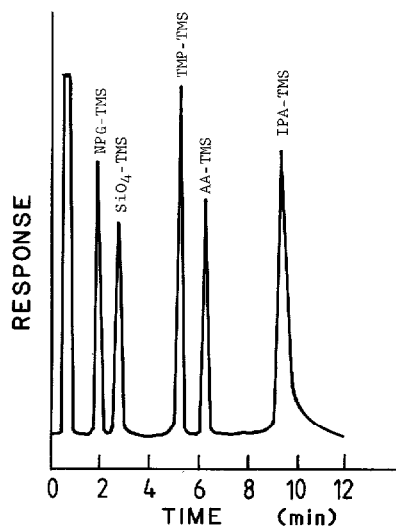


Fig. 2. Gas chromatogram showing simultaneous determination of polyols, dicarboxylic acid and silicate TMS derivatives from sample 3. Compound abbreviations given in Table I.

additional component trimethylolethane is shown in Fig. 2. The separations are not treated in detail in this work as the results are substantially as previously reported<sup>16,17</sup>.

N-Trimethylsilylimidazole (TMSI), used earlier for silicates by Verzele and co-workers<sup>24-26</sup> was first evaluated in this work. While the reagent is less sensitive to moisture than many other silylating reagents and the products are less susceptible to hydrolysis, reaction with dicarboxylic acids was not achieved. The reagent works well for silicates and polyols. With the silylation reagents used the moisture content was reduced by preliminary drying. The excess of silylation reagent reacts vigorously with moisture to form hexamethyldisiloxane which is eluted with the solvents used and does not interfere with the chromatogram.

The work of Wu *et al.*<sup>21</sup> with silicate minerals showed the separation of several anions, *i.e.* monomer  $\text{SiO}_4^{4-}$ , dimer  $\text{Si}_2\text{O}_6^{6-}$ , trimeric ring  $\text{Si}_3\text{O}_9^{6-}$ , tetrameric ring  $\text{Si}_4\text{O}_{12}^{8-}$ , and trimeric chain  $\text{Si}_3\text{O}_{10}^{8-}$ . In the present work the silicate produced a single peak. Results comparable to the previous ones<sup>16,17</sup> were obtained for the analysis of alkyl and aryl substituents of the resin by headspace analysis and resolution of the liberated hydrocarbons via gas-solid chromatography. Methane and benzene were eluted at 0.28 and 3.4 min, respectively, equivalent to elution temperatures of 76 and 238°C. Fusion reactions have been described in earlier papers as providing semi-quantitative data when reagents aggressive enough to allow complete cleavage are used. Although the analytical scheme presented in this work is a qualitative one, the extraction steps are eliminated and errors can be minimized in the analysis of polyol, carboxylic acid, and silicate fragments of the silicone polyester. An examination of possible quantitation of polymer analyses after acid or alkali hydrolytic fusion has recently been reported<sup>30</sup>, and limitations including the lack of purity of some initial reactions indicated. However the analysis of the alkyl and aryl groups however, was carried out without extraction steps, and with the use of an internal standard quantitative results have been demonstrated.

## CONCLUSION

Alkali-fusion-reaction gas chromatography has been described for the qualitative analysis of silicone polyester resins. Simultaneous separation of polyol, carboxylic acid and silicate fragments as their trimethylsilyl derivatives allow a simple and rapid analysis of the silicone polyester resins to be achieved.

## REFERENCES

- 1 G. J. Glading and J. K. Haken, *J. Chromatogr.*, 157 (1978) 404.
- 2 J. K. Haken and J. A. Obita, *J. Oil Colour Chem. Assoc.*, 63 (1980) 194.
- 3 J. K. Haken and J. A. Obita, *J. Macromol. Sci. Chem.*, A17 (1982) 202.
- 4 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 213 (1981) 55.
- 5 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 244 (1982) 259.
- 6 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 244 (1982) 265.
- 7 J. K. Haken and J. A. Obita, *J. Chromatogr.*, 239 (1982) 377.
- 8 J. K. Haken and M. A. Rohanna, *J. Chromatogr.*, 298 (1984) 263.
- 9 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 319 (1985) 121.
- 10 J. K. Haken, R. P. Burford and P. A. D. T. Vimalasiri, *J. Chromatogr.*, 349 (1985) 347.
- 11 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 355 (1986) 141.

- 12 R. P. Burford, J. K. Haken and P. A. D. T. Vimalasiri, *J. Chromatogr.*, 321 (1985) 295.
- 13 R. P. Burford, J. K. Haken and P. A. D. T. Vimalasiri, *J. Chromatogr.*, 329 (1985) 132.
- 14 P. A. D. T. Vimalasiri, J. K. Haken and R. P. Burford, *J. Chromatogr.*, 361 (1986) 231.
- 15 J. K. Haken, P. A. D. T. Vimalasiri and R. P. Burford, *J. Chromatogr.*, 362 (1986) 391.
- 16 J. K. Haken, N. Harahap and R. P. Burford, *J. Chromatogr.*, 387 (1987) 223.
- 17 J. K. Haken, N. Harahap and R. P. Burford, *J. Coat. Technol.*, 59 (1988) 73.
- 18 B. Laurinat and J. Hellwig, *Plaste Kautsch.*, 29 (12) (1982) 710.
- 19 J. K. Haken, N. Harahap, R. P. Burford, *J. Coat. Technol.*, 60 (1988) in press.
- 20 C. Lentz, *Inorg. Chem.*, 3 (1964) 579.
- 21 F. F. H. Wu, J. Götz, W. D. Jamieson and C. R. Masson, *J. Chromatogr.*, 48 (1970) 515.
- 22 J. Gotz and C. R. Masson, *J. Chem. Soc. A.*, (1970) 2683.
- 23 G. Garzó, D. Hoebell, Z. Ecsery and K. Ajszaszi, *J. Chromatogr.*, 167 (1978) 321.
- 24 M. Verzele, P. Mussche and P. Sandra, *J. Chromatogr.*, 190 (1980) 331.
- 25 P. Sandra, M. V. Roelenbosch, I. Temmerman and M. Verzele, *Chromatographia*, 16 (1982) 63.
- 26 I. Temmerman, P. Sandra and M. Verzele, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 8 (1985) 513.
- 27 J. H. Wetters and R. C. Smith, *Anal. Chem.*, 41 (1969) 379.
- 28 J. McFadden and D. S. Scheung, *J. Chromatogr. Sci.*, 22 (1984) 310.
- 29 D. D. Schleuter and S. Siggia, *Anal. Chem.*, 49 (1977) 15.
- 30 J. K. Haken, *J. Chromatogr.*, 406 (1987) 167.