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FT-NMR DETERMINATION OF THE
SILANE HYDROGEN CONTENT OF SILOXANE
PRE-POLYMERS

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DEVELOPMENT DIVISION

OCTOBER 1978

Process Development
Endeavor No. 101

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ABSTRACT

The application of proton FT-NMR methods for the determination of the silane hydrogen content of several siloxane pre-polymers has shown itself to be a relatively rapid procedure with excellent precision.

INTRODUCTION

A study of the potential application of proton FT-NMR methods, for use in the determination of the silane hydrogen content in siloxane pre-polymers, was undertaken to develop an alternate and rapid method of analysis for these systems.

Several selected siloxane pre-polymer 'catalyst' mixtures were analyzed in this study and include the following:

Sylgard 182 B	Lot EF 076062
Sylgard Catalyst	184-36B
Sylgard Catalyst	186-47B

EXPERIMENTAL

A weighed amount of the pre-polymer (500 - 800 mg) along with a weighed amount of p-dioxane (internal quantitative standard approximately 10 mg, 1 - 2%)^a was dissolved in deuteriochloroform (CDCl₃), and the resulting

^aEastman Spectro Grade.

mixture was run in a 5 mm tube on a Nicolet NT-150 FT-NMR at 150.0588 MHz. Six samples of each of the three materials were analyzed. An ¹H spectrum of Sylgard 184-36B/p-dioxane, in CDCl₃, is shown in Fig. 1. The major peaks centered at 0.18, 0.13, and at 0.09 ppm, are due to the methylsiloxane proton resonances. Silane hydrogen is centered at 4.72 ppm, while p-dioxane is at 3.71 ppm.

Unlike typical cw NMR systems, the Nicolet NIC-1180 computer system does not necessitate that the spectrum and the integral be plotted, with the subsequent manual measurement of the integral regions. All operations are accomplished with the computer, in conjunction with the computer scope display. This is accompanied by digital read out and print out of the integral region magnitudes. In addition, computer scope display cursors allow a more precise determination of the correct spectral sweep region by nearly exact determination of the actual resonance peak entry and peak exit positions. These are the limits

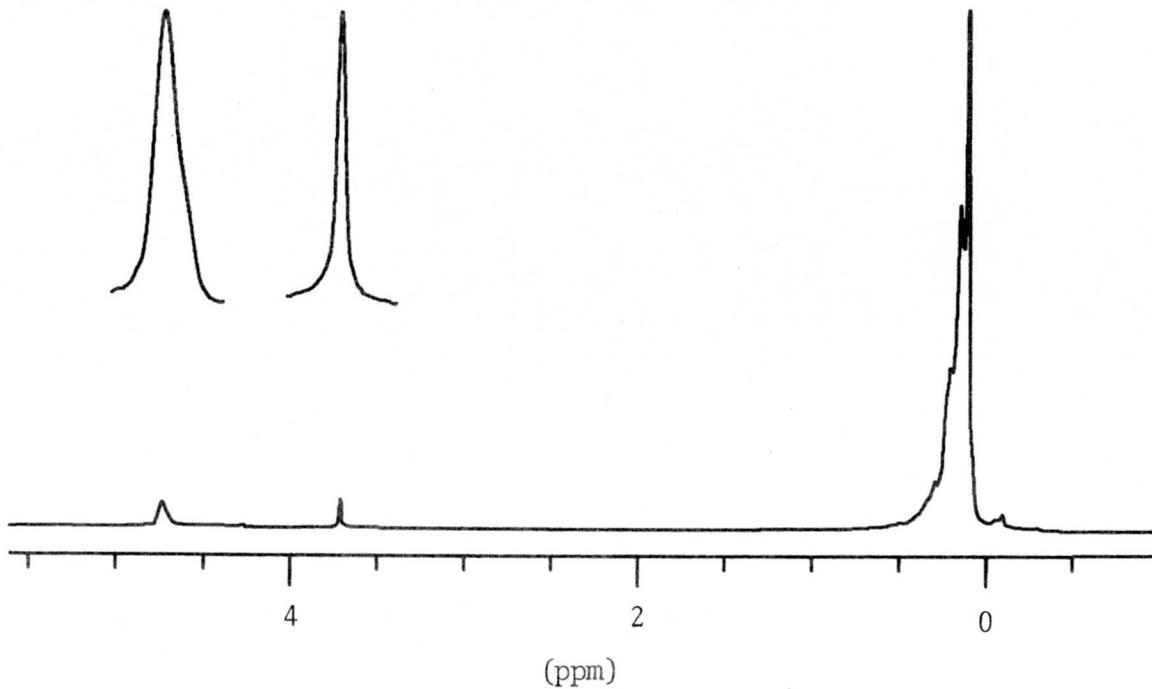


Fig. 1. ^1H NMR Spectrum of Sylvard 184-36B in CDCl_3 , with p-Dioxane

of the region of the displayed integral measured, and results in a considerably more precise technique than former methods. The use of a superconducting magnet also eliminates any field drift over the period of the experiment. With the FT system, rf saturation problems are not a concern, although the post acquisition/pre-pulse delay must be long enough to compensate for the difference in relaxation times between the resonant species. In this experiment, it was found that a pre-pulse delay of 5 seconds was more than adequate.

Table I presents the NMR results for the 182B system, while the results for the 184-36B and the 186-47B are seen in Tables II and III, respectively. Wet chemical analytical results for the latter two are presented for comparison.

The time required for one sample was found to be about 20 minutes, from

sample weigh up through percentage calculation. A set of six samples required one hour and twenty minutes.

Table I. Silane Hydrogen Content of Sylvard 182B (Lot EF-076062)

Run No.	Percent Silane Hydrogen	Average (\bar{X})	Standard Deviation (σ)
1	0.437		
2	0.433		
3	0.442	0.435	0.004
4	0.429		
5	0.436		
6	0.434		

Wet chemical results not available.

Table II. Silane Hydrogen Content of Sylgard 184-36B

Run No.	Percent Silane Hydrogen	Average (\bar{X})	Standard Deviation (σ)
1	0.427		
2	0.433	0.434	0.005
3	0.429		
4	0.437		
5	0.434		
6	0.441		

Wet chemical results (0.442%).

Table III. Silane Hydrogen Content of Sylgard 186-47B

Run No.	Percent Silane Hydrogen	Average (\bar{X})	Standard Deviation (σ)
1	0.082		
2	0.094		
3	0.090	0.091	0.007
4	0.100		
5	0.093		
6	0.084		

Wet chemical results (0.088%).

COMMENTS

The precision of this method appears to be quite acceptable. The accuracy is yet to be determined, although the results are quite close to those reported by the Quality Division using a wet chemical method. Silane hydrogen standards, such as those used in Sylgard pre-polymer compositions, have been ordered from Silar Corpor-

ation, and include 1,1,3,3,5,5-hexamethyltrisiloxane and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane. Upon their receipt, the accuracy of the method will be determined and subsequently reported. Additional work in this area of analysis is now underway, with a study of the potential application of NMR methods to the determination of siloxane vinyl content.

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