

# General Procedures to Determine the Composition of Commercial, Two-Part Polysulfide Aircraft Sealants

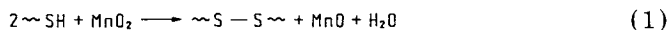
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## Synopsis

Interpretation of the chemical processes which polysulfide sealants undergo either on storage or when the cured material is subjected to environmental influences requires detailed knowledge of formulations. Procedures have been developed to isolate and identify a range of additives in two-part commercial aircraft sealants of both the dichromate and manganese dioxide cure types. Solvents, curing agent dispersants, and cure rate modifiers were separated chemically and thermal analysis was demonstrated to provide a ready means to estimate carbon in fillers. The phenolic resin adhesion enhancers were conveniently determined using  $^{13}\text{C}$ -NMR spectroscopy and could also be identified using size exclusion chromatography. It was shown that virtually no interaction occurred between polysulfide liquid polymers and phenolic resins following aging at  $70^\circ\text{C}$  for 7 days. The most appropriate methods for determining curative levels were established and new means of assessing thiol content of the polysulfides by both  $^{13}\text{C}$ -NMR and PMR spectroscopy are described. The significance of aspects of the sealant formulations is discussed.

## INTRODUCTION

The principal application of aircraft sealants is in the sealing of fasteners and seams of integral fuel tanks. Specialized materials are required and polysulfide sealants based on Thiokol liquid polymers have provided reliable service for many years when used within their performance limitations. These sealants are usually cured by oxidation of a thiol-terminated prepolymer (1) with inorganic oxidants such as manganese dioxide or dichromate salts,<sup>1-3</sup> a process which introduces new disulfide links:



Commercial polysulfides are presented as two-part systems with the prepolymer and curing agent packaged separately. The base polymer components are often produced from blends of various prepolymers which are available in a range of molecular weights and with differing proportions of crosslinking sites. As a result of the thiol-disulfide interchange reaction<sup>4,5</sup> the prepolymers interact and reach an equilibrium molecular weight distribution. Incorporation of numerous other compounding agents, however, leads to formulations of con-

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siderable complexity. Typical additives include fillers, cure rate modifiers, adhesion enhancers, plasticizers, viscosity adjusters, and curing agent dispersants. The functions of these constituents and the general classes of compounds used in these roles have been reviewed.<sup>2,3,5-8</sup>

To a considerable degree, the effectiveness of polysulfide sealants is controlled by slow chemical reactions which occur either on storage of the uncured formulation or through the influence of environment on the cured material.<sup>9</sup> Although many of the compounding additives may be considered to be chemically inert, some conceivably can participate in reactions which result in modified sealant properties. Any program to improve sealant performance, and particularly one which involves interpretation of the processes leading to degradation, demands as a prerequisite detailed knowledge of the sealant composition. Some specific instances where such information has been crucial are mechanistic studies of long term ageing of polysulfides,<sup>9</sup> acceptability of time-expired sealants, and investigations of desealing procedures,<sup>10,11</sup> hot water immersion,<sup>12,13</sup> and thermal degradation.<sup>1,9</sup>

Consequently, there is a need for a general scheme to permit the separation and identification of the individual components of polysulfide formulations. Appropriate techniques to achieve this requirement are now presented together with details of the most effective procedures for analysis of critical reagents and properties, such as curing agent concentrations and thiol content of the liquid polymer.

## EXPERIMENTAL

### General

<sup>1</sup>H and <sup>13</sup>C magnetic resonance spectra were obtained in CDCl<sub>3</sub> using a Bruker AM300 instrument, and all chemical shifts are reported in ppm relative to tetramethylsilane as internal standard. Infrared spectra were determined using a Perkin-Elmer 580B double beam ratio recording infrared spectrophotometer equipped with a Model 3600 data station and associated software. X-ray fluorescence spectroscopy was carried out with a Philips Model PW 1400 sequential spectrometer using compressed disc samples of 10% mixture in pure cellulose. Mass spectra were obtained using a Vacuum Generators Model 7035 instrument interfaced with a Varian 3700 gas chromatograph operated using a 15 m × 0.2 mm bonded phase (BP 10)-fused silica column and SGE universal injector. Thermal analysis was conducted using a DuPont thermal analyzer Model 1090 comprising a 910 DSC and a modified 950 TGA, and for spectrophotometric analysis a Pye Unicam SP8-150 UV/visible instrument was used together with 10 mm quartz cells. Size exclusion chromatography (SEC) was undertaken using an Altex 110A pump and a Beckman variable, dual-channel UV detector.

Melting points (uncorrected) were determined in a Buchi apparatus (Tottoli model) using open capillary tubes.

### Materials

#### *Commercial Sealants*

Two-part polysulfide sealants meeting the specifications MIL-S-8802 (dichromate cure type) and MIL-S-83430 (manganese dioxide cure type) were

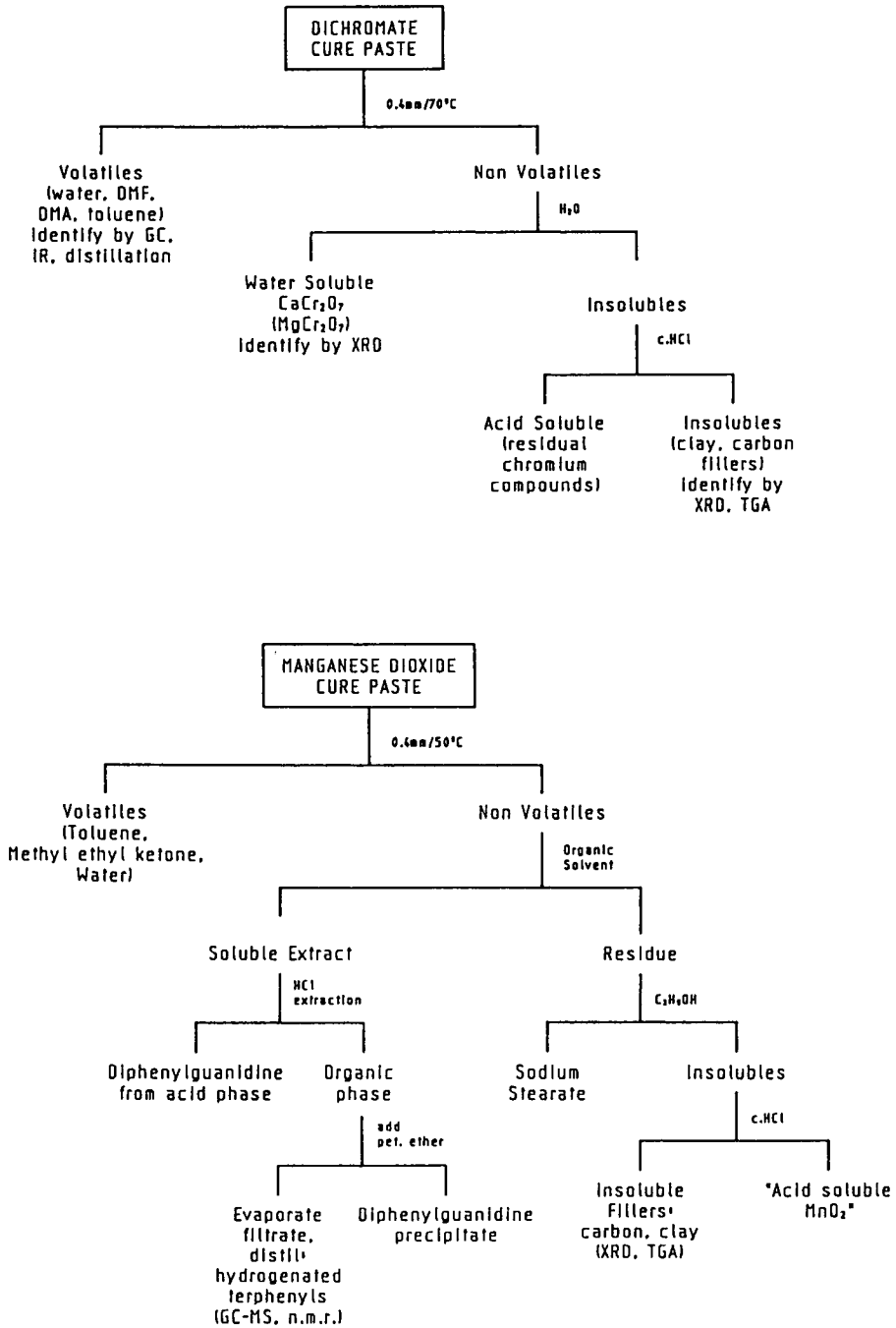


Fig. 1. Separation of cure paste components.

obtained from a range of commercial sources. The sealants consisted of a base polymer component (polysulfide polymer blend, fillers and adhesion additive) and a separately packaged cure paste (curing agent, dispersant, fillers, and

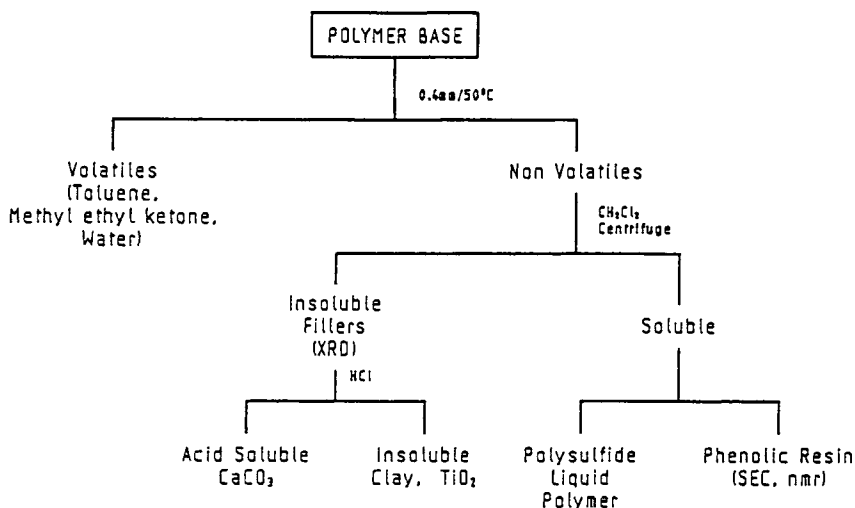


Fig. 2. Separation of base polymer components.

accelerator). Two types of sealants were examined: A class, a low viscosity, brushable grade, and B class, a more viscous mixture which is applied by extrusion gun or spatula. Within each class, differing cure rates are designated by dash number, e.g., B-2 denotes a B class sealant with a minimum application time of 2 h.

### Reference Materials

Materials used for comparison with components of commercial sealant formulations were the liquid polysulfide polymers, LP-2, LP-3, and LP-32, acquired from Toray Thiokol, and the phenolic resins Methylon 9484 (General Electric) and Durez 10694 (Hooker Chemical Corp.), which were examined as models for the adhesion additives.

TABLE I  
Compositions of Polymer Bases

Component or property	Dichromate sealants				Manganese dioxide sealants				
	A-1/2	A-2	B-1/2	B-2	A-1/2	A-2	B-1/2	B-2	B-6
Polysulfide	61.1	59.4	58.9	59.2	51.6	50.8	59.3	60.1	59.8
Water	0.3	0.2	0.4	0.6	0.5	0.5	0.6	0.3	0.8
Toluene-MEK <sup>a</sup>	6.6	7.9	0.6	1.5	8.5	8.7	—	—	—
Phenolic resin	7.5	7.5	7.5	7.5	4.0	4.0	4.0	4.0	4.0
Calcium carbonate	24.5	25.0	32.6	31.2	35.4	36.0	36.1	35.6	35.4
Titanium dioxide	—	—	—	—	<i>p</i> <sup>b</sup>	<i>p</i> <sup>b</sup>	<i>p</i> <sup>b</sup>	<i>p</i> <sup>b</sup>	<i>p</i> <sup>b</sup>
[SH]%	1.12	1.08	1.27	1.22	2.20	2.15	2.15	2.13	2.20

<sup>a</sup> Methyl ethyl ketone.

<sup>b</sup> *p* indicates present in small quantities.

TABLE II  
Compositions of Manganese Dioxide Cure Pastes

Component	A-1/2	A-2	B-1/2	B-2	B-6
"Acid-soluble MnO <sub>2</sub> "	56.8	52.3	57.1	55.0	52.4
Carbon black	7.1	14.6	5.4	12.4	14.5
Hydrogenated terphenyls	29.8	29.3	30.3	29.4	30.0
<i>N,N'</i> -diphenylguanidine	3.6	1.6	4.7	1.7	1.0
Sodium stearate	2.3	1.9	1.9	2.1	1.5
Water	0.4	0.3	0.6	0.4	0.6
MnO <sub>2</sub> <sup>a</sup>	45	44	44	46	43

<sup>a</sup> By potentiometric titration.

Manganese dioxide for curing studies was from Riedel-de Haën (Type FA) and was dispersed in Cerechlor AS52 (ICI Chemicals). 2-Ethoxyethane thiol had <sup>1</sup>H-NMR  $\delta$  1.22, t, CH<sub>3</sub>; 1.60, t, SH; 2.68, m, CH<sub>2</sub>SH; 3.50, q, CH<sub>3</sub>CH<sub>2</sub>; and 3.56, t, OCH<sub>2</sub>CH<sub>2</sub>; all assignments confirmed by spin decoupling experiments, while di(2-ethoxyethane) disulfide had  $\delta$  1.07, t, CH<sub>3</sub>; 2.74, t, CH<sub>2</sub>SS; 3.39, q, CH<sub>3</sub>CH<sub>2</sub>; and 3.53, t, OCH<sub>2</sub>CH<sub>2</sub>.

## Examination of Cure Pastes

### *Manganese Dioxide-Based Systems*

By use of a vacuum line (operated at 0.4 mm of Hg) volatile components from a tared sample of the cure paste maintained at 50°C were collected using a series of liquid nitrogen traps. The residual paste was dispersed in dichloromethane, centrifuged, and the solvent decanted. The bulked solvent from three such operations was extracted twice with 1*N* HCl to remove the basic accelerator (1,3-diphenylguanidine, mp and mmp 148–150°C and infrared spectrum identical to that of an authentic sample). Following the extraction, the dichloromethane solution was dried and then evaporated to dryness to give a brown oil. This was dispersed in petroleum spirit (bp 40–60°C) and filtered

TABLE III  
Compositions of Dichromate Cure Pastes

Component or property	A-1/2	A-2	B-1/2	B-2
Water		25.8		21.3
Dimethylacetamide	51.0	25.4 <sup>a</sup>	50.1	30.0
"Dichromate"	37.1	28.1	37.3	25.1
% Mg <sup>b</sup>	3.0	1.2	2.5	0.08
% Ca <sup>b</sup>	2.2	3.7	2.3	3.8
Clay		20.1		22.6
Carbon black	11.9	0.6	12.6	1.0
[Cr VI]	14.1	11.4	14.3	9.9

<sup>a</sup> Mixed DMA, DMF.

<sup>b</sup> On total cure paste by atomic absorption spectroscopy.

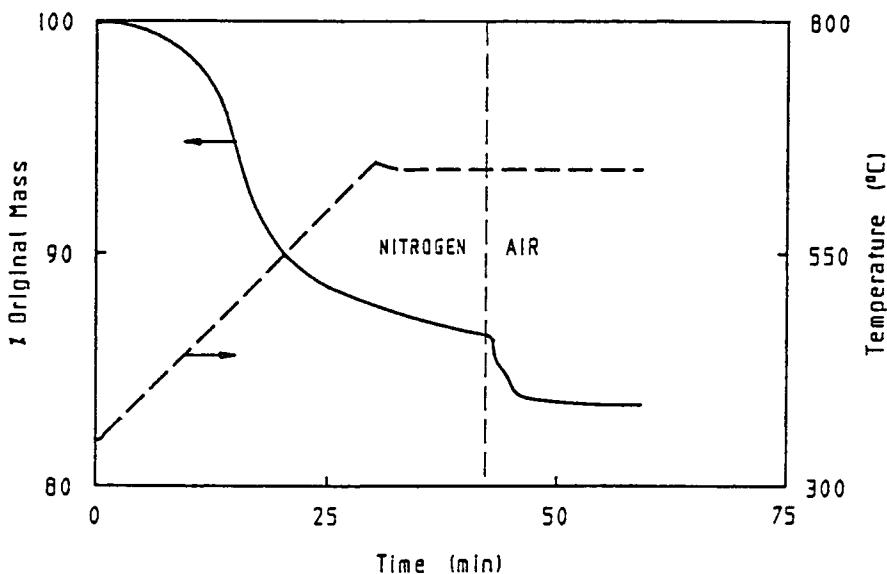


Fig. 3. TG analysis of fillers from a dichromate cure paste.

to give further 1,3-diphenylguanidine. Removal of solvent from the filtrate followed by distillation gave the yellow carrier oil which was shown to be mixed hydrogenated terphenyls comprised of approximately equal proportions of mono- and dicyclohexyl isomers. GC-MS showed 10 resolved peaks of which a minor component with  $m/z$  230 was spectrally indistinguishable from terphenyl; five peaks showed  $m/z$  236 (monocyclohexyl isomers) and four peaks had  $m/z$  242 (dicyclohexyl isomers).  $^1\text{H-NMR}$ :  $\delta$  7.25, m (aromatics); 0.75–3.0, m, major signals centered at  $\delta$  2.5, 1.8, and 1.3;  $\nu_{\text{max}}$  (film) 2925, 2850, and  $1605\text{ cm}^{-1}$ .

The dark residue from the centrifugation was dried in air and extracted several times with hot ethanol. Removal of the solvent from the bulked extracts gave sodium stearate, mp 220–285°C, lit mp gradual melt from 220 to 305°C;  $\nu_{\text{max}}$  (KBr disc)  $1565\text{ cm}^{-1}$ , infrared spectrum identical with an authentic sample. Acidification of an aqueous solution afforded stearic acid. Examination by X-ray fluorescence and atomic absorption spectroscopy confirmed that the cation was sodium.

The ethanol-insoluble material remaining after extraction was digested overnight in concentrated hydrochloric acid. The residue, mainly carbon, was analyzed by the thermal analysis technique described in the Results section.

#### *Dichromate-Based Curing Systems*

Removal of volatiles under vacuum afforded first water at 30–40°C and then a mixture of water with dimethylformamide and/or dimethylacetamide at temperatures of 60–100°C. The amide derivatives were identified by subtractive infrared spectroscopy and the ratio of water to amide was shown by GC to be around 2 : 1. Repeated grinding of the caked residue facilitated removal of the solvent but many days were necessary to complete the process. The entire

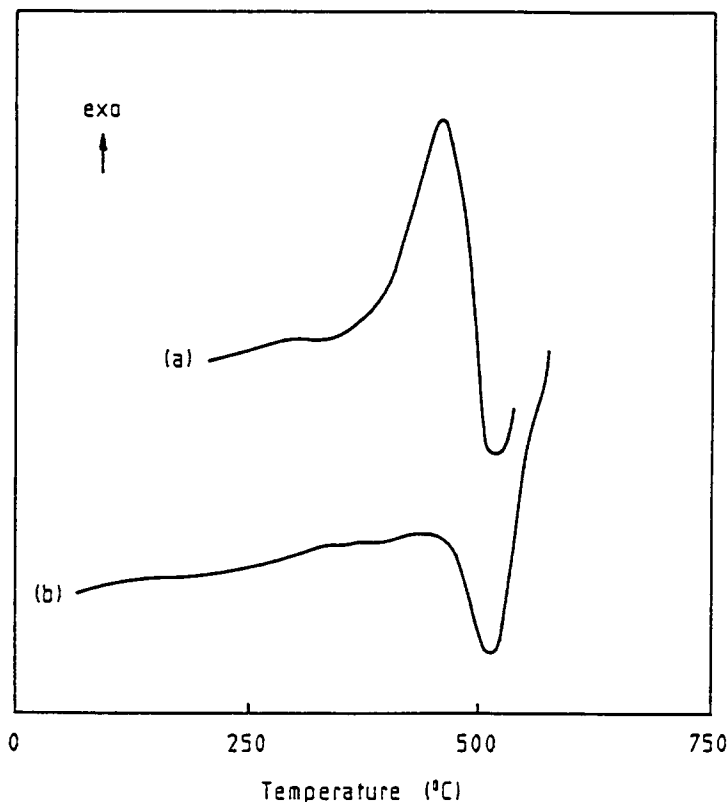


Fig. 4. DSC curves, in air, 10°C/min, of fillers from a dichromate cure paste: (a) unwashed; (b) washed with HCl.

estimation was therefore conducted only on the A-2 and B-2 cure pastes, the remainder being only partially assessed by this procedure. The residual solid was heated with water to extract the dichromate, and XRF and standard analytical methods were used to identify the cations. The water-insoluble fillers were treated with 1N hydrochloric acid to remove any remaining chromium compounds and the dried solid was examined by thermal analysis.

#### Examination of Base Polymer Mixtures

Removal of volatiles under vacuum at ambient temperatures afforded either a mixture of toluene and ethyl methyl ketone (1 : 1 w/w by GC analysis) followed by water, or in some cases water alone. The remaining mixture was repeatedly stirred with dichloromethane and centrifuged until all fillers had separated. Examination by XRF together with standard analysis indicated that the fillers were essentially calcium carbonate. Digestion of the solids in hydrochloric acid produced small quantities of insoluble material, some of which was soluble in chloroform and was shown to be polysulfide polymer (presumably high MW species). The solvent-washed samples were then examined by XRF to establish the presence of titanium dioxide or clay.

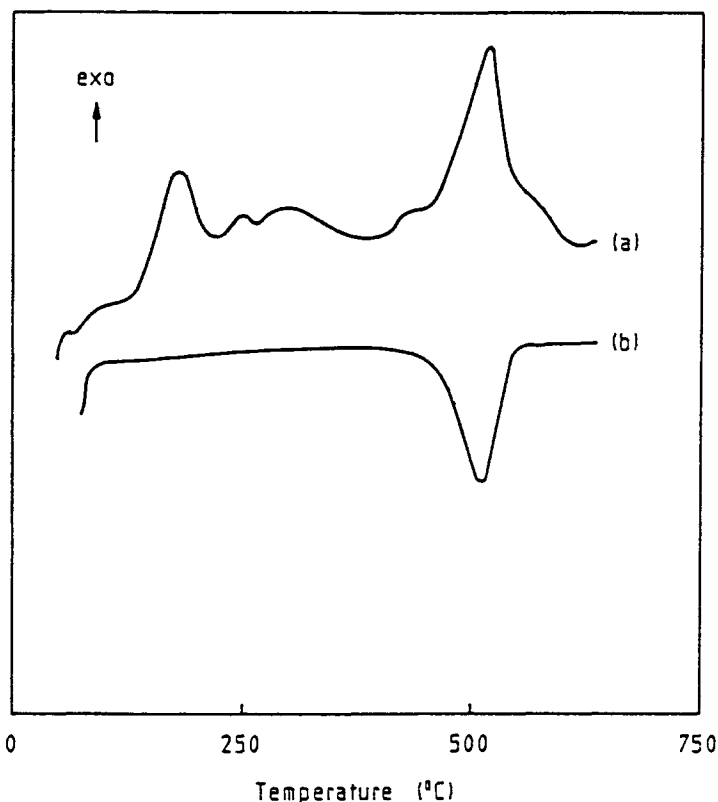


Fig. 5. DSC curves in nitrogen, 10°C/min, of (a) unwashed MnO<sub>2</sub> cure paste and (b) MnO<sub>2</sub>.

### Adhesion Additive

Chloroform solutions of the filler-free polysulfide polymer were repeatedly extracted with 5% aqueous sodium carbonate to give small quantities of material with infrared spectra virtually identical with those of commercial phenolic resins. Use of sodium hydroxide led to a mixed extract of polysulfide and phenolic resins. Control experiments with LP-32 containing 6% Methylon 9484 afforded only 10–15% recovery of resin on extraction with sodium carbonate.

Gated-decoupled <sup>13</sup>C-NMR spectra of the filler-free prepolymers showed a series of unassigned peaks in the 110–160 ppm range arising from aromatic carbons of the phenolic resin. For the polymer bases of the manganese dioxide cured series the major resin peaks were located at 156.1, 143.3, 127.6, and 113.8 ppm with other signals at 133.5, 133.0, 128.3, 127.3, 126.8, 117.7, 117.4, 114.5, and 111.2 ppm; the aliphatic carbons were obscured by the polysulfide spectrum. The equivalent dichromate series polymer base exhibited its principal peaks at 156.2, 143.4, 128.9, 128.1, 127.6, 125.2, and 113.8 ppm with additional peaks at 137.3, 134.2, 133.6, 133.1, 128.4, 127.3, 126.8, 117.5, 117.4, 115.2, 114.5, and 111.2 ppm. Methylon 9484, used for comparison purposes, afforded a complex spectrum with major aromatic carbon signals at 153.3, 137.0, 134.0, 133.5, 133.2, 129.5, 128.7, 127.1, 118.0, 117.7, 115.7, 114.7, and 111.5 ppm together with aliphatic carbon peaks at 34.0, 39.0, and 59–69 ppm. Phenolic resin contents



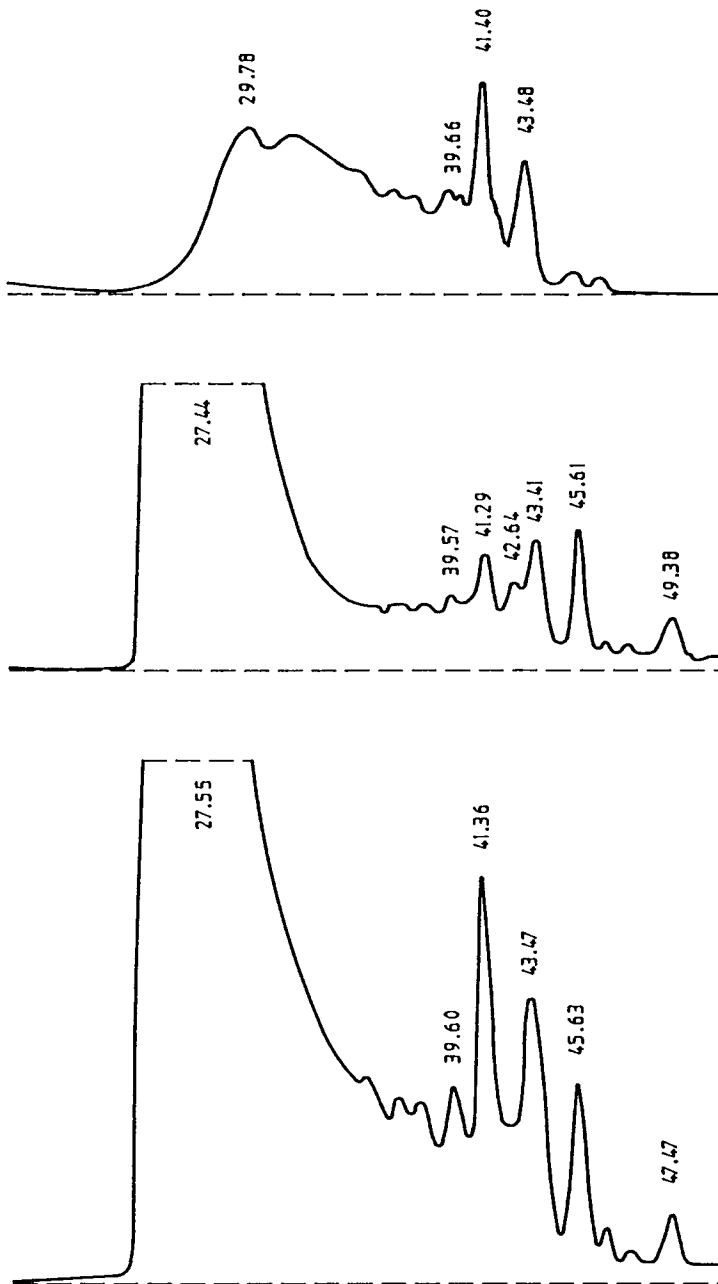


Fig. 6. Size exclusion chromatograms: (top) methylon resin; (center) liquid polymer from a commercial MnO<sub>2</sub>-cured sealant system; (bottom) commercial liquid polymer with 3% added methylon resin.

of filler-free polymer base formulations were determined from peak intensities of the gated-decoupled <sup>13</sup>C spectra after application of suitable line broadening (5 Hz).

TABLE IV  
Effect of Aging at 70°C on the Thiol Content of Polysulfide Liquid  
Polymers Containing Phenolic Resin Adhesion Additive

Exposure time (h)	Thiol content (%)				
	LP-32 70°C	LP-32 + resin <sup>a</sup> (4.8%)		Commercial polysulfide <sup>b</sup> 70°C	Commercial polysulfide <sup>b</sup> + resin <sup>a</sup> (2.3%) 70°C
		70°C	25°C		
0	1.64	1.63	1.63	1.87	1.91
18	1.67	1.65	1.65	1.76	1.61
48	1.72	1.59	1.67	1.61	1.45
72	1.72	1.67	1.72	1.56	1.40
168	1.75	1.62	1.73	1.26	1.09

<sup>a</sup> Methylon 9484.

<sup>b</sup> Filler-free polymer base of a manganese dioxide-cured sealant.

Size exclusion chromatography (SEC) studies were conducted on LP-32, Methylon 9484, LP-32 containing 4.8% added Methylon 9484, and the polysulfide prepolymer from a manganese dioxide-cured sealant both alone and with 2.3% added Methylon 9484. All were examined using four Waters microstyrigel columns (nominal porosity  $2 \times 500\text{A}$  and  $2 \times 100\text{A}$ ) with stabilized THF as solvent and the UV detector operated at 290 nm.

### Analysis for Mn(IV), Cr(VI), and Thiol Content

#### *Manganese IV Content*

The method suggested by Riedel-de Haën<sup>14</sup> was modified by changing the dispersion agent from an aqueous medium to acetone which dissolved the carrier oil. The solids were separated by centrifugation, taken up in phosphoric acid and the Mn IV determined by titration of iodine liberated through the addition of potassium iodide and disodium hydrogen phosphate.

#### *Chromium VI Content*

A solution of the dichromate in 1N sulfuric acid was obtained by dispersing the cure paste in the acid with stirring and ultrasonic shaking. Fillers were removed by centrifugation and the resulting solutions were assayed spectrophotometrically<sup>15</sup> by measuring absorbance at 450 nm or through modifications to two methods described by Vogel. In the procedure involving titration with ferrous ammonium sulfate,<sup>16a</sup> 1,10-phenanthroline was used as the indicator while the potentiometric titration<sup>16b</sup> was undertaken using a platinum and calomel electrode and measurements were made with a digital voltmeter reading to 0.001 V.

### Thiol Content of Liquid Polymers

Both the infrared procedure<sup>17</sup> and the potentiometric technique developed by Thiokol Corporation<sup>2</sup> gave self-consistent results but the following approach

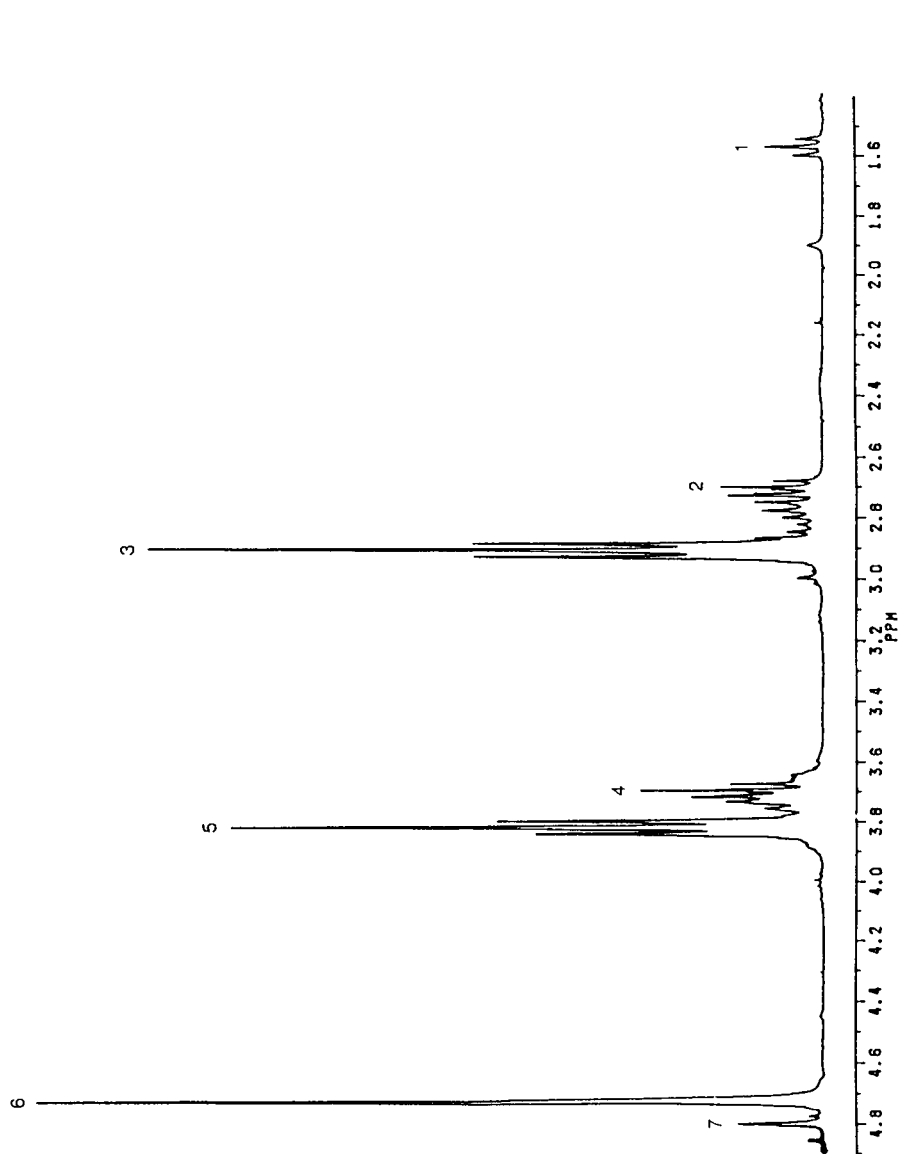


Fig. 7.  $^1\text{H-NMR}$  spectrum of LP-3 with assignments as follows: (1)  $\text{SH}$ ; (2)  $\text{CH}_2\text{SH}$ ; (3)  $-\text{OCH}_2\text{CH}_2\text{SS}-$ ; (4)  $-\text{OCH}_2\text{CH}_2\text{SH}$ ; (5)  $\text{OCH}_2\text{CH}_2\text{SS}-$ ; (6)  $-\text{OCH}_2\text{O}-$ ; (7)  $-\text{OCH}_2\text{OCH}_2\text{O}-$ .

using  $^{13}\text{C}$ -NMR spectroscopy was preferred. The gated-decoupled spectrum of the liquid polymer in  $\text{CDCl}_3$  shows a well-separated peak for the  $\text{CH}_2\text{SH}$  carbon around 24 ppm. The thiol content is obtained from the ratio of the intensity of this peak relative to the summed intensities of all peaks in the spectrum after suitable line broadening (3–5 Hz) and results are in excellent agreement with those from the alternative techniques.

### Cure Rate Studies

LP-32 (3 g) was separately mixed with pastes of manganese dioxide and Cerechlor AS52 (1 : 1 w/w, 0.18 g) containing 0%, 2%, and 4% of added sodium stearate. Cure rates were followed by monitoring hardness during the development of cure and were practically identical for all three mixes. After 4 days all sealants had Rex A hardness readings of 32.

## RESULTS AND DISCUSSION

### General Separation Procedures

Sequential physical and chemical processes were evaluated to provide indicative compositions of commercial aircraft sealants of various viscosities (A or B Class), application times and curing systems. These processes, which were logically premised upon available sealant compounding data, were subsequently refined and the resulting separation procedures are depicted in Figures 1 and 2. Although the same procedure was applicable to the polymer base of all sealants regardless of the associated curative, selective techniques were necessary for the cure pastes and depended on the type of inorganic oxidant present. Although reasonable estimates of the proportions of most components could be obtained by these approaches, for reasons to be discussed the analysis of curing agents must be conducted separately. The compositions of the various polysulfide sealants determined by these means are listed in Tables I–III. Specific aspects of the separation techniques are considered below.

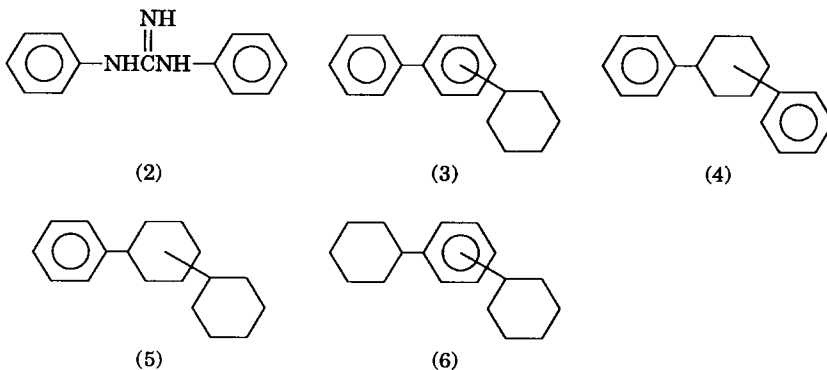
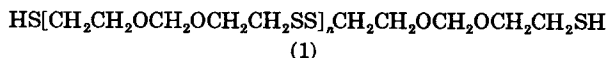
#### *Removal of Solvent*

Volatile components from both the polymer bases and the cure pastes were effectively removed under reduced pressure using a vacuum line and collected using in-line traps. To avoid degradation reactions, temperatures were generally kept below  $60^\circ\text{C}$ . Complete removal of volatiles was therefore often a protracted process, particularly with dichromate cure pastes which contain the higher boiling dipolar solvents dimethylformamide (DMF) or dimethylacetamide (DMA). At temperatures in excess of  $100^\circ\text{C}$  the dichromate appeared to react with DMF (or DMA) and significant quantities of chromium trioxide were produced.

#### *Cure Pastes: Soluble Components*

The fillers and curing agent of the manganese dioxide-based cure pastes were readily separated from the dispersant by solvent treatment. Straightforward chemical manipulations allowed isolation of the cure rate activators diphenyl-

guanidine (2) and sodium stearate together with the dispersing oil which was identified by spectroscopic means as a complex mixture of hydrogenated terphenyls, for example (3)-(6). For the dichromate-based curing systems the oxidant was readily separated from the distillation residue by aqueous extraction and the cations were identified both by X-ray fluorescence and by qualitative analysis:



#### *Analysis of Cure Paste Fillers by Thermal Techniques*

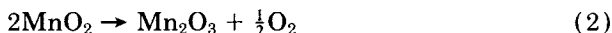
After the determination of volatiles and extractables, the residual solids were examined first by XRD which indicated the absence of calcium carbonate, and then by thermal analysis to estimate the relative amounts of carbon and clay present. The thermogravimetric procedure is illustrated in Figure 3. The sample was heated under nitrogen to 650°C and when weight loss had stabilized air was admitted and the carbon estimated by combustion. In the example shown, the weight loss of 13–14% is attributed to the dehydroxylation of the clay in the dichromate cure paste and corresponds to the similar losses for kaolinites,<sup>18</sup> although at a slightly lower temperature, 450–650°C. The small (2–3%) loss on combustion was due to the carbon black colorant present, and the clay was confirmed by the identification of both silicon and aluminium in the residue.

The vigor of ignition and combustion of carbons can vary widely depending on the source and pretreatment<sup>19,20</sup> and in the case of a high proportion of an active carbon it might be desirable to lower the temperature before air is admitted to prevent sputtering and mass loss.<sup>19</sup> Weight changes due to reactions other than dehydroxylation or combustion would need to be investigated through analysis of the residue after combustion.

It is important that the oxidants are thoroughly removed by acid extraction before thermogravimetric analysis is attempted. Swaine<sup>20</sup> considered the possibility of carbon combustion being affected by mineralization or catalyzed by specific metal ions. It is probable that this is the explanation for the premature oxidation of incompletely washed fillers from a dichromate cure paste, which was already colorless by 550°C and lost no further weight when air was admitted.

The promotion of oxidation in the unwashed material is shown in the DSC curves in air (Fig. 4), where it can be seen that oxidation precedes dehydroxylation, although it follows it in the well-washed carbon/clay mixture. It appears that there is sufficient oxygen in the thermobalance to oxidize small amounts of carbon if catalysis is efficient.

The fillers from pastes containing manganese dioxide give uninterpretable results when acid digestion is incomplete. Figure 5 shows the DSC curve, under nitrogen, of such a material. It can be seen that the reaction is complex and extensively exothermic. The thermogravimetric curves in either air or nitrogen are similarly complex and several reactions could contribute to this. Manganese dioxide is unstable in this temperature range, decomposing as in eq. (2) from 530°C in air and at lower temperatures in oxygen-deficient conditions<sup>21</sup>:



It could be expected that the oxygen so generated would react with the carbon to compound the weight loss, particularly if catalytic amounts of manganese ions are absorbed on the carbon as a result of the digestion. Consequently, the reaction is exothermic rather than endothermic (Fig. 5). The reaction is exothermic from quite low temperatures, however, and to explain this it seems likely that extraction, digestion, and drying processes in the pretreatment have partially "activated" the manganese dioxide, in which case the oxidative capacity and weight loss of the dioxide would be unpredictable.<sup>22</sup>

It is concluded that thermogravimetry is a useful tool for analysis of carbon black in the absence of oxidative inorganic fillers. DSC is needed to ensure that this condition has been achieved.

#### *Analysis of Fillers from the Base Polymer*

The fillers were readily separated from the polysulfide prepolymer and adhesion additive by treatment with dichloromethane. In each case the filler was predominantly calcium carbonate; treatment with hydrochloric acid left less than 3% of insoluble material, some of which was shown by extraction with chloroform to be virtually elastomeric polysulfide. High molecular weight species of low solubility in common organic solvents separate from the polysulfide blend on centrifugation, and this would account for contamination of the filler by polysulfide. Analysis of the solvent-washed residues indicated that silicon, aluminum, and iron were present in the acid-insoluble component from the fillers associated with dichromate cures whereas titanium was the major component of the equivalent material from the manganese dioxide systems. These observations suggest the presence of small quantities of calcined clay and titanium dioxide, respectively. Additional evidence for the presence of titanium dioxide in manganese dioxide-cured sealants has been provided by electron microscopy, which clearly reveals particles of this material in the cured sealant matrix.

#### *Adhesion Additive*

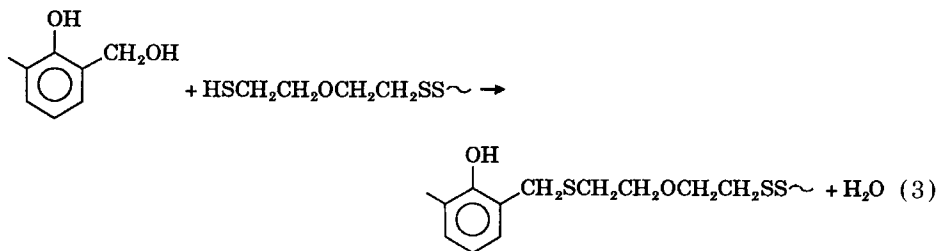
Although both phenolic resins and silanes are commonly used to promote adhesion of polysulfide sealants,<sup>3,5-7</sup> for aircraft applications the phenolic resins

are preferred as they provide better adhesion to airframe metals, have superior fuel resistance, and are more compatible with the reinforcing fillers. This was verified by examination of the NMR spectra of the filler-free polysulfide components. Weak aromatic signals were evident in the 6.6–7.3 ppm region of the  $^1\text{H}$ -NMR spectrum while the  $^{13}\text{C}$  spectrum displayed a complex series of aromatic signals between 113 and 156 ppm, characteristic of disubstituted phenols and well separated from the remainder of the spectrum. The adhesion additives from both types of polymer bases afforded essentially equivalent spectra. A representative phenolic resin, Methylon 9484, while different from the materials used in the formulations, exhibited many similar spectral features. The less diagnostic infrared spectra of all three resins were indistinguishable. A reasonable estimate of the phenolic resin content in the filler-free prepolymers was obtained from the peak intensities of the gated-decoupled spectra, usually after repeated scans to intensify the signals of the resin. After judicious line broadening,<sup>23</sup> summation of the intensities of the aromatic signals (which represent six of approximately eight carbons per repeat unit) relative to the total intensities of the polysulfide resonances provides a simple, convenient determination of the level of adhesion additive present in the formulation. By this means it was established that the phenolic resin contents of the polymer bases of dichromate systems was 7.5% whereas for manganese dioxide cured systems the level was near 4%.

Attempts to isolate the phenolic resins by alkaline extraction were unsatisfactory since, even with a weak base such as sodium carbonate, some polysulfide was obtained together with the adhesion additive. Moreover, control experiments with LP-32 and added phenolic resin gave very poor recovery of the resin by base extraction presumably due to the poor water solubility of the higher molecular weight phenolates.

An alternative means for examining the degree of incorporation of phenolic resin was by use of size exclusion chromatography (SEC). Methylon 9484 afforded a typical chromatogram<sup>24</sup> with a broad peak ( $R_t$  about 30 min) corresponding to the high molecular weight fraction together with two well-separated intense peaks at  $R_t$  41 and 43 min ascribed to low MW species (Fig. 6). Under similar conditions the polysulfide LP-32 was characterized by a major peak (> 98%) of  $R_t$  28 min and a series of minor peaks at  $R_t$  37, 39, 44, and 50 min. Examination of LP-32 with 4.8% added Methylon 9484 clearly showed new peaks at  $R_t$  41 and 43 min corresponding to the phenolic resin. Application of this technique to the filler-free commercial polysulfide prepolymers corresponding to both types of curing system also revealed peaks at  $R_t$  41 and 43 min, which were substantially increased by addition of further Methylon 9484 (Fig. 6). Although this technique readily identifies the presence of phenolic resin and allows subjective assessments of the relative proportions present (for example, the higher loading in the dichromate polymer base), it is not particularly suitable for accurate estimations. Interference from the low molecular weight tail of the polysulfide introduces base line errors while the use of a reference phenolic resin different to that in the formulations adds to the difficulties.

At elevated temperatures, phenolic resins can react with thiol compounds and this has been exploited<sup>3,5</sup> in endeavours to modify the properties of polysulfide sealants.



The likelihood of a similar reaction occurring during long term storage therefore has been of concern. The above samples of LP-32 and filler-free polysulfide together with those containing added Methylon 9484 were aged at 70°C for 168 h and reexamined by SEC and NMR. No indication of any interaction could be detected. Concurrently all were periodically monitored for changes in thiol concentration. Although the commercial polysulfide appears to undergo partial curing, the presence of additional phenolic resin caused only a marginal decrease in thiol content under reaction conditions which are particularly severe in the context of long-term aging (Table IV). Interactions of the type shown in eq. (3) are therefore considered to have no significant influence on the storage of polysulfide sealants at ambient temperatures.

### Cured Sealants

Little information can be obtained about the composition of cured polysulfide sealants without resorting to degradative procedures. Heating in acetone yields 6–7% of extractable material, which was shown to be principally uncured polysulfide prepolymer together with either hydrogenated terphenyl or DMA/DMF depending on the curing system. Chemical degradation can be accomplished by application of the thiol–disulfide interchange reaction. A 5–10% solution of thiophenol or thiophenolate salt in a hydrocarbon solvent rapidly degrades the sealant to soluble low molecular weight species.<sup>25</sup> The residue of fillers, unreacted curing agent and inorganic curing products can be analyzed, as described earlier, to indicate the type of curing system used.

### Specific Analyses

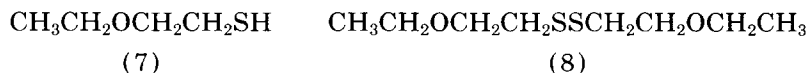
#### *Thiol Content of Polysulfide Polymer*

Knowledge of the thiol group concentration in the polysulfide prepolymer is necessary both for characterization purposes and for evaluation of the curing reaction. The potentiometric procedure, ASTM D1323-62, was unsuitable due to the limited solubility of the prepolymer in the recommended solvent mixture. An alternative potentiometric method developed by the Thiokol Corp.<sup>2</sup> did, however, give satisfactory results but required the unpleasant solvent system of benzene–pyridine. Attempts to replace benzene by toluene led to inconsistent results presumably due to side reactions between iodine and toluene. The infrared procedure of Davidson and Mathys<sup>17</sup> was shown to be particularly convenient for determining thiol contents on samples which had been separated from the fillers, but this method can be affected by interference bands from other materials. For example, solvents such as toluene and ethyl methyl ketone which are commonly used in prepolymer formulations (particularly the A-class



sealants) exhibit overtone bands in the 2550–2700  $\text{cm}^{-1}$  range. Of these the band arising from toluene is the most intense. In order to avoid interference with the SH stretching vibration at 2588  $\text{cm}^{-1}$  and the reference polysulfide combination peak at 2645  $\text{cm}^{-1}$ , it is essential to remove any such solvents prior to measurement. Additionally, sulfenothioic acids (hydrodisulfides) may possibly be present in liquid polymers or be produced during reactions. Available data indicates that the SS–H band could also lead to complications since absorptions of these compounds are shifted only 50  $\text{cm}^{-1}$  to higher wavenumbers relative to the equivalent thiol.<sup>26</sup>

These problems can be overcome by using resonance intensities of the gated-decoupled  $^{13}\text{C}$ -NMR spectrum in a similar manner to that for estimation of the phenolic resin component. The  $\text{CH}_2\text{SH}$  peak at 24 ppm is well separated from the remainder of the spectrum, and, after suitable line broadening is introduced, the technique provides results which correlate well with other methods but is simple and avoids interferences. It should be noted that the pmr spectrum cannot be used as effectively in this manner. Spectra of the model compounds (7) and (8) indicate that the  $\text{CH}_2\text{SH}$  methylene peak (2.68 ppm) is nearly coincident with the  $\text{CH}_2\text{SS}$  peak (2.74 ppm):



The thiol SH in (7), however, appears as a triplet at 1.60 ppm, and since this chemical shift is well removed from those of the principal polysulfide peaks, opportunity for further analysis was perceived. The spectrum of the liquid polymer LP-3, which has a relatively high thiol content (approx. 6%), showed a well-defined triplet centered at 1.63 ppm which is assigned to the SH group (Fig. 7). Decoupling experiments then permitted identification of signals due to the terminal groups in the polymer. The SH triplet collapsed to a singlet upon irradiation of a group of small peaks centered at 2.70 ppm while the reverse decoupling resulted in the formation of a triplet at 2.70 ppm. Irradiation of the multiplet centered at 3.68 ppm generated a doublet centered at 2.70 ppm. These results conclusively establish that the methylenes of the  $\text{CH}_2\text{SH}$  and  $\text{OCH}_2\text{CH}_2\text{SH}$  terminals are centered at 2.70 and 3.68 ppm, respectively. Neither is sufficiently separated from the main peaks to allow analysis. Integration of the SH peak relative to the methylenes in the spectrum and use of the generalized polysulfide formula (1) enables the thiol content to be estimated to a reasonable approximation. For samples with lower thiol contents (1–2%), it would be necessary to undertake several scans to increase signal intensity and improve the reliability of the peak integrals. Thiol contents of 6.3, 5.7, and 5.2% were obtained from the same sample of LP-3 using infrared,  $^{13}\text{C}$ -NMR and  $^1\text{H}$ -NMR, respectively. Of these results, that from  $^1\text{H}$ -NMR is considered to be least precise while the infrared value may include a small contribution from hydrodisulfide.

#### *Manganese(IV) and Chromium(VI) Content of Cure Pastes*

Physical separation of the inorganic oxidants is tedious and is valuable principally as a means of identifying the materials employed. In the case of man-

ganese dioxide, the total acid soluble material obtained from the cure paste residues after removal of the organic compounds exceeded the quantity of manganese dioxide determined by analytical methods. The nature of the extra material was not pursued. The most satisfactory method for assessing Mn(IV) was based on a procedure outlined by Riedel-de Haën.<sup>14</sup> As the compounded cure paste could not be satisfactorily dispersed in the recommended aqueous medium, the curing agent was suspended in acetone, which allowed ready separation of the insoluble solids. Chromium(VI) was conveniently and reproducibly assayed by minor modifications to standard spectrophotometric or volumetric titration procedures,<sup>15,16</sup> which were considered necessary to meet the specific requirements imposed by the compounded cure paste.

### Discussion of Formulations

The compositions of the polymer bases shown in Table I indicate differences in compounding approach. For example, the A class (brushable) formulations of the dichromate series are developed by inclusion of solvent at the expense of the filler whereas in the manganese dioxide cases the polysulfide levels are reduced. Some observations on the blends of liquid polymers are possible from consideration of thiol contents. Within the manganese-dioxide-cured group these are practically uniform, which implies that the same mixture is used in each case. The relatively high thiol content also points to the use of some LP-3 in this blend. The prepolymer for the dichromate-cured sealants is clearly different. Although there are minor variations between the thiol levels of the A and B classes, they are insufficient to substantiate the use of specific blends for each class.

Considerably less adhesive additive is present in the manganese-dioxide-based systems. This is ascribed to the weak acidity of the phenolic resins, which are known<sup>7,27</sup> to retard the base catalyzed manganese dioxide cures. It is therefore likely that only the minimum proportion consistent with obtaining adequate adhesion is incorporated into the sealant formulation. Another interesting comparison between the polymer bases concerns the relative basicities. The pH of mixtures derived from compounded prepolymer (30 g) and water (400 mL) were 8.1 for the manganese dioxide system prepolymer and 7.1 for the dichromate equivalent. Separate experiments showed that the fillers from each produced aqueous extracts of similar pH. The lower pH of the polymer base in the dichromate series is considered to result from the higher proportion of phenolic resin in the formulation since no basic material could be isolated by acid extraction.

One method of improving thermal stability of polysulfide sealants, particularly those cured by lead dioxide, is through addition of small quantities of sulfur to the formulation.<sup>1-5</sup> Techniques to identify the presence of sulfur in the polymer base have been developed and will be reported subsequently. No evidence for such an addition was noted in the sealants used in the present investigation.

Small quantities of water were found in both the polymer base and cure paste of the manganese dioxide sealants. Whether adventitious or deliberate, the presence of water is important as it appears to participate in the curing reaction.<sup>9</sup>

Approaches to modification of cure rates varied with the type of curative (Tables II and III). Rates of manganese dioxide cures were enhanced by increasing the proportion of diphenylguanidine while retaining the same concentration of curative. The levels of accelerator used with the A classes of these sealants reflect the lower amount of polysulfide in the polymer base. The role of sodium stearate is less clear. Although it has been cited as a cure rate enhancer,<sup>3</sup> this was not borne out in curing studies using LP-32. Curing behavior with laboratory prepared sodium stearate–manganese dioxide mixtures was markedly influenced by the activity of the oxidant. With highly active manganese dioxide, addition of sodium stearate had little effect on rate of cure. Greater discrimination was possible, however, with a less active grade (Riedel-de Haën, Type FA) for which it was found that the presence of sodium stearate inhibited curing. It is considered that sodium stearate may be used in formulations to partially offset the effect of diphenylguanidine and allow minor adjustments to cure rate and application time. With the dichromate systems, rate enhancements were achieved both by increasing the proportion of calcium dichromate and also by introducing magnesium dichromate as a cocurative. The percentage of Cr(VI) in the cure pastes was also found by titration to be less than would be expected if all calcium and magnesium was in the dichromate form. Either some reduction of dichromate could have occurred or, more probably, the reagents used were slightly impure.

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