

Water Immersion of Polysulfide Sealants. II. An Interpretation of the Influence of Curing Systems on Water Resistance*

PETER J. HANHELA, ROBERT H. E. HUANG, D. BRENTON
PAUL,[†] and THEODORE E. F. SYMES, *Department of Defence,
Defence Science and Technology Organisation, Materials Research
Laboratories, P.O. Box 50, Ascot Vale, Victoria, Australia 3032*

Synopsis

Dichromate cured polysulfide sealants have superior resistance to swelling in hot water than those cured with manganese dioxide and examinations to identify the reasons for this difference were undertaken. The commercial sealants PR-1422, PR-1750, and Pro-Seal 899 were shown to contain similar types and loading of fillers. Crosslink densities were compared through a procedure involving an oscillating disc cure meter modified to accommodate mobile mixtures. No relationship between stability and crosslinking was observed. Formation of large voids in MnO₂-cured sealants after prolonged immersion at 70–90°C, suggests the formation of a water-soluble acid which then reacts with the CaCO₃ filler, and this was supported by pH measurements. The acid was shown to arise through autoxidation of formal groups in the polysulfide, and this process can be suppressed by radical scavengers (including ammonium dichromate). When PR-1750 was examined under nitrogen or with carbon black as filler, a similar time–swell curve to that of PR-1422 was produced. It was concluded that abnormal swell does not result simply from autoxidation: a filler capable of reacting with the acid must also be present.

INTRODUCTION

The use of polysulfide sealants in the integral water tanks of the environmental control system in some military aircraft constitutes one of the few examples in which sealants are exposed to hot water for long periods. An earlier study designed to identify the most satisfactory sealants for this purpose established that the nature of the curing system had a dominant influence on the performance of polysulfides in hot water.¹ Examination of both commercial and laboratory formulated sealants revealed that dichromate-cured materials exhibit marginally greater swell at 25°C than those cured with manganese dioxide. At 50–90°C, however, this trend is reversed. Dichromate-cured sealants display a typical saturation type time–swell relationship whereas that of the manganese dioxide cured products is linear. With time the manganese-dioxide-cured sealants become so swollen that they no longer perform a sealing function due to excessive permeability and loss of adhesion to metal substrates. These effects become significant when volume

*Presented at Adhesives, Sealants and Encapsulants 85 (Network Events), London, U.K., November 1985.

[†]To whom all correspondence should be addressed.

swell approaches 100% and are associated with the development of large voids in the sealant.

The underlying reasons for the superior stability of the dichromate-cured sealants in hot water were not readily evident. Possible contributing factors such as crosslink density, filler type and loading, and chemical degradation have now been considered in an endeavor to rationalize the observed stability differences.

EXPERIMENTAL

General

Atomic absorption analysis was conducted using a Perkin-Elmer Model 403 double beam instrument, X-ray fluorescence with a Philips Model PW1400 sequential spectrometer and a Perkin-Elmer 580B double beam, ratio recording infrared spectrometer was used to determine thiol contents of the polysulfide polymers. Hardness of cured sealants was monitored with a Rex indenter model 1700, type A. A Monsanto oscillating disc cure meter Model LSD, modified to the capabilities of the R900 model was used to follow the sealant curing processes. Number average molecular weights were determined with a Hewlett Packard 302B vapor pressure osmometer.

Materials and Reagents

a. Commercial sealants. The two part polysulfide sealants PR-1750 B-2 and B-6, PR-1422 B-2 (Products Research Corporation), and Pro-Seal 899 B-2 and B-6 (Essex Chemical Corporation, Coast Pro-Seal Division) were mixed using a Semco pressure mixer, Model S-1350. The general compositions of these sealants have been indicated previously.¹ Recorded hardnesses of PR-1422 B-2 and PR-1750 B-2 were 66 and 54, respectively.

b. Laboratory formulated sealants. The materials used for such preparations have been described elsewhere.¹ The unfilled liquid polysulfides of the commercial materials PR-1422 and PR-1750 were obtained by suspending the polymers in chloroform, and repeatedly centrifuging the mixtures until no further solids settled out, followed by removal of the solvent under reduced pressure. With PR-1750 the product still contained small amounts of finely dispersed filler, and this was removed by prolonged high speed centrifugation. Thiol contents of the liquid polymers as determined by the infrared procedure² were PR-1422, 1.54%; PR-1750, 2.13%; and LP-2, 1.69%. The curing systems were the pastes of PR-1422 and PR-1750, a solution of ammonium dichromate, dimethylformamide (DMF) and water (10:35:1 w/w) and a mixture of manganese dioxide (Riedel de Haën, Type C) in di-2-ethylhexyl phthalate (EHP; 1:1 w/w). The minimum ratios of curing agent to liquid polymer were calculated using standard curing reaction stoichiometry and measured thiol concentrations. Where necessary, adjustments for filler loadings were made. The normal curing conditions were 24 h at 25°C and 50% RH followed by 2 days at 50°C and 1 day at 70°C, although this was varied as appropriate depending on condition of the sealant. In order to optimize the cure, increased proportions of the curing agent were sometimes employed. The following formulations were used to prepare the sealants for volume swell and

pH studies. The mix ratio (w/w) of curing agent to 10 parts of polymer is given in parentheses together with the hardness of the product (Rex A). (a) LP-2/PR-1750 (1.54), hardness 40; (b) LP-2/PR-1422 (1.77), 46; (c) LP-2/MnO₂-EHP (0.69), 42; (d) LP-2/MnO₂-DMF (0.69), 43; (e) LP-2/ammonium dichromate-DMF (2.4), 40; (f) PR-1422 (unfilled)/PR-1422 (1.58), 40; (g) PR-1750 (unfilled)/PR-1750 (1.54), 32; (h) PR-1422 (unfilled)/ammonium dichromate-DMF (1.2), 34; (i) PR-1750 (unfilled)/ammonium dichromate-DMF (1.2), 45; (j) PR-1750 filled with 25% Tintacarb 90 (Australian Carbon Black)/PR-1750 (1.11), 57.

c. Model compounds for hydrolysis experiments. Bis-*n*-pentyl disulfide (70%, b_p(7 mm) 119°C) was prepared from 1-pentanethiol by adaptation of the general oxidative procedure of Price and Stacy.³ An unbranched liquid polysulfide was obtained from 2-mercaptoethyl ether (Aldrich) in a similar manner and formaldehyde di-*n*-butyl acetal (bp 181°C) was synthesized using the method of Vogel.⁴

d. The ferrocene (bis(cyclopentadienyl)iron (Alfa Products)) and 2,4,6-tri-*t*-butylphenol (Aldrich) employed in the autoxidation study were used without further purification. Eldorado Chemical desealer SR-51 was used to depolymerize cured polysulfide sealants.

Solids Content of Liquid Polymers and Sealants

Each liquid polymer was separated from filler as described above. The collected solid deposits were Soxhlet-extracted with chloroform, dried at 70°C and weighed to establish the percentage loading. Examination by atomic absorption, X-ray fluorescence spectroscopy, and qualitative analysis showed that all the fillers were composed primarily of calcium carbonate.

Strips of cured sealant (total weight, 100 g) were added to a solution of SR-51 desealant (500 mL) which had been enhanced by additional thiophenol (10 g), stirred at 50°C for 48 h, cooled, and filtered. The crude inorganic residue was extracted with hot chloroform (3 × 100 mL), dried and analyzed as above.

Volume Swell Measurements (ASTM D471)

Measurements were carried out on the sealants PR-1422/ammonium dichromate, (h), and PR-1750/ammonium dichromate, (i), in both benzene and trichloroethylene at 25°C. The optimum mix ratio, 10 : 1.2 w/w, was selected after assessing the hardness of sealants prepared with component ratios varying from 0.7 to 1.5 parts by weight of the curing system to 10 parts by weight of liquid polymer. Swell measurements were also carried out in distilled water at 90°C using the following sealants: LP-2/PR-1750, (a); PR-1750 (unfilled)/PR-1750, (g); and PR-1750 (25% carbonate black)/PR-1750, (j). PR-1750 B-2 was also examined in the presence and absence of air. Degassing of the sample was achieved over several days using a vacuum line maintained at 5×10^{-3} mm and intermittently the sample vessel was purged with nitrogen. Swell experiments were conducted with sealed vessels containing a nitrogen atmosphere and sufficient were prepared to permit duplicate samplings at each withdrawal.

Assessment of Cure of Sealants with an Oscillating Disc Cure Meter

In normal operation, low viscosity materials such as freshly mixed sealants flow from the sample cavity of the cure meter before the upper and lower dies can be closed. To overcome this problem, the following modification was used.

Dies were constructed which provided a square cavity ($50 \times 50 \times 10$ mm). A reversed configuration to that generally specified for rubber samples was used with the sides of the cavity being formed by the lower die and the upper die acting as a cover plate. A rotor of larger diameter (45 mm) and thickness than is standard with rubber specimens was produced, which necessitated a deeper cavity. With the slow cure time for sealants, this extra thickness would not significantly affect heat transfer rates from the heated dies to the specimens. Radial grooves were machined into the dies and both faces of the rotor to minimize slippage. The cavity was sealed with a Viton O-ring (PTFE was unsatisfactory), but occasional exudation of the sealant mixture past the seal was noted; this effect can lead to variable torque readings in the lower ranges. To permit ready removal of the specimens after curing, the dies and rotor were coated with PTFE before each run. Care was also necessary to ensure that the rotor was centered relative to the cavity to prevent contact with dies. Normal operating conditions were: die temperature, $50 \pm 1^\circ\text{C}$; air pressure, 300 kPa; torque range, 2.8 Nm (25 in. lb); oscillating frequency, 100 Hz and arc angle, 1° . For convenience the torque scale was adjusted to zero at the commencement of each test. A graph of torque vs. time was provided by a chart recorder. Smooth and reproducible curing curves were obtained from which the time to any specific state of crosslinking could be determined. Only minimal air entrapment was noted in the cured specimens, and this was considered to be within expected limits for sealants.

Effect of Sealants and Their Components on pH of Immersion Solutions

Cured sealants, their base polymers and curing systems were immersed in distilled water (190 mL) maintained at 90°C , and at intervals the pH was determined using a meter fitted with a glass and calomel electrode. Stopped Pyrex glass containers, pretreated with boiling distilled water for 2 h, were used to avoid contributions to alkalinity which occur with soda-glass. A control run using distilled water was included to monitor such effects. The following materials were assessed under the above conditions.

a. Cured Sealants. PR-1422 B-2, PR-1750 B-2 and the polysulfides (a)–(g) described under Materials and Reagents were examined as discs (22×5 mm; average weight 2.7–2.9 g).

b. Base Polysulfide Polymers. PR-1422 B-2, filled (5.0 g), PR-1422 B-2, unfilled (3.5 g), PR-1750 B-2, filled (5.0 g), PR-1750 B-2, unfilled (3.2 g), LP-2 (6.0 g) and a mixture of LP-2 (6.0 g) in DMF (0.78 g) were separately immersed. Samples of fresh LP-2 and LP-2 which had been in contact with water at 90°C for 49 days (2.6 g) were each mixed with the ammonium dichromate paste (0.26 g) and cured for 19 h at 25°C and 50% RH followed by 30 h at 70°C . The volume swell of each resulting elastomer was measured after immersion in distilled water at 90°C for 24 days.

c. Curing agents. Manganese dioxide (Riedel-de Haën, Type C) was examined in its unused state and also after either complete or partially complete reaction with an alkyl thiol as follows. The manganese dioxide (2.0 g) and butanethiol (2.4 mL) ($\text{MnO}_2 : \text{SH} = 2 : 1$) were stirred for 4 h; the solid residues were collected by filtration and washed with both ether and acetone to afford incompletely reacted curing agent. The process was repeated with manganese dioxide (1.0 g) and butanethiol (5.0 mL) to obtain the completely reacted material. The cure pastes of PR-1422 B-2 and PR-1750 B-2 (1.0 g) were also made to react with butanethiol (5.0 g), and the residues after removal of volatile components under vacuum were collected for examination. For the pH assessments, these curing agents (0.66 g; equivalent to the quantity of manganese dioxide in the cured sealants above) those of PR-1422 B-2 (0.79 g), PR-1750 B-2 (0.79 g), ammonium dichromate (0.79 g), and the ammonium dichromate–dimethylformamide–water (10 : 35 : 1) mixture (1.8 g) were interacted with water (190 mL).

Interaction of Disulfides and Ethers with Water

Bis-*n*-pentane disulfide, di-*n*-butyl ether, and the unbranched polysulfide obtained by oxidation of 2-mercaptoethyl ether (each 2.0 g) were separately heated at 90°C with distilled water (90 mL). The pH of each aqueous solution was regularly monitored over 14 days.

The pH values of the aqueous solutions produced after separately interacting dioxan, LP-2, or formaldehyde di-*n*-butyl acetal (4) (each 1.0 g) with water (100 mL) at 90°C were monitored over several weeks. Comparative studies were also undertaken with the following materials also present: manganese sulfate, cuprous chloride, cupric chloride, chromium (III) chloride, and ammonium dichromate using ether–oxygen to metal ion ratios of 10,100 and 1000 to 1. Ferrocene and tri-*t*-butylphenol were also used in a 5% m/m ratio to the ether links. Control experiments with these additives in water (100 mL) gave the following pH values: $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.105 g), 4.8; CuCl (0.356 g), 4.8; $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ (0.16 g), 4.3; ferrocene (0.115 g), 6.6 after 3 days, 5.1 after 40 days, 3.6 after 58 days; tri-*t*-butylphenol (0.165 g), 6.2 after 3 days, 5.3 after 58 days.

RESULTS AND DISCUSSION

Effect of Filler Type and Loading

Any rationalization of the disparate swell behavior of polysulfides produced by the different curing agents must include consideration of the type and level of incorporation of fillers, crosslink densities, extraction of components by the swelling agent, and chemical interaction with the swelling medium. Each of these factors was examined using the commercial sealants PR-1750 and ProSeal 899 (manganese dioxide-cured) and PR-1422 (dichromate-cured) and in some instances with laboratory formulations prepared using Thiokol liquid polysulfide polymers.

Addition of fillers to rubbers has long been known to reduce swell, and this is attributed to the lower volume fraction of polymer which is available to the swelling agent.⁵ The swell results reported earlier¹ confirmed the expectation

of greater swelling from sealants without fillers. When immersed in water at 90°C, these products exhibited 50–75% greater swell than their filled counterparts. Treatment of cured sealants with a proprietary desealing solution based on thiophenol⁶ allowed the inorganic solids (filler and reduced curing agent) to be isolated from the crosslinked polysulfide. There was little variation in loading between the sealants with the solid contents (w/w) being PR-1422 B-2, 34.0%; PR-1750 B-2, 41.0%; and Pro-Seal 899 B-2, 40.3%. The fillers, which were isolated from the prepolymers by solvent extraction and centrifugation were mainly comprised of calcium carbonate and the loadings in each prepolymer were: PR-1422 B-2, 29.8% (w/w); PR-1750 B-2, 35.5%; and Pro-Seal 899 B-2, 36.9%. Filler loading was therefore considered unlikely to influence the relative swell performance particularly since the dichromate-cured sealants had the lowest solids content of those examined.

The possibility that prolonged immersion of the sealants in hot water would lead to extraction of essential components was also examined. After 35 days immersion in water at 90°C the mass losses after drying the sealants to constant weight (24 h at 90°C) were: PR-1422 B-2, 2.3%; PR-1750 B-2, 1.6%; PR-1750 B-6, 1.8%. Spectroscopic analysis showed calcium to be the major element extracted into the aqueous solution with concentrations (wt% of polymer) in the range 0.65–0.92% for all sealants. Chromium (0.05–0.1%) was detected in the PR-1422 B-2 extract, and trace quantities of manganese were observed in the solutions in which the PR-1750 and Pro-Seal 899 sealants were immersed. X-ray fluorescence indicated the presence of sulfur-containing compounds in all extracts. These findings did not suggest that extraction of components from the sealants would have any bearing on the swell results.

Comparison of Crosslink Densities

Earlier investigations based on swelling in organic solvents,⁷ and water, together with comparative hardness measurements, indicated that the crosslink density in PR-1750 was higher than that of PR-1422 and that, for the polymer blends studied, dichromate cure systems were more effective than those using manganese dioxide.¹ Although the thiol contents in the polysulfide base polymers can be readily determined (PR-1750, 2.13% SH; PR-1422, 1.54% SH) without details of molecular weight distributions the relative proportions of sidechain thiol groups cannot be reliably gauged. In order to obtain an estimate of this relationship, volume swell data in organic solvents was obtained for the dichromate-cured sealants prepared from the unfilled prepolymers of PR-1422 and PR-1750. Procedures for calculating crosslink densities of network structures through swelling techniques are well documented,^{8–10} but these require knowledge of polymer–solvent interaction parameters. A more convenient approach may be developed from the work of Lorenz and Parks,¹¹ who observed that for peroxide-cured natural rubber a linear relationship existed between crosslink density, $1/2(M_c)$, and the swelling ratio (Q) in benzene. These results were later reviewed by Saville and Watson,¹⁰ who derived a simple expression [eq. (1)] to relate the effective crosslinks $[X]_{\text{chem}}$ with the swelling ratio. In this equation the figure 0.475 allows for the difference between actual and effective crosslinks and the value 11.5 represents the slope of the line (Fig. 2 of Ref. 12) which relates $10^4/2M_c$ and $1/Q^2$.

For two similar elastomers a and b cured by the same system, the ratio of their crosslink densities will be given by eq. (2). Assuming that a linear relationship will also apply for elastomers such as polysulfides, measurement of specific gravity, ρ , and swell will permit ready comparison of crosslink densities:

$$\frac{10[X]_{\text{chem}}}{\rho} = 0.475 \times \frac{11.5}{Q^2} \quad (1)$$

$$\frac{[X_a]_{\text{chem}}}{[X_b]_{\text{chem}}} = \frac{\rho_a Q_b^2}{\rho_b Q_a^2} \quad (2)$$

Satisfactory application of this approach requires that optimally cured materials be used. For the unfilled polysulfide sealants PR-1750 and PR-1422, the effect of varying the stoichiometry was first examined to ensure that appropriate cure ratios were selected (Table I). Swelling was conducted using both benzene and trichloroethylene, and with these solvents equilibrium volume swell was achieved after 48 h. The comparative crosslink densities (Table II) were in good agreement with both solvents and indicate that there are substantially more crosslinking sites present in PR-1750 than in PR-1422.

TABLE I
Effect of Stoichiometry on Cure of Polysulfide Sealants^a

Time (h) ^b	Hardness ^c													
	PR-1422 cure ratio ^d							PR-1750 cure ratio ^d						
	0.7	0.8	0.9	1.0	1.1	1.2	1.5	0.7	0.8	0.9	1.0	1.1	1.2	1.5
15	—	—	—	4	11	16	19	3	25	27	31	34	35	36
20	—	—	3	11	15	18	20	12	31	33	36	39	40	40
39	—	3	11	18	23	25	25	19	40	40	42	43	43	42
62	—	10	15	22	25	26	26	22	41	42	43	44	43	42
118	12	22	21	35	37	39	41	34	51	50	51	52	54	52

^a Fillers removed from polysulfide polymers; cure solution: ammonium dichromate (1.0 g), dimethylformamide (3.5 g), water (0.1 g).

^b For 0–62 h: temperature 25°C, relative humidity 50 ± 5%; for 62–118 h: temperature 70°C.

^c Rex A.

^d Ratio (w/w) of cure mixture to 10 parts of polysulfide.

TABLE II
Crosslink Ratios of Polysulfides by Swelling in Organic Solvents

	Benzene		Trichloroethylene	
	PR-1422	PR-1750	PR-1422	PR-1750
Volume swell (%)	310	220	440	280
Q	2.29	1.47	4.75	3.13
Specific gravity	1.291	1.326	1.291	1.326
$\frac{[X_{1750}]}{[X_{1422}]}$		2.5		2.3

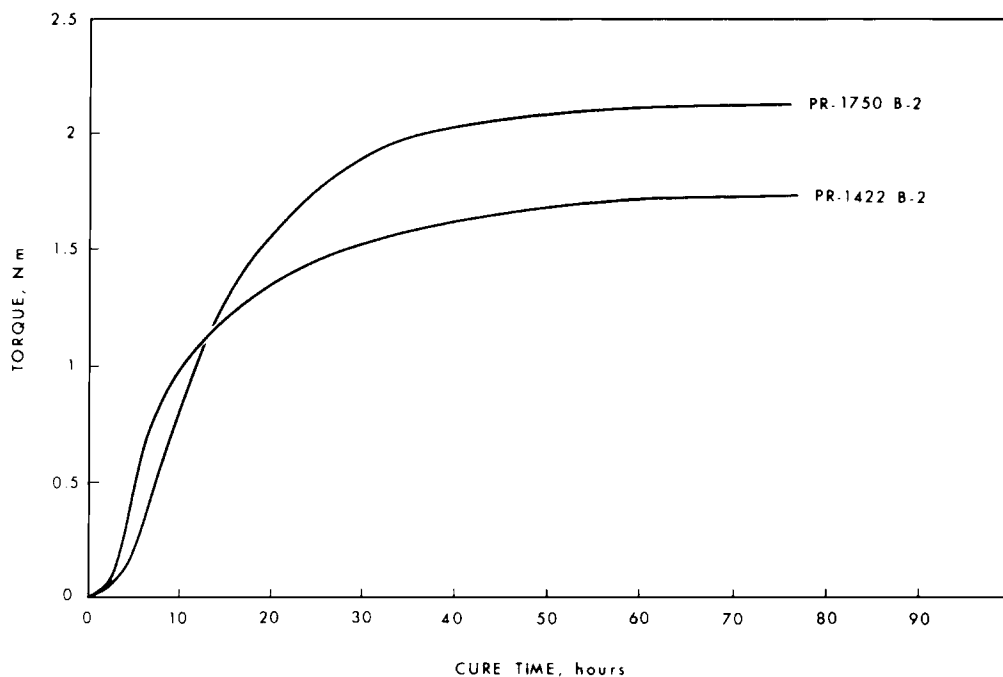


Fig. 1. Comparative curing performances of PR-1422 and PR-1750 using an oscillating disc cure meter.

A new approach to the assessment of crosslink densities of sealants has been developed through use of an oscillating disc cure meter. For solid rubber cure processes this method provides essential information about the rate and degree of vulcanization. Sealant cure mixtures, however, are initially of very low viscosity, and the monitoring of cure requires low torque. Use of a modified die and rotor operated in an inverted position relative to the normal procedure, however, permitted satisfactory assessment of the sealant cure. Preliminary results indicate that this technique can provide similar cure parameters for sealants to those generated for rubbers. The curing curves obtained with PR-1750 B-2 and PR-1422 B-2 at 50°C (Fig. 1) resulted in torque maxima of 2.2 Nm (19.3 in. lb) for PR-1750 and 1.7 Nm (15.5 in. lb) for PR-1422 with the times to achieve 90% crosslinking being 32 and 35.4 h, respectively. Although this supported the relative crosslinking densities inferred from swelling, a detailed comparison could not be drawn since the sealant substrates differed in curing systems and the presence or absence of fillers. These aspects are to be considered further during a survey of the scope of this technique.

Effect of Components on pH of Immersion Solutions

The water swell results obtained with PR-1750 and Pro-Seal 899 are anomalous when compared with the performance of these sealants in organic solvents. The linear time-swell relationships over a prolonged period, the absence of any saturation curves, and the findings that crosslink densities, filler loadings, and extraction of components have no direct influence on this

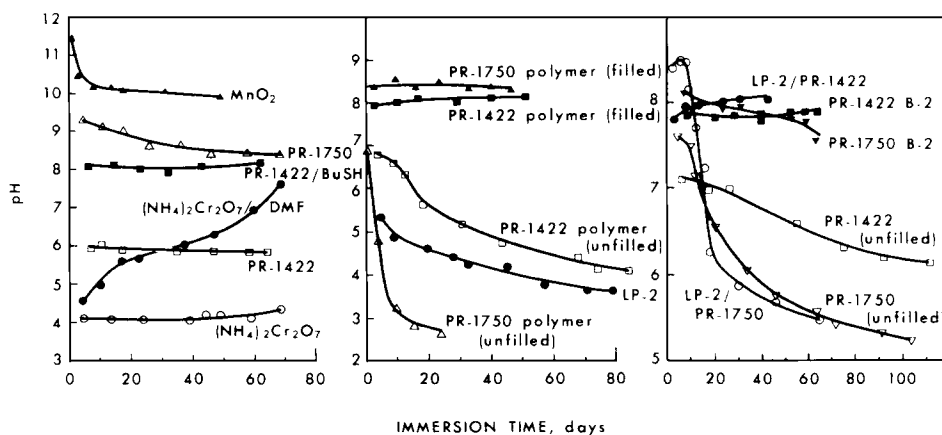
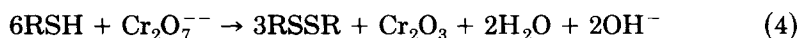


Fig. 2. (a) Effect of curing agents on pH of aqueous immersion medium. (b) Effect of polysulfide liquid polymers on pH of aqueous immersion medium. (c) Effect of cured sealants on pH of aqueous immersion medium.

abnormal behavior leads to the conclusion that polymer degradation could be involved. Moreover, unlike PR-1422, the manganese dioxide-cured sealants PR-1750 and Pro-Seal 899 form pronounced voids after prolonged immersion in water at elevated temperatures. Since this effect could be related to chemical degradation, a rationalization of the void forming process was sought.

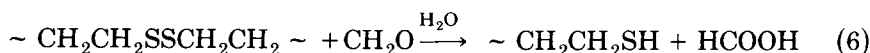
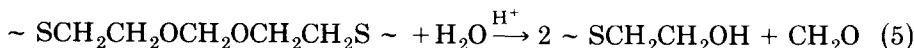
It was considered possible that with the manganese dioxide-cured products an acid solution could be generated which would react with the calcium carbonate filler to release carbon dioxide. The effects of a series of curing agents (unreacted, partially reacted, and fully reacted), base polymers, and cured sealants, on the pH of hot water were therefore surveyed (Fig. 2). The results indicate that manganese dioxide cure pastes are weakly alkaline [Fig. 2(a)]. Moreover, the reacted manganese dioxide and PR-1750 pastes performed in similar fashion to the unreacted reagents, indicating that the extent of cure has little influence on the pH. The curing reaction is considered to be a complex process which eventually leads to the water insoluble manganese(II) oxide¹² [eq. (3)]. The basicity of this system is due to retention on the oxide surface of residual alkali used in its preparation. In contrast, aqueous solutions of ammonium dichromate are acidic. In the presence of dimethylformamide this acidity is reduced over the longer term due to amine formation. The end product of oxidations with dichromate is considered to be the insoluble chromic oxide [eq. (4)]. Removal of the volatile disulfide from a mixture obtained by dichromate oxidation of *n*-butanethiol afforded a residue of reacted curing agent and prolonged immersion of this material in hot water produced only a weakly alkaline solution.



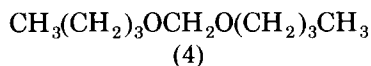
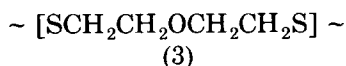
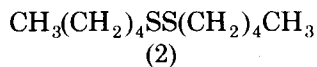
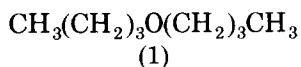
Immersion of polysulfide liquid polymers in water at 90°C slowly generates acidic solutions [Fig. 2(b)]. With compounded liquid polymers, the carbonate

filler neutralizes any acid which is formed and the pH of the water remains virtually constant at about 8. The results obtained with cured sealants are of particular interest [Fig. 2(c)]. The presence of calcium carbonate again buffers the system, and the water solution becomes very weakly alkaline. With unfilled sealants, however, a difference between manganese dioxide- and dichromate-cured materials is evident. This is exemplified by the results from sealants prepared from LP-2 for which the manganese dioxide-cured products afford an acidic solution whereas the materials cured by dichromate do not. Hence, a parallel exists between this behavior and the stability of the sealants in hot water as assessed by swell measurements.

The susceptibility to hydrolysis of formal groups in polysulfides is recognized¹³ and has been exploited¹⁴ in the preparation of hydroxyl terminated polymers [eq. (5)]. This process, together with the subsequent reaction shown in eq. (6), has been suggested to account for degradation of polysulfide sealants at elevated temperatures.¹⁵ Generation of formic acid in this manner would explain the slow development of acidic solutions after prolonged inter-



actions of the polysulfide polymers and sealants in hot water. Reactions at 90°C between water and the model compounds (1)–(4) confirmed that the ether linkages are prone to produce acid solutions whereas the disulfide groups remain unaffected. After 14 days immersion the aqueous solutions of compounds (1), (2), (3) and (4) afforded pH readings of 3.8, 7.1, 2.1, and 2.7, respectively.



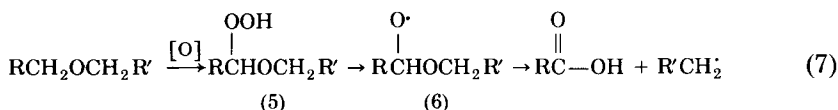
Aqueous hydrolyses would, however, require acid catalysis, and thiol groups would not be expected to promote the process. Impurities in the polysulfide polymers conceivably could account for the presence of strong acid catalysts since during synthesis of the polymers an acidification with mineral acid is performed.¹³ Potentiometric titration of the aqueous extract from a chloroform solution of LP-2, however, established that no water soluble acid was present. An alternative sequence which could lead to a mineral acid catalyst would be aqueous hydrolysis of compounds such as bis-2-chloroethyl formal retained from earlier steps in the polysulfide synthetic scheme. Successive replacements of the water during prolonged interaction with LP-2 at 90°C were conducted to determine whether the observed acidity could result from such residues in the polysulfide polymer. The supernatant liquid was exchanged for distilled water after 49, 63, and 100 days at which times the pH values of the reacted solutions were 4.2, 4.9, and 4.3, respectively. It is

therefore deduced that the acidity results from a chemical process and not the presence of an artifact. Moreover, qualitative analysis of immersion solutions indicated the absence of both hydrochloric and formic acids.¹⁶ Distillation of a solution at atmospheric pressure, however, led to loss of more than 60% of the acidity which suggested that decarboxylation of a carboxylic acid could have occurred.

As these findings eliminated the involvement of mineral acid catalyzed hydrolysis, attention was directed to the possibility of anchimerically assisted processes. Ions of either chromium or manganese will be present during the sealant curing reaction and complexes between these metals and ethers have been reported.¹⁷ The observed discrimination in sealant performance would occur if a hydrolytically susceptible manganese complex was formed. No increase in rate of acid formation was observed, however, during reaction of either LP-2 or formaldehyde di-*n*-butyl acetal (4) with water in the presence of manganous sulfate.

AUTOXIDATION STUDIES

Ethers do not hydrolyze under neutral conditions. Since both the ethers and formal compounds formed acidic solutions with equal facility, hydrolysis is therefore unlikely to initiate the degradation. Production of a carboxylic acid would require an oxidation step, and the susceptibility of ethers to autoxidation is widely recognized.^{18,19} The unstable peroxides which result from such oxidations could participate in a complex series of reactions leading to a variety of products.²⁰ One sequence is shown in eq. (7) in which the peroxide (5) thermally decomposes to an alkoxy radical (6) and subsequent β -scission would result in the production of a carboxylic acid:



In addition, electron abstraction from thioethers by hydroxyl radicals has been reported to generate sulfur radical-cations.²¹ Similar interactions between alkoxy radicals, such as (6), and an alkyl disulfide moiety of the polysulfide would lead to oxidation of methylene groups adjacent to the disulfide bonds.

Many transition metal salts can inhibit autoxidations by intercepting radicals through single electron transfer processes.²⁰ They are also known to catalyze alkylperoxide decompositions and in this context Mn(II) is particularly effective. The formal derivative (4), dioxan, and LP-2 were therefore interacted with water at 90°C in the presence of copper, iron, and chromium salts and the changes in pH of the aqueous solutions were compared with those of reference mixtures without the radical scavengers (Fig. 3). The organic inhibitor, tri-*t*-butylphenol, was also briefly examined. Representative results from a range of additive concentrations are shown for the case of formaldehyde di-*n*-butyl acetal (4). All additives produced an acidic solution in the absence of the substrate which somewhat masked the degree of protection. The aqueous solutions from chromium (III) chloride and ferrous

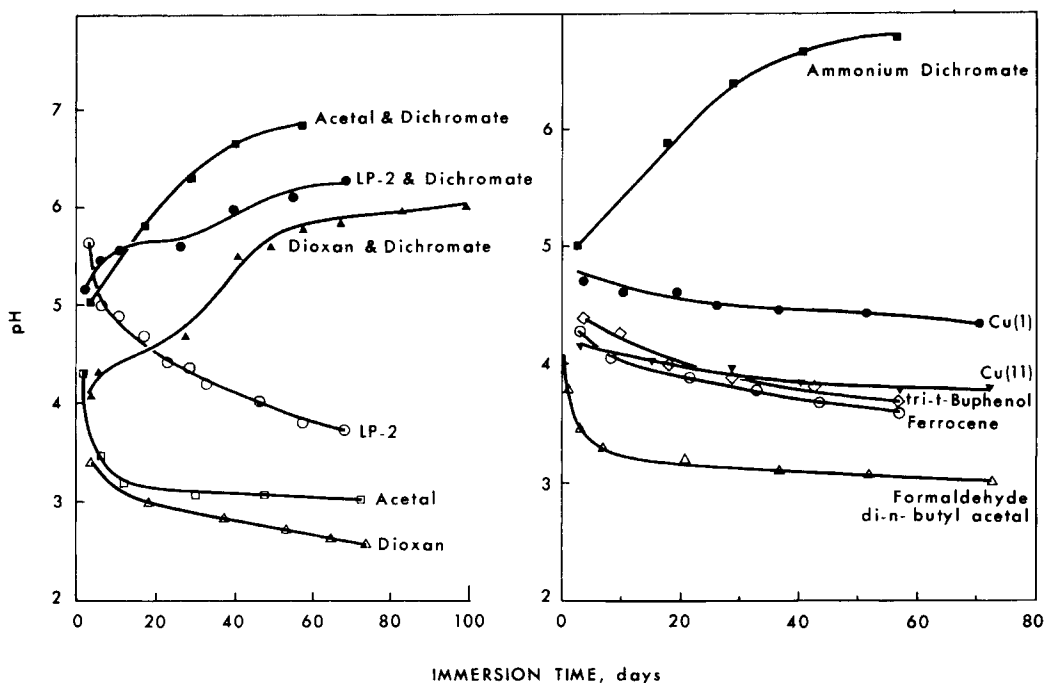


Fig. 3. (a) Effect of ammonium dichromate on pH of mixtures of water with LP-2, dioxan, or formaldehyde di-*n*-butyl acetal. (b) Effect of autoxidation inhibitors on pH of mixture from formaldehyde di-*n*-butyl acetal and water. The pH levels of inhibitor-water mixtures are given in the Experimental Section.

sulfate in fact were of lower pH (2.0–2.4) than those produced from the substrates in water, thereby preventing any conclusions. In addition the low solubility of additives such as ferrocene and tri-*t*-butylphenol limited their effectiveness. A measure of protection was provided with Cu (II), Cu (I), ferrocene, and tri-*t*-butylphenol, and these effects were further confirmed by experiments with cupric chloride, dioxan, and water (0.12:3:100) which produced a steady pH of 4.0 after 75 days whereas the mixture without the radical trapping agent had a pH of 2.4. Of the radical scavengers examined the most effective inhibition of autoxidation was provided by ammonium dichromate, and this was shown with LP-2 as well as the model compounds [Fig. 3(a)]. With this reagent there was a clear trend to increased pH values at longer immersion times, and, although the reasons for this effect are unknown, secondary chemical reactions (e.g., decarboxylation) and slow generation of a different oxidation state of chromium may be involved.

These results support the assertion that acid generation is due to autoxidation but do not indicate the extent of degradation which occurs. A practical assessment was made by preparing sealants from both fresh LP-2 and LP-2 which had been heated with water at 90°C for 49 days. Firm elastomers were produced from both liquid polymers with that from fresh LP-2 having an initial hardness of 43, volume swell (water, 90°C, 24 days) of 90%, and final hardness of 16, whereas that from the water immersed LP-2 gave values of 41, 84%, and 13, respectively. It was also observed that prolonged contact of the

base polymers with hot water led to an increase in viscosity and in the case of the PR-1750 and PR-1422 polymers elastomeric solids resulted. For the LP-2 polymer the thiol content, determined by the infrared technique, dropped from 1.61% before immersion to 0.87% after 37 days contact with water at 90°C. The only difference observed from the subtractive infrared spectra of LP-2 and the immersed LP-2 was a reduction in the SH absorbance at 2545 cm^{-1} , and no distinctive changes were evident between the ^1H NMR spectra of the two samples in CHCl_3 . Two competing processes must therefore occur: an autoxidation leading to chain scission and oxidation of thiol groups which results in chain extension and increase in viscosity. Number average molecular weights by the VPO procedure indicate that thiol oxidation is significant since the \overline{M}_n for LP-2 was increased from an initial value of 1880 to 2510 and 2880 for samples which had been immersed in water at 90°C for 18 and 62 days, respectively.

Confirmation of Degradation Sequence

It is therefore argued that the performance differences which occur following hot water immersion of the differently cured sealants result from two concurrent effects. First, in manganese dioxide-cured sealants an autoxidation takes place which results in the formation of an acidic solution. This process is inhibited with dichromate-cured sealants since the chromium ion acts as a radical scavenger. Second, the extent of chemical degradation is minor and not directly responsible for the abnormal swelling with manganese-dioxide-cured products. It is the further reaction of the acid with the calcium carbonate filler which is considered to lead to the excessive swelling.

These points were separately confirmed by a series of volume swell experiments on manganese dioxide-cured sealants carried out (a) with calcium carbonate filler in the absence of air, (b) with an inert filler in air, and (c) without a filler in air. The results (Fig. 4) justify the above conclusions. Exclusion of air during swell measurements precludes autoxidation and a normal saturated time-swell curve is observed with PR-1750 [Fig. 4(a)]. In accordance with the crosslink density data, the swell produced under these conditions is less than for PR-1422. The time-swell curve of a sealant produced from the PR-1750 base polymer after replacement of the calcium carbonate filler (35% loading) by carbon black (25% loading) is also shown in Figure 4(a). Under these circumstances polymer degradation can occur, but no further interaction is possible. A normal curve results which signifies that involvement of the calcium carbonate filler is necessary to produce the anomalous swelling. This hypothesis was further corroborated by swell data for the unfilled sealants cured with the PR-1750 system. Absolute swell values are high with such sealants due to absence of filler but even though some degradation must occur, a normal time-swell relationship results [Fig. 4(b)].

Two possible explanations of the void forming process may be advanced. Release of carbon dioxide within the sealant would subject the softened matrix to pressures resulting from gas expansion in the hot environment and a cellular-like structure would develop. This suggestion requires that generation of the carbon dioxide occurs faster than its loss from the sealant by diffusion. It consequently follows that all voids must form concurrently with gas

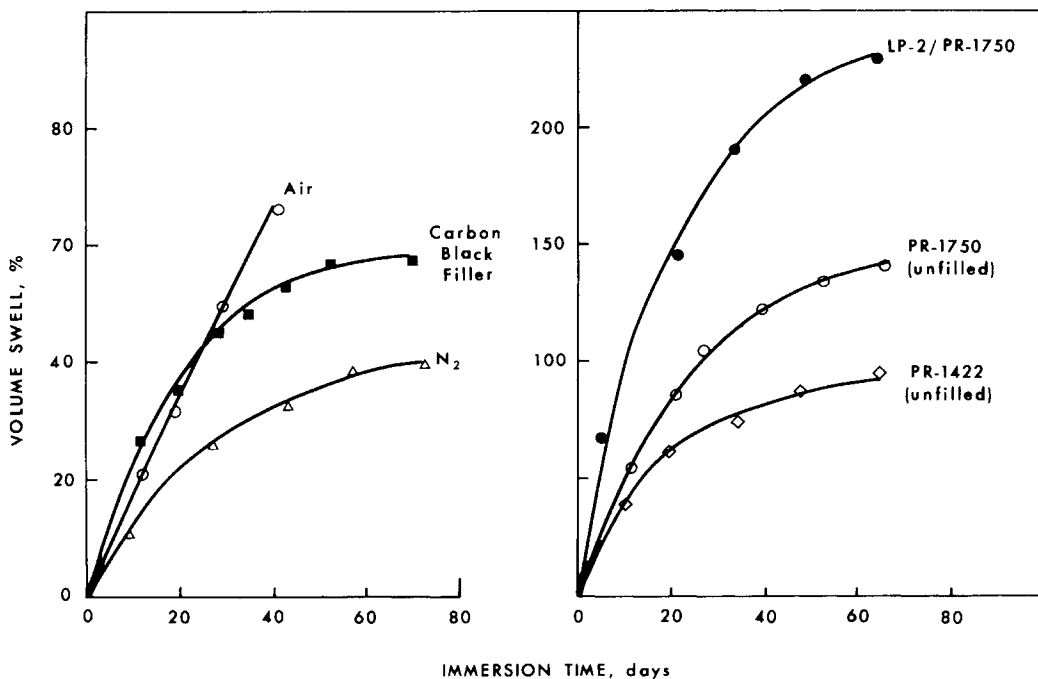


Fig. 4. (a) Influence of air and filler type on volume swell of PR-1750 in water at 90°C. (b) Time-swell curves for the unfilled sealants PR-1750 and LP-2/PR-1750 in water at 90°C.

evolution. In practice, however, large voids were developed only after approximately 3 months immersion, and therefore this mechanism is not considered to be convincing.

Alternatively, it may be envisaged that the interaction between calcium carbonate and the organic acid will produce localized high concentrations of a soluble calcium salt. The sealant could then be considered as a membrane, and swelling by osmosis would ensue. Voids would form in areas where the water-soluble salts had replaced the original filler. The relatively good solubility of calcium salts of aliphatic carboxylic acids supports this proposed rationalization.

Having established that unfilled sealants cured with manganese dioxide do not undergo abnormal swell, and given the earlier finding that the base polymer of PR-1750 has more crosslinking sites than does that of PR-1422, the relative effectiveness of the two curing systems can be assessed. Data generated previously¹ for unfilled sealants in water at 90°C indicates that sealants from PR-1750 and ammonium dichromate exhibit less swelling than those using manganese dioxide. Further, the swell of unfilled PR-1422 is comparable with that from the more highly crosslinked PR-1750. It is therefore inferred that, with the liquid polymer blends studied, dichromate curing systems are more effective than those involving manganese dioxide.

Finally the role of water in these processes is of interest. Normal swell curves are produced from manganese dioxide-cured sealants with organic solvents as the swelling agents, although autoxidation reactions must still operate. It is probable that water acts not only as a swelling agent but also as

a solvent for the carboxylic acid. Moreover, its presence would also be fundamental to the postulated osmotic process.

CONCLUSIONS

These results demonstrate that the significant swell differences which occur between dichromate- and manganese dioxide-cured sealants when immersed in hot water derive from the respective abilities of these sealants to counter autoxidation. Ammonium dichromate performs as an efficient radical scavenger and sealants cured with this system are stable. Manganese dioxide-cured sealants, however, do not exhibit this protection, and acidic degradation products are formed. In itself the autoxidation does not greatly affect swelling, but, if a component is present which is capable of releasing carbon dioxide through reaction with the acidic oxidation products, the normal swelling of the sealant will be augmented most probably by osmosis. An alternative rationalization involving carbonation is considered less plausible. The abnormal swell of manganese dioxide-cured sealants filled with calcium carbonate was explicable in these terms and swell measurements (a) with an inert filler, (b) without fillers, and (c) with calcium carbonate filler under nitrogen confirmed this interpretation.

References

1. P. J. Hanhela, R. H. E. Huang, and D. B. Paul, *Ind. Eng. Chem., Prod. Res. Dev.*, to appear.
2. R. G. Davidson and G. I. Mathys, *Anal. Chim. Acta*, **160**, 197 (1984).
3. C. C. Price and G. W. Stacy, *Org. Synth., Coll. III*, 86 (1955).
4. A. I. Vogel, *J. Chem. Soc.*, **1948**, 616.
5. W. Hofmann, in *Polymer Chemistry of Synthetic Elastomers*, Wiley-Interscience, New York, 1968, Part 1, p. 185.
6. P. J. Hanhela and D. B. Paul, Materials Research Laboratories (Australia), Report MRL-655, 1979.
7. P. J. Hanhela and D. B. Paul, Materials Research Laboratories (Australia), Report MRL-658, 1984.
8. P. J. Flory and J. Rehner, *J. Chem. Phys.*, **11**, 512 (1943); P. J. Flory, N. Rabjohn, and M. C. Schaffer, *J. Polym. Sci.*, **4**, 225 (1949); P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
9. C. G. Moore and W. F. Watson, *J. Polym. Sci.*, **19**, 237 (1956).
10. B. Saville and A. A. Watson, *Rubber Chem. Tech.*, **40**, 100 (1967).
11. O. Lorenz and C. R. Parks, *J. Polym. Sci.*, **50**, 299 (1961).
12. P. C. Colodny and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **2**, 39 (1959).
13. M. B. Berenbaum, in *Polyethers*, N. G. Gaylord, Ed., Wiley-Interscience, New York, 1962, Part III, p. 43.
14. J. C. Patrick and H. R. Ferguson, U.S. Pat. 2,527,374 (1950).
15. R. H. Gobran and M. B. Berenbaum, in *High Polymers*, J. P. Kennedy and E. G. M. Tornqvist, Eds., Wiley-Interscience, New York, 1969, Vol. XXIII, Part II, p. 826.
16. F. Feigl, *Spot Tests In Organic Analysis*, 6th ed., Elsevier, Amsterdam, 1960.
17. S. Searles and M. Tamres, in *The Chemistry of the Ether Linkage*, S. Patai, Ed., Interscience, London, 1967, p. 243.
18. C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957.
19. E. Schmitz and I. Eichhorn, Ref. 17, p. 309.
20. J. K. Kochi, Ed., *Free Radicals*, Vol. 1, Wiley-Interscience, New York, 1973.
21. B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc. Perkin II*, 1748 (1973).

Received December 12, 1985

Accepted January 16, 1986