COMPREHENSIVE EXAMINATION OF SILICONE
MEMBRANE MATERIALS FROM W68

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QUALITY DIVISION

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INTRODUCTION

Proper performance of the W68 depends, among other factors, upon a functional silicone membrane. It is known that the LX-09 releases deleterious products which may be incompatible with other components of the system. If the chemistry of decomposition of the membranes can be clearly elucidated, preventive measures may be taken in system construction to optimize shelf lives of the units. Therefore, a project was initiated to examine this decomposition. Initially, several key tests were performed. These included: (1) toluene swell, (2) thermogravimetric analysis, (3) ionic fluoride determination and total fluoride assay, (4) total amine analysis, (5) total acrylate determination and (6) functional group analysis of extractables. The results of analyses on W68 membranes are compared with control assays of membranes in units not containing the LX-09.

CROSS LINKAGE OF POLYMER BY TOLUENE SWELLS

Toluene swell tests (Table I) are polymer cross link indicators. With the single exception of BBN-10344-L71, all W68 membranes had a lower toluene swell, indicating a greater polymeric cross linkage. This would lead to embrittlement of the membranes.

THERMOGRAVIMETRIC ANALYSES

A series of thermogravimetric analyses were run on the W62 and W68 membranes, both with and without the silastic remaining (Table II). A few broad generalizations can be made. In general, the W68 membranes show greater decomposition at the test temperatures of 200 and 350 C than do the W62 control membranes. This is true for membranes from which silastic had been removed and on which silastic remained. Also, the differences are more pronounced at 200 C, indicating greater loss of more volatile (lower molecular weight) components. There are, however, several obvious exceptions to these generalizations. No apparent correlation between age of membrane and thermogravimetric decomposition could be noted on these tests.

INORGANIC AND TOTAL FLUORIDE ASSAY

For the total fluoride measurement, the sample is totally combusted in a Paar Bomb and the fluoride liberated is measured spectrophotometrically. This is a measure of inorganic plus organic fluoride in the membrane. For the purposes of this report all covalently bound fluoride was assumed to be present as FEFO . The inorganic fluoride is extracted from the ground membrane and measured spectrophotometrically. Table III shows the results of the fluoride analyses. As can be seen, nearly all fluoride present in the membranes is covalent. This implies that the FEFO has migrated into the membrane.

TOTAL AMINES

A likely product of membrane decomposition is the organic amine. Therefore, a method for detecting and quantitatively measuring these amines has been adapted to assaying the membranes. Several spectrophotometric techniques were considered. Although these methods were extremely sensitive they were specific to only one type of amine (primary, secondary or tertiary). Therefore, a less specific acid-base titration was adapted for assaying micro quantities of amine. The technique includes successive extractions of 10 g of the membrane with ethyl alcohol, acetone, cyclohexane and toluene. Each extract is evaporated to dryness, the residue is taken up in acetic acid, and the solution is potentiometrically titrated with HClO_4 in acetic acid. This technique is standard for macro amounts, but a little work was necessary to determine the feasibility of utilizing the techniques for micro amounts of amines. Two materials, aniline and N,N-dimethylaniline, were used to test the adaptation to micro analysis of amines. The HClO_4 was initially standardized against potassium acid phthalate. Results of titrations are illustrated in Table IV and Fig. 1. At the semi-micro level (0.05 meq) accuracy and precision are adequate. At the micro level (0.0005 meq) results have a 5.9 percent positive bias, but precision is excellent. At both levels, endpoint detection is excellent, and accuracy and precision are adequate for the job at hand. Examinations of the W68 membrane (Table V) showed two which contained detectable quantities of amines, showing decomposition of the membrane itself. The physical amount of NH_2 is of the order of 4 $\mu\text{g-NH}_2$, which does not represent a large amount of deterioration.

TOTAL ACRYLATES

A spectrophotometric method for determining acrylates was derived from a general procedure for esters. The procedure is applicable in a range of 0.001 M to 0.01 M concentrations. Ethanol is used as a solvent for samples. The samples are refluxed for five minutes with an alkaline hydroxylamine solution. Color is developed on addition of ferric perchlorate solution as a diluent to volume. The concentration of ester (acrylate) is determined spectrophotometrically from this solution. Amyl acetate was used as a primary test material. Results were excellent in consistency and reproducibility. This is shown in Table VI and Fig. 2. Methyl acrylate was also used to test specifically for acrylate and recovery was essentially 100 percent. Analysis of the membranes includes successive extraction of 10 g of membrane with ethanol, acetone, cyclohexane and toluene. The residues are taken to dryness and redissolved in ethanol and then analyzed for acrylate (Table VII). All the W68 membranes showed appreciable traces of acrylate, indicating migration of PDNPA into the membrane.

EXTRACTABLES

Portions of test membranes were successively extracted with ethanol, acetone, cyclohexane, and toluene. The solvent was then evaporated under vacuum and total extractables determined. Infrared spectra of each extract were then examined for major functional group analyses. Table VIII shows the amounts of total extractables. Fig. 3 shows the IR scan of the extracts of the W62 (control) and W68 membranes. The major peaks are identified in Fig. 3, most of which are from the silicone rubber of the membrane itself. However, peaks at 1725 cm^{-1} and 1575 cm^{-1} change significantly from the control to the 68 membranes. The 1725 cm^{-1} peak is an ester peak, while the 1575 cm^{-1} peak is a nitro peak. The ratio of ester to nitro is not constant, indicating that some of the nitro is due to HE clinging to the membrane. The ester probably comes from the PDNPA in the plasticizer. This is in agreement with the total acrylate analysis.

CONCLUSION

From the foregoing tests it is obvious that some HE is migrating into the membranes. This is shown by fluoride (FEFO) and acrylates (PDNPA) which were detected in the W68 membranes. However, these amounts are negligible and, as yet, observed deterioration of these membranes is insignificant.

ACKNOWLEDGEMENT

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Table I. Toluene Swell Tests on W68 Membranes

<u>Membrane</u>	<u>Program</u>	<u>Toluene Swell (%)</u>
BBN-13658-C73	62	2.72
BBN-14485-C73	62	2.50
BBN-8501-H71	62	2.52
BBN-8504-H71	62	2.74
BBN-9239-I71	62	2.83
BBN-2577-F0	68	2.36
BBN-6078-C1	68	2.33
BBN-6313-C1	68	2.42
BBN-5158-L0	68	2.46
BBN-1615-L9	68	1.70
BBN-2461-F0	68	2.36
BBN-10344-L71	68	3.83

Table II. Thermogravimetric Analyses on Membranes

<u>Membrane</u>	<u>Program</u>	<u>Wt. Loss, 200 C (%)</u>	<u>Wt. Loss, 350 C (%)</u>
<u>W/O Silastic</u>			
BBN-13658-C73	62	0.122	0.575
BBN-14485-C73	62	0.067	0.467
BBN-8501-H71	62	0.075	0.453
BBN-8504-H71	62	0.134	0.590
BBN-9239-I71	62	0.465	0.484
BBN-2577-F0	68	0.163	0.618
BBN-6078-C1	68	0.304	0.835
BBN-6313-C1	68	0.374	0.934
BBN-5158-L0	68	0.096	0.680
BBN-1615-L9	68	0.281	0.906
BBN-2461-F0	68	0.130	0.519
BBN-10344-L71	68	0.192	0.684
<u>With Silastic</u>			
BBN-13658-C73	62	0.135	0.830
BBN-14485-C73	62	0.039	0.698
BBN-8501-H71	62	0.138	0.674
BBN-8504-H71	62	0.170	0.775
BBN-9239-I71	62	0.076	0.674
BBN-2577-F0	68	0.153	0.751
BBN-6078-C1	68	0.474	1.190
BBN-6313-C1	68	0.511	1.250
BBN-5158-L0	68	0.419	1.301
BBN-1615-L9	68	0.338	1.072
BBN-2461-F0	68	0.193	0.741
BBN-10344-L71	68	0.292	0.927

Table III. Fluoride Analysis of W68 Membranes

<u>Membrane</u>	<u>Program</u>	<u>Inorganic F (ppm)</u>	<u>Total F (ppm)</u>	<u>FEFO (ppm)</u>
BBN-13658-C73	62	0	0	0
BBN-14485-C73	62	0	0	0
BBN-8501-H71	62	0	0	0
BBN-8504-H71	62	0	0	0
BBN-9239-I71	62	0	0	0
BBN-2577-F0	68	0.6	12	96
BBN-6078-C1	68	0.6	11	89
BBN-6313-C1	68	0.6	12	96
BBN-5158-L0	68	0.6	24	197
BBN-1615-L9	68	0	0	0
BBN-2461-F0	68	0.6	25	206
BBN-10344-L71	68	0.6	12	96

Table IV. Titration of N,N-Dimethylaniline

<u>Analysis</u>	<u>Titrant Added (mℓ)</u>	<u>meq. Found</u>
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Titration of 0.5 mℓ N,N-Dimethylaniline with 0.00880 N HClO₄

1	5.25	0.0462
2	5.25	0.0462
3	5.45	0.0480
4	5.35	0.0471
5	5.50	0.0484
6	5.45	0.0480
7	5.35	0.0471
8	5.25	0.0462
9	5.30	0.0466
10	5.45	0.0480
11	5.50	0.0484

Avg. = 0.0473 ± 0.0009

1.90% Relative

Titration of 0.005 mℓ N,N-Dimethylaniline with 0.000880 N HClO₄

1	0.575	0.000506
2	0.575	0.000506
3	0.575	0.000506
4	0.550	0.000484
5	0.575	0.000506

Avg. = 0.000501 ± 0.000003

0.6% Relative

Table V. Total Amine Content of Membranes

<u>Membrane</u>	<u>Program</u>	<u>meq. Amine/g Membrane</u>
BBN-9239-I71	62	0
BBN-2577-F0	68	0
BBN-2461-F0	68	0.00048
BBN-5158-L0	68	0
BBN-1615-L9	68	0.00054

Table VI. Spectrophotometric Determination of Ester

<u>Concentration</u>	<u>λ, mμ</u>	<u>Absorbance</u>
0.002	527	19.8
0.002	527	19.9
0.002	545	20.0
0.002	545	19.0
0.002	545	18.5
0.002	545	18.3
0.002	545	18.3
0.004	527	40.0
0.004	527	40.7
0.004	527	40.0
0.004	545	39.0
0.004	545	40.0
0.004	545	38.8
0.004	545	40.7
0.004	545	40.7
0.006	527	62.8
0.006	527	63.0
0.006	527	60.1
0.006	527	60.3
0.006	545	67.5
0.006	545	62.6
		62.6

Table VII. Total Acrylate Contents of Membrane

<u>Membrane</u>	<u>Program</u>	<u>g Acrylate/g Membrane</u>
BBN-9239-I71	62	0
BBN-2577-F0	68	98
BBN-2461-F0	68	73
BBN-5158-F0	68	79
BBN-1615-L9	68	118

Table VIII. Total Extractables from Membranes

<u>Membrane</u>	<u>Program</u>	<u>Wt. Extractables in mg/g Membranes</u>							
		<u>Ethanol</u>		<u>Acetone</u>		<u>Cyclohexane</u>		<u>Toluene</u>	
BBN-9239-I71	62	17.1	15.7	3.6	3.3	28.8	31.6	3.4	2.6
BBN-2577-F0	68	13.7	14.5	4.6	4.3	26.1	22.5	3.1	4.3
BBN-2461-F0	68	14.4	14.1	3.3	4.3	26.5	30.2	2.5	2.3
BBN-5158-L0	68	16.0	16.5	4.8	4.4	44.2	44.5	2.7	5.1
BBN-1615-L9	68	26.2	27.5	5.5	5.2	88.4	88.3	3.7	4.7

Fig. 1. Titration of N,N-Dimethylaniline

Fig. 2. Titration of Amyl Acetate

Fig. 3. IR Spectra of the Extracts of the W62 (Control) and W68 Membranes