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LAWRENCE LIVERMORE LABORATORY

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CHEMICAL ANALYSES OF CELLULAR SILICONE MATERIALS

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MASTER

CHEMICAL ANALYSES OF CELLULAR SILICONE MATERIALS

ABSTRACT

We performed comprehensive chemical analyses on 22 batches of cellular silicone (14 as raw material and finished parts and eight at intermediate stages of processing). The results are consistent enough to form the basis for a chemical specification, if needed. The occasional deposition of hard-water ions such as Ca and Mg is the only significant change resulting from the processing operations. The retention of 0.2 wt% chlorine in the product was unexpected, but the chloride ion was present to the extent of only 25 ppm. Although active peroxide content varied considerably and averaged only 70% of the theoretical amount, the recipe includes a sizable excess and the consistently low extractables content of finished parts indicated adequate cure of all batches.

INTRODUCTION

This report contains the analytical data obtained from 18 consecutive batches of cellular silicone compound delivered in a one-year period to Bendix Corporation, Kansas City Division. Additional data on four batches analysed at LLL are also included. Materials involved were Y-3333, Y-3260 and Y-3223. Raw material received from Union Carbide and finished parts fabrication at Bendix were analyzed in addition to a few batches that were examined during intermediate stages of processing.

The work described in this report developed from three considerations:

1) variations in mechanical properties of cellular silicone stress cushions generally have been ascribed by the fabricator to material variability and by the material supplier to fabrication problems, 2) the contribution of processing to the final composition has not been assessed, and 3) the limitations on components for nuclear devices have become more stringent in terms of compatibility and other requirements. All of these problems came to a head in the W-71 program. A very extensive analytical study was formulated at LLL to examine all the batches of materials and parts used in the Spartan development assemblies. The specific objectives were to determine the composition and consistency of the starting material and finished parts so that 1) we could write a chemical specification if needed, 2) we could try to relate compositional variations to mechanical property differences, and 3) we would learn much more about the composition, properties, and responses of the product.

The analytical program for cellular silicone is shown in Table 1. Manpower, time and dollar limitations precluded completion of the whole study; only those analyses for which reasonably established procedures existed were undertaken. These included

Table 1. Analytical program for cellular silicones.

Tests and procedures	Fabrication stage ^a				Finished (post-cured) product
	Raw material	Pre-forms	Molded, cured	Washed, dried	
<u>Chemical</u>					
1. Elemental analysis	A	B	B	B	A
2. Peroxide content	A	B	B	B	B
3. Urea content	A	B	B	B	A
4. Urea analysis	A				
5. Outgassing					A
6. Peroxide distribution (polymer/urea)	A	A	A		
7. Extractables	A	B	B	B	A
8. Washing deposits				B	A
9. Acidity-alkalinity			B	B	A
10. Analysis for polymerization catalyst	B				
11. Peroxide by-products			B	B	A
12. Analysis of extractables	B		B		B
<u>Physical</u>					
1. Friction					A
2. Load deflection					A
3. Solvent swell	B	B	B	B	A
4. Thermo-mechanical study (DTA, TGA, etc.)	A	B	B	B	A
5. Surface and cell configuration study					B
6. Rheology	B	B			
7. Urea size distribution	B	B	B		
8. Hardness	B	B	B	B	B
9. Physical/mechanical properties	B	B	B	B	A
10. Density distribution			B	B	B

^aA = prime priority, B = secondary priority.

items 1, 2, 3, 5, 7, and 9 under "Chemical" and 1, 2, and 3 under "Physical" in Table 1.

The description of the basic analytical methods and their accuracy are contained in the Appendix.

MATERIALS

The materials used in this study are proprietary and are produced under a patent to Union Carbide Corporation.¹ The sequence of compounding and fabrication steps is outlined below with certain, agreed-upon specific terminology enclosed by quotation marks.

The cellular structure is obtained by incorporating the essentially spherical urea particles before molding the material to size and shape, curing it and then removing the urea in the washing step. Designations such as Y-3333 are used for the appropriate material all the way through from the cellular silicone compound purchased from Union Carbide to the final, cellular product. Because the three density grades are produced from the same base compound, their compositions after removal of the urea should be essentially identical.

The only processing difference among the three grades involves the handling of the material immediately upon receipt from Union Carbide. During storage, Y-3333 undergoes a hardening and consequent loss of processability that is reduced by a cold-pressing operation performed as soon as possible; the lesser change in Y-3260 and Y-3223 can be offset, just before molding, by a brief milling step. Thus, the processing histories and exposure of the different materials and batches should be very similar.

A combination letter-digit(s)-digit code is used to identify the separate batches of material. The letter refers to a month, the first digit(s) to the day of the month and the last digit indicates the chronological order of the batches of the same type mixed on that day. For the sequence of batches included here, batch "F" was made in June, 1970, and the last is batch "P-22-1" made the 22nd of April, 1971.

DISCUSSION AND RESULTS

Major Elements

Table 2 lists the analytical data for the major elements. Carbon, hydrogen, nitrogen and silicon are determined directly; oxygen is calculated as the remainder after allowing for the chlorine and trace elements. The data of Table 2 agrees reasonably well with calculations based on our limited knowledge of the identity and concentration of the components in cellular silicone compounds.

Table 2. Major element analysis of finished cellular silicones^a

Batch No.	Percent by weight				
	C	H	Si	O	N
<u>BKC</u>					
<u>Y-3333</u>					
F- 5-1	25.9	5.6	35.8	32.4	<0.1
F-15-1	25.7	5.5	36.2	32.3	<0.1
F-19-1	25.5	5.3	36.3	32.6	<0.1
G- 1-1	25.5	5.4	37.7	31.1	<0.1
G-14-1	25.4	5.3	36.9	32.0	<0.1
H- 3-1	26.3	5.6	36.5	31.2	<0.1
H- 7-1	26.3	5.6	36.7	31.2	<0.1
I -15-1	26.1	5.5	36.5	31.5	<0.1
L- 3-1	26.2	5.4	36.6	31.5	<0.1
L-11-1	26.1	5.4	37.2	30.8	<0.1
N-18-1	26.3	5.6	36.3	31.4	<0.1
N-24-1	26.3	5.5	36.4	31.4	<0.1
O- 5-1	26.1	5.5	37.5	30.6	<0.1
P-22-1	26.1	5.5	37.4	30.7	<0.1
<u>Y-3260</u>					
L-15-1	26.2	5.4	36.3	31.7	0.1
N-18-1	26.3	5.5	37.0	30.9	<0.1
O-12-2	26.2	5.5	37.0	31.0	<0.1
<u>Y-3223</u>					
O-12-2	26.2	5.6	37.6	30.4	<0.1
Average: ^b	26.0 ± 0.6	5.5 ± 0.2	36.8 ± 1.1	31.4 ± 1.3	<0.1
<u>L.L.L</u>					
<u>Y-3333</u>					
6-7	26.6	5.6	36.4	31.1	<0.1
	26.6	5.4			
R-18-1	25.2	5.1	36.3	31.4	<0.1
	26.7	5.4			
<u>Y-3260</u>					
SAA-1	26.5	5.6	36.6	31.0	0.0
	26.4	5.6			0.0
2-2-68	26.8	5.4	36.3	31.5	0.0
	26.8	5.2			0.0

^aSee Appendix for precision of methods.

^bThe limits represent to; i.e., the range within which one has a 95% confidence that 95% of the values will fall.

Trace Elements

The trace element results in Table 3 are generally as expected. The only anomalies are the occasional high values for calcium and magnesium. It should be mentioned that no statistically sound average value or limits can be calculated for any of the elements in this table because of the wide range of values found.

Table 3. Minor element analysis of finished cellular silicones.^a

Batch No.	Parts per million (ppm)											Total
	Al	Ca	Cr	Cu	Fe	Mg	Na	Ni	Pb	Sr	Ti	
<u>BKC</u>												
<u>Y-3333</u>												
F- 5-1	53.	200.	n.d. ^b	4.	80.	160.	b.d. ^c	n.d.	n.d.	b.d.	7.	500
F-15-1	55.	275.	n.d.	4.	108.	40.	b.d.	n.d.	n.d.	b.d.	7.	500
F-19-1	56.	230.	n.d.	4.	70.	32.	b.d.	n.d.	n.d.	b.d.	6.	400
G- 1-1	99.	560.	n.d.	9.	87.	42.	b.d.	n.d.	n.d.	b.d.	8.	800
G-14-1	160.	550.	4.	9.	23.	98.	690.	n.d.	n.d.	10.	22.	1550
H- 3-1	130.	475.	4.	7.	30.	125.	650.	n.d.	n.d.	10.	11.	1450
H- 7-1	115.	456.	5.	9.	34.	78.	225.	n.d.	n.d.	7.	10.	950
I -15-1	140.	605.	7.	8.	8.	127.	120.	1.	1.	10.	26.	1050
L- 3-1	80.	195.	2.	6.	70.	27.	58.	4.	n.d.	b.d.	10.	450
L-11-1	110.	1500	4.	13.	160.	>500	168.	n.d.	n.d.	b.d.	20.	2500
N-18-1	320.	170.	1.	14.	91.	73.	56.	n.d.	4.	6.	20.	750
N-24-1	250.	670.	1.	10.	141.	93.	65.	2.	6.	16.	20.	1300
O- 5-1	195.	360.	2.	10.	178.	57.	34.	n.d.	1.	7.	15.	850
P-22-1	210.	263.	1.	11.	161.	100.	53.	4.	1.	20.	18.	850
<u>Y-3260</u>												
L-15-1	549.	277.	n.d.	10.	66.	>630.	155.	n.d.	1.	10.	17.	1750
N-18-1	119.	127.	1.	10.	19.	52.	69.	n.d.	5.	6.	16.	450
O-12-2	340.	370.	n.d.	7.	17.	75.	98.	n.d.	1.	13.	20.	950
<u>Y-3223</u>												
O-12-2	140.	150.	n.d.	4.	36.	63.	11.	n.d.	n.d.	8.	21.	450
<u>LLL</u>												
<u>Y-3333</u>												
6-7	60.	1800.	n.d.	10.	200.	200.	<200.				20.	2500
R-18-1	20.	200.	n.d.	10.	60.	60.	<200.				20.	400
<u>Y-3260</u>												
SAA-1	50.	1500.	n.d.	10.	50.	150.	<200.				25.	1800
2-2-68	50.	300.	n.d.	10.	15.	60.	<200.				15.	500

^aSee Appendix for precision of methods.

^bNot detectable.

^cBarely detectable.

Past experience has shown that the level of several metallic species, Ca and Mg in particular, is directly related to the leaching or urea-removal operation because of deposition of these ions from the wash water. This is substantiated by the data in Table 4 that shows the progressive changes in metallic ion contents during processing. The only difference between "as-received" and "molded-cured" levels should be pick-up during cold-pressing, handling, and exposure to the molds (batch F-5-1 shows a slight increase). If one assumes that all the metallic contaminants are in the polymer phase and none in the urea, then washing (which removes 3/4 of the total mass of Y-3333 as urea) should result in an increase in metallics to no more than four times the pre-wash level; instead, the major metallics appear to increase by several times the expected four-fold jump. The high values of elements such as Ca, Mg, and Fe reported for the washed-dried material may be questioned since there seems no reason for the indicated decrease in these elements after the subsequent post-cure step, assuming no volatility of the salts at 480°F. However, regardless of whether the "washed-dried" contaminant levels or the "post-cure" values are accepted, the increase from earlier processing stages is very significant.

The various cellular silicone parts spend from 4 to 24 hr in the washing tank, depending on their thickness, etc.; these tanks contain water drawn from the Kansas City municipal supply which, in turn, is drawn from the adjacent Missouri River. In examples of extremely long wash periods, parts "crusted" with hard-water residues have been encountered in the past. Thus, it seems reasonable that the build-up of metallic contaminants occurs during washing and that deposition of various salts will vary with the seasonal variations in the content of these ions in the water supply. The

Table 4. Metallic contamination at various processing stages.

Y-3333 Batch No.	Processing stage	Content, ppm					
		Al	Ca	Cu	Fe	Mg	Ti
F- 5-1	As received	4.	4.	4.	3.	3.	1.
	Molded, cured	20.	13.	3.	10.	6.	2.
	Washed, dried		960.	16.	105.	120.	40.
	Post-cured	53.	200.	4.	80.	160.	7.
F-15-1	As received	16.	24.	2.	30.	7.	2.
	Post-cured	55.	275.	4.	108.	40.	7.
F-19-1	As received	14.	90.	10.	6.	4.	2.
	Post-cured	56.	230.	4.	70.	32.	6.
G- 1-1	As received	15.	35.	4.	5.	9.	1.
	Washed, dried	70.	515.	9.	140.	57.	15
	Post-cured	99.	560.	9.	87.	42.	8.

new Bendix facility, that is under construction, will use de-ionized water for washing and the problem concerning metallic salts in production parts will soon be eliminated.

Chlorine

The chlorine levels, shown in Table 5, column 6, were much higher than the few ppm expected. Although a chlorine-containing peroxide (Cadox TS-50, 50 wt% 2,4-dichlorobenzoyl peroxide + 37.5 wt% silicone oil + 12.5 wt% dibutyl phthalate) is used to cross-link the vinyl-containing polymer, the post-cure period of 24 hr at 480°F in a circulating-air oven is supposed to volatilize out the peroxide by-products. Since the chlorine content of the finished material is fairly consistent and cannot be washed out or extracted, it is assumed that the chlorine is still bound to the phenyl nucleus which must be grafted onto the polysiloxane. This chlorine should be organically-bound and inactive; titrations for chloride ion showed an average of only 1-2% of the total chlorine in ionic form (see Table 5, column 7).

Following the total chlorine content through the various processing stages produced some interesting results. Theoretically, there is no change until the post-cure operation is carried out; this assumption is based on the premise that all of the peroxide and its decomposition by-products are in the polymer phase and none are in the urea phase. Data to be presented in the section under "Peroxide" indicates that this assumption is incorrect; that perhaps 25-30% of the by-products and that possibly peroxide also is contained in either the urea or associated with the surface of the urea particles. This conclusion is supported by the information in Table 5, columns 2, 4, and 5 where the total chlorine of the washed product is only twice, rather than four times, the level prior to washing. That is, removing a chlorine-free fraction equivalent to 75% of the mass should produce a remainder with four times the prior chlorine. Because the values of 0.33 and 0.27% represent only two-fold increases over the respective values of 0.16 and 0.13% in the molded-cured product, washing has resulted in removal of one-half the total chlorine. The post-cure step to the finished part reduces the residual chlorine levels by approximately one-third, rather than eliminating it altogether.

Peroxide

The conversion of the cellular silicone compounds to useful products requires a "curing" operation—the introduction of chemical cross-links between the polymer chains. This is done by incorporating a peroxide that decomposes in an appropriate temperature range. Both physical and chemical properties of the final product reflect the degree of cross-linking and this is dependent on the amount of peroxide and the cure conditions. Assuming the latter to be either constant or adequate to decompose all the peroxide, the initial amount of peroxide can be critical. The "recipe" for Y-3333 calls for 4.5 parts of Cadox TS-50 per hundred parts of the compound. This is equivalent to 0.556 wt% in the cellular compound $\left(\frac{4.5 \times 0.5}{100 + 4.5 + 300} \right)$. This amount is

Table 5. Chlorine and peroxide analyses of cellular silicones.

Batch No.	Chlorine, wt. percent					Peroxide,		Peroxide/Cl ratio (theoretical = 2.65)	
	As received		Molded, cured	Washed, dried	Finished part		As received material		
	wt% ^a	% theoretical ^a			Total	Ionic	wt%		% theoretical ^b
Y-3333									
F- 5-1	0.16	77.	0.16	0.33	0.21	0.0022	0.39	70.	2.44 (+0.5, -0.4) ^c
F-15-1	0.17	82.			0.19	0.0026	0.42	76.	2.47 (+0.45, -0.35)
F-19-1	0.18	87.			0.20	0.0038	0.35	63.	1.94 (+0.4, -0.3)
G- 1-1	0.16	77.	0.13	0.27	0.18	0.0028	0.35	63.	2.18 (+0.45, -0.35)
G-14-1	0.14	68.			0.15	0.0030	0.35	63.	2.50 (+0.55, -0.45)
H- 3-1	0.14	68.			0.18	0.0030	0.43	77.	3.06 (+0.7, -0.5)
H- 7-1	0.20	97.			0.10	0.0017	0.44	79.	2.20 (+0.35, -0.3)
I -15-1	0.21	101.			0.18	0.0020	0.47	85.	2.24 (+0.35, -0.3)
L- 3-1					0.22	0.0015			
L-11-1					0.17	0.0010			
N-18-1					0.24	0.0006			
N-24-1					0.19	0.0025			
O- 5-1					0.15	0.0003			
P-22-1					0.15	0.0004			
Y-3260									
L-15-1					0.15	0.0017			
N-18-1					0.18	0.0060			
O-12-2					0.18	0.0014			
Y-3223									
O-12-2					0.11	0.0041			

^aBased on 0.207 wt% calculated from theoretical loading of 4.5 phr Cadox TS-50.^bBased on 0.556 wt% calculated from theoretical loading of 4.5 phr Cadox TS-50.^cLimits based on precision of chlorine and peroxide determinations.

several times the theoretical that is necessary to react with all of the vinyl groups present. It is included for several reasons: 1) if the peroxide distributes itself uniformly through the compound, 75% is wasted or unavailable since it would be contained in the particulate urea phase that constitutes 3/4 of the mass, 2) the efficiency of the reaction between the peroxide radicals and the vinyl groups on the chains and subsequent cross-linking is not known, and 3) many basic and acidic materials decompose peroxides, reducing the effective concentration. The simplest assessment of the initial catalyst loading is through chlorine determinations since there should be no other source of this element. However, the decomposition products per 3) above also contain chlorine without any peroxide functionality and so a direct analysis for peroxide functionality is included.

Only one test of the peroxide content of urea from a compound was run, per 1) above. A sample was physically removed from a molded, cured pad of Y-3333 and the chlorine content determined to be 0.06 wt%. This translates into a figure of 25-30% of the peroxide by-product associated with the urea phase of the mix.

The peroxide data is listed in Table 5, columns 8 and 9. Whether assessed by chlorine or direct peroxide titration, the catalyst loadings are generally grossly below theoretical level. The estimates based on chlorine might be subject to sampling problems because only 0.2 g are used in the analysis and a couple of "extra" urea particles in one or another sample would introduce a sizable error. This is not so with the direct titration that utilized a 4- to 5-g sample. The implication is that the catalyst loading was much below the proper, or recipe, level. Furthermore, since the values for "percent of theoretical" chlorine are greater than those for "percent of theoretical" peroxide, it also appears that either the initial peroxide activity of the catalyst was low or decomposition, subsequent to mixing into the compounds, had occurred.

Urea

Analysis of five lots of Union Carbide Y-3333 cellular silicone compound for urea loading did not produce as consistent results as expected. Material samples were ground under liquid nitrogen to homogenize them before sampling for analysis. Table 6 lists the findings for urea content.

Table 6. Urea content of cellular silicone compounds.

Y-3333 Batch No.	Wt% urea ^a		
	As received	Cold-pressed	Molded, cured
F- 5-1	75.3		
F-15-1	72.5	76.3	71.5
F-19-1	80.5		
G- 1-1	72.3		
G-14-1	74.0		

^aNominally 74.

The value for batch F-19-1 as received material appears questionable. There is no confirmation in density or load deflection tests for a 10% reduction in density implied by this high nitrogen value. Furthermore, the carbon, hydrogen, and silicon values are all normal. The sequence of urea contents for the F-15-1 series is also questionable and may indicate sampling difficulties. Urea particles are only loosely bound into the matrix so that they may fall out to readhere later in a localized concentration or the shearing that occurs during cold-pressing and molding may bring about some separation of urea and matrix leading to heterogeneity. Whatever the cause, a sampling problem does seem to exist for urea loading determinations.

Extractables

This test was included for three reasons: 1) as a check of the efficiency or completeness of the cure, 2) to determine if there was significant oxidative degradation during the rigorous post-cure, and 3) to determine how much potentially-migratable material is present. The values of 2.2-3.3 wt% listed in Table 7 agree well with other determinations at LLL on numerous samples including batches and parts. Relatively little difference results from using any of a wide range of solvents—pentane, toluene, chloroform, acetone, etc. This reasonably low average value of 2.7% indicates that the cure does incorporate almost all of the polymer and that, if there is any degradation, the products are volatilized out. The extract has not been identified beyond being primarily a polysiloxane of fairly high viscosity—probably close to a thousand centistokes.

Acidity-Alkalinity

Some acidic by-products will result from the peroxide decomposition and some may form by oxidation of the organic groups on the silicon of the polymer during post-cure. To check for the presence of these in the final product, the pH of an extracting solvent mix was examined before and after soaking cushion samples. Table 7 shows that slight acidification did occur since there was a drop of about 1 pH unit, but there was negligible titratable acid in the solvent.

Outgassing

The predominant species in all the materials were water and absorbed atmospheric gases. Six batches showed additional trace species: hydrocarbons in L-3-1, L-11-1, N-24-1, and O-5-1; siloxane fragments in N-18-1; some Cl^+ and HCl^+ , increasing in intensity at 400°F, in P-22-1. The N-18-1 batch of Y-3260 showed the same siloxane fragments, but to lesser degree, seen in the N-18-1 batch of Y-3333.

The results of the quantitative determination of moisture on finished cushions, shown in Table 7, column 6, agree very well with prior Bendix data.

Table 7. Moisture content, amount and pH of extractables in cellular silicones.

Batch No. and stage	Weight percent extractable			pH ^a	Moisture content, wt%
	Chloroform	Toluene	Acetone		
<u>Y-3333</u>					
F- 5-1					
Molded, cured ^b				7.7	
Washed, dried				6.3	
Post-cured	2.4	2.6		5.6	0.34
F-15-1 Post-cured	2.5	2.7		5.5	0.32
F-19-1 Post-cured	2.6	2.4		5.7	0.32
G- 1-1 Post-cured	2.9	2.7		5.6	0.31
G-14-1 Post-cured	2.7	2.8		5.5	0.32
H- 3-1 Post-cured	2.4	2.6		5.6	0.32
H- 7-1 Post-cured	2.6	2.8		5.5	0.33
I -15-1 Post-cured	2.4	2.5	3.3	5.4	0.32
L- 3-1 Post-cured	2.4		2.9		0.30
L-11-1 Post-cured	2.6		2.8		0.32
N-18-1 Post-cured	2.6		2.7		0.32
N-24-1 Post-cured	2.6		2.8		0.31
O- 5-1 Post-cured	2.6		2.9		0.32
P-22-1 Post-cured	2.7		2.8		0.30
<u>Y-3260</u>					
L-15-1 Post-cured	2.5		2.7		0.32
N-18-1 Post-cured	2.7		2.7		0.31
O-12-2 Post-cured	2.8		3.2		0.32
<u>Y-3223</u>					
O-12-2 Post-cured	2.2		2.5		0.32
Average: ^a	2.6 ± 0.2	2.6 ± 0.1	2.8 ± 0.2	5.5 ± 0.1	0.32 ± 0.01

^aRatio of toluene, distilled water, and isopropyl alcohol are 50, 0.5, and 49.5, respectively. The blank registered a pH of 6.6.

^bContains urea.

^cThe limits represent $\pm \sigma$; i.e., the range within which one has a 95% confidence that 95% of the values will fall.

COMMENTS AND CONCLUSIONS

An overall assessment of the analytical data shows a reasonably consistent chemical composition that is not significantly altered by Bendix processing. The chlorine retained by the product was a surprise, but should not be of concern because only 5-40 ppm was in active, ionic form. The apparent gross variation in peroxide level was the most disturbing finding. However, three factors that possibly diminish

the importance of the peroxide variation are (1) the excessive recipe loading, (2) the indication that only a minor fraction migrates into the urea phase, and (3) the fairly steady extractable level.

Pick-up of calcium and magnesium salts during the washing stage was the most significant change resulting from the fabrication sequence. This can affect mechanical properties when present in large amounts, but not at the levels encountered here — although the effect on long-term properties has not been considered in this study.

Some additional study of sampling methods and/or homogenization seems necessary before implementation of a regular analytical program or specification for cellular silicones.

Two different approaches were unsuccessful in correlating analytical data with mechanical properties such as load deflection or compression set. Neither "factor analysis"² nor "pattern recognition"³ could be applied primarily because of either insufficient data — number of samplings, number of replicates, or because of the wide ranges of analytical values encountered that made "averages" meaningless. Additional difficulty arose from minor variations in test procedures and from the fact that we have very little quantitative understanding of such fundamental factors as polymer-filler interactions and the part played by processing aids.

ACKNOWLEDGMENTS

The majority of the chemical data was generated under the direction of Fred N. Larsen at Bendix Corporation, Kansas City Division. Specific questions on the analytical procedures and their limitations should be directed to Fred N. Larsen.

REFERENCES

1. F. A. Smith, Method of Making a Filled Cellular Silicone Elastomer and Cellular Product Obtained Thereby, U.S. Patent 3,238,157 (March, 1966).
2. H. H. Harman, Modern Factor Analysis (University of Chicago Press, Chicago, Ill. 1967), 2nd ed., revised.
3. C. F. Bender and B. R. Kowalski, Pattern Recognition, A Powerful Approach to Interpreting Chemical Data, Lawrence Livermore Laboratory, Rept. UCRL-73590 (1972).

APPENDIX

ANALYTICAL METHODS

Note: The values listed for the precision of the various elemental determinations are based on the claims of the instrument manufacturers and have not been separately established; it should not be assumed that these are any better than 1σ limits.

Elemental Analyses

C, H, N: Automated combustion analyses were performed by Elek Microanalytical Laboratory for Bendix. (Fred Larsen reports that Elek Microanalytical Laboratory data agree with Bendix data). Precision: ± 0.1 wt%.

Si: Peroxide combustion followed by colorimetric analysis. Precision: ± 0.2 wt%.

Trace elements: a one-gram sample was wet ashed to eliminate C, H, N, treated with HF to eliminate Si, and then arc emission spectroscopy was performed on remainder of ash. Triplicate runs were made on a single ash sample. Sodium was determined separately by atomic absorption. The following table indicates the individual factors to be applied to the elemental concentration to obtain the maximum and minimum limits at a 95% confidence level.

Element ^a	Factor	
	Upper limit	Lower limit
Al	1.43	0.57
Ca	1.16	0.84
Cr	1.26	0.74
Cu	1.56	0.44
Fe	1.28	0.72
Mg	1.24	0.76
Na	1.10	0.90
Ni	1.33	0.67
Pb	1.50	0.50
Sr	1.26	0.74
Ti	1.18	0.82

^aApplicable ranges: 1-500 ppm for Ca, Mg, Ti; 1-100 ppm for remaining elements. Precision has not been established for levels higher than those indicated. Possibly present, but not analyzed for, at the ppm level are P, S, As, K, Ba, Zn, Sn.

Cl: Total halogen determined by oxygen combustion in a Parr bomb of a 0.2-g sample, adding 7-ml 5% aqueous sodium carbonate, washing out with distilled water, concentration to 5 ml and subsequent dilution to 25 ml for titration in a "Cotlove Chloridometer." Precision: ± 0.02 wt%. Ionic chloride determined by an aqueous ethanol extraction of a 1.5-g cushion sample and coulometric titration.

Peroxide: A 4 to 5-g sample refluxed for 4-5 min in a solution of 100-ml isopropyl alcohol, 10-ml acetic acid and 1-ml aqueous saturated sodium iodide. After cooling, 10-ml isopropyl alcohol and 25-ml distilled water added before titrating with 0.025 N sodium thiosulfate. Precision: ± 0.02 wt%.

Urea: This value was calculated from the nitrogen content on two assumptions: urea is the only source of nitrogen and the urea is 100% H_2NCONH_2 . The first is justified to the best of our knowledge; the second assumption is only slightly incorrect based on Union Carbide analytical results that indicate about a 98% urea content with the remainder probably biuret, $\text{H}_2\text{NCONHCONH}_2$.

$$\text{Wt\% urea} = \frac{\text{Wt\% N}}{0.4665^a}$$

^a wt% N in urea

Extractables: A 3 to 5-g sample was extracted with 150 ml of solvent (as indicated in Table 7) in a Soxhlet apparatus for 8 hr. Extractables content was calculated both from remaining weight after drying and also by determining non-volatiles in an aliquot of the extraction solvent.

Acidity-Alkalinity: Ten grams of cushion were shaken for 1 hr with 100 ml of a 50:0.5:49.5 volume percent mixture of toluene, distilled water, and isopropyl alcohol. After standing overnight, the supernatant liquid was checked with a Beckman meter to determine the pH.

Outgassing: A small sample was placed in the direct probe solids sampler of a CEC 110 mass spectrometer. With pressure at 10^{-5} to 10^{-6} Torr, spectra were run at various temperatures from ambient to 400°F for masses to 600.

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