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MIDLAND, MICHIGAN

DEPARTMENT	SECTION	REPORT NUMBER
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TITLE: FURTHER CHARACTERIZATION OF SAN AND SARAN MICROSPHERES

SUMMARY:

To further characterize Saran (vinylidene chloride - acrylonitrile copolymer) and SAN (styrene - acrylonitrile copolymer) microspheres, a number of comparative tests were performed. Specifically (1) a paper yellowing test, (2) resilience in an asbestos sheet, (3) hydraulic compression tests and (4) solvent resistance were the four properties studies.

Briefly, SAN MS were found superior in the paper yellowing and resilience tests whereas Saran MS were considered best in the compression and solvent resistance tests. This report describes the procedures and results of each test.

Ecological Considerations: The information contained in this report is simply comparative data between two types of microspheres and consequently has no significant ecological impact.

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TYPE OF REPORT	DATE	PROBLEM NUMBER
Lab Report	May 23, 1973	0023999

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REPORT NO.

TITLE:

FURTHER CHARACTERIZATION OF SAN AND SARAN MICROSPHERES

PURPOSE:

To identify additional, physical differences between SAN and Saran Microspheres.

CONCLUSIONS AND RECOMMENDATIONS:

Conclusions:

1. Paper yellowing test - Saran microsphere paper shows a greater loss in brightness than SAN microsphere paper when subjected to 94 hrs of intense U.V. radiation.
2. Resilience in an asbestos sheet - Greater bulk was obtained with Saran MS, however the compression set of the SAN MS was far superior to the saran product. For example, a 50% increase in caliper at a compression set of <15% can only be obtained using SAN microspheres.
3. Hydraulic compression tests - Saran microspheres were found to be softer and more flexible than SAN microspheres. Consequently, they collapse at lower pressures, and can survive higher pressures without rupturing than the SAN microspheres.
4. Solvent effects - Saran microspheres were able to withstand aromatic solvents better than the SAN microspheres (at room temp.). At 60°C, however, the saran product would also deteriorate. Aliphatic hydrocarbons seemed to be the only organic solvents that do not damage either type of microsphere.

Introduction

Other than differences in foaming properties and the thermal stabilities of SAN and Saran microspheres, very little comparative data has been generated. So, early in 1973 a list of "comparisons" was drawn up

- A. Paper Yellowing
- B. Asbestos Sheets, Resilience
- C. Hydraulic Compression
- D. Solvent Resistance
- E. Non-Wovens
- F. "K" Factor
- G. Foamability - Latex & Solvent Based Systems
- H. Odor Development

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for further evaluation. Although the program is not yet complete, this report describes the procedures and results of the first four tests. The report is sectioned into four parts, one for each of the four "comparisons" studies.

LIGHT STABILITY OF MICROSPHERES IN PAPER

The following procedure was used to prepare microsphere-containing paper hand sheets for comparing the U.V. light stability of our SAN and Saran Microspheres.

300 Grams of Great Lakes Bleached Softwood was beat to a Canadian Standard Freeness (CSF) of 454 which gave a 3.0 gm. sheet and a consistency of 1.5%. In like manner 300 gms. of Bowaters Hardwood Bleached Kraft was beat to a CSF of 479 which gave a 2.7 gm. sheet and a consistency of 1.36%. The two pulp slurries were combined to give a total of 71 lbs. of slurry with a corrected freeness of 444. A sample hand sheet weighed 2.95 gms. which means we had a consistency of 1.48%. 1% Rosin (based on pulp weight = 4.78 g) was then stirred in followed by 1% Alum (4.78 g). The pH was then adjusted to 4.5 with 1.0 N sulfuric acid (15 ml).

One liter of prepared pulp (14.8 gms) was added to the proportionator which contained enough DI water to make four 8 inch hand sheets. In all cases .05% (by wt. of the pulp) Separan CP-7 was added to the proportionator as a retention aid (14.8 cc of a .05% solution), followed by the appropriate amount of microspheres. The following chart is a summary of the designed experiment.

<u>SHEET #</u>	<u>MS TYPE</u>	<u>%MS*</u>	<u>WT OF MS (gms)</u>	
			<u>Dry</u>	<u>Wet</u>
C-1 Thru C-3	None	Controls	0	0
1-1 Thru 1-9	SAN	1.0	.148	1.1
2-1 Thru 2-9	SAN	2.0	.296	2.2
3-1 Thru 3-9	SAN	4.0	.592	4.4
4-1 Thru 4-9	SARAN	1.0	.148	1.03
5-1 Thru 5-9	SARAN	2.0	.296	2.06
6-1 Thru 6-9	SARAN	4.0	.592	4.12
C-4 Thru C-9	None	Controls		

*Based on wt. of pulp

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Each of the 63 sheets was checked on the brightness tester to give the following data.

	<u>Wire Side</u>	<u>Felt Side</u>		<u>Wire Side</u>	<u>Felt Side</u>
C-1	83.0		4-1	86.2	
-2	82.7		-2	85.5	
-3	84.2	83.9	-3	86.5	86.4
1-1	84.5		-4	86.6	
-2	82.5		-5	86.2	
-3	80.0	82.8	-6	85.8	86.2
-4	84.4		-7	85.8	
-5	82.6		-8	86.0	
-6	83.5	84.7	-9	86.0	86.4
-7	82.8-85.0		5-1	86.2	
-8	78.6-84.3		-2	86.6	
-9	85.0	85.0	-3	86.0	86.9
2-1	85.2		-4	86.3	
-2	85.6		-5	86.5	
-3	85.3	86.2	-6	87.3	87.3
-4	84.0		-7	87.6	
-5	80.9-84.2		-8	87.8	
-6	86.5	85.7	-9	87.3	87.3
-7	86.0		6-1	87.8	
-8	86.2		-2	87.8	
-9	85.7	86.3	-3	87.8	87.9
3-1	85.6		-4	88.0	
-2	87.0		-5	87.7	
-3	86.8	87.0	-6	87.9	88.0
-4	86.0		-7	87.9	
-5	84.5		-8	87.8	
-6	86.3	86.3	-9	87.0	88.1
-7	86.5		C-4	85.4	
-8	86.2		-5	85.2	
-9	86.3	87.0	-6	85.2	85.6
			-7	84.9	
			-8	85.1	
			-9	85.3	85.6

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To investigate the U.V. stability differences between the SAN and Saran MS, selected hand sheets were subjected to U.V. radiation in the fade-ometer for up to 93.7 hours. The following brightness readings were taken after the U.V. exposure.

	BLANK	24 HRS	94 HRS	Δ	
C-3	81.3	79.0	78.8	2.5	No Microspheres
C-9	83.1	81.0	80.4	2.7	
1-9	83.1	81.2	80.7	2.4	SAN Microspheres Lot #110621
2-9	83.5	80.8	81.1	2.4	
3-9	83.0	81.0	80.6	2.4	
4-9	83.4	81.2	80.0	3.4	SARAN Microspheres Lot #05182
5-9	83.9	80.8	80.7	3.2	
6-9	84.4	82.0	80.8	3.6	

Conclusion

Although the bulk of the "yellowing" seemed to occur during the first 24 hrs (indicating the test may have been too severe) the data does show a greater drop in brightness of the Saran MS paper than the SAN.

MICROSPHERE RESILIENCE IN ASBESTOS SHEETS

To compare the "compression set" characteristics of the SAN and Saran MS, a series of asbestos hand sheets were made containing from 1 to 7% (by wt) microspheres. The following procedure was used for preparing the hand sheets:

Asbestos	57.9 g
H ₂ O	2340 ml
Latex (10% Soln)	87.0 g
Ethomeen C-15 (5% Soln)	2.5 ml
Drew 169 A (DeFoamer)	2.5 ml
Microspheres (Foamed wet cake)	As Needed

The crumbed asbestos was agitated in 2340 ml of H₂O with an air driven agitater for 1 minute. The latex was then poured in and agitated for 3 more minutes followed by the addition of the Drew 169 A (defoamer) and the Ethomeen C-15 (surfactant) and an additional 1 minute of agitation - total of 5 minutes of agitation. The microspheres were then slurried in just prior to pouring the formulation into the sheet former. After each sheet was pressed and dried, four two-inch squares were cut out for compression set analysis.

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This test is performed by subjecting the samples to 50% compression at 70°C (158°C) for 22 hours. The sample is then allowed to recoil at room temperature for 30 minutes before the final thickenss is read. The following data was generated -

SARAN MICROSPHERES LOT #05182 14.4% SOLIDS 1.24 ATD

	<u>Sample</u>	<u>Wt.(g)</u>	<u>Int. Thick.</u>	<u>Final Thick.</u>	<u>Set</u>	<u>% Set</u>
1% Saran MS	1	2.3595	.0540	.0430	.0110	20.4
	2	2.3252	.0510	.0380	.0130	25.5
	3	2.3517	.0540	.0435	.0105	19.5
	4	2.3030	.0545	.0415	.0130	24.0
2% Saran MS	1	2.2675	.0730	.045	.028	38.4
	2	2.3227	.0770	.051	.026	33.8
	3	2.3101	.0785	.053	.0255	32.6
	4	2.3165	.0800	.054	.026	32.5
3% Saran MS	1	2.5165	.1100	.077	.033	30.0
	2	2.2208	.1120	.0765	.0355	31.8
	3	2.1828	.0925	.062	.0305	33.0
	4	2.2231	.0900	.060	.030	33.3
4% Saran MS	1	2.3714	.1255	.0950	.0305	24.3
	2	2.4382	.1240	.0960	.0280	22.6
	3	2.4089	.1240	.0950	.0290	23.4
	4	2.3912	.1105	.0850	.0255	23.1

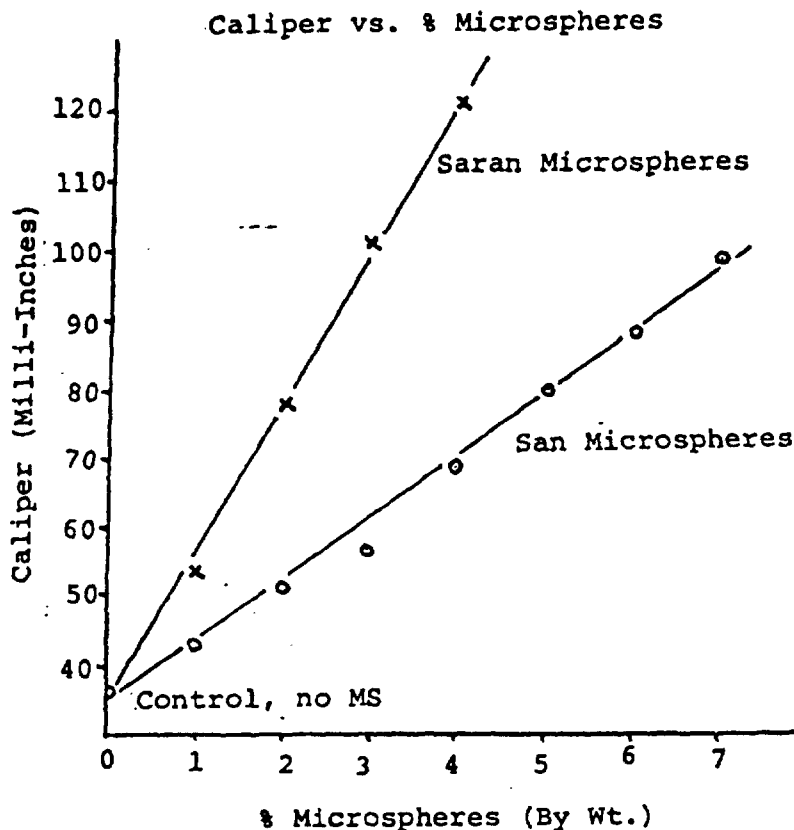
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SAN MICROSPHERES LOT #110621 13.4% SOLIDS 3.00 ATD

	<u>Sample</u>	<u>Wt.(g)</u>	<u>Int. Thick.</u>	<u>Final Thick.</u>	<u>Set</u>	<u>% Set</u>
1% SAN MS	1	2.1610	.0405	.0400	.0005	1.2
	2	2.3850	.0450	.0400	.005	11.0
	3	2.4430	.0445	.0415	.003	6.7
	4	2.3660	.0445	.0420	.0025	5.6
2% SAN MS	1	2.2129	.0475	.0415	.006	12.6
	2	2.2800	.0495	.0450	.0045	9.1
	3	2.4410	.0585	.0450	.0135	23.1
	4	2.4982	.0560	.0500	.006	10.7
3% SAN MS	1	2.0630	.0555	.0440	.0115	20.7
	2	2.3887	.0570	.0470	.0100	17.5
	3	2.2683	.0535	.0460	.0075	14.0
	4	2.3151	.0570	.0460	.0110	19.5
4% SAN MS	1	2.4739	.0645	.053	.0115	17.8
	2	2.4421	.0700	.060	.010	14.3
	3	2.4251	.0675	.053	.0145	21.5
	4	2.3667	.0695	.057	.0125	18.0
5% SAN MS	1	2.2978	.0795	.064	.0155	19.6
	2	2.3660	.080	.061	.019	23.8
	3	2.6070	.081	.063	.018	22.2
	4	2.3055	.080	.058	.022	27.5
6% SAN MS	1	2.4850	.089	.066	.023	25.8
	2	2.4962	.088	.067	.021	23.8
	3	2.4958	.087	.0665	.0205	23.6
	4	2.4660	.087	.067	.020	23.0
7% SAN MS	1	2.7168	.100	.074	.026	26.0
	2	2.6621	.101	.074	.025	24.7
	3	2.4480	.094	.072	.022	23.4
	4	2.5526	.096	.073	.023	24.0

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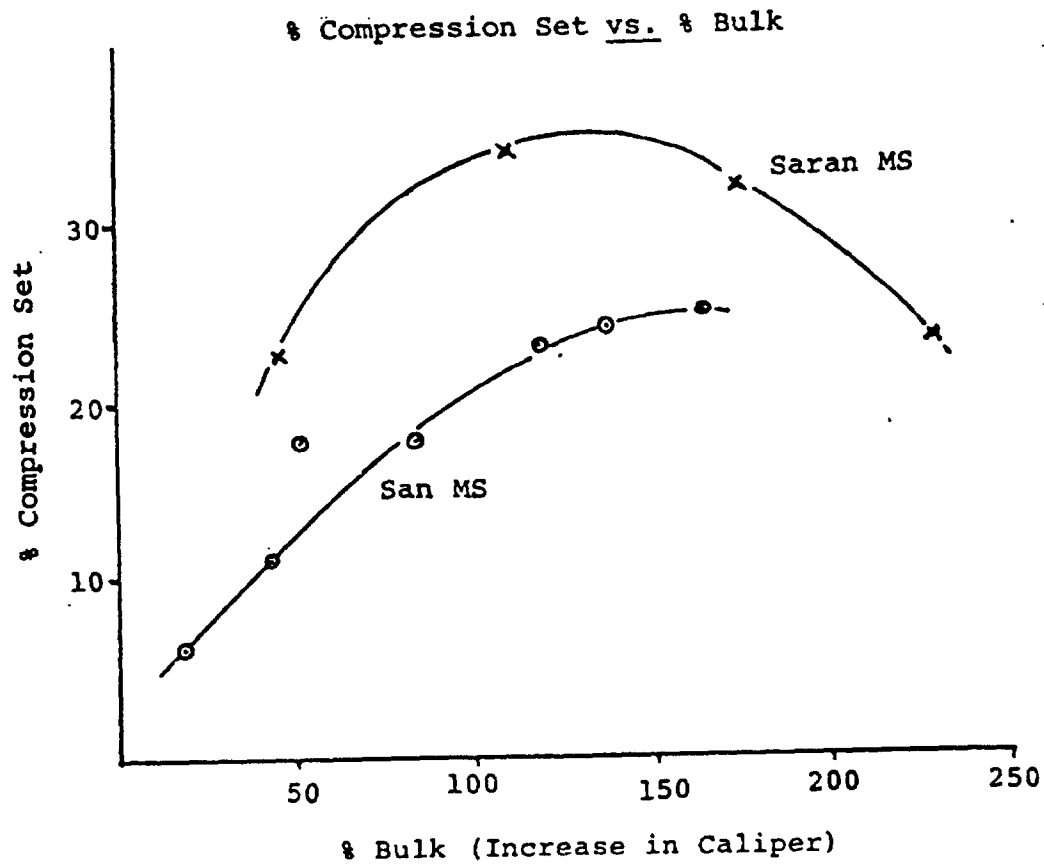
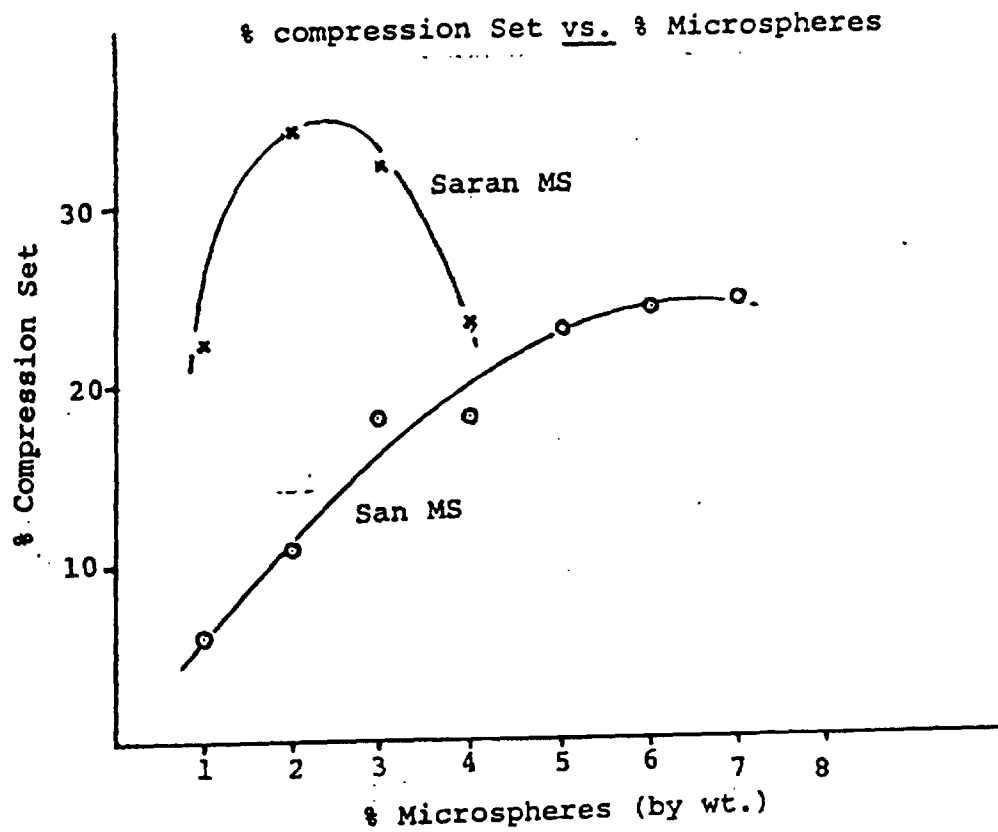
The following charts display this data graphically.



This first diagram shows the relationship between amount of microspheres added and the additional thickness of the sheet. The dramatic difference in slopes between the SAN and Saran MS is probably due to their different densities - the SAN has a density of 3.00#/ft^3 whereas the Saran only a 1.24#/ft^3 density.

The next two graphs show the amount of compression set compared first to % microspheres and then to % increase in caliper (bulk).

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Both graphs show that the Saran MS containing sheets reach a maximum compression set of 35% at the 2% MS level. Also, the SAN MS sheets seemed to have reached a maximum of 25% set at the 6-7% level, however the experiment wasn't carried far enough to confirm whether this is indeed a maximum or a plateau.

Conclusion

SAN Microspheres show superior compression set characteristics to Saran Microspheres in the asbestos sheet formulation. The Saran MS do add more bulk to the sheet, but the corresponding compression set is much larger than that of the SAN MS sheets. For example, a 50% bulk with <15% set can only be achieved using SAN Microspheres.

HYDRAULIC COMPRESSION TESTS

Compression bulking tests were run on both the SAN and Saran expanded microspheres. The first series of tests were run in a thick walled, glass bomb with a 60 psig pressure limit. Both dry microspheres and a MS-glycerin slurry were subjected to pressures up to 60 psig in this apparatus.

In general, the procedure was to place the MS sample in a calibrated test tube, which was then sealed in the bomb. As the pressure increased (by the introduction of air) the volume of the sample would decrease due to the buckling of the microspheres. When the pressure was released, the sample would again assume its original volume. The following data was collected when each sample was run in duplicate.

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SAN (Freon) Microspheres Lot #110621 Air Dried

Initial Wt. = 0.3459 gms
Initial Vol. = 23.0 ml
Initial Density = 15×10^{-3} gms/cc

<u>Press. (psig)</u>	<u>Vol. (cc)</u>	<u>Density (10^{-3} gms/cc)</u>	<u>% Increase in Density</u>
5	21.2	16.3	8.5
9	20.5	16.9	12.1
13	20.0	17.3	15.0
15	19.5	17.7	17.9
19	19.0	18.2	21.0
25	18.5	18.7	24.3
29	18.2	19.0	26.3
39	17.5	19.8	31.4
46	17.1	20.2	34.5
56	16.4	21.1	40.2

Initial Wt. = .3504 g
Initial Vol. = 23.2 ml
Initial Density = 15.1×10^{-3} gms/cc

2	22	15.9	5.4
4	21.5	16.3	7.9
9	20	17.5	16.0
13	19.4	18.1	19.5
16	18.9	18.5	22.7
22	18.3	19.1	26.7
27	17.8	19.7	30.3
36	17.0	20.6	36.5
50	16.5	21.2	40.6
59	16.2	21.6	43.2

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Saran Microspheres Lot #05182 Air Dried

Initial Wt. = 0.1895
Initial Vol. = 22.7 ml
Initial Density = 8.35×10^{-3} g/cc

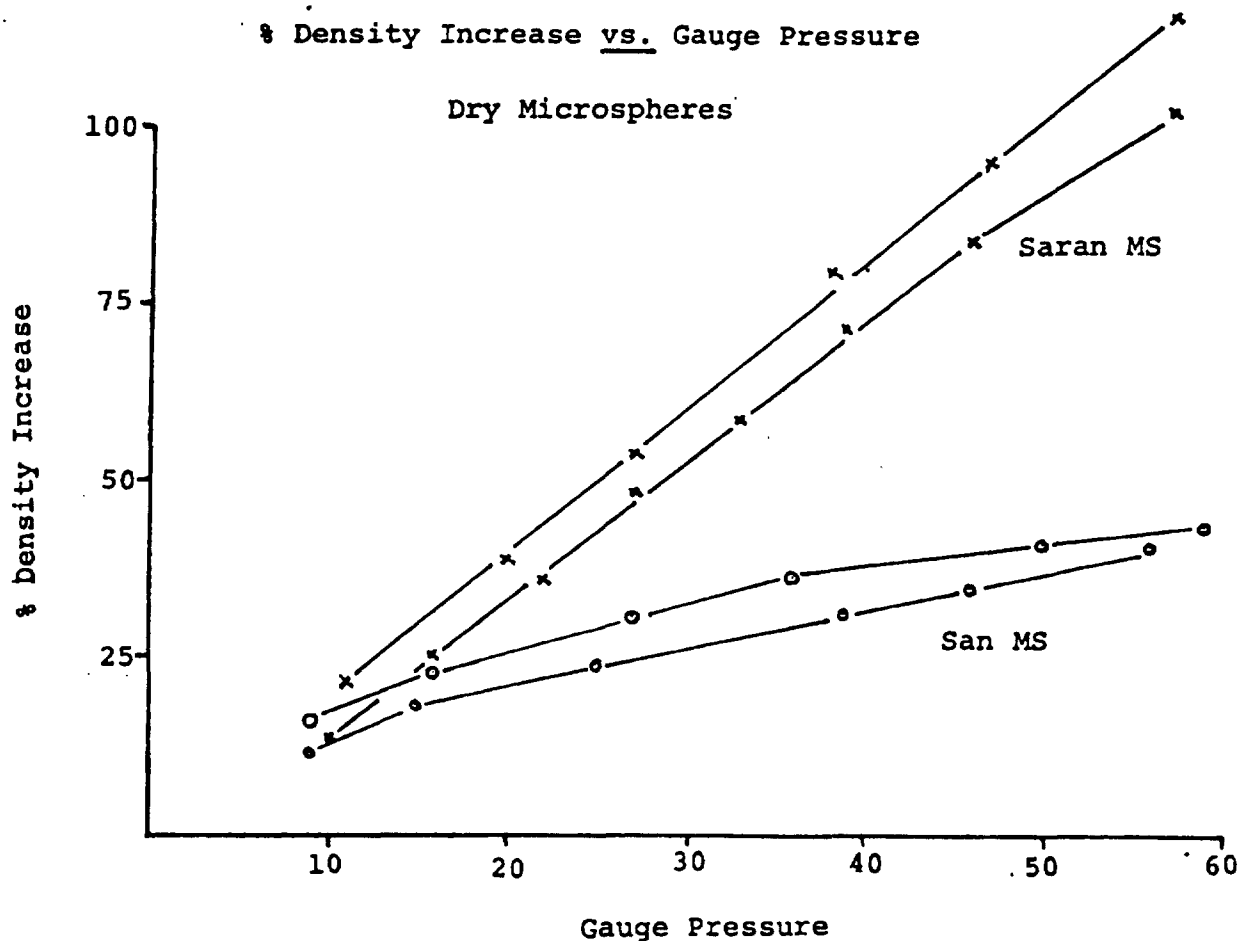
<u>Press. (psig)</u>	<u>Vol. (cc)</u>	<u>Density (10^{-3} g/cc)</u>	<u>% Increase in Density</u>
2	20	9.5	11.1
10	19.5	9.7	13.9
14	19	10.0	16.9
16	18.5	10.2	20.0
22	16.4	11.5	35.5
25	15.5	12.2	43.5
27	15.0	12.6	48.1
33	14.0	13.5	58.7
39	13.0	14.6	70.9
46	12.1	15.7	83.7
57	11.0	17.2	102.0

Initial Wt. = 0.1775
Initial Vol. = 21.5 ml
Initial Density = 8.26×10^{-3} g/cc

4	19.2	9.2	11.9
11	17.6	10.1	22.2
15	16.8	10.6	28.0
20	15.5	11.4	38.6
24	14.6	12.2	47.1
27	14.0	12.7	53.6
31	13.0	13.6	65.3
38	12.0	14.8	79.2
47	11.0	16.1	94.9
57	10.0	17.8	115.0

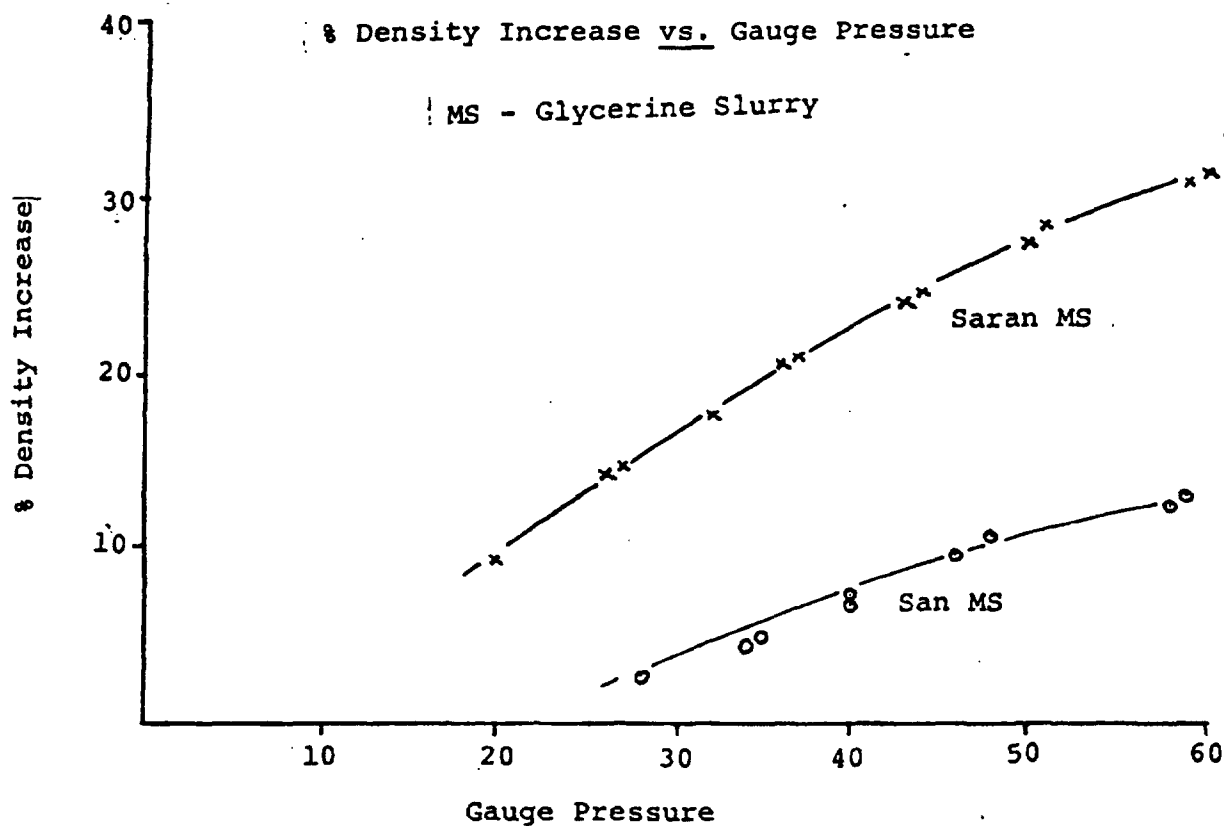
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When this data is presented graphically, one can readily see the more pronounced effect of pressure on the Saran Microspheres compared to the SAN product.



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A similar set of data was generated using a glycerine slurry of expanded microspheres instead of the dry material. Here, too, we see the same pronounced effect of pressure on the Saran microspheres.



The following charts show the raw data used to generate this graph.

ST0284310

Saran Microspheres Lot #05182 14.4% Solids

Initial Wt. = 16.5 gms of MS - Glycerine Slurry
Initial Vol. = 21.2 ml
Initial Density = 0.778 g/cc

<u>Press. (psig)</u>	<u>Vol. (cc)</u>	<u>Density (g/cc)</u>	<u>% Increase in Slurry Density</u>
20	19.4	.85	9.3
23	19.0	.87	11.6
27	18.5	.89	14.6
32	18.0	.92	17.8
37	17.5	.94	21.2
44	17.0	.97	24.7
51	16.5	1.00	28.5
59	16.2	1.02	30.9

Initial Wt. = 17.6 gms slurry
Initial Vol. = 22.8 cc
Initial Density = .772 g/cc

17	21.5	.82	6.1
20	21	.84	8.6
22	20.5	.86	11.2
26	20	.88	14.0
30	19.5	.90	16.9
34	19	.93	20.0
39	18.5	.95	23.2
46	18	.98	26.7
57	17.5	1.01	30.3

ST0284311

SAN Microspheres Lot #110621 13.4% Solids

Initial Wt. = 22.3 g of MS-Glycerine Slurry
Initial Vol. = 22.6 cc
Initial Density = .987 g/cc

<u>Press (psig)</u>	<u>Vol. (cc)</u>	<u>Density (g/cc)</u>	<u>% Increase in Slurry Density</u>
28	22	1.014	2.7
35	21.5	1.037	5.1
40	21	1.062	7.6
48	20.5	1.088	10.3
59	20	1.115	13.0

Initial Wt. = 21.7 g of Slurry
Initial Vol. = 21.9 cc
Initial Density = .991

34	21	1.033	4.3
40	20.5	1.059	6.8
46	20	1.085	9.5
58	19.5	1.113	12.3

ST0284312

At these low pressures, 0-60 psig, no permanent damage, or rupturing, occurred to the microspheres. In order to determine the maximum pressures these spheres can withstand, experimentation was done in a small, (50 ml.) Parr bomb equipped with a 1000 psi pop valve. A glycerine slurry of known microsphere concentration and density was poured into the bomb and subjected to 900# psig (air pressure) for 15 minutes. The sample was removed and the density checked. Theory: If a significant number of microspheres are ruptured, their loss of volume will cause the slurry density to increase. In this manner the following data was collected.

Effect of 900# Air Pressure on Microspheres
Time = 15 Minutes Temp. = Room Temp.

	<u>Initial Density</u>	<u>Final Density</u>	<u>% Change</u>
Saran Lot #05182	1.24#/ft ³	1.12#/ft ³	-9.6
Saran Lot #111811	1.78#/ft ³	1.77#/ft ³	-0.5
SAN Lot #110621	2.54#/ft ³	5.23#/ft ³	+105.9
SAN Lot #092021	1.84#/ft ³	2.13#/ft ³	+15.8
SAN-Neo Lot #1553-15	1.53#/ft ³	1.67#/ft ³	+9.2

Microscopic examination of all five samples confirmed that no rupturing had occurred with the Saran Microspheres, but the SAN samples showed unusual looking platelets, presumably the ruptured microspheres.

Conclusion

Saran Microspheres buckle at lower pressures than SAN and can survive higher pressures without rupturing. Saran Microspheres, in general, seem to be a softer, more flexible sphere than SAN Microspheres.

ST0284313

SOLVENT EFFECTS ON MICROSPHERES

The solvent compatibility of microspheres has been a major concern of many of our customers doing developmental work in non-aqueous systems. To examine the solvent effects on microspheres, a series of test tubes were filled with dry, expanded microspheres and treated with the solvent in question. The following table shows the effect of fourteen different solvents at room temperature and at 60°C.

Conclusion

Aliphatic hydrocarbons seem to be the only organic solvents that do not soften or solvate the microsphere shell. The saran product is more resistant to aromatic solvents than the SAN material at room temperature, but at 60°C it too will decompose.

SOLVENT RESISTANCE OF MICROSPHERES

<u>BP°C</u>	<u>SOLVENT</u>	<u>SARAN</u>		<u>SAN</u>	
		R.T.	60°C	R.T.	60°C
?	Mineral Spirits	Good	Good	Good	Good
68.7	Hexane	Good	Good	Good	Good
80.7	Cyclohexane	Good	Good	Good	Good
64.7	Methanol	Good	Poor	Good	Poor
78.4	Ethanol	Good	Good	Good	Poor
82.4	Isoprcpanol	Good	Good	Good	Poor
80.1	Benzene	Good	Poor	Poor	
110.6	Toluene	Good	Poor	Poor	
140	Xylene	Good	Good (?)	Poor	
56.2	Acetone	Poor		Poor	
79.6	Methyl Ethyl Ketone	Poor		Poor	
118	Methyl Isobutyl Ketone	Poor		Poor	
40.2	Methylene Chloride	Poor		Poor	
113	Trichloroethane	Good		Poor	
		(Slight Color)			

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