Monsanto

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SUBJECT Polysulfides

REFERENCE

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Summary

Evaluations of polysulfide sealant formulations show that benzyl phthalates are in the position of performing less well than chlorinated paraffin in some critical tests. Cost parameters favor chlorinated paraffin, particularly when compared to Santicizer® 278. Long term viability of our position with benzyl phthalates in polysulfide sealants will probably require development of new blends, new blending and sealant technology, and possibly synthesis of new molecules.

Detailed Summary

1) Santicizer 278 is inferior to Cereclor S-52 (chlorinated paraffin, ICI) in fogging to glass. Blending Santicizer 8 with Santicizer 278 reduces fogging but Santicizer 8 does not improve the adhesion of Santicizer 278.

2) In glass adhesion and in aluminum adhesion Santicizer 278 is worse than Santicizer 261. Again, chlorinated paraffin is the best of all materials evaluated. All materials respond to epoxy silane adhesion promoters. No filler effects are seen. Santowax® Q and Montars will increase Santicizer 278 aluminum adhesion but not to the point where it is competitive with chlorinated paraffin.

3) Santicizer 278 is reasonably stable with heat and this stability is also shown by Santicizer 261 and by chlorinated paraffin. Heating any of the plasticizers tends to increase the cure rate slightly. Heating any benzyl phthalate plasticizer with manganese dioxide catalyst will reduce the catalytic efficiency and retard curing of the polysulfide. This does not occur as dramatically with chlorinated paraffins or DUP. Lead dioxide will deactivate when heated with Santicizer 278. This does not occur with Santicizer 261, Santicizer 160, Cereclor S-52 (chlorinated paraffin), or DUP. It has also been shown that alcohols will lower the cure time and reduce adhesion of the systems. Any high alcohol levels in plasticizers are detrimental in this respect.

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Tentative Conclusions, Options, Leads, etc.

1) Santicizer® 261 seems less reactive to manganese dioxide than Santicizer 278. The switch of the polysulfide industry to manganese dioxide rather than lead dioxide has allowed the use of chlorinated paraffins in a number of applications, and Santicizer 278's advantages are limited with manganese dioxide. It seems possible that Santicizer 261 may be the benzyl phthalate of choice for blends. The use of Santicizer 8, Santowax® Q, or Montar 9 with Santicizer 261 may indicate a viable blending lead.

2) The cost of chlorinated paraffins indicates that a low cost blend stream for benzyl phthalates may be advantageous. Alkylates as H-230-L seem to be a possibility providing adhesion problems can be solved. These materials blended with Santicizer 261 may be viable candidates and should be screened further.

3) Adhesion promoters include calcium oxide generators, iron halide materials, unsaturated polyesters for cross-linking, anhydrides, sulfonamides, etc. No materials evaluated to date, however, are as efficient as epoxy silene adhesion promotion. This may indicate a need for synthesis to help generate new leads. The material could be reactive with mercaptans, contain methoxy silane groups, be multi-functional, or possibly have phosphorus in the backbone.

4) The chlorinated paraffin threat to the benzyl phthalate position seems to be mostly in calcium carbonate filled systems. The black filled system will probably be less threatened. It is recommended that some defensive research be carried out to protect our position in black filled systems, and to maintain our technology level in the use of benzyl phthalates in catalyst dispersions.

5) The loss of adhesion by Santicizer 278 and the surprisingly good performance of chlorinated paraffin is a complex situation. Work has shown that low molecular fragments of polysulfide rubber appear on the surface when rubber is exposed to moist heat or U.V. A chain terminating complex of manganese with the rubber is postulated. One customer has indicated this hypothesis may be valid. The low molecular fragments would be easily solvated by Santicizer 278, increasing moisture pick-up and decreasing adhesion.

Chlorinated paraffin will, however, dehydrohalogenate leaving olefins that can crosslink the rubber thus preventing migration of fragments which may form. Incorporation of low levels of PVC or polybutadiene in Santicizer® 278 may improve performance by the same mechanism.

6) It has been learned in discussions with Norton Co. and PRC (see J. H. Orem reports) that the commercial ratio of rubber to plasticizer is nearly 1:1 instead of the 3:1 ratio recommended by Thiokol. This increases the problems possibly dependent on plasticizer but also allows the use of other polymeric blends with benzyl phthalates.

Proposed Technical Topics

1) Compare Santicizer 261 and Santicizer 278 in blends with Santowax® Q, Montar 9, Santicizer 8, etc.

2) Determine properties and suitability of H230L and other alkylates as a blending agent with benzyl phthalates.

3) Determine utility of latent crosslinkers (as PVC, polybutadiene, etc.) with benzyl phthalates.

4) Evaluate new molecules as available, particularly those containing unsaturation or otherwise reactive to the polysulfide resin.

Discussion

The current threats and questions pertaining to our benzyl phthalate position in polysulfide sealants have been well documented (J. H. Orem). In general the use of manganese dioxide as a catalyst has allowed the use of chlorinated paraffin in what was previously a proprietary benzyl phthalate market. This catalyst, the new coated fillers which compensate for the chlorinated paraffin viscosity variations, and "cleaner" chlorinated paraffins have led to the current situation where chlorinated paraffins are equivalent or better in many tests when compared to Santicizer 278 or Santicizer 261. Table 1 describes recent Monsanto laboratory evaluations.

Basically, Table 1 shows that chlorinated paraffin is superior in fogging, adhesion, cure stability, and physicals to Santicizer 278. Considering the wide variation in cost it is apparent why chlorinated paraffins are under evaluation as a Santicizer 278 replacement. It is noteworthy in Table 1, particularly in adhesion, that Santicizer 261 is very close to chlorinated paraffin in performance and is somewhat superior to Santicizer 278 in this effect.

The most critical factors, other than cost, in a polysulfide sealant are adhesion, low moisture vapor transmission, good cure stability, and very low fogging results. Adhesion promoters are conventionally added to improve the adhesion of such systems. In Table 2 A189 (epoxy silanes) were evaluated with chlorinated paraffin and with Santicizer® 278. In this evaluation the results were essentially equivalent for Santicizer 278 and for chlorinated paraffins. It was shown that Santolite® MHP would not cure with Santicizer 278 with the Inmont manganese dioxide catalyst. However, Santicizer 8 was shown to greatly improve the fog value of Santicizer 278, particularly on long-term aging in the Fadeometer. Further data in Table 2 indicates that Santicizer 8 did not give the hoped for increase in adhesion. This effect of Santicizer 8 in improving the fog value should be investigated further.

In Table 3 a number of other materials were evaluated. Montar 9 and Santowax® Q blended with Santicizer 278 and Santicizer 261 showed that a slight increase in adhesion can be achieved with Montar 9 or Santowax Q particularly in the case of aluminum. This system should be followed up.

H-230L was evaluated with Santicizer 278. Stick times were progressively improved with H-230L but the adhesion fell off precipitiously. This should not be much different than the effects usually found with diluent addition and should be over-ridden by the addition of epoxy silane. This particular system may lead to a blend which may be cost competitive with chlorinated paraffin. The use of Santicizer 261 with H-230L should be evaluated for this type of blend. Montar 9, Santowax Q, Santicizer 8 may be evaluated with a blend of this type to hopefully improve its performance.

The second half of Table 3 further indicates that HOE, PBSA, or Texanol will lower the adhesion of Santicizer 278 polysulfide system, up to 50-75%. It also indicates anhydride groups will deactivate the catalyst and prevent cure, which eliminates this potential method of increasing adhesion.

Table 4 covers the effect of per se heating on the plasticizer involved. It is seen that benzyl phthalates and chlorinated paraffin readily decrease stick times (cure up the polysulfide faster) after the plasticizers have been heated.

In Table 5 the acidity of these systems was measured and it is seen that chlorinated paraffin is stable. Santicizer 160, Santicizer 261, and Santicizer 278 are all relatively low in acidity and seem to be very stable.

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Table 6 is the crux of the technical problem facing us. Here the individual plasticizers (benzyl phthalates, chlorinated paraffins, and DUP) were heated with manganese dioxide and lead dioxide. The resulting systems were decanted and the refractive indicies measured. There were only moderate changes in the refractive index, but severe deactivation of the catalyst occurred. Thus, the stick times of manganese dioxide catalyst with benzyl phthalates are radically changed. DUP shows very little interaction but, as is common for most dialkyl phthalates, gives a very sticky tacky surface.

Comment

One of the big problems with getting up to speed after inactivity in this area for 8 to 9 years is the long evaluation time required for polysulfide sealants. Thus, a sample based on an idea one has today will require 3-5 months before a complete evaluation can be achieved. The technical odds of success are not encouraging and some new technology or innovation is certainly indicated. Defensive effort is certainly warranted to maintain our current business as much as possible. Overall success in regaining market share lost to chlorinated paraffin will require that this program in sealants be continued for at least another year in order to gain enough data so that suitable blends or compounds can be generated.

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/vw

TABLE I

		1	2	3	4	5	6	7	8
Thiokol LP-2		100	→	→	→	-	-	-	-
Thiokol LP-32		-	-	-	-	100	→	→	→
Hakuenka CC		30	→	→	→	→	→	→	→
Santicizer 278		-	30	-	-	-	30	-	-
Santicizer 261		-	-	30	-	-	-	30	-
Cereclor S52		-	-	-	30	-	-	-	30
Inmont Catalyst		15	→	→	→	→	→	→	→
Stick time (minutes)		90	115	80	90	60	20	10	10
Stick time (minutes (after 1 mo. aging)		45	80	70	90	25	35	25	35
Adhesion to Glass (lbs.)		1	0.6	0.6	0.8	1.4	1.3	2.0	2.1
Specular Reflectance									
Orig. No UV Number Side (1)		79	81	82	86	75	86	85	89
No UV + Corrora glass (2)		81	83	84	89	79	89	88	93
UV Blank side (3)		69	81	83	85	82	84	86	85
Blank side + Corrora glass (4)		71	84	86	88	85	88	89	88
115 hrs.	1	OS	40	37	74	33	72	58	57
	2	OS	37	38	79	34	75	61	59
	3	67	76	68	83	61	75	72	73
	4	67	79	68	88	61	78	74	76
233 hrs.	1	74	80	71	OS	71	89	86	83
	2	74	81	71	OS	72	90	86	85
	3	OS	OS	→	→	→	→	→	→
	4	OS	OS	→	→	→	→	→	→
334 hrs.	1	73	72	72	83	70	79	90	80
	2	73	72	72	83	70	79	91	80
	3	OS	→	→	→	→	→	→	→
	4	OS	→	→	→	→	→	→	→
Shore A (10 Sec.)		51	30	29	30	38	19	20	17
Instantaneous		52	32	32	32	42	24	24	24
100% Mod. PSI		697	407	805	686	1286	563	557	523
200% Mod. "		863	583	1070	955	1587	724	719	678
300% Mod. "		981	617	-	-	1921	853	854	816
Elongation, %		598	274	193	205	306	482	621	686
Tensile PSI		1319	1315	1061	985	1802	1021	1188	1283
Moist UV (failures)	5 day	-	-	-	20%	-	-	0	-
	7 day	(Swollen)		OK	20%	Sticky	20%	(Swollen)	
	12 day	80%	10%	OK	20%	20%	20%	20%	20%
	18 day	80%	20%	OK	80%	(20%	→	→	→)

TABLE 2

	Control	1	2	3	4	5	6	7	8
Thiokol LP32		100 ⟶							
Hakuenka CC		40 ⟶							
A 187		-	-	2	2	-	-	-	-
A 189		-	-	-	-	2	2	-	-
Santicizer 278		20	-	20	-	20	-	15	15
Cereclor S 52		-	20	-	20	-	20	-	-
Santicizer 8		-	-	-	-	-	-	5	-
Santolite MHP		-	-	-	-	-	-	-	5
Inmont Catalyst		15 ⟶							
Stick Life (min.)		35	30	35	25	360	330	40	305
Stick Life (1 mo. min.)		25	25	30	20	90	90	30	(didn't cure)
Adhesion to glass (lbs.)		2.2	2.1	3.5*	3.8*	4.0*	2.4*[1]	1.3	-
Adhesion to metal (lbs.)		1.2	1.1	> than tensile of polymer				0.7	-
100% Mod.		796	760	993	787	861	780	757	-
200% Mod.		871	958	1396	1139	1185	1092	954	
300% Mod.		1096	1103	-	-	-	-	1088	-
Elongation, %		517	627	218	259	258	223	527	-
Tensile PSI		1315	1500	1448	1304	1296	1144	1355	-
Shore A 10 sec.		28	27	34	30	34	31	29	-
Instantaneous		34	35	37	35	37	35	35	-
Specular Reflectance									
1) Orig. No UV, Number Side	93	89	92	86	94	84	95	93	90
2) No UV, Corrora Glass	97	91	94	88	97	86	98	96	92
3) UV, Blank Side	96	86	91	89	97	85	96	95	92
4) UV, Blank, Corrora Glass	100	88	93	91	99	87	99	99	95
1) 47 Hrs.		85	90	76	85	69	95	94	Fail ↓
2)		87	92	77	89	71	99	97	
3)		87	89	87	94	86	98	95	
4)		89	91	89	97	87	OS	99	
1) (94 hrs)		84	84	66	68	59	93	93	
2)		86	86	67	70	60	97	96	
3)		83	82	85	91	83	97	94	
4)		85	84	86	93	84	OS	98	
1) 139 hrs.		86	90	53	59	55	85	94	
2)		88	92	54	60	56	89	97	
3)		89	90	81	85	81	97	97	
4)		91	92	82	87	82	OS	100	

* = broke, 1 = tacky

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TABLE 3

	1	2	3	4	5	6	7	8	9
Thiokol LP32	100 →								
Santicizer 278	27	27			30	25	20	10	-
Santicizer 261			27	27					
Montor 9	3		3						
Santowax Q		3		3					
H-230-L						5	10	20	30
Inmont Catalyst	15 →								
Stick Time (min.)	105	120	75	60	120	85	80	55	25
Glass Adhesion (lbs.)	1.2	1.4	1.0	1.3	1.2	1.8	.9	0	.3
Aluminum Adhesion (lbs.)	.25	.6	.6	.5	0.1	0	0	0	0

TABLE 3A

	1	2	3	4	5	6	7	8
Thiokol LP32	100 →							
Hakuenka CC	30 →							
Santicizer 278	30		30	25	25	25	25	
Cereclor S52		30						
Montor 9				5				
Santowax Q					5			
HOE						5		
PBSA							5	
A-189		1	1					
2% Texanol in Santicizer 278								30
Thiokol Catalyst	15 →							
Stick Time (min.)	20	20	15	10	5	8	>48 Hrs.	5
Glass Adhesion (lbs.)	.4	3.6	.8	.4	.3	.2	-	.1
Aluminum Adhesion (lbs.)	.6	(> than polymer)		.6	.7	0	-	.3

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TABLE 4

	1	2	3	4	5	6	7	8
Thiokol LP-2	50	→	→	→	→	→	→	→
S-278	15							
S-261		15						
S-160			15					
Cereclor S52				15				
S-278 (72 hrs 100°C)					15			
S-261 "						15		
S-160 "							15	
Cereclor S52 "								15
Inmont Catalyst	7.5	→	→	→	→	→	→	→
Stick Life (min)	190	135	190	170	145	110	145	140

TABLE 5

Acidity (meg/100 g)

Hours at 100°C	Cereclor S52	Santicizer 160	Santicizer 261	Santicizer 278
0	0.44	0.90	0.17	0.42
12	0.45	0.88	0.23	0.44
24	0.45	0.90	0.26	0.40
48	0.50	0.90	0.32	0.38
72	0.60	0.89	0.32	0.38

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TABLE 6

Aged One Week, 100°C

	1	2	3	4	5	6	7	8	9	10
Santicizer 278	50	50								
Santicizer 261			50	50						
Santicizer 160					50	50				
Cereclor S52							50	50		
DUP									50	50
Manganese Dioxide	50		50		50		50		50	
Lead Dioxide		50		50		50		50		50
Refractive Index	1.5161	1.5162	1.5243	1.5244	1.5379	1.5376	1.5061	1.5063	1.4792	1.4790
Stick Times (In 50 LP-2, 15 Plasticizer, 7.5 Inmont Catalyst)	>24 hr	>24 hr	>24 hr	335 min	>24 hr	170 min	275 min	115 min	85* min	80* min

*Sticky to touch.

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