

Monsanto

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DATE

October 26, 1979

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SUBJECT

POLYSULFIDES

REFERENCE

TO

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SUMMARY

Scriptset 808, dissolved in polysulfide rubber, improves adhesion and moisture sensitivity. Standard plasticizers, especially Santicizer 261, Santicizer 278 and XA-1112 work well with this system and were somewhat better than chlorinated paraffin. A blend of Scriptset 808/plasticizer, could not be made. The Scriptset must be dissolved in the polysulfide prior to compounding for best results. Standard compounding techniques can be used.

RECOMMENDATION:

1. If patent approval is obtained, distribute the Scriptset 808 data to the field and push for evaluation with XA-1112, Santicizer 261 and Santicizer 278.
2. Terminate further efforts in polysulfide sealant research except for specific work requests.

DETAILS

Attached

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/vw -gl's
Att.

DSW 588344

STLCOPCB4093680

Details

Previous work has shown that XA-1112 is a good way of modifying the adhesion characteristics of polysulfide adhesives and sealants. However, the normal use of amine-type accelerators in such polysulfide sealants prevents the effective use of XA-1112 in most commercial applications. As the whole purpose for the XA-1112 development was to achieve cross-linking of the polysulfide, to increase the cohesive energy density, which results in an improvement in water permeability it was then necessary to look for alternate methods of obtaining cross-linking. One of the best methods known in the literature is, of course, phenolic resins or anhydride or polyacid-type resins. In the polysulfide window sealing caulks the use of such resins has a tendency to give infinitely long cure times and this is not advantageous. An amine, ammonium salt, amide, imide, etc. salt of a polyanhydride resin, however, was apparently a previously unevaluated method of obtaining cross-linking. For this reason work was done with Scriptset 808. Figure 1 describes the physical properties and gives a structural formula for Scriptset 808.

Initially, it was attempted to dissolve Scriptset 808 in Santicizer® 278 or Santicizer 261. No successful method was found. Attempts to co-solvate with tetrahydrofuran, butanol, or with very fine physical dispersions (paint mill, ball mill, etc.) were all unsuccessful. Separation or infinitely long stick lives or poor adhesion was found. This occurred whether the Scriptset 808 was put in on the catalyst (manganese dioxide) side or on the resin (polysulfide) side. Table 1 shows the problems of straight physical blending of Santicizer 278, Scriptset 808, with or without Santicizer 8 in a typical polysulfide screening formulation. It is to be noted that very short stick lives are obtained showing the acceleration possible with Scriptset. Initial adhesion to glass and aluminum strips was quite good, but upon water soaking the adhesion failed badly.

In Table 2, attempts to improve water adhesion were made by incorporating wire and cable modifier (WCM) or phenolic plastics with the Scriptset resin and with benzyl phthalate. In this case, the phenolics prevent the cure and WCM prevents good adhesion even with organo silane ester additive as an adhesion promoter.

In Table 3, the successful method of dispersing Scriptset 808 is first described. The blend of Scriptset 808 with the polysulfide rubber forms a clear homogeneous solution. The blending may occur at any temperature up to the decomposition temperature of the polysulfide rubber. We found 100°C with stirring to be convenient although room temperature stirring will also eventually result in a clear solution.

In Table 3, very good stick lives are seen and, it is to be noted, that superior adhesion was found to glass and aluminum even after a 72 hour water soak. It is seen that organo silane ester adhesion promoter is not necessary, a small amount of epoxy resin (Epi Rez 510) is beneficial. Based on this screening data a complete screening series was run. This is shown in Table 4.

From this data the wide use of the Scriptset/LP-32 combination may be seen. The control is sample #1. This "State of the art" sample shows relatively rapid loss in the water immersion beads test. It shows good results in the fogging test (Table 5). The use of the LP-32 - Scriptset 808 blend without organo silane promoters is shown in Table 4. Epi-Rez. 510 is used in this system also. Here the good results found in the screening from Table 3 did not show to the extent hoped for, although the water beads test shows a definite improvement over the control.

Sample 3 is exactly the same as 2 except organo silane ester is added. This sample shows very good results particularly in adhesion in the water beads test.

Sample 4 is a state of the art competitive control using chlorinated paraffin. It is seen, as previously reported that this sample is superior to our current "benzyl phthalate" state of the art system. It is also seen that the use of Scriptset 808 with LP-32 and chlorinated paraffin (Sample #7) does also work. Overall evaluation (subjective, least swell) show however that the benzyl phthalates work better than the chlorinated paraffins with Scriptset/LP-32 modification.

Sample 5 shows the substitution of Santicizer® 261 for Santicizer 278 in our preferred formulation. Unfortunately, while very good moisture vapor transmission results were found, a fall-off in glass adhesion and a slight fall-off in water immersion is seen. This is still a very good sample, however, and could be of use and might possibly be worthwhile evaluating.

Samples 6 and 8, which use XA-1112 and the Scriptset 808/LP-32 modification were superior. Sample 6 incorporates everything we now know which would give improved performance in a polysulfide system. Overall, based on visual inspection of the water beads sealant test, Sample 6 was rated the best and showed superiority to the chlorinated paraffin control (Sample 7). Sample 8, while quite good, was not quite as good as the sample 6 test which shows an accumulative advantage of organo silane ester adhesion promoter.

It does seem that we have a strong possibility of selling:

- A) Scriptset 808
- B) XA-1112 or other benzyl phthalate
- C) A possible reduction of the organo silane ester level to come close to a Class 1 (Class A) adhesive or sealant.

It is hoped that this Scriptset modification will eliminate the problems noted previously with XA-1112 where accelerator interference was seen. It is recommended that this data, as soon as it is cleared with Patent personnel, be taken to the field for evaluation.

FIGURE 1

Scriptset 808

Styrene/Maleic Anhydride Ratio	1:1
Molecular Weight Distribution	Broad
Physical Form	Powder
Sp. Gravity (dried film)	1.27 - 1.29
Soft. Pt. °C	225 - 230°C
Acid Number (Alc. KOH Titration)	290
Viscosity 10% So'n. (cps)	4200 (Brookfield, #1, 25°C)
p ^H 10% Sol'n.	5.7

FORMULA:

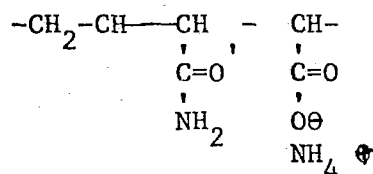


TABLE ONE

<u>COMPONENTS</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Scriptset 808	10	20	10	10	50
Santicizer 278	90	80	85	80	50
Santicizer 8	-	-	5	10	-
	↓	↓	↓	↓	↓
Blend #1	25	-	-	-	-
Blend #2	-	25	-	-	-
Blend #3	-	-	25	-	-
Blend #4	-	-	-	25	-
Blend #5	-	-	-	-	25
LP-32 Liquid Polysulfide Polymer	50	----->			
CaCO ₃ (Atomite)	30	----->			
Hakuenka CC	10	----->			
Chemetals Catalyst 1443665	10	----->			
Stick Life (min.)	0	2	15	5	0
Initial Adhesion					
Glass	Good	----->			
Aluminum	Fair	----->			
Water Soak Adhesion					
Glass	Fail	----->			
Aluminum	Fail	----->			

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TABLE TWO

<u>COMPONENTS</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
LP-32 Liquid Polysulfide Polymer	50	----->				
CaCO ₃ (Atomite)	30	----->				
Hakuenka CC	10	----->				
W.C.M. (Wire & Cable Modifier) AS-2	25	22.5	22.5	20	15	-
Scriptset 808	-	2.5	-	2.5	2.5	-
Phenolic Plastic Bakelite CK-0036	-	-	2.5	2.5	2.5	-
Santicizer 278	-	-	-	-	5	25
A-189 Organo Silane Ester	0.5	----->				
Chemetals Catalyst 1443665	10	----->				
Stick Life (min.)	1	1	∞	∞	∞	20

Initial Adhesion

Glass	Fail	Fail	-	-	-	Good
Air	Fail	Fail	-	-	-	Good

Water Soak Adhesion

Glass	Fail	Fail	-	-	-	Good
Air	Fail	Fail	-	-	-	Good

TABLE THREE

<u>COMPONENTS</u>	<u>1</u>	<u>2</u>	<u>3</u>
5:1/LP-32:SCRIPTSET 808*	30	30	50
LP-32 Liquid Polysulfide Polymer	20	20	-
Santicizer 278	25-----		
Hakuenka CC	10-----		
CaCO ₃ (Atomite)	30-----		
A-189 Organo Silane Ester	0.5	-	-
Chemetals Catalyst 1443665	10-----		
Epi Rez 510 B5-26438	2.5-----		
Stick Life (min.)	60	20	20
Initial Adhesion			
Glass	Good	Good	Good
Aluminum	Good	Good	Poor
Water Soak (72 hours)			
Glass	Good	Good	Good
Aluminum	Fail	Good	Good

* Blend prepared 100°C with stirring until clear.

TABLE FOUR

COMPONENTS	1	2	3	4	5	6	7	8
LP-32 Liquid Polysulfide Polymer	100	40	40	100	40	40	40	40
5:1/LP-32:SCRIPTSET 808	-	60	60	-	60	60	60	60
Santicizer 278	50	50	50	-	-	-	-	-
Santicizer 261	-	-	-	-	50	-	-	-
Hakuenka CC	20	----->						
CaCO ₃ (Atomite)	60	----->						
A-189 Organo Silane Ester	1	-	1	1	1	1	1	-
Epi Rez 510 B5-26438	-	2.5	2.5	-	2.5	-	-	-
S-52 Cereclor	-	-	-	50	-	-	50	-
XA-1112	-	-	-	-	-	50	-	50
Chemetals Catalyst 1443665	20	----->						
Stick Life (min.)	10	10	15	15	45	30	30	10
Adhesion to Glass (all exceed tensile strength of polymer) PSI	-	-	-	3.1	2.2	2.2	3.2	3.3
Adhesion to Aluminum PSI	0.4	-	-	-	-	-	-	-
(all but sample 2 exceed tensile strength of polymer)								
Permeability (Honeywell) g.cm/24 hr. 2.mm Hg m	.107	.117	.107	.084	.086	.083	.069	.088
8 Week Water Immersion (Wet U.V.)								
Weeks to Edge Lift	4 weeks plus	----->						
Weeks to 5% Loose	4	3	-	-	3	-	-	3
Weeks to swelling	1	1	1	2	1	1	1	1

Best overall (least swell) -- #6

TABLE FIVE

			Standard Black Carrara Glass		Not Exposed to Ultra-Violet Rays (cold side) Number Side with Carrara Glass		Exposed to Ultra-Violet Rays (Hot Side) Blank Side with Carrara Glass	
Started			Zero in	Blank Side	Number Side		Blank Side	
July 12, 1979 3:30pm	1443695-1	0		100	85	87	87	91
	-2	0		100	83	87	77	81
	-3	0		100	90	96	91	97
	-4	0		100	85	89	87	92
	-5	0		100	86	91	88	93
	-6	0		100	87	92	89	94
	-7	0		100	92	98	92	98
0 Hours Total	-8	0		100	84	87	85	89
CONTROL			0	100				
July 26, 1979	1443695-1	0		100	88	92	89	93
	-2	0		100	86	90	88	92
	-3	0		100	90	95	90	96
	-4	0		100	84	88	88	93
45704 Hours on indicator	-5	0		100	88	93	88	93
	-6	0		100	84	87	82	84
	-7	0		100	88	93	88	93
232 Hours Total	-8	0		100	86	90	87	92
August 1, 1979	1443695-1	0		100	87	92	87	91
	-2	0		100	85	89	88	92
	-3	0		100	92	98	93	98
	-4	0		100	84	88	88	92
45771 Hours on indicator	-5	0		100	88	92	88	93
	-6	0		100	84	88	84	87
	-7	0		100	90	95	89	94
299 Hours Total	-8	0		100	84	88	86	89
August 13, 1979	1443695-1	0		100	88	91	87	91
	-2	0		100	88	92	89	94
	-3	0		100	90	96	91	96
	-4	0		100	84	88	87	92
	-5	0		100	86	92	89	94
	-6	0		100	84	87	82	85
	-7	0		100	87	92	86	92
584 Hours Total	-8	0		100	84	88	86	90
August 20, 1979	1443695-1	0		100	87	91	87	91
	-2	0		100	85	89	85	90
	-3	0		100	90	96	91	96
	-4	0		100	84	89	88	92
	-5	0		100	88	92	89	93
	-6	0		100	84	87	82	85
	-7	0		100	87	92	86	91
685 Hours Total	-8	0		100	84	88	85	89
September 4, 1978	1443695-1	0		100	88	92	87	92
	-2	0		100	85	89	86	91
	-3	0		100	92	97	92	98
	-4	0		100	84	87	87	91
	-5	0		100	88	92	88	93
	-6	0		100	84	87	82	85
	-7	0		100	87	92	86	91
	-8	0		100	84	88	86	90

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