CRAY VALLEY
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APPLICATION BULLETIN

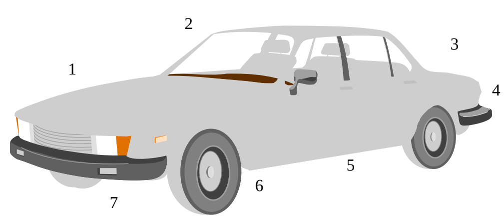
The Use of Cray Valley Metallic Coagents in Pumpable Sealants

Introduction

Sealants function as load-bearing elastic jointing materials that exclude dust, dirt, moisture and chemicals. Sealants also serve to reduce noise, vibrations (anti-flutter) and to insulate or serve as space fillers, as well as prevent corrosion.

Applications

A major application area for sealants is the auto industry where sealants are used as body-seam sealers and as undercoatings in wheel wells and other areas; for glazing, bonding and sealing windshields, back-lights, in self-sealing tires, for watershields, doors, engine components, weather strips, threaded pipe fittings, air conditioners and heaters, tail lights, and numerous others.



1. Hood Antiflutter
2. Windshield Seal
3. Trunk Sound Proof
4. Panel Seams
5. Underbody Undercoat
6. Wheel Well Antichip
7. Headlight Seal

Sealant Performance Properties

Sealants must satisfy many requirements to be effective in automotive applications. These requirements include:

(1) Excellent metal, glass, plastic adhesion
(2) High cured modulus
(3) High elongation/flexibility
(4) Good aging characteristics
(5) Adhesion to oily substrates such as CRS, aluminum
(6) Pumpable viscosity
(7) Chemical resistance including alkali, phosphate
(8) Water resistance

Elastomers

PVC plastisols have been the predominant sealant used for these applications. Other useful elastomers include SBR, urethanes, and EVA copolymers (non-cured). Formulations with high molecular weight elastomers require significant levels of plasticizers to obtain the necessary low final viscosity suitable for pumping. The presence of non-reactive plasticizers presents a potential problem with long term aging (heat) properties. Thus problems can be overcome by formulating with liquid low molecular weight elastomers which do not require plasticizers to achieve pumpable viscosities. As a result, all the major formulation ingredients are cured into a permanent network leading to improved aging performance and maintenance of resilience.

Coagent Benefit

Saret® SR633, is a metallic diacrylate coagent, which when added to peroxide-containing sealant formulations co-cures to provide the necessary properties for good sealant performance, especially adhesion. The **Saret® SR633** is a fine free flowing white powder which can be added directly to the formulation. The ionic nature of the metallic portion of the coagent molecule results in strong bonding to polar substrates such as metal and polar plastics. In addition, the metallic bond under stress can

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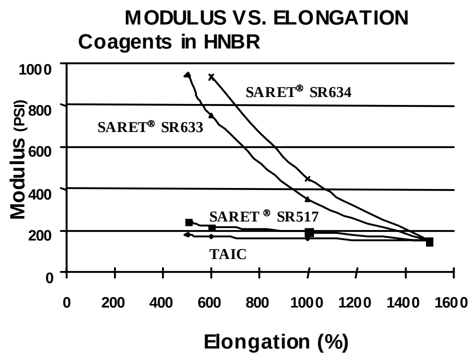
undergo cleavage with subsequent reformation resulting in improved elongational characteristics similar to sulfur cure as illustrated below in Figure 1.

Figure 1



For a given modulus or crosslink density, the **Saret® SR633** gives higher elongation (resilience) than the TAIC. **Saret® SR634**, a metallic dimethacrylate, gives even higher elongation and is less sensitive to moisure, but provides lower adhesion than **Saret® SR633**.

The metallic diacrylate can also be obtained in dispersion form (liquid) wherein the metallic diacrylate is dispersed in a monofunctional acrylate. The monofunctional acrylate acts to reduce the sealant viscosity and reacts in the cure process to provide a stable good aging sealant system. The dispersion facilitates addition of the **Saret® SR633** to the formulation. This is another example of a reactive plasticizer. Thus, the **Saret® SR633** can be utilized in both liquid and high molecular weight elastomer formulations.

Peroxide Selection

The sealant cure conditions can be varied from low (R.T.) to high (200°C) temperatures by proper selection of peroxide. RT cures can be effected with MEK peroxide and a metal accelerator such as cobalt naphthenate. High temperature peroxides include Triganox 145 or Lupersol 130.

Starting Point Formulations

The benefits of **Saret® SR633** in several liquid elastomeric sealant formulations is given below for liquid EPDM, natural rubber, polybutadiene, and NBR. A control comparison is shown without the **Saret® SR633** in each case.

EPDM Sealant (Uniroyal) Cured 160°C, 25 minutes

FORMULATION	**Saret® SR633**	**CONTROL**
Trilene 56	100	100
$CaCO_3$	50	50
Zinc Oxide	7.5	7.5
Stearic Acid	1.0	1.0
Maglite D	2.0	2.0
Resin D	0.5	0.5
t-b-perbenzoate	7.7	7.7
Saret® SR633	20	0
LAP SHEAR ADHESION PROPERTIES		
CRS/CRS, lb [1]	710C	20C
Thru ASTM 3 oil CRS/CRS, lb	620C	30C50%
Heat age, 130°C/two weeks, CRS/CRS, lb	950C	70C
Heat age ASTM 3 oil, 130°C/two weeks, CRS/CRS, lb	990C	40C

[1] C=cohesive failure

Lap shear adhesion was run with cold rolled steel (CRS) coupons overlapped one inch and spacers to achieve a sealant thickness of about 0.070 inches. Pressure (light) was applied to bring the upper coupon to bear on the spacer. For oily steel testing, both coupons were coated with ASTM 3 oil and the excess oil removed before applying the sealant.

The table above shows the **Saret® SR633** increasing CRS adhesion with and without oil compared with the control. Heat age values (130°C/two weeks) for both oily and non-oily steel increased significantly over the RT tests. Failure mode was cohesive in all cases with the **Saret® SR633** coagent. Sealant viscosity was approximately 1.5 million cp.

Of course temperature can be used to control viscosity should formulation changes be undesirable.

Natural Rubber Sealant (Hardman) Cure 160°C, 25 minutes

FORUMULATION	Saret® SR633	CONTROL
DPR 40 NR	100	100
CaCo3	50	50
Zinc Oxide	7.5	7.5
Stearic Acid	1.0	1.0
Maglite D	2.0	2.0
Resin D	0.5	0.5
t-b-perbenzoate	7.7	7.7
Saret® SR633	30	0
LAP SHEAR ADHESION PROPERTIES		
CRS	660C	0
Heat age, 130°C/two weeks, CRS/CRS, lb	710C	-

Liquid polybutadiene (PBD) was evaluated as a base elastomer for sealants with the evaluation shown below.

FORMULATION	Saret® SR633	CONTROL
R45HT	100	100
CaCo3	50	50
Zinc Oxide	7.5	7.5
Stearic Acid	1.0	1.0
Maglite D	2.0	2.0
Resin D	0.5	0.5
t-b-perbenzoate	7.7	7.7
Saret® SR633	30	0
LAP SHEAR ADHESION PROPERTIES		
CRS/CRS, lb	760C50%	40A
Caustic Soak (1) Lap Shear 5%, 70hr, 70°C CRS/CRS, lb	510C80	40A
Heat age, 130°C/two weeks, CRS/CRS, lb	>1000	40A

Again, lap shear adhesion values for the **Saret® SR633** formulation improved from the control 40A to 76°C/50 psi. Heat age testing again showed an increase in strength while exposure to a caustic bath for 70 hr at 70°C gave a lap shear strength only slightly less than the control **Saret® SR633** results. Liquid PBD was also evaluated as a glass sealant with **Saret® SR633** with the data shown below.

FORMULATION	160°C CURE	100°C CURE	CONTROL
R45HT	100	100	100
HiSil 230	50	50	50
Zinc Oxide	7.5	7.5	7.5
Stearic Acid	1.0	1.0	1.0
Maglite D	2.0	2.0	2.0
Resin D	0.5	0.5	0.5
Saret® SR633	30	30	0
CADOX BS	10	--	10
CADOX Ts 50S	--	10	--
Cure Temperature, °C	160	100	160
LAP SHEAR ADHESION PROPERTIES			
Glass/CRS	150C	110C	0
Glass/E-Coat	250C	100C	0

Polybutadiene Glass Sealant (Elf Atochem)

Adhesion testing resulted in cohesive failure at the two cure tempertures of 160°C and 110°C with the **Saret® SR633** vs zero for the control. Higher adhesion values are possible with increased crosslink density. The glass was untreated.

Liquid NBR elastomer from Zeon was evaluated at 30 PHR **Saret® SR633** coagent as shown below.

FORMULATION	Saret® SR633	CONTROL
NBR 1312LV	100	100
CaCo3	50	50
Zinc Oxide	7.5	7.5
Stearic Acid	1.0	1.0
Maglite D	2.0	2.0
Resin D	0.5	0.5
t-b-perbenzoate	7.7	7.7
Saret® SR633	30	0
LAP SHEAR ADHESION PROPERTIES		
CRS/CRS, lb	500C	0
Glass/CRS, lb	>270	-
Glass/E-Coat, lb	460C	-
Heat age,130°C/two weeks CRS/CRS, lb	950C	-

NBR Sealant (Zeon) Cure 160°C, 25 minutes
Results for CRS were similar to the previous evaluations. Glass as well as E-coat steel were evaluated as a substrate with bond strengths exceeding 460 lb.

Saret® SR633 also enhanced the adhesion properties of a PVC plastisol sealant as illustrated in the data below:

PVC Plastisol Automotive Body Sealant Cured @325°F for 15 minutes

Component		Chemical Name	SR9011	Saret® SR633
Oxy 521	1.	PVC Dispersion Resin1	60.00	60.00
Oxy 565	2.	PVC Extender Resin1	40.00	40.00
	3.	Di-Oxtyl Phthalate2	20.05	20.05
	4.	Calcium Carbonate3	50.05	50.05
	5.	Titanium Dioxide4	50.05	50.05
SR9011	6.	TrifunctionalMethacrylateEster	5.00	-
Saret® SR633	7.	Metallic Diacrylate	-	5.00
	8.	t-Butyl Perbenzoate	0.5	0.5
LAP SHEAR ADHESION PROPERTIES				
CRS, psi			10	500
Thin Film Adhesion to Electroplated Steel			No pick-off @ 6mil film thickness	No pick-off @ 6mil film thickness

Mixing Conditions: Disperse components 1,2,4, & 5 into components 3,6,& 7 using high shear mixer until homogeneous. Add 8 last.

1-Occidental Chemical
2-Eastman Chemical
3-Ashland Chemical
4-DuPont Chemical
5-Atochem North America
6-Cray Valley
7-Cray Valley
8-Elf Atochem

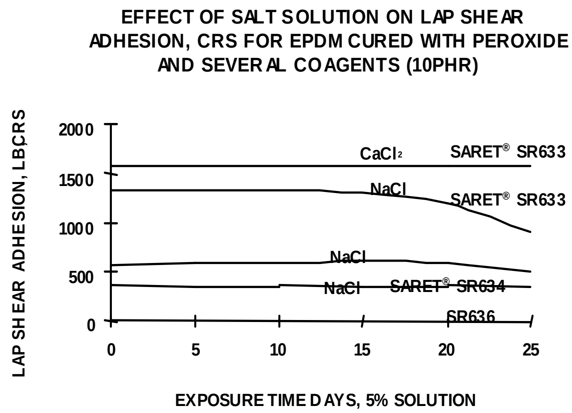
Lap shear adhesion was 10 psi for the SR9011 control while the **Saret® SR633** was 500 psi.

Environmental Testing

Testing has been conducted with both 5% caustic solution and 5% NaCl and CaCl2 solutions. For the caustic solution, the elastomer's resistance to caustic is controlling and PBD gave the best results (see PBD starting formulation).

Salt solution testing was done with a high molecular weight EPDM (Nordel 1040) to determine the sensitivity of the **Saret® SR633**. The salt solution is considered a more severe test than the salt spray testing. Results in Figure 2 show that CaCl2 does not effect the lap shear adhesion to 25 days while a small drop-off occurs with NaCl.

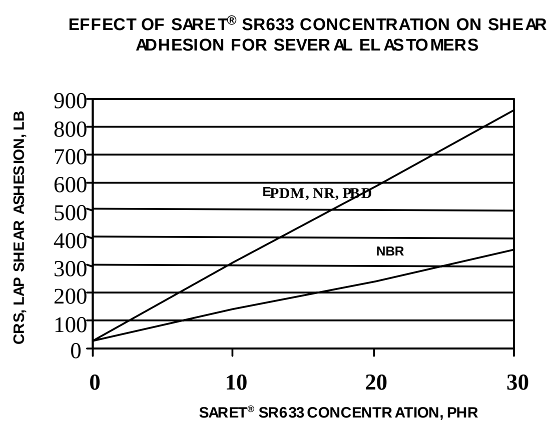
Figure 2



Adhesion Summary

Lap shear adhesion was found to be correlate to the concentration of **Saret® SR633** used in the formulation as shown in Figure 3.

Figure 3



The NBR liquid elastomer did not cure to the same crosslink density as the EPDM, NR, and PBD and gave a slightly lower lap shear adhesion. The starting formulations were listed with 20-30 phr **Saret® SR633**.

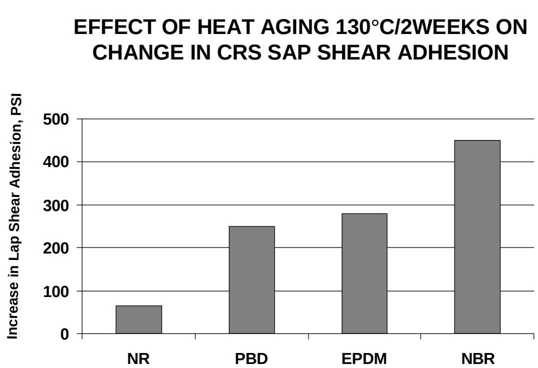
Adhesion improvement with **Saret® SR633** was demonstrated with several substrates:

(1) CRS
(2) Oily CRS
(3) Dura Steel
(4) E-Coat
(5) Glass

Heat Age Summary

In every case, heat aging the lap shear adhesion coupons cured with the several elastomers resulted in increased adhesion values. The increase in value over the unaged control for each elastomer is shown below in Figure 4.

Figure 4

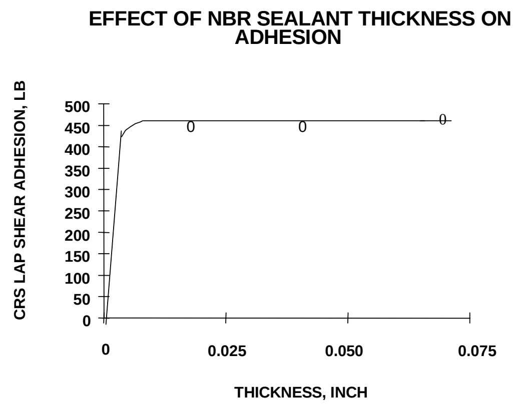


The large change in adhesion on aging for NBR may reflect an incomplete cure for the unaged control.

Sealant Thickness

Several sealant thicknesses were evaluated with the liquid NBR sealant formulation to determine if any sensitivity to thickness is present. Figure 5 below shows that adhesion was essentially independent of thickness. The sealants, if desired could be used as adhesives where thickness is minimized.

Figure 5



Sealant Summary
Improvement With Saret® SR633 (ZDA)

- Excellent adhesion to steel, E-Coat, and Dura Steel with several elastomers, EPDM, NBR, PBD, NR
- Good adhesion to oily steel
- Good adhesion to glass (NBR, PBD)
- Pumpable viscosities, 800,000-1,500,000 cp. Conntrollable with monofunctional liquid monomer.
- Cure capability 100°C-200°C
- Excellent heat age performance, 130°C/2 weeks
- High cure modulus
- Caustic resistance with PBD elastomers
- 100% solids formulations
- Benefits of **Saret® SR633** apply to high molecular weight elastomers cut with plasticizer (for adhesion and modulus)