

## Effects of Ester Plasticizers on Neoprene Crystallization Rate

### Summary

Six Hallstar ester plasticizers were mixed into a neoprene WK compound and evaluated to assess the plasticizer effects on the crystallization rate. The results show Paraplex® G-62 interferes with the cure system used in our standard neoprene WK recipe. The remaining plasticizers showed varying degrees of crystallization resistance at -20°C in the neoprene WK compound tested. The plasticizers examined were Plasthall® TOTM, Plasthall® DOS, Plasthall® 4141, Plasthall® 7041 and Plasthall® 503. In addition to crystallization resistance, the cure properties, tensile properties, low-temperature brittle point and low-temperature torsional flexibility were measured for all compounds.

Among synthetic elastomers, the ability to crystallize under suitable conditions of stress and temperature is confined to relatively few materials, one of which is neoprene rubber. Crystallization is the ability of the rubber chains, or portions thereof, to align themselves into a well-ordered crystalline structure. This phenomenon differs from the glass transition common to all high molecular weight polymeric materials that is characterized by the well-known parameter Tg and that is associated with simple thermal stiffening of the polymer. Crystallization effects and Tg must both be considered when designing neoprene materials for low-temperature service.

Unfortunately, the use of ester plasticizers, so commonly used to lower the Tg of a material, does not usually help prevent crystallization and, in many cases, will actually accelerate the crystallization rate. The retardation or prevention of neoprene crystallization is a practical concern as its development is accompanied by increases in hardness and stiffness, as well as loss of resiliency. Controlling the microstructure of a neoprene elastomer provides a means by which to control the crystallization tendencies. However, such changes also have adverse effects on other properties of the polymer. This study attempts to discover methods of controlling the crystallization tendencies by using suitable plasticizers without also deteriorating other low-temperature properties of the neoprene compound. The initial phase of the study assesses the effects of six Hallstar ester plasticizers on the neoprene crystallization rate. The materials evaluated include Plasthall® 4141, Plasthall® 503, Plasthall® TOTM, Plasthall® 7041, Plasthall® DOS and Paraplex® G-62.

### Conclusion

1. The WK grade of neoprene is not suited for use as a base polymer in neoprene compounds subjected to crystallization testing designed to determine the effects of plasticizers on the crystallization rate. It is designed to have maximum crystallization resistance, thus resulting in an unacceptably long time to obtain experimental results.

2. The effect of Paraplex<sup>®</sup> G-62 on the crystallization rate cannot be fairly evaluated in the present recipe due to the reduced state of cure for the G-62 compound.
3. The crystallization resistance of neoprene WK compounds at -20°C in an unstressed state is considered excellent for TOTM, good for DOS, fair for 4141 and 7041, and poor for 503.

## Experimental

The compounds for performance testing were mixed in a BR Banbury internal mixer following normal mixing procedures. Curatives, with the exception of magnesium oxide, were withheld from the Banbury charge and added on a two-roll, 611 x 1311 laboratory mill during finishing operations. Scorch and cure properties were determined in accordance with ASTM D1646-81 and ASTM D2084-81. Sheets for physical testing were pressed in a Wabash press at a pressure of 833 psi and a temperature of 150°C. Cure times were taken as 1.25 x t'<sub>c</sub>(90) from rheometer testing. The conditioning period for vulcanized sheets was a minimum of 16 h under standard laboratory conditions.

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Appropriate ASTM test procedures were used to measure the physical properties and low-temperature flexibility characteristics. Crystallization tendencies were determined using a hardness increase test and a resiliency retention test. Hardness increase was measured as a function of time at -20°C using a Shore Leverloader, Model 71300, equipped with a 600-gram weight and a 4000-gram weight. Resiliency retention was determined by placing 111 x 1/411 x 0.07511 samples folded in half into a pinch clamp. Release paper was used to separate adjoining rubber surfaces. Initial resiliency was measured by immersing clamped samples into a -65°C methanol bath. After a five minute conditioning period, samples were released from the clamps and the bath slowly warmed. The temperature at which samples attained a 90°C opening was recorded as the 50 percent recovery temperature. The crystallization rate was measured by conditioning clamped samples for the indicated time period at -20°C. Conditioned samples were transferred to a -30°C methanol bath and the clamps were released. Slow warming of the bath followed to determine the 50 percent recovery temperature. All samples for crystallization testing were heated at 70°C for 1 hour, followed immediately by a 1 hour conditioning period at room temperature to remove all traces of crystallinity prior to beginning the crystallization testing.

## Discussion

Extensive literature is available discussing both the mechanism of crystallization and the effects on neoprene compound performance at low temperatures. An excellent article for review is a paper published by Murray and Detenber of DuPont, which is available in the TSL library at Hallstar.<sup>1</sup> More recent work is also available but was not readily accessible for consultation prior to beginning this work. In the work by Murray and Detenber, it was concluded that neoprene crystallization occurs most rapidly at -2°C for vulcanized compounds. It was also pointed out that the maximum rate of crystallization for raw polymer occurs at -50°C. Thus, the temperature needed to

maximize the rate of crystallization would appear to vary slightly, depending on the specific formulation tested.

In the present work, -20°C was the temperature chosen at which to measure the rate of neoprene crystallization. This temperature was selected based on the recommended operating range of -18°C to -73°C for the Model No. A18-100 SO-LOW Chilling Machine supplied by the SO-LOW Environmental Equipment Company of Cincinnati, Ohio. Because a large number of plasticizers was scheduled for testing, it was decided screening tests run at -20°C would allow the selection of candidates imparting the greatest retardation of the neoprene crystallization rate. The best candidates can then be used in subsequent testing to determine the temperature at which our formulation shows the maximum rate of crystallization.

The neoprene grade used in this phase of the study was neoprene WK, which is recommended by DuPont for applications requiring maximum crystallization resistance. The results obtained confirm the excellent resistance to crystallization claimed by DuPont for this polymer. A review of the data for hardness increase shows only the compound containing butyl oleate (503) registered a 20-point hardness increase over the 106 d duration of the test. The best crystallization resistance was found with TOTM, as this compound registered a mere six-point hardness increase after exposure of 106 d at -20°C. A relative comparison of plasticizers in this phase of the study with regards to crystallization resistance is shown below in Table I. Comparisons are based solely on the results of hardness increase measurements using the descending order of performance, excellent, good, fair and poor.

TABLE I

## Relative Crystallization Resistance of Neoprene WK Compounds Containing Various Ester Plasticizers

<u>Plasticizer</u>	<u>Relative Crystallization Resistance</u>
Plasthall® TOTM	Excellent
Plasthall® DOS	Good
Plasthall® 4141	Fair
Plasthall® 7041	Fair
Paraplex® G-62	Poor
Plasthall® 503	Poor

The poor performance of Paraplex® G-62 is more likely attributable to the low state of cure for this compound, inasmuch as reduced crosslink density is known to increase the rate of crystallization. The results for the remaining plasticizers are consistent with the notion advanced by DuPont that highly efficient low-temperature plasticizers also enhance the crystallization rate.

Resiliency retention tests tend to support the findings of hardness increase testing, although the apparent rate of crystallization is considerably enhanced. Stress is known to considerably enhance crystallization when the temperature is held constant. However, interpretation of the resiliency tests requires considerably greater caution due to a lack of knowledge about stress relaxation mechanisms at the test temperature. Unlike results for hardness increase testing, resiliency retention behavior can be

explained on the basis of effects other than crystallization. Due to the ambiguity of the test results, the resilience retention tests will not be considered further.

Time to a 20-point hardness increase was not determined for all materials due to the excessive duration of the test. Testing was terminated at 106 d upon attainment of a 20-point hardness increase for compounds containing 503. Subsequent testing is planned for compounds containing neoprene GN as the base polymer. Crystallization occurs within a more reasonable time frame for the GN grade of neoprene, thus allowing the screening of plasticizers at a faster rate.

Tested by: Fred A. Farnell, Selwyn R. Mather

Written by: Fred A. Farnell

## References

<sup>1</sup>Murray, R. M., Detenber, J. D., "First and Second order Transitions in Neoprene," Rubber Chemistry and Technology, 34, 668 (1961).  
Data Book FF-8, pgs. 11, 29, 31, 50-53, 72, 79, 80, 248.

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## DATA

<b>Recipe FF8-11</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Neoprene WK	100.0	100.0	100.0	100.0	100.0	100.0
Stearic Acid	0.5	0.5	0.5	0.5	0.5	0.5
Stabiwhite Powder	3.0	3.0	3.0	3.0	3.0	3.0
Maglite® D Powder	4.0	4.0	4.0	4.0	4.0	4.0
N-774	67.0	67.0	67.0	67.0	67.0	67.0
Crown Clay	35.0	35.0	35.0	35.0	35.0	35.0
Plasticizer	32.0	32.0	32.0	32.0	32.0	32.0

### **Mill Addition**

St. Joe 922	5.0	5.0	5.0	5.0	5.0	5.0
Na22F	0.75	0.75	0.75	0.75	0.75	0.75
TMTD	0.50	0.50	0.50	0.50	0.50	0.50
TOTAL	247.75	247.75	247.75	247.75	247.75	247.75
Plasticizer	4141	503	TOTM	7041	G-62	DOS

### **Viscosity and Curing Properties**

#### **Mooney Viscosity: at 125°C**

**(257 °F)**

Minimum Viscosity	29.0	26.0	35.0	28.0	33.0	29.5
t5, min	12.8	14.5	14.5	13.8	21.0	16.0
t35, min	19.0	22.5	24.8	21.3	58.5	26.8

## **Cure Characteristics: at 150°C**

**(302 °F)**

ML, lbf/in.	18	17	21	18.5	20.5	19.0
MH, lbf/in.	69.5	60	70	66.5	47.5	7.0
ts2, min.	5.5	5.6	5.8	6.0	6.5	6.0
t'c(90), min.	34.3	40.5	44.0	39.5	45.3	41.8
1. 25 x t'c(90), min.	42.8	50.6	55.0	49.4	56.7	52.2
Cure Time, min.	43	51	55	49	57	52
Cure Rate Index, min <sup>-1</sup>	3.47	2.87	2.62	2.99	2.58	2.79

## **Physical Testing**

### **Original Physical Properties**

Stress at 100% Elong., Mpa	2.76	2.41	2.41	2.41	1.38	2.41
psi	400	350	350	350	200	350
Stress at 300% Elong., MPa	-	-	-	-	6.21	-
Tensile, Ultimate, MPa	11.4	10.3	11.7	10.7	10.0	10.3
psi	1650	1500	1700	1550	1450	1500
Elongation at Break, %	260	290	290	270	420	280
Hardness, Duro A, pts.	68	65	70	68	63	68
Specific Gravity	1.478	1.451	1.483	1.465	1.487	1.460
Tear Resistance, lbf/in.	76	77	104	76	126	89
Brittle Point, °C	-49	-57	-39	-49	-35	-50
<b>Recipe FF8-11</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
<b>Plasticizer</b>	<b>4141</b>	<b>503</b>	<b>TOTM</b>	<b>7041</b>	<b>G-62</b>	<b>DOS</b>

**Low-Temperature Stiffening:** by Gehman Torsion Wire Apparatus, type A specimens, torsion wire constant, K-0. 152, gf-cm/deg.

T <sub>2</sub> , °C	-20	-32	-28	-34	-14	-28
T <sub>5</sub> , °C	-29	-43	-37	-42	-28	-43
T <sub>10</sub> , °C	-39	-46	-40	-45	-33	-46
T <sub>100</sub> , °C	-52	-54	-46	-51	-40	-55
G <sub>23</sub> °C, psi	231	230	270	217	105	244

## **Crystallization Resistance**

### **Hardness Increase after -20°C**

#### **Exposure**

Initial Hardness, pts.	72	68	77	70	78	72
<b>Increase After:</b>						
1 d Exposure, pts.	+1	+2	+1	+3	+4	+2
3 d Exposure, pts.	+1	+3	+1	+3	+6	+2
7 d Exposure, pts.	+2	+6	0	+4	+8	+2
12 d Exposure, pts.	+4	+10	0	+5	+11	+3
15 d Exposure, pts.	+6	+13	+2	+5	+13	+4
20 d Exposure, pts.	+8	+14	+2	+7	+14	+5
26 d Exposure, pts.	+8	+15	+1	+7	+12	+3
34 d Exposure, pts.	+13	+17	+1	+11	+16	+6
44 d Exposure, pts.	+12	+17	0	+12	+14	+6

56 d Exposure, pts.	+15	+17	+1	+15	+16	+8
66 d Exposure, pts.	+16	+17	+4	+16	+17	+10
75 d Exposure, pts.	+18	+19	+5	+17	+17	+13
83 d Exposure, pts.	+16	+19	+3	+17	+17	+13
91 d Exposure, pts.	+13	+17	+3	+16	+14	+12
99 d Exposure, pts.	+18	+19	+5	+18	+17	+13
106 d Exposure, pts.	+18	+20	+6	+18	+18	+13

**Resiliency Retention:** temperature to recover 50% of 180° Bend Stress.

**Recovery Temperature**

Initial, °C	-34	-40	-34	-37	-16	-42
<b>After -20 °C Exposure</b>						
21 h, °C	-9	-8	-19	-11	-6	-15
3 d, °C	-7	-5	-14	-8	-1	-9
1 week, °C	-4	-3	-8	-5	0	-6