

# TECHNICAL Bulletin

**Subject:** Tire Curing Bladders

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## MEDIUM THERMAL BLACK N990 IN TIRE CURING BLADDERS

### Background

Cancarb Limited has introduced the concept of high loadings of thermal black in halobutyl inner liners to the tire industry. This concept can theoretically be applied to other similar applications, including curing bladders, inner tubes and sports ball inner liners. This technical bulletin provides the results of Cancarb's evaluation of N990 in butyl tire curing bladders.

### Tire Curing Bladders: General Information

Tire curing bladders (membranes) are sealed flexible rubber bags inflated inside of uncured tires during the vulcanization process. Curing bladders are one of the most severe rubber applications in terms of heat and flexing resistance. Bladder compounds have some of the most stringent and exacting requirements of any rubber compound. These requirements can be summarized as follows:

1. Mix well and process easily
2. Mold satisfactorily
3. Good physical properties
4. Good aging properties
5. Good flex and tear resistance
6. Low tension set
7. Excellent steam aging properties
8. Good thermal conductivity

## Standard Curing Bladder Formulation

The carbon black loading in butyl curing bladders has typically been 50 or 55 parts of N330, high abrasion furnace type. The HAF type provides the necessary tear strength and has been well accepted over GPF or FEF grades. A typical formulation is as follows:

Butyl 268	100 phr	Exxon
Neoprene WRT	5 phr	Dupont*
HAF N330 Carbon Black	50 phr	
Castor oil	5 phr	
Zinc Oxide	5 phr	
Reactive phenol formaldehyde resin	10 phr	butyl curing resin, Schenectady SP1045

\*5 phr of Neoprene is added in resin cured butyl compounds. It is used to activate the resin cure reaction by donating halogen.

To achieve optimum performance of the bladder compound, good dispersion of the Neoprene, carbon black, zinc oxide and curing resin is critical.

Based on the above formulation, compounds with the following filler loadings were tested at the BFGoodrich Laboratory in Breckville, Ohio. (This lab is an A2LA accredited lab and is ISO 9001 certified).

- Compound #1 - 50 phr N330 HAF carbon black (control)
- Compound #2 - 110 phr N990
- Compound #3 - 90 phr N990, 20 phr N660 GPF carbon black
- Compound #4 - 80 phr N990, 30 phr N330
- Compound #5 - 90 phr N990, 20 phr N330
- Compound #6 - 40 phr N990, 40 phr N330
- Compound #7 - 50 phr N990, 40 phr N330
- Compound #8 - 60 phr N990, 40 phr N330
- Compound #9 - 90 phr N990 Ultra-Pure\*, 20 phr N330

\*Compound #9 is identical to Compound #5, except that the Ultra-Pure grade of Thermax® N990 was used so that the effect of the lower pH thermal black on the cure time could be evaluated. Thermax® N990 Ultra-Pure has a typical pH of 5 compared to 10 for standard N990.

Results are as attached in Table 1.

## Comments

All results are indicative of the typical effects of using thermal carbon black in a rubber compound. Due to the large particle size and low structure, N990 is in general a non-reinforcing carbon black and while it will enhance the dynamic properties of rubber, it does not provide the strength or reinforcement that the furnace grades do. Furthermore, the higher pH will in general lead to longer cure times.

Compound #2, with 110 phr of N990, had the lowest viscosity, as expected. The similarity of the modulus to the control compound may be interest to some bladder producers.

Compound #5, #6 and #8 are similar to the control compound. Processing properties for #5 are generally equal to the control compound except the T<sub>min</sub>+5 indicates a longer cure time. This is also evident in the other compounds that are loaded with N990, as N990 tends to provide more scorch safety than other carbon blacks. This was confirmed with #9, which had 90 phr of Thermax® N990 Ultra-Pure, the low pH thermal carbon black.

Tensile properties – original, aged and elevated temperature – for the N990 compounds are in general lower than the control but are considered to be sufficient for this application. Elongation, however, is noticeably lower than the control and is a point of concern. However, #6 should have sufficient elongation.

Tear strength for the #5 compound is also noticeably lower than the control compound. However, with 40 phr N330 and 60 phr N990, #8 has equivalent tear strength.

Thermal conductivity improved (i.e. was higher) with the higher black loadings in all of the test compounds. Compound #8 showed exceptional results. This is generally a function of the higher carbon loading which is allowed with the thermal black, rather than a property specific to the thermal blacks. Higher thermal conductivity is a benefit in bladder compounds in which higher heat flow can result in faster tire cure times. Estimates of the increase in cure times range from 10 – 20 seconds per tire.

The DeMattia crack growth results, for all compounds including the control, were poor and showed insufficient crack growth resistance. Experience with this test suggests that more than two samples should be used for a valid indication of the true crack growth resistance.

The compounds containing the thermal blacks had slower cure rates than the control. One possible explanation for the slower cure tests is the surface activity of the thermal blacks, or that the high pH (10) of the thermal blacks inhibited the rate of resin cure in the butyl rubber. The T95 results confirm this, with compound #9, the low pH compound, having the shortest cure time of the thermal black compounds. Adding more Neoprene or Stannous Chloride to the formulation should increase the cure rate.

### **Cost Benefit Analysis**

Calculations of cost savings should theoretically include the material costs, tire cure time, press downtime and any increase (or decrease) in productivity due to the changes in throughput.

For raw materials cost savings, Table 2 provides an estimate of savings of approximately US \$0.94 per curing bladder. This is due to the substitution of the higher cost butyl rubber with the thermal carbon black.

### **Conclusion**

Compound #6 and #8 provide the best balance of physical properties compared to the control compound. The main advantages seen thus far would be the improved thermal conductivity and reduced compound cost. Final judgment on the above results will naturally be subject to bladder life.

## Supplementary Notes

Thermal conductivity is measured according to ASTM C 518-91, Vol. 04.06. Q is the heat flow through the rubber test piece at a thickness of approximately 13 mm (0.51 in.). K is the measurement of thermal conductivity expressed in  $\text{BTU}\cdot\text{in}/(\text{ft}^2\cdot\text{hr}\cdot^\circ\text{F})$ . It is normally expressed in degrees Kelvin. mV is a milli-volt value of the heat flow meter output. This value is not converted to temperature. The results have been indexed based on the control compound for ease of understanding. BFGoodrich uses a Dynatech Rapid-k meter and a Haskris recirculating chiller.

For further information please contact Cancarb @ fax #: 1-403-529-6093  
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**Table 1: Curing Bladder Compound Data**

Compound #	#1 Control	N990 #2	MT-GPF #3	MT-HAF #4	MT-HAF #5	MT-HAF #6	MT-HAF #7	MT-HAF #8	MT-HAF #9
N330 HAF	50			30	20	40	40	40	20
N660 GPF			20						
N990 Thermax®		110	90	80	90	40	50	60	
N990 UP Thermax®									90
<b>Compound Properties (ASTM D 1646-96a)</b>									
Mooney Viscosity	66	59	65	76	69	76	75	77	70
ML (1 + 4) @ 100°C									
<b>Mooney Scorch @ 137.8°C (ASTM D 1646-96a)</b>									
Minimum	49	40	45	58	52	59	58	60	53
Tmin + 5 min.	24.5	32.8	37.8	26.8	35.8	14.3	14	15.8	17.4
<b>Monsanto R100 Oscillating Disk Rheometer @ 190°C, 1° arc (ASTM D 2084-95)</b>									
ML dNm	9.9	7.6	8.7	10.2	9.9	11.9	11.3	11.5	10.2
MH dNm	34.4	36.7	38.5	40.7	40.2	38	39.4	38.7	38.6
T (2) min	3.2	3.5	3.7	3.2	3.3	3.1	2.8	3	2.6
T (90) min	29.2	36.5	40.7	37.1	37.6	33.6	34.5	34.9	30.7
T (95) min	36.9	45.5	48.9	45.2	46.3	42.8	43.5	43.2	40.1
<b>Stress-Strain, Originals @ RT, Cure Conditions T95 @ 190°C (ASTM D 412-97)</b>									
100% Modulus MPa	1.8	2.2	2.4	2.2	2.8	2.3	2.3	3.1	2.6
300% Modulus MPa	5.5	5.5	5.7	6.5	7.9	7.2	7.6	8.9	7.9
Tensile Strength MPa	15	6.5	6.7	7.9	8.9	11.2	10.5	10	8.9
Elongation %	647	414	403	425	415	490	450	420	400
Shore A Hardness	66	70	70	71	74	69	71	73	72
<b>Stress-Strain, Originals @ 100°C, Cure Conditions T95 @ 190°C (ASTM D 412-97)</b>									
100% Modulus MPa	1.9	1.9	1.7	1.9	2.3	2.1	2.4	2.3	2.2
300% Modulus MPa	5.6	4.2	3.8	5.2	6.3	6.1	7.1	6.5	-
Tensile Strength MPa	9.1	4.3	4	5.7	6.3	6.7	7.1	6.7	6
Elongation %	460	315	325	335	305	330	310	310	290
<b>Stress-Strain, Oven-Aged 48 hours @ 170°C, Cure Conditions T95 @ 190°C (ASTM D 412-97)</b>									
100% Modulus MPa	4.6	4.4	4.8	5	4.9	4.6	5.3	5.1	5.2
200% Modulus MPa	7.6	6.8	7.6	8.2	8.1	7.7	8.8	8.2	8.3
Tensile Strength MPa	10.3	7.5	8.1	8.7	9.1	9.4	6.9	8.9	8.3
Elongation %	280	240	215	205	230	255	155	220	200
Shore A Hardness	90	96	94	94	93	90	90	93	91
<b>Tear Strength, Die C (ASTM D 24-96), RT</b>									
kN/m	38.9	34.0	33.6	35.1	33.1	34.5	33.9	40.7	32.3
<b>Tension Set, 100% Elongation, @ 200°C – Held 10 minutes (ASTM D 412-97)</b>									
% Tensile Set	13.4	25.0	27.4	25.9	20.5	24.1	26.6	29.3	26.1
<b>DeMattia Crack Growth: 23°C, aged 7 days @ 100°C; average of two samples, inches (ASTM D 813-95)</b>									
5,000 cycles	2.5	5.0	6.0	7.0	3.5	3.5	6.5	5.5	5.5
10,000 cycles	2.5	5.5	6.5	7.5	4.5	5.5	6.5	6.5	6.5
15,000 cycles	3.5	6.5	7.5	8.5	5.5	6.5	7.5	7.0	7.5
25,000 cycles	5.0	8.0	9.0	10.0	7.0	7.5	9.0	7.5	10+
<b>Thermal Conductivity, 100°C (ASTM C 518-91)</b>									
Q: Heat Flow, mV	3.610	3.953	4.153	4.200	4.157	4.095	4.282	4.440	4.420
K: Thermal Conductivity BTU in/(hr.sq.ft .F)	0.786	0.844	0.892	0.900	0.891	0.856	0.885	0.910	0.917
Index	100	110	115	116	115	113	118	120	122

**Table 2: Cost Benefit of Thermax® N990 in Tire Curing Bladder Compound - USA**

Curing Bladder Formulation	Traditional Formulation		Thermax® Formulation	
	Parts by Weight	Parts by Volume	Parts by Weight	Parts by Volume
Exxon Butyl 268	100.00	108.70	100.00	108.70
Neoprene W	5.00	4.00	5.00	4.00
HAF Carbon Black N330	50.00	27.78	20.00	11.11
Thermax® N990	0.00	0.00	90.00	50.00
Castor oil	5.00	5.21	5.00	5.21
Zinc oxide	5.00	0.89	5.00	0.89
Curing Resin SP 1045	10.00	9.52	10.00	9.52
<b>Totals</b>	<b>175.00</b>	<b>156.10</b>	<b>235.00</b>	<b>189.43</b>
<b>Specific Gravity (calculated)</b>	<b>1.121</b>	<b>-</b>	<b>12.41</b>	<b>-</b>
Compound Cost (USD)	1.99/kg	2.23/litre	1.76/kg	2.18/litre
Savings per curing bladder (USD), based on 4 kg compound: 0.94				

### Ingredient Cost Assumptions

Prices are listed in September 1997 Rubber World Compounding Ingredients Price List. Prices are used for bulk quantities.

	<u>USD/kg</u>	<u>Spec. Gravity</u>
Exxon Butyl 268	2.390	0.92
Neoprene W	4.09	1.25
HAF N330 Carbon Black	0.83	1.80
Thermax® N990	0.99	1.80
Castor oil	1.58	0.96
Zinc oxide	2.18	5.60
Curing Resin SP 1045	2.88	1.05