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TECHNICAL BULLETIN

Standard and High ACN Nitrile Rubber

Thermax® N990 medium thermal carbon black is manufactured by the thermal decomposition of natural gas. The thermal process provides a unique carbon black that is characterized by a large particle size and low level of particle aggregation (structure). Thermax® N990 is widely used in applications that require superior heat, oil and chemical resistance, along with good dynamic properties. The large particle size (low surface area) and low structure allow for high loadability, low compression set, high rebound and low hysteresis, maintaining the inherent elastomeric properties of the rubber compound. As a non-reinforcing black, thermal black is often blended with furnace carbon blacks and/or mineral fillers to achieve cost reduction and specific physical properties in the rubber compound.

Thermax® N990 can be used in all polymers and is commonly used in NBR, HNBR, CSM, CR, EPDM, ACM, FKM and ECO. In these polymers, comparatively high loadings of Thermax® N990 are possible, while maintaining low viscosity, thereby providing the opportunity to improve aging properties and reduce compound cost.

The use of high loadings of carbon black to improve resistance to heat, oils and other aggressive fluids is well known in the rubber industry. Generally, the higher the loading of carbon black, the better the compound's resistance to heat, fuels and oils (with the resultant less loss of tensile strength and other crucial properties). Higher volumes of fillers may also serve to reduce compound cost. The loadability of the carbon filler is therefore critical and is dependent on the specific grade and its properties, namely particle size and structure.

Nitrile rubbers are high molecular weight amorphous random copolymers of 1, 3 butadiene and acrylonitrile. The ACN content may vary from a minimum of 15% to a maximum of 50%. As the level of acrylonitrile increases, such properties as hardness, tensile, resistance to fuels, oils and gas impermeability increases.[1] However, as the level of ACN increases, the material becomes more brittle in nature (higher Tg). This is associated with poorer compression set performance, higher hardness and higher modulus.[2] As well, higher ACN content grades of NBR are generally 20 - 50% more expensive than low/medium ACN content grades.

Due to its unique properties, Thermax® N990 is used in numerous NBR applications for several reasons, including cost reduction, to obtain lower compression set and to improve oil and fuel resistance (reduce volume swell). It may also be used to enhance the aging resistance of standard ACN-content NBR to the equivalent of high ACN-content NBR and to improve the dynamic properties of high ACN content NBR to be similar to that of standard ACN-content NBR.

The combination of Thermax® N990 and NBR provides excellent oil and chemical resistance and excellent high temperature properties. NBR compounds filled with Thermax® N990 are used for applications such as:

- Seal, gaskets, o-rings, packings
- Tubing, hose, belts
- Roll coverings, tank linings

In this report, the use of Thermax® N990 in medium (standard) acrylonitrile content NBR is compared to the use of N650 furnace carbon black in a high ACN content NBR fuel hose compound.

[1]Jones, M.S., "Solvent Resistant Elastomers – Nitrile Rubber (NBR), in Basic Elastomer Technology, ACS Rubber Division, 2001, Ch. 10, pp. 359
[2]Dewar, J., Krista, R., Tsou, D., "Benefits of High Molecular Weight NBR Elastomers in Soft Printing Rolls," Paper No. 119, ACS Rubber Division Pittsburgh Meeting, October 2002, p. 7

Part I: NBR Fuel Hose Compound Study

An NBR formulation for low permeation fuel filler hose was obtained from Bayer Corp. This formulation calls for Krynac 4560 (45% ACN) and 80 phr of N650 furnace carbon black. Krynac 3370 is Bayer's standard ACN content NBR grade. Thermax® N990 was evaluated at a high and low loading in Krynac 3370. The test formulation is shown in Table 1 below. The carbon black loadings are provided in Table 2. The carbon black loadings were calculated for equal hardness.

Table 1: NBR Fuel Filler Hose Test Formulation[3]

Ingredient	Parts phr	Supplier
Krynac 4560 or 3370	100.0	Bayer Canada
Hi-Sil 233	20	PPG
Merrol 4221	18.0	Harwick Standard
Plasticizer SCB	12.0	Harwick Standard
Zinc Oxide	5.0	Zo Chem
Coumin 100	5.0	St. Lawrence Resins
Wingstay 29	2.5	Goodyear Chemical
TMQ	1.5	Uniroyal/Compton
Sunproof Canadian Wax	2.0	Uniroyal/Compton
Sulphur H15	0.5	L.V. Lomas
TMTD	1.0	Uniroyal/Compton
MBS	1.5	Uniroyal/Compton
DTDM	1.5	Uniroyal/Compton
Carbon Black	As Shown	Cancarb/Cabot

Table 2: NBR Grade and Carbon Black Grade/Loadings in Test Formulations

Compound ID	HACN #1	SACN #2	SACN #3
Krynac 4560	100.0	-	-
Krynac 3370	-	100.0	100.0
Thermax® N990	-	75	150
N650	80.0	60	35

HACN + high acrylonitrile; SACN + standard acrylonitrile

[3]Original test formulations for compounds in Tables 1 & 2 provided by Bayer, Tube Compound for Low Permeation Fuel Filler Neck Hose

The results are provided in the following tables, with general comments

Table 3: Compound Data[4]

	HACN #1	SACN #2	SACN #3
Mooney Viscosity, ML 1 + 4 @ 100°C	20.5	48.1	50.2
Mooney Scorch, t5 @ 121°C	26.7	26.5	25.8
Rheometer @ 160°C			
Minimum Torque, lbs. – in.	2.6	7.91	7.68
Maximum Torque, lbs. – in.	61.81	91.19	97.07
t2, minutes	2.4	2.5	2.6
t90, minutes	6.1	6.4	7.3

There is a major difference in Mooney Viscosity with the compounds for the two types of NBR, due to the different polymer viscosities between the Krynac 4560 and 3370. However, the t5 scorch time was roughly equivalent. For the rheometer properties, there was a large difference in the torque readings, but minimal difference in the SACN compounds in spite of the different carbon black loading. The data clearly demonstrates the inert nature and non-reinforcing property of the Thermax® N990 and the potential to increase loading without affecting processability.

Table 4: Unaged Physicals, Cured 15 minutes @ 166°C

	HACN #1	SACN #2	SACN #3
Hardness	71	71	74
100% Modulus, MPa	4.69	4.93	5.93
200% Modulus, MPa	10.82	11.13	10.58
Tensile, MPa	12.27	12.24	10.72
Elongation (%)	260	230	205
Compression Set, 70 hours @ 125°C			
Compression Set (%)	27.8	21.8	23.9

[4]All compound mixing and testing was performed at Canadian Rubber Testing & Development Limited

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Hardness is essentially equal, with slightly higher hardness for the highly loaded SACN compound. This again demonstrates the loadability of Thermax® N990 in comparison to other carbon blacks. Tensile strength declined as the carbon black loading was increased, due to saturation of the polymer. The higher compression set with the HACN compound is evident. There was little loss in compression set at the 150/35 loading and this may provide cost savings due to the higher loading if the slight loss in tensile strength is acceptable. In comparing compound #1 (HACN-N650 control) and compounds #2 and #3 (SACN), overall better physical properties were provided by the standard NBR grade in #2 and #3, in terms of tensile strength and lower compression set, at equal hardness.

Table 5: Oven Aged, 70 hours @ 125°C (+ change from originals)

Compound ID	HACN #1	SACN #2	SACN #3
Krynac 4560	100.0	-	-
Krynac 3370	-	100.0	100.0
Thermax® N990	-	75	150
N650	80.0	60	35
Hardness	91	88	90
Points Change	+20	+17	+16
100% Modulus, MPa	11.07	10.93	10.3
% Change	+136.0	+121.7	+73.6
Tensile Strength, MPa	14.24	12.86	11.31
% Change	+16.0	+5.1	+5.5
Elongation (%)	155	135	125
% Change	-40.4	-41.3	-39.0

In the oven aging test, substantially better resistance, as measured by the percent change from the originals, was provided overall by the standard ACN-content NBR with the blend of Thermax® N990 and N650.

Compound ID	HACN #1	SACN #2	SACN #3
Krynac 4560	100.0	-	-
Krynac 3370	-	100.0	100.0
Thermax® N990	-	75	150
N650	80.0	60	35

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Table 6: Oil Aged, 70 hours @ 125°C, ASTM D 471

	HACN #1	SACN #2	SACN #3
Hardness	79	71	75
Points Change	+7	0	+1
100% Modulus, MPa	7.17	5.65	6.83
% Change	+52.9	+14.7	+15.1
Tensile Strength, MPa	13.34	12.31	10.82
% Change	+8.8	+0.6	+1.0
Elongation (%)	190	195	175
% Change	-26.9	-15.2	-14.6
Volume Swell (%)	-5.4	-1.6	-2.1

Better oil aging resistance was provided by the standard acrylonitrile NBR compounds. Substantially higher hardness was evident with the high ACN compound. There was significantly less change in the modulus and tensile with the standard NBR compounds. Lower volume swell with the higher carbon black loadings was seen in both of the SACN compounds, thus it is very notable with the oil aging data that there is not a clear benefit to using the higher acrylonitrile content NBR.

Table 7: Aged in Fuel C, 48 hours @ RT, ASTM D 471

	HACN #1	SACN #2	SACN #3
Hardness	55	59	62
Points Change	-16	-12	-12
100% Modulus, MPa	3.41	4.52	4.55
% Change	-27.2	-8.4	-23.3
Tensile Strength, MPa	8.55	8.41	8.45
% Change	-30.3	-31.3	-21.2
Elongation (%)	185	165	175
% Change	-28.8	-28.3	-14.6
Volume Swell (%)	+23.5	+25.8	+22.4

As with the oil aging test, overall better fuel aging resistance was seen with the highly loaded Thermax® N990 compound in the SACN NBR compound. There was less change in hardness, and less loss in modulus, as compared to the HACN. Volume swell was roughly equal, with slightly less change seen in the compound which had the highest loading of carbon black. The aged elongation and tensile were noticeably better with the compound with the high loading of Thermax® N990.

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Table 8: Aged in Fuel C/Methanol (85/15), 48 hours @ RT, ASTM D 471

	HACN #1	SACN #2	SACN #3
Hardness	53	56	62
Points Change	-18	-15	-12
100% Modulus, MPa	3.41	3.93	4.55
% Change	-27.2	-20.2	-23.3
Tensile Strength, MPa	8.83	6.48	7.62
% Change	-28.1	-46.9	-28.9
Elongation (%)	195	140	152
% Change	-25.0	-39.1	-25.9
Volume Swell (%)	+33.5	+39.9	+33.1

The severity of this test is evident in the data. There is some variation in the results but the compound with the high loading of Thermax® N990 had the best overall properties, in terms of hardness and volume swell. The higher loading of carbon black and the higher ACN content served to provide better aging resistance than compound #2.

Summary

The results indicate that it would be technically beneficial to use a high loading Thermax® N990 with the N650 in standard acrylonitrile content NBR, as opposed to the high acrylonitrile grade of NBR. The loadability of Thermax® N990 serves to enhance the aging resistance of the 3370 NBR grade.

Part II: ASTM Compounds

To support/clarify the above results with the fuel hose formulation, additional compounds were prepared using the ASTM standard D 3848, Evaluation of NBR mixed with carbon black. This is a very simple formulation without other fillers and plasticizers and better isolates the effects of the polymer and carbon black together.[5]

The formulations used, per ASTM D 3848, are shown in Table 9. Carbon black loadings were designed for equal hardness and to demonstrate the effect of a high and low loading of Thermax® N990 in a blend with N650.

[5]Mixing and testing for the ASTM compounds was provided by Akron Rubber Development Lab

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Table 9: Test Formulations

	HACN #1	SACN #2	SACN #3
Krynac 3370	-	100.0	100.0
Krynac 4560	100.0	-	-
N650	40.0	25.0	12.5
Thermax® N990	-	57.0	86.0
Zinc Oxide	3.0	3.0	3.0
Sulphur	1.5	1.5	1.5
Stearic Acid	1.0	1.0	1.0
Accelerator TBBS	0.7	0.7	0.7
TOTAL	**146.2**	**188.2**	**204.7**

Table 10: Rheometer Data, ASTM D 2084, 160°C, 1° arc, 1.7 Hz

	HACN #1	SACN #2	SACN #3
Maximum, MH, dN.m	30.1	50.4	52.1
Minimum, ML, dN.m	6.2	14.1	14.3
Scorch Time, Ts1, minutes	2.6	1.8	1.9
Cure Time, t50, minutes	4.9	2.8	2.9
Cure Time, t90, minutes	18.8	13.9	13.5

Table 11: Mooney Viscosity, ASTM D 1646, ML 1 + 4 @ 100°C

	HACN #1	SACN #2	SACN #3
Initial Torque, MU	80.8	95.2	93.3
Viscosity	49.6	65.8	67.0

As seen in the hose compound, there are differences in rheometer torque, scorch time, cure times and Mooney Viscosity. However it is notable that there is minimal difference between compounds #2 and #3, in spite of the higher carbon black loading for SACN #3. This is due to the low surface area and inert nature of the Thermax® N990.

Compounds were cured for 50 minutes @ 145°C.

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Table 12: Original Physical Properties, ASTM D 412, D 2240

	HACN #1	SACN #2	SACN #3
Hardness	75	76	76
Tensile Strength, MPa	23.9	20.4	17.0
100% Modulus, MPa	3.3	4.5	4.3
300% Modulus, MPa	13.9	18.0	15.9
Elongation (%)	540	400	390

The target hardness of 75 was obtained in the three compounds. There is some unexplained variability in these results, such as the high 300% modulus in SACN #2. It is evident that the NBR attains a state of saturation in the highly loaded compounds, as shown by the loss in tensile strength.

Table 13: Heat-Aged, ASTM D 573, 70 hours @ 125°C in Forced Air Oven

	HACN #1	SACN #2	SACN #3
Hardness	82	89	89
Tensile Strength, MPa	+7	+13	+13
100% Modulus, MPa	15.8	3.3	3.3
300% Modulus, MPa	-33.9	-83.8	-80.6
Elongation (%)	150	30	30
% Change	-72.3	-93.8	-93.0

Much better heat aging resistance is provided by the high acrylonitrile, with no difference amongst the compounds with the high loadings of carbon black. The significant loss in tensile strength due to heat aging suggests that a higher performance polymer, such as ACM or ECO should be considered for high heat applications.

Table 14: Compression Set, ASTM D 395, Aged 70 hours @ 125°C, 25% deflection, 30 minutes recovery

	HACN #1	SACN #2	SACN #3
Compression Set (%)	87.3	74.2	75.0

Poorer compression set is evident with the high ACN type NBR. The compression set did not worsen with the higher loading of carbon black, demonstrating the non-reinforcing nature of the Thermax® N990.

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Fluid Immersion Properties, ASTM D 471

	HACN #1	SACN #2	SACN #3
Krynac 3370	-	100.0	100.0
Krynac 4560	100.0	-	-
N650	40.0	25.0	12.5
Thermax® N990	-	57.0	86.0

Table 15: 70 hours @ 125°C in IRM 903 Oil

	HACN #1	SACN #2	SACN #3
Hardness	70	65	65
Points Change	-5	-11	-11
Tensile Strength, MPa	23.7	20.5	17.7
% Change	-0.8	+0.5	+4.1
Elongation (%)	370	310	290
% Change	-32.2	-22.4	-25.5
Volume Change (%)	+5.7	+15.9	+15.0

The above results demonstrate the benefit of using the higher acrylonitrile content. The SACN #2 compound had somewhat similar results and should be considered in light of the better compression set.

Table 16: 48 hours @ 23°C in ASTM Fuel C

	HACN #1	SACN #2	SACN #3
Hardness	51	52	52
Points Change	-24	-24	-24
Tensile Strength, MPa	12.2	10.0	10.2
% Change	-49.0	-51.0	-40.0
Elongation (%)	300	180	210
% Change	-43.9	-54.4	-45.5
Volume Change (%)	+40.0	+56.1	+53.9

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Table 17: 48 hours @ 23°C in 85% ASTM Fuel C, 15% Methanol

	HACN #1	SACN #2	SACN #3
Hardness	40	49	49
Points Change	-35	-27	-27
Tensile Strength, MPa	6.4	8.3	8.0
% Change	-73.2	-59.4	-52.9
Elongation (%)	160	140	140
% Change	-69.7	-63.9	-62.6
Volume Change (%)	+80.2	+89.9	+85.9

Tables 16 & 17 demonstrate that while the high acrylonitrile content provides some protection against the fuel attack, in some cases better resistance is provided by the higher carbon black loading. This is especially evident in terms of the change in hardness. The ASTM formulation is able to better isolate the effects of the acrylonitrile content and the loading and type of carbon black. A higher carbon black loading may provide better fuel resistance than a higher ACN content in some applications.