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(54) Title: HYDROGENATED NITRILE RUBBERS WITH IMPROVED LOW-TEMPERATURE PROPERTIES

(57) Abstract: Hydrogenated copolymers of an unsaturated nitrile, butadiene and isoprene, wherein the molar ratio of butadiene to isoprene is less than 3:1, display valuable low temperature properties.



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## PROPERTIES

The present invention relates to novel nitrile rubbers that have improved low temperature properties.

5 Background of the Invention

Hydrogenated nitrile butadiene rubber (HNBR) is a valuable elastomer known for its combination of unique properties, including high tensile strength, resistance to abrasion, high oil resistance and resistance to oxidation.

10 There is an increasing demand for elastomers that display these  
valuable properties at low temperatures. Car manufacturers are  
requesting elastomers that can be used over a temperature range  
from -40°C to +155°C. For aerospace applications elastomers are  
sought whose working temperature range extends down to -60°C or  
15 even -70°C.

There are known HNBR's that are useful at low temperature. There are commercially available HNBR's that have good low temperature properties. Thus, Therban<sup>®</sup> XN 535C is a terpolymer, available from Bayer, composed of 21% acrylonitrile, 20 acrylate, and butadiene, that has a residual double bond content (RDB) of 5.5% and a glass transition temperature (Tg) of -38°C. Therban<sup>®</sup> VP KA 8798 is similar, but differs in having an RDB of less than 0.9%, and, again, has a Tg of -38°C.

European Patent No. 471,250 of Bayer AG, issued  
25 February 1992, the disclosure of which is incorporated herein by  
reference, discloses hydrogenated  
butadiene/isoprene/(meth)acrylonitrile copolymers. The patent  
teaches that isoprene-modification of HNBR improves compression  
set at low temperature (for 97.1 to 98.6% hydrogenation, i.e.  
30 2.9 to 1.4% RDB). The patent discloses copolymers containing  
3.5 to 22% by weight of copolymerized isoprene and 18 to 50% by

weight of copolymerized acrylonitrile or methacrylonitrile, and having a degree of hydrogenation, based on the C=C double bonds of the polymer, of at least 85%, that is, an RDB not greater than 15%. The examples used copolymers with acrylonitrile contents of 34.1%, 33.3% and 33.5% and isoprene contents of 4.1%, 7.9% and 12.0%, respectively, the balance in each case being butadiene. The degrees of hydrogenation of isoprene were 86.3%, 86.6% and 82.9%, respectively.

### Summary of the Invention

It has now been found that by careful selection of the content of the copolymer there can be obtained an elastomer whose low temperature properties are markedly improved, as compared with the copolymers disclosed in European Patent No. 471,250. In particular, the inventors have surprisingly found significant improvement in low temperature flexibility as shown by Gehman and Temperature Retraction tests, and lowered glass transition temperature values identified by Differential Scanning Calorimetry (DSC).

Accordingly, the present invention provides a hydrogenated copolymer of an unsaturated nitrile, butadiene and isoprene, wherein the molar ratio of butadiene to isoprene is less than 3:1.

### Description of Preferred Embodiments

It has surprisingly been found that by lowering the butadiene:isoprene molar ratio in the hydrogenated copolymer there is effected an improvement in low temperature properties without a significant deleterious effect in the other properties of the HNBR. The lowest butadiene:isoprene molar ratio exemplified in the above-mentioned European patent 471,250 is greater than 4.5:1. In accordance with this invention the butadiene:isoprene ratio is below 3:1, preferably below 2:1. The ratio can be as low as 0.1:1, but is preferably not less

than 0.5:1. Good results are obtained with a ratio of 1:1 and the preferred range is 0.75:1 to 1:0.75.

The butadiene plus isoprene usually constitute about 50 to about 85% of the copolymer, and the nitrile usually  
5 constitutes about 15 to 50% of the copolymer. For this invention, which is concerned with low temperature properties the nitrile content does not normally exceed 36% and is preferably below 30%. The normal lower limit on the nitrile content is 15%, because copolymers with lower nitrile contents  
10 lose their oil resistance. For applications where oil resistance is not of importance, however, lower nitrile contents are acceptable, down to 10% or even 5%. For most purposes a nitrile content of 15 to 25% is preferred.

The nitrile is normally acrylonitrile or  
15 methacrylonitrile or  $\alpha$ -chloroacrylonitrile, of which acrylonitrile is preferred.

The polymer may also contain an amount, usually not exceeding about 10%, of another copolymerisable monomer, for example, an ester of an unsaturated acid, say ethyl, propyl or  
20 butyl acrylate or methacrylate, or a vinyl compound, for example, styrene,  $\alpha$ -methylstyrene or a corresponding compound bearing an alkyl substituent on the phenyl ring, for instance, p-alkylstyrene such as p-methylstyrene. Other copolymerisable monomers include  $\alpha,\beta$ -unsaturated acids, for example, acrylic,  
25 methacrylic, ethacrylic, crotonic, maleic (possibly in the form of its anhydride), fumaric or itaconic acid, and other conjugated dienes, for example 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and piperylene. The copolymer preferably is a solid that has a molecular weight in excess of about 60,000, most  
30 preferably in excess of about 100,000.

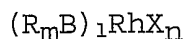
The copolymer that is to be hydrogenated can be made in known manner, by emulsion or solution polymerisation,

resulting in a statistical polymer. The copolymer will have a backbone composed entirely of carbon atoms. It will have some vinyl side-chains, caused by 1,2-addition of the conjugated diene during the polymerisation. It will also have double  
5 bonds in the backbone from 1,4-addition of the diene. Some of these double bonds will be in the cis and some in the trans orientation. These carbon-carbon double bonds are selectively hydrogenated by the process of the invention, without concomitant hydrogenation of the nitrile groups present in the  
10 polymer. If carboxyl groups (from an  $\alpha,\beta$ -unsaturated acid) are present, it is desired that these should not undergo hydrogenation.

Processes for the hydrogenation of NBR are known and may also be used for the production of the hydrogenation  
15 products according to the invention. Rhodium or titanium is generally used as the catalyst, although platinum, iridium, palladium, rhenium, ruthenium, osmium, cobalt or copper in the form of the metals, but preferably in the form of metal compounds, may also be used, cf. for example US 3,700,637; DE-PS  
20 2,539,132; EP 134 023; DE-OS 35 41 689; DE-OS 35 40 918; EP-A 298 386; DE-OS 35 29 252; DE-OS 34 33 392; US 4,464,515; and US 4,503,196.

Suitable catalysts and solvents for hydrogenation in homogeneous phase are described in the following, and in GB  
25 1558491 of Bayer AG and in EP 471,250, previously incorporated herein by reference. It is not intended to restrict the catalysts and solvents for hydrogenation useful for the invention, and these are provided only by way of example.

The selective hydrogenation can be achieved by means  
30 of a rhodium-containing catalyst. The preferred catalyst is of the formula:



in which each R is a C<sub>1</sub>-C<sub>8</sub>-alkyl group, a C<sub>4</sub>-C<sub>8</sub>-cycloalkyl group  
a C<sub>6</sub>-C<sub>15</sub>-aryl group or a C<sub>7</sub>-C<sub>15</sub>-aralkyl group, B is phosphorus,  
arsenic, sulfur, or a sulphoxide group S=O, X is hydrogen or an  
anion, preferably a halide and more preferably a chloride or  
5 bromide ion, l is 2, 3 or 4, m is 2 or 3 and n is 1, 2 or 3,  
preferably 1 or 3. Preferred catalysts are tris-  
(triphenylphosphine)-rhodium(I)-chloride,  
tris(triphenylphosphine)-rhodium(III)-chloride and tris-  
(dimethylsulphoxide)-rhodium(III)-chloride, and tetrakis-  
10 (triphenylphosphine)-rhodium hydride of formula ((C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P)<sub>4</sub>RhH,  
and the corresponding compounds in which triphenylphosphine  
moieties are replaced by tricyclohexylphosphine moieties. The  
catalyst can be used in small quantities. An amount in the  
range of 0.01 to 1.0% preferably 0.03% to 0.5%, most preferably  
15 0.1% to 0.3% by weight based on the weight of polymer is  
suitable.

It is known to use the catalyst with a co-catalyst  
that is a ligand of formula R<sub>m</sub>B, where R, m and B are as defined  
above, and m is preferably 3. Preferably B is phosphorus, and  
20 the R groups can be the same or different. Thus there can be  
used a triaryl, trialkyl, tricycloalkyl, diaryl monoalkyl,  
dialkyl monoaryl diaryl monocycloalkyl, dialkyl monocycloalkyl,  
dicycloalkyl monoaryl or dicycloalkyl monoaryl co-catalysts.  
Examples of co-catalyst ligands are given in US Patent No  
25 4,631,315, the disclosure of which is incorporated by reference.  
The preferred co-catalyst ligand is triphenylphosphine. The co-  
catalyst ligand is preferably used in an amount in the range 0.3  
to 5%, more preferably 0.5 to 4% by weight, based on the weight  
of the copolymer. Preferably also the weight ratio of the  
30 rhodium-containing catalyst compound to co-catalyst is in the  
range 1:3 to 1:55, more preferably in the range 1:5 to 1:45.  
The weight of the co-catalyst, based on the weight of one  
hundred parts of rubber, is suitably in the range 0.1 to 33,

more suitably 0.5 to 20 and preferably 1 to 5, most preferably greater than 2 to less than 5.

The hydrogenation reaction can be carried out in solution. The solvent must be one that will dissolve butadiene nitrile rubber. This limitation excludes use of unsubstituted aliphatic hydrocarbons. Suitable organic solvents are aromatic compounds including halogenated aryl compounds of 6 to 12 carbon atoms. The preferred halogen is chlorine and the preferred solvent is a chlorobenzene, especially monochlorobenzene. Other solvents that can be used include toluene, halogenated aliphatic compounds, especially chlorinated aliphatic compounds, ketones such as methyl ethyl ketone and methyl isobutyl ketone, tetrahydrofuran and dimethylformamide. The concentration of polymer in the solvent is not particularly critical but is suitably in the range from 1 to 30% by weight, preferably from 2.5 to 20% by weight, more preferably 6 to 15% by weight and most preferably 10 to 15% by weight. The concentration of the solution may depend upon the molecular weight of the copolymer rubber that is to be hydrogenated. Rubbers of higher molecular weight are more difficult to dissolve, and so are used at lower concentration.

The reaction can be carried out in a wide range of pressures, from 10 to 250 atm and preferably from 50 to 100 atm. The temperature range can also be wide. Temperatures from 60 to 160°, preferably 100 to 160°C, are suitable and from 110 to 150°C are preferred. Under these conditions, the hydrogenation is usually completed in about 3 to 7 hours. Preferably the reaction is carried out, with agitation, in an autoclave.

Hydrogenation of carbon-carbon double bonds improves various properties of the polymer, particularly resistance to oxidation. It is preferred to hydrogenate at least 70% of the carbon-carbon double bonds present. For some purposes it is desired to eliminate all carbon-carbon double bonds, and

hydrogenation is carried out until all, or at least 99%, of the double bonds are eliminated. For some other purposes, however, some residual carbon-carbon double bonds may be required and reaction may be carried out only until, say, 90% or 95% of the  
5 bonds are hydrogenated. The degree of hydrogenation can be determined by infrared spectroscopy or  $^1\text{H}$ -NMR analysis of the polymer.

In some circumstances the degree of hydrogenation can be determined by measuring iodine value. This is not a  
10 particularly accurate method, and it cannot be used in the presence of triphenyl phosphine, so use of iodine value is not preferred.

It can be determined by routine experiment what conditions and what duration of reaction time result in a  
15 particular degree of hydrogenation. It is possible to stop the hydrogenation reaction at any preselected degree of hydrogenation. The degree of hydrogenation can be determined by ASTM D5670-95. See also Dieter Brueck, Kautschuk + Gummi Kunststoffe, Vol 42, No 2/3 (1989), the disclosure of which is  
20 incorporated herein by reference.

To extract the polymer from the hydrogenation mixture, the mixture can be worked up by any suitable method. One method is to distil off the solvent. Another method is to inject steam, followed by drying the polymer. Another method is to add  
25 alcohol, which causes the polymer to coagulate.

The catalyst can be recovered by means of a resin column that absorbs rhodium, as described in US Patent No 4,985,540, the disclosure of which is incorporated herein by reference.

30 The hydrogenated isoprene nitrile butadiene rubber (HINBR) of the invention can be crosslinked. Thus, it can be vulcanized using sulphur or sulphur-containing vulcanizing



agents, in known manner. Sulphur vulcanization requires that there be some unsaturated carbon-carbon double bonds in the polymer, to serve as reactions sites for addition of sulphur atoms to serve as crosslinks. If the polymer is to be sulphur-  
5 vulcanized, therefore, the degree of hydrogenation is controlled to obtain a product having a desired number of residual double bonds. For many purposes a degree of hydrogenation that results in about 3 or 4% residual double bonds (RDB), based on the number of double bonds initially present, is suitable.

10 The HINBR can be crosslinked with peroxide crosslinking agents, again in known manner. Peroxide crosslinking does not require the presence of double bonds in the polymer, and results in carbon-containing crosslinks rather than sulphur-containing crosslinks. As peroxide crosslinking  
15 agents there are mentioned dicumyl peroxide, di-t-butyl peroxide, benzoyl peroxide, 2,2'-bis(ter-butylperoxy)disopropyl benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexyne-3 and 2,5-dimethyl-2,5-di(benzoylperoxy)hexane and the like. They are suitably used in amounts of about 0.2 to 20 parts by weight,  
20 preferably 1 to 10 parts by weight, per 100 parts of rubber.

The HINBR of the invention can be compounded with any of the usual compounding agents, for example fillers such as carbon black or silica, heat stabilisers, antioxidants, activators such as zinc oxide or zinc peroxide, curing agents  
25 co-agents, processing oils and extenders. Such compounds and co-agents are known to persons skilled in the art.

The low temperature properties of the hydrogenated copolymers of the invention renders them suitable for many specialised applications. They are suited for extreme  
30 conditions of under-the-hood automotive applications, including belts, hoses and mountings such as engine mounts. Mention is made of rolls, especially high-hardness roll applications in, for instance, metal-working rolls, paper industry rolls,

printing rolls and elastomer components for textile rolls.

Resistance to fluids, especially fluids with aggressive additives renders the hydrogenated copolymers of the invention useful for seals, and also in oil well specialties as a

5 consequence of low swell and explosive decompression resistance.

They are also useful in wire and cable applications that demand excellent mechanical properties and high flexibility under critical ambient conditions. They are also suitable for use in vibration dampeners and torque struts.

10           The invention is further illustrated in the following non-limiting examples:

Example 1

Various copolymers of acrylonitrile, butadiene and isoprene were hydrogenated to different RDB values and then

15 subjected to differential scanning calorimetry (DSC).

Hydrogenation reactions were carried out in a 2 US gallon Parr high-pressure reactor in the laboratory under the following conditions:

	Cement solids	6%
20	H <sub>2</sub> pressure	1200 psi
	Agitator speed	600 rpm
	Reactor temperature	138 °C
	Catalyst	
	(Tris(triphenylphosphine) -	
25	rhodium(I)chloride) loading	0.13-0.4 phr
	Co-catalyst	2-2.33 phr
	(triphenylphosphine) loading	
	Solvent	Monochlorobenzene

Results are given in Table 1

TABLE 1

HINBR	BD/IP wt. %	BD/IP ratio	ACN wt. %	Tg °C (1)	H (J/g) (2)	% RDB (3)
A	65/20	3/1	15	-44	19	4
B	42/38	1/1	20	-47	0	23
C	43/44	1/1	13	-51	0	11
D	na	na	21	-38	0	5.5
E	na	na	17	-25	37	4.7

(1) Glass transition temperature determined from DSC (midpoint).

5 (2) Melting Enthalpy- a high value indicates crystallinity, which is undesired; a lower value indicates a better result. A value of zero indicates an amorphous polymer (no crystallinity). Values were determined using DSC.

10 (3) Residual double bond content, determined by <sup>1</sup>H-NMR spectroscopy.

The above descriptions (1), (2) and (3) apply equally to the results shown in Example 2, Table 2.

Samples D and E are comparative, and contain no isoprene. Sample D is the commercially available  
15 butadiene/acrylonitrile/acrylate terpolymer Therban<sup>®</sup> XN 535C. Sample E is a hydrogenated copolymer of 17% acrylonitrile and 83% butadiene, with 4.7 % RDB.

In particular, Example 1 shows that sample B having a BD:IP ratio of 1:1 has a lower Tg value than comparative sample  
20 D, a commercially available low temperature polymer.

### Example 2

Copolymers of acrylonitrile, butadiene, and isoprene were prepared with three levels of acrylonitrile, namely, 19%,

23% and 25% and three ratios of butadiene to isoprene (BD/IP), namely, 3:1, 2:1 and 1:1, and then hydrogenated to different RDB values. Results are given in Table 2. Samples F to K are in accordance with the invention and sample D is again used as a comparative sample.

Table 2

HINBR	BD/IP % wgt	BD/IP ratio	ACN wt. %	Tg °C*	H (J/g)	% RDB
F	61/19	3/1	20	-33	16.0	3.8
G	50/25	2/1	25	-38	1.0	6.6
H	37/38	1/1	25	-36	0	3.8
I	37/40	1/1	23	-40	0	5.6
J	54/26	2/1	19	-39	6.5	2.8
K	42/39	1/1	19	-46	0	7.6
D	na	na	21	-38	0	5.5

Sample K, which may be compared to Sample B in Table 1 for composition, shows an improved Tg value, confirming the results of Example 1, Table 1.

Isoprene is less readily hydrogenated than butadiene, and as the isoprene content of a polymer is increased hydrogenation becomes more difficult. To achieve a desired RDB increased catalyst loading, or longer reaction time, or both, may be required. Details of the hydrogenation of samples I, J and K are given in Table 3.

Table 3

HINBR	BD/IP ratio	Cat loading (phr)	TPP loading (phr)	Reaction time (h)	% RDB*
I	(1/1)	0.3	2	11	5.6
J	(2/1)	0.3	2	9	2.8
K	(1/1)	0.3	2	9	7.6

\* % RDB of HINBR determined by <sup>1</sup>H-NMR.

Example 3

HINBR's of Example 1 were compounded and subjected to peroxide cure. The recipe used is set forth in Table 4.

Table 4

Compound	phr
HINBR or HNBR* or other	100
Carbon Black, N 660 Sterling-V	50
Maglite D (MgO activator)	3
Naugard 445 (antioxidant)	1
Plasthall TOTM (plasticizer)	5
Vulkanox ZMB-2/C5 (ZMMBI) (antioxidant)	0.4
Zinc Oxide (Kadox 920)	3
Diak #7 (coagent for peroxide)	1.5
Di-cup 40KE (peroxide curative)	7.5

5 \*Base polymer

The low temperature properties of the cured compounds are given in Table 5. Samples A, B & C are from Example 1 and in accordance with the invention. Samples D, E, also from Example 1, and Therban<sup>®</sup> C 3467 are comparative.

10

Table 5

Sample Identification	BD:IP	ACN wt. %	Compression Set @-30°C (Cure Temp 170°C)	Gehman LT Stiffness at 170° Cure Temp		
				T2	T10	T100
A	3:1	15	88	-11	-35	-44
B	1:1	20	42	-30	-40	-46
C	1:1	13	41	-33	-44	-49
D	na	21	81	-28	-37	-42
E	na	17	97	3	-25	-37
Therban <sup>®</sup> C 3467	na	34	93	-20	-27	-31

Table 5 shows that HINBR samples containing either 13 wt.% (sample C) or 20 wt.% (sample B) acrylonitrile with a 1/1 BD to IP ratio have very low compression set properties at low

temperature. The high content of butadiene in the 15 wt.% ACN sample (sample A) explains the higher compression set value.

The HINBR samples containing the 13 and 20 wt.% ACN content again show the best low temperature properties as seen by Gehman test results. Both samples have a BD/IP ratio of 1/1. Due to low temperature crystallinity, which hinders flexibility at low temperature, the Gehman temperatures are higher in the 15 wt.% ACN HINBR sample (sample A).

The Gehman test determines the relative stiffness characteristics of vulcanized rubber by measuring the angle of twist between -70°C and room temperature. The first measurement is taken at room temperature. The sample is then cooled down to -70°C and twisted while it is warming up. The T2 value is the temperature at which the sample is two times as stiff (or the sample is 1/2 of its original angle).

#### Example 4

Samples of HINBR from Example 2 were compounded and subjected to peroxide cure. The recipe is set forth in Table 6.

Table 6

Compound	phr
HINBR or HNBR*	100
Carbon Black, N 660 Sterling-V	50
Maglite D	3
Naugard 445	1
Plasthall TOTM	5
Vulkanox ZMB-2/C5 (ZMMBI)	0.4
Zinc Oxide (Kadox 920)	3
Diak #7	1.5
Di-cup 40KE	7.5

\*Base polymer

Sample J formulation varied in the amount of Diak #7 (5 phr) and Dicup 40KE (9.4 phr) used.

The MDR @ 170°C cure behaviour and Stress Strain Data of the samples are shown in Table 7.

Table 7

	K	I	G	H	THER- BAN <sup>®</sup> C 3467	THER- BAN <sup>®</sup> VP KA 8798	THER- BAN <sup>®</sup> XN 535C
<b>MDR CURE CHARAC- TERISTICS</b>							
Test Temp (°C)	170	170	170	170	170	170	170
MH (dN.m)	35.82	26.22	37.59	31.02	36.03	23.59	27.84
ML (dN.m)	3.01	2.2	3.91	5.75	1.59	2.54	2.14
Delta MH- ML (dN.m)	32.81	24.02	33.68	25.27	34.44	21.05	25.7
<b>Stress Strain (Dumbel ls)</b>							
Stress @ 25 (Mpa)	0.9	0.9	1.1	0.9	1.1	0.9	1.0
Stress @ 50 (Mpa)	1.4	1.3	1.7	1.4	1.6	1.4	1.5
Stress @ 100 (MPa)	3.1	2.8	4.0	2.9	3.5	3.0	3.4
Stress @ 200 (MPa)	10.8	9.4	13.5	10.5	12.4	9.2	10.1
Stress @ 300 (MPa)		16.0			21.5	15.2	16.0
Ultimate Tensile (MPa)	16.0	16.3	18.7	19.0	23.9	18.0	17.4
Ultimate Elonga- tion (%)	266	302	253	299	345	358	325
Hard. Shore A2 Inst. (pts.)	59	60	63	60	63	63	63

The state of cure as measured by delta torque is comparable to current commercial Therban<sup>®</sup> grades.

The Low Temperature Flexibility - Gehman Test and Temperature Retraction (TR) are shown in Table 8.

Table 8

	J	K	I	G	H	THER- BAN® C 3467	THER- BAN® VP KA 8798	THER- BAN® XN 535C
<b>GEHMAN LOW TEMP STIFFNESS (at 170°C cure temperature)</b>								
Cure Time (min)	14	13	14	13	12	13	14	14
Start Temperature (min)	-70	-70	-70	-70	-70	-70	-70	-70
Temperature @ T2 (°C)	-23	-32	-22	-23	-20	-21	-20	-21
Temperature @ T5 (°C)	-32	-39	-31	-32	-28	-26	-32	-34
Temperature @ T10 (°C)	-35	-41	-33	-33	-30	-28	-35	-36
Temperature @ T100 (°C)	-42	-47	-40	-40	-37	-32	-41	-42
<b>TEMPERATURE RETRACTION (at 50% elongation /170°C cure temperature)</b>								
Cure Time (min)	14	13	14	13	12	13	14	14
TR 10 (°C)	-32	-41	-32	-32	-29	-23	-31	-32
TR 30 (°C)	-26	-36	-26	-29	-25	-19	-26	-28
TR 50 (°C)	-21	-32	-22	-24	-22	-15	-21	-24
TR 70 (°C)	-15	-26	-15	-19	-19	-11	-16	-19
Temp Retraction TR 10 - TR 70	17	15	17	13	10	12	15	13

5 Sample K reaches the lowest temperatures in the Gehman test. The temperature retraction tests also support the



improved low temperature flexibility properties of sample K, giving a TR 10 value of -41 °C compared to the value of -32 °C for Therban® XN 535C. In the temperature retraction test the rubber test piece is elongated to 50% (by locking it) followed by cooling it in an ethanol/dry ice liquid bath (-70 °C). The temperature of the bath is then increased by 1 °C per minute. The elastic retraction was measured by recording the temperature at which the test piece retracts to 10, 30, 50 and 70% of its original shape.

The properties of sample K are compared to Therban® XN 535C in Table 9.

Table 9

	Sample K	Therban® XN 535C
% ACN	19	21
% RDB	7.6	5.5
<b><u>Peroxide Cure:</u></b>		
Tensile (MPa)	16	17.4
Elongation (%)	266	325
M 100 (MPa)	3.12	3.35
H (Shore A)	59	63
<b><u>LT Flexibility:</u></b>		
Gehman (°C) T2	-32	-21
T10	-41	-36
T100	-47	-42
<b>Temp. Retraction (°C)</b>		
TR10	-41	-32
TR70	-26	-19
Tg (°C)	-46	-38

Although the elongation @ break % is reduced slightly, the low temperature properties of the HINBR of this invention are improved over current commercial grades of hydrogenated nitrile rubbers for low temperature applications.

The following advantages were obtained in a hydrogenated nitrile/isoprene/butadiene copolymer having a butadiene:isoprene ratio of 3:1 or less:

- 5       • improved, lowered glass transition value (amorphous polymer from thermal analysis, DSC)
- improved compression set properties at low temperatures
- increased low temperature flexibility

It should be noted that phr as used herein means parts per hundred parts of rubber, and is generally understood in the art.

10 Further, the term copolymer used herein is intended to include polymers composed of two, three or more monomers, as appropriate.

CLAIMS:

1. A hydrogenated copolymer comprising an unsaturated nitrile, butadiene and isoprene, wherein the molar ratio of butadiene to isoprene is 3:1 or less.
- 5 2. A copolymer according to claim 1, wherein the molar ratio of butadiene to isoprene is 2:1 or less.
3. A copolymer according to claim 1, wherein the molar ratio of butadiene to isoprene is not less than 0.1:1.
4. A copolymer according to claim 1, wherein the molar  
10 ratio of butadiene to isoprene is not less than 0.5:1.
5. A copolymer according to claim 1, wherein the molar ratio of butadiene to isoprene is in the range 0.75:1 to 1:0.75.
6. A copolymer according to any one of claims 1 to 5, wherein the unsaturated nitrile is acrylonitrile.
- 15 7. A copolymer according to any one of claims 1 to 5, wherein the unsaturated nitrile is methacrylonitrile.
8. A copolymer according to any one of claims 1 to 7, wherein the copolymer contains not more than 36% of the nitrile.
9. A copolymer according to any one of claims 1 to 7,  
20 wherein the copolymer contains from 15 to 30% of the nitrile.
10. A copolymer according to any one of claims 1 to 9, which has a residual double bond content of 30% or less.
11. A copolymer according to claim 10, wherein the residual double bond content is 10% or less.
- 25 12. A process for preparing a hydrogenated copolymer according to any one of claims 1 to 11 which comprises copolymerising an unsaturated nitrile, butadiene and isoprene, wherein the molar ratio of butadiene to isoprene is 3:1 or less

and subjecting the obtained copolymer to selective hydrogenation.

13. A process according to claim 12, wherein the selective hydrogenation is carried out in the presence of a rhodium-  
5 containing compound as catalyst and a co-catalyst ligand.
14. A process according to claim 13, wherein the rhodium-containing compound is tris(triphenylphosphine)-rhodium (I) chloride and the co-catalyst ligand is triphenylphosphine.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 01/01189

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08C19/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 471 250 A (BAYER AG) 19 February 1992 (1992-02-19) cited in the application abstract; claims page 2, line 40 - line 48 ----	1,2,6-12
A	T. KOBATAKE ET AL.: "improvement of low-temperature flexibility of hydrogenated nitrile-butadiene rubber" RUBBER CHEMISTRY AND TECHNOLOGY., vol. 70, no. 5, 1997, pages 839-854, XP002185139 RUBBER DIVISION ACS. AKRON., US ISSN: 0035-9475 abstract; figure 12; table IV page 849 ----- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

10 December 2001

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# INTERNATIONAL SEARCH REPORT

Internat. Application No  
PCT/CA 01/01189

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 631 315 A (BUDING ET AL)  23 December 1986 (1986-12-23)  cited in the application  abstract; claims; example 1  column 3, line 52 - line 63  -----</p>	12-14

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern: il Application No

PCT/CA 01/01189

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			JP 61078802 A	22-04-1986
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