

## Naphthenic Tire Oils: Excellent Tool to Modify Rubber Compound Performance

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#### Oil in a tyre

Oil is not so important?!

- Formulation work is done with polymers, fillers and coupling agents (+resins)
- Oils have limited possibilities to contribute to compound performance
- Oils are intrinsincly cheap and do thus not offer big saving potential
- Oils are logistically difficult in a tyre/polymer plant
- Oils destroy productivity in a polymer production

#### Process oils are used in the rubber industry to,

- improve the processability of rubbers and rubber compounds
  - ----> process aids
- increase the bulk of rubber in order to lower cost
  oil-extended rubbers

Main application is process aid.











### **Oil is an excellent tool to affect**

- 1) Rolling resistance
- 2) Traction in varying conditions
- 3) Durability and mechanical strength
- 4) Processing and manufacturing efficiency
- 5) Utilization of other novel raw materials





- Naphthenic rubber oils / Features, Nynas product offering and global sustainability requirements and trends
- Tire industry approaches: how to utilize the naphtenic potential
  - Rolling resistance improvement with naphthenic oil
  - Winter and all-season tire traction boost with naphthenics
  - Naphthenics in mixing machine lubrication



### Global Technology Center at Nynäshamn Refinery



**Technical Development and Market Support** 



- Global technical support to customers from 5 locations:
  - Nynäshamn
  - Singapore
  - São Paulo
  - Buenos Aires
  - Harburg
- 42 Employees
  - ▶ 9 PhD
  - 17 MSc
  - 2 Professors
  - 13 Languages



Process Technology: Pilot Scale Hydrotreating Units



- Three units are running 24/7 and are used for a wide variety of applications
  - Research and competence build-up
  - Catalyst evaluations
  - Crude evaluations
  - Process development
  - Product related investigations
- Investment: 37.5 MSEK





### Application Testing: Rubber Lab

Opening planned for January 2017

 Compounding and testing of rubber and tire formulations









#### Naphthenic rubber oils:

Sand Contraction

Features, Nynas product offering and global sustainability requirements and trends



#### Which oils are used in rubber goods?

Heavy Naphthenics		RAE	SRAE
Vegetable Oils	DAE	TDAE	MES
Paraffinic Gr I, Gr II, Gr III	TRAE	Naphthenic I	Black Oil





#### Rubber Oil preferences today









#### Naphthenic Oil Refining at Nynas







### Naphthenic or Paraffinic crude?

- Based on the relative amount of paraffinic molecules (C<sub>P</sub>)
  - ▶ C<sub>P</sub> (IR) 42-50% Naphthenic
  - ▶ C<sub>P</sub> (IR) 56-67% Paraffinic

Aromatic molecules confer high solvency to the oil, but if in conjugated formations they are toxic and harmful to the environment so therefore removed during the refining process. Mono and di-aromatics are not harmful.



Styrene-Butadiene Rubber



### More realistic molecules present in oil

Paraffinic oils

Naphthenic oils



• Aromatic oils



#### Base oils classification



\* American Petroleum Institute



#### **API Base Oil Groups**

Group I	Group II	Group III			
Solvent Extraction Processing	Severe Hydrogen Processing	Severe Hydrogen Processing /			
VI: ~ 80-100 Max. visc. @ 40 °C: ~1000 cSt Sulphur ~1 %	VI: ~80-120 Max. visc. @ 40 °C: 100 cSt Sulphur < 10 ppm	Wax Isomerization VI: >120 Max. visc. @ 40 °C: 50 cSt Sulphur < 5 ppm			

Driver: Higher quality engine oils and fuels

Group I refineries closing

New capacity in Group II, III and Naphthenics



# General features of naphthenic oils

Produced via hydrotreatment of vacuum distilled crude oil cuts

- Comply with all global health and safety regulations
  - PAH content even lower than that of RAE and TDAE
  - Sulphur content low



- Very good low temperature properties (both transportation and product performance)
- Ensured availability in short and long term



### General features of naphthenic oils

- Solubility matches extremely well to that of tyre polymers (NR, BR, SBR, CIIR/BIIR)
- Offer improvement in rolling resistance and mileage
- Offer potential also in

- winter tyre tread / all season tyre tread formulations



- subtread / thick undertread compounds
- compounds containing NR/BR (e.g. sidewall)
- innerliner formulations

# Solubility parameters as a tool for predicting compatibility

Solubility parameter,  $\delta$  is proportional to the strength of intermolecular interactions between molecules

- Elastomers have δ values
- Plasticisers have δ values

If they are similar to each other they are more likely to be compatible





# Hydrocarbon structure and solvent power

- Solvent Power usually refers to the ability of dissolving a substance of higher polarity
- "Like dissolves like"
- But mineral oil consists basically only of hydrocarbons which does not exhibit polarity
- What do we mean with polarity when talking about hydrocarbons then?
- Van der Waals or/and dispersive forces





### Hydrocarbon structure and solvent power





### Polymer compatibility





### Oil glass transition

- Mineral oil is clearly not a polymer but does still undergo Glass Transition
- The glass transition are determined with DSC according to ASTM E 1356
- When the oil and polymer system is fully compatible the Fox Equation should apply

If the nature of the components being mixed are not "too different", then the "Inverse rule of mixtures" can be applied, also called the Fox equation . This equation is commonly used to predict Tg of polymer blends.

$$\frac{1}{Tg} = \frac{w1}{Tg1} + \frac{w2}{Tg2} + \frac{w3}{Tg3}$$



## **Oil Glass Transition**

- Dependent on molecular structure
  - Hydrocarbon distribution
  - Molecular weight





#### **Oil Glass Transition**





### Product Portfolio: Rubber Process Oils (RPO)

Property	Unit	Method ASTM	Nytex 810	Nytex 820	Nytex 832	Nytex 840	Nytex 230	Nytex 4700	Nytex 459
Viscosity, 40°C	cSt	D 445	22.3	109	225	375	440	710	5400
Viscosity, 100°C	cSt	D 445	3.7	8.3	14.2	18	19.9	29	98
Flash Point, PM	°C	D 93A	174	212	226	256	221	220	241
Aniline Point	°C	D 611	75	86	94	98	88	90	95
Pour point	°C	D 97	-45	-30	-24	-21	-12	-15	0
Volatility, 107°C, 22h	wt%	D 972	7	0.5	0.2	0.1	0.2	0.6	-
Sulphur	%	D 2622	0.06	0.06	0.06	0.12	1.8	0.5	0.9
Density, 15°C	kg/dm <sup>3</sup>	D 4052	0.902	0.917	0.921	0.922	0.931	0.94	0.962
Refractive Index, 20 °C		D 1747	1.494	1.502	1.505	1.507	1.512	na	na
Viscosity-Gravity-Constant		D 2501	0.861	0.859	0.853	0.847	0.858	0.866	0.872
Colour		D 1500	<0.5	<1.0	<2.5	<2.5	5	>8.0	>8.0
Carbon-Type Composition, C <sub>A</sub>	%	D 2140	10	11	12	12	12	25	26
Carbon-Type Composition, $C_N$	%	D 2140	43	41	36	34	29	24	17
Carbon-Type Composition, CP	%	D 2140	47	48	52	54	59	51	57
Tg	°C	E 1356	-75	-62	-60	-56	-52	-55	-46



### **Tire Labelling**





#### Tire industry approaches: how to utilize the naphtenic potential





# **Tire Industry Trends and Signals**

- Rolling resistance & fuel economy pursuit continues
- Sustainability pursuit becomes stronger
- Weight reduction targeted
- Use of functionalized polymers in tread compounds increases
- Increase of silica SSA and loading in tread compounds
- Expansion of silica to non-tread compounds
- Studded tyre usage will be restricted







#### Tire industry approaches: how to utilize the naphtenic potential

#### **Rolling resistance reduction with naphthenic oils**



#### **Rolling resistance and fuel consumption**



Source: Umweltbundesamt

#### Tire's rolling resistance:

- Tyre rubber compounds are viscoelastic
- They dissipate energy on deformation
- Contribution to total fuel consumption varies from 15% to 30%





Tread	Undertread	≡ Belt	≡ Side wall
■ Carcass	Bead	Innerliner	



### **Rolling resistance reduction**

- Environmental impact of tyre use
  - Since 1990 there has been a global drive to lower CO<sub>2</sub> emissions.
  - Vehicle emissions are a significant contribution.
- Tyre manufacturers challenged by automotive industry
  - To reduce the carbon footprint of road vehicles.
  - To improve tyre/vehicle performance.
  - To lower costs.
- Tyre manufacturers challenged by legislators
  - To improve safety.
  - To reduce product environmental impact.
- Tyre replacement market
  - Achieve a greater share of replacement tyre market.



		Wanli	Debica	Sava	Fulda	GT Radial	Uniroyal	Vredestein	Bridge- stone	Dunlop	Goodyear	Conti- nental	Michelin
		S-1063	Furio	Intensa hp	Carat Progresso	Champiro 228	Rain Expert	Sportrac 3	Turanza ER 300	SP Fast- response	Optigrip	Premium Contact 2	Primacy HP
Reifendimension 205/55 R 16 91 V													
Sicherheit, nass													
Bremsen, nass	30	6	24	27	27	21	27	24	27	27	27	30	24
Reifenlabel für den Nassgriff		E	С	В	В	С	В	С	В	В	В	A	В
Handling, nass (Zeitmessung)	10	4	6	9	9	8	9	9	10	10	9	10	9
Handling, nass (sujektive Wertung)	20	5	15	18	16	15	18	16	18	20	18	20	18
Aquaplaning, quer	10	3	6	8	8	5	9	9	8	8	10	9	7
Aquaplaning, längs	10	4	6	8	8	7	10	9	9	9	10	9	8
Kapitelwertung	80	22	57	70	68	56	73	67	72	74	74	78	66
Sicherheit, trocken													
Bremsen, trocken	20	10	16	17	17	18	18	17	20	20	17	20	19
Handling, trocken (Zeitmessung)	10	8	7	7	8	9	8	8	10	9	8	9	10
Handling, trocken (subjektive Wertung)	20	14	15	15	16	18	18	18	20	18	16	20	20
Vorbeifahrgeräusch	10	10	10	9	9	10	9	10	10	10	9	10	10
Kapitelwertung	60	42	48	48	50	55	53	53	60	57	50	59	59
Wirtschaftlichkeit													
Rollwiderstand	20	16	10	6	10	18	10	8	10	10	10	10	20
Reifenlabel für den Rollwiderstand		E	E	F	E	E	E	F	E	E	E	E	E
Preis für 4 Reifen*	10	200,-€ 10	230,-€ 9	240,-€ 8	260,-€ 7	260,-€ 7	260,-€ 7	270,-€ 7	280,-€ 6	280,-€ 6	280,-€ 6	300,-€ 5	340,-€ 3
Kapitelwertung	30	26	19	14	17	25	17	15	16	16	16	15	23
Gesamtwertung	170	90	124	132	135	136	143	135	148	147	140	152	148
GTÜ-Urteil				0	+	0**	++	+	++	++	+	++	++

\* Preise stichprobenartig im Internet ermittelt (Stand: 02/2010), Angaben ohne Montage und inkl. MwSt. • \*\* Abwertung wegen schlechter Nässeeigenschaften

++ sehr empfehlenswert • + empfehlenswert • o bedingt empfehlenswert • – nicht empfehlenswert







### Rolling resistance reduction

- Competition and legislation changes as drivers
- Work not limited to eco tyres, tread compounds or high sales volume sizes

UN Regulation 117 version 02										
Imple	mentation dates	1.11.2012	1.11.2014	1.11.2016	1.11.2018	1.11.2020				
	Requirements and implem	entation dat	es for new	and existing t	yre types					
New tyre types	S2 = Sound, level 2. W = Wet Grip R1 = Rolling Resistance, level 1. R2 = Rolling Resistance, level 2.	S2 for class C1, W for class C1 R1 for class C1,		R2 for class C1, C	2,63					
Existing tyre types Sale or entry into service R1 = Rolling Resistance, level 1.			W for class C1 R1 for class C		R2 for class C1, C2					
Jan Mar	R2 = Rolling Resistance, level 2.			R1 for class C3		R2 for class C3				
	Combination markings a	ind impleme	entation da	tes for new	tyre types					
C1 R 30 + R 117 c	ombination approval mark	E4 02303030 +02	S2WR1 segrete	E4 02303030 +0252	WR2					
C2 R 54 + R 117 cr	ombination approval mark	E4 0054 5454 +02	S2R1 vpgude	E4 00545454 +0252	R2					
C3 R54+R117 c	ombination approval mark	E4 0054 5454 +02	S2R1 upgende	E4 00545454 +0252	R2					






# Rolling resistance reduction

- Various stages of tread compound development
  - Carbon black / ESBR
  - Carbon black / SSBR, Silica / ESBR
  - Silica / SSBR
  - Silica / fx-SSBR
  - ► Ti-BR → Ni-BR, Co-BR → Nd-BR → fx-Nd-BR
  - Silica surface area development
  - Silica coupling development
  - Carbon black nanostructure development
  - Aromatic oils  $\rightarrow$  naphthenic oils (natural oils)



0.8

0.7

0.6

0.5

0.4

0.3 0.2 0.1 0.1



# **Rolling resistance reduction**

Two-way approach:

- 1) Tread compound development
- 2) Development of other compounds and materials

One of the first A-tyres (2012)

- new tread compound
- new sidewall, carcass and apex compounds
- new textile cord
- new tread design, new tyre profile
- significant weight reduction
- Most work done with polymers and fillers, yet other ingredients can support significantly



### Rolling resistance (RR) pursuit

- Competition and legislation changes as drivers
- Work not limited to eco tyres, tread compounds or high sales volume sizes
- Tan d an excellent indicator: 30% drop in tan delta at 60-70 C leads
  - in tread to
  - in thick subtread (undertread)
  - in steel belt compound

7-12% drop in RR2-4 % drop in RR2-3 % drop in RR

→ Oils yielding a low tan delta offer a benefit → Nytex 4700, Nytex 459



#### Nytex 4700 in f-SSBR

#### **Tire Tread Formulation**

	phr	phr	phr	phr	phr
SSBR, Sprintan SLR 4602	70	70	70	70	70
Nd-BR, Buna CB 24	30	30	30	30	30
Silica, Ultrasil 7000 GR	90	90	90	90	90
TESPT, Si 69	8.0	8.0	8.0	8.0	8.0
Carbon Black, N234	5.0	5.0	5.0	5.0	5.0
NBO (Nytex 4700)	35.0				
MES		35.0			
TDAE			35.0		
RAE				35.0	
DAE					35.0
Zinc Oxide	2.5	2.5	2.5	2.5	2.5
Stearic Acid	3.0	3.0	3.0	3.0	3.0
Sulfur	1.5	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5	1.5
DPG	2.0	2.0	2.0	2.0	2.0
6PPD	2.0	2.0	2.0	2.0	2.0
TMQ	1.0	1.0	1.0	1.0	1.0
Wax, Antilux 654	1.0	1.0	1.0	1.0	1.0

#### **Oil Properties**

Properties	Test Method	NBO	MES	TDAE	RAE	DAE
Visc., 40 °C / mm <sup>2</sup> s <sup>-1</sup>	ASTM D 445	710	195	437	4383	1062
Visc., 100 °C / mm <sup>2</sup> s <sup>-1</sup>	ASTM D 445	29.8	15.1	19.4	67.0	24.8
Density, 15 °C / Kg dm <sup>-3</sup>	ASTM D 4052	0.945	0.909	0.952	0.987	0.979
Sulfur / wt%	ASTM D 2622	0.6	0.5	0.8	4.4	1.3
Aniline Point / °C	ASTM D 611	90	98	66	62	43
Refractive Index	ASTM D 1747	1.525	1.502	1.526	1.539	1.576
VGC	ASTM D 2501	0.869	0.839	0.890	0.921	0.923
C <sub>A</sub> / %	ASTM D 2140	25	12	22	31	40
C <sub>N</sub> / %	ASTM D 2140	24	28	34	15	25
C <sub>P</sub> / %	ASTM D 2140	51	61	45	54	35
<i>T</i> g / ℃	ASTM E 1356	-55	-63	-50	-38	-40











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Slightly faster curing
Excellent mechanical properties (incl. abrasion)



Nytex 4700 in f-SSBR

Wet traction comparable with TDAE/MES, yet rolling resistance the lowest







#### **ESBR 1500**



	phr	phr	phr	phr
SBR 1500	100	100	100	100
Carbon Black (N234)	70	70	70	70
Nytex 4700	37.5			
TDAE		37.5		
RAE			37.5	
DAE				37.5
Stearic Acid	2	2	2	2
ZnO	3	3	3	3
Wax (Antilux 500)	1	1	1	1
6PPD	2	2	2	2
TMQ	1	1	1	1
DPG	0.4	0.4	0.4	0.4
Sulfur	1.75	1.75	1.75	1.75
CBS	1	1	1	1



175

RAE

DIN Abrasion (mm<sup>3</sup>) 20 20

0

136

Nytex 4700

137

TDAE

147

DAE

# Rolling resistance reduction



- Development of tread compounds: <u>an example</u>
  - SSBR tread compound for summer tyres
  - Provides traction, contributes significantly to RR, provides wear resistance, etc. etc.

	Tread A	Tread B	Tread C
SSBR	70	70	
Fx-SSBR			75
BR	30	30	
Fx-BR			25
Silica	80	80	80
Oil	35 (TDAE)	34 (napht)	34 (napht)
Tan delta at 60 C	100	88-92	72-75
Tan delta at 0 C	100	97	103-108

#### Naphthenic oils in butyl compounds



- Butyl rubber compatible with naphthenics
- Rolling resistance reduction potential low

- Yet other advantages might be available
  - ► Faster oil take-up → more efficient mixing
  - Enables higher filler loadings
  - Dust stop oil compatibility with butyl (innertube / bladder compounds)







#### Rolling resistance reduction: Summary

- ▶ 50% of RR is affected by tread compound development
- To reach highest RR classes in European and Asian labelling, work with other compounds is needed too
  - Even a significant weight reduction helps only a little (yet it helps in controlling raw material costs)
- A decrease of 10-30% in tan delta at 60-70 C can be obtained by selecting an appropriate oil
  - For tread compounds, corresponding loss in wet traction is a lot smaller
- Innerliner compatibility with naphthenics is excellent even if RR reduction is not significant



#### Tire industry approaches: how to utilize the naphtenic potential

#### Winter tire performance boost with naphthenics





# Winter tyre landscape changes

- Winter tire legislation changes as development driver
  - Winter tyre usage has become "more mandatory" (Germany, Italy, Czech Republic etc.)
  - Studded winter tires under heavy pressure in certain countries
  - EU tire labelling not descriptive of performance
  - Simultaneously a new tire segment "Cross-Climate" appeared in Europe
  - Strong shift from premium to economy in Russian winter tyre market











#### Winter tyre performance boost: winter vs. summer tyre materials

Materials used in a winter tyre are selected to ensure an excellent performance on extremely difficult conditions - snow and ice – and at temperatures significantly below 0 ° C

- Polymers which remain elastic at low temperatures are selected (NR, high-cis BR, low styrene-low vinyl SSBR)
- Polymers having excellent friction on icy and snowy surfaces are selected (in particular NR)
- Content of reinforcing filler is adjusted to ensure sufficient mobility of polymer chains
- Appropriate vulcanization system is selected to ensure sufficient softness of the tread
- Plastizicers such as naphthenic oils are used to increase elasticity even further



# Winter tyre performance boost: winter vs. summer tyres...

- Naturally tyre design and tyre construction are affected
  - Typically a tread block design is used instead of a rib design
  - ► Tread compound is designed to match all the essential features (e.g. sipes, grooves) of the tread design → optimizes the performance
  - A stiff undertread compound is used to support the soft and elastic tread
  - In case of studded winter tyres, the undertread provides support to stud body
  - Tyre construction is more flexible (e.g. reinforcing steel cord is more "elastic", or not as stiff as in summer tyres)



#### The Magic Triangles of Tire Development:



#### Naphthenics in winter tyres

- Oils contribute significantly to low temperature stiffness
- An appropriately selected oil can improve winter performance
  - ▶ Dynamic stiffness at extremely cold decreases → ice braking distance can be 2-5% shorter
  - Tan delta at 60-70 C may decrease 8-20% → rolling resistance drop
  - Corresponding loss in wet traction is often negligible







# Naphthenics in winter tyres

- Polymers should/could also be extended with appropriate oil
  - Nytex 810, Nytex 820, Nytex 840 enable decreasing the oil content
    - 0, Nytex 620, Nytex 640 enable decreasing the oil content
  - No compatibility issues between different oils (i.e. polymer extended with other oil blends well with naphthenic "free" oil

- For rolling resistance reduction and stud retention improvement, thick undertread offers also potential
  - ESBR 1753, ESBR 1763

# tent

Curing characteristics, productivit

# Winter tyre performance boost



#### Development of tread compounds: <u>an example</u>

- NR/BR tread compound for winter tyres
- Provides traction in different conditions, contributes significantly to RR, provides wear resistance, etc. etc.

	Tread A	Tread B	Tread C
NR	70	70	70
BR	30	30	30
Carbon black	60	60	5
Silica			60
Oil	40 (TDAE)	40 (naphth)	40 (naphth)
E* at -25 C	100	82-87	75-80
Tan delta at 60 C	100	85-90	70-75
Tan delta at 0 C	100	92-95	85-95 *



#### Naphthenics in winter tyres: Summary

- Winter tyre legislation changes set new requirements to tyre materials
- An appropriately selected oil can improve winter performance and decrease rolling resistance
  - Corresponding loss in wet traction is often small (and increasing silica loading slightly can compensate the loss)
- For rolling resistance reduction and stud retention improvement thick undertread offers also potential
- European All Season is an interesting segment with naphthenics offering a performance jump
  - Higher mileage accompanied with improved traction in mild winter conditions



# Winter tyre performance boost: Summary

- Winter tyre legislation changes set new requirements to tyre materials
- An appropriately selected oil can improve winter performance and decrease rolling resistance
  - Corresponding loss in wet traction is often small and increasing silica loading enhances the effects of naphthenics
- For rolling resistance reduction and stud retention improvement thick undertread offers also potential
- European All Season is an interesting segment with naphthenics offering a performance jump
  - Higher mileage accompanied with improved traction in mild winter conditions



#### Tire industry approaches: how to utilize the naphtenic potential

#### Naphthenic oils in rubber mixing machine lubrication





# Rubber mixer lubrication with naphthenic oils



- Nytex 4700, Nytex 832 and Nytex 840 offer a cost-effective solution
  - Recommended e.g. by Harburg-Freudenberger
  - Right viscosities at operating temperatures
  - Also compatible with butyl compounds



Fig. 1. Spring-loaded dust seal – GA (courtesy of ThyssenKrupp Elastomertechnik GmbH)

Fig. 2. Hydraulic dust seal – WYH (courtesy of ThyssenKrupp Elastomertechnik GmbH)



# Naphthenics as compounding tools: Summary

- Tyre compounder and polymer producer can get a performance boost with oil in a number of ways
  - Rolling resistance reduction of ca. 3-7% with a only small compromise in traction
  - Winter tyre performance improvement
  - Processing benefits with novel SSBR grades
  - Increased compatibility with butyl and halobutyl compounds



# It's amazing how far a drop of oil can take you.

www.nynas.com