NYCO
INDUSTRY & AUTOMOTIVE

Synthetic ester as dielectric fluids Ecological and high performing solutions - Nycodiel

National Conference on Environmental Friendly Insulating Liquids

November 2013
New Delhi - India

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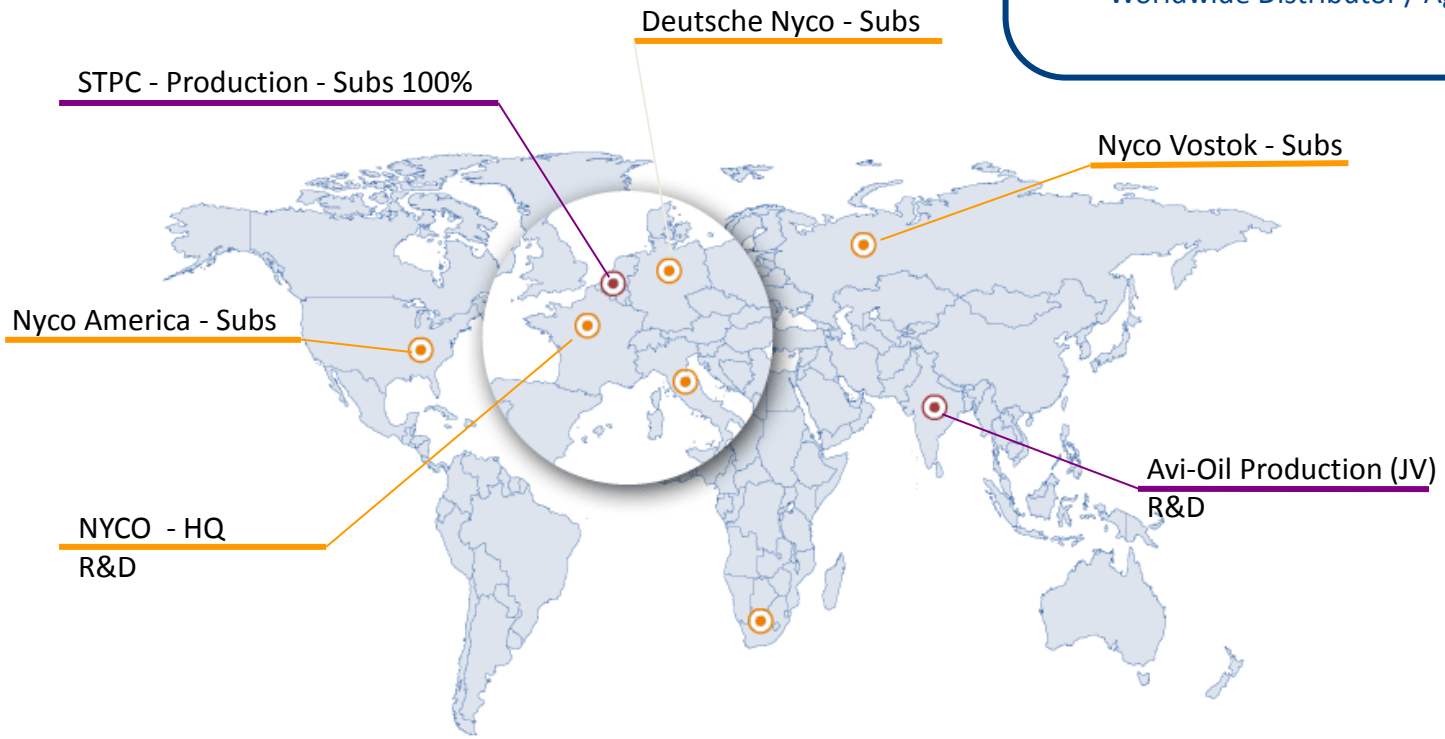
1- THE GROUP

Nyco worldwide

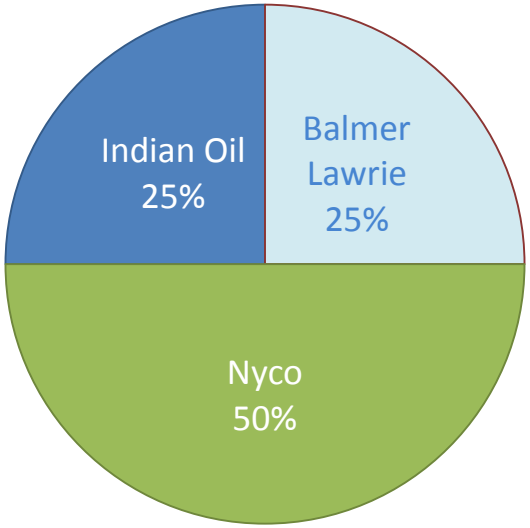
NYCO

- French independent and privately-owned company
- 80% export to more than 90 countries
- 220 people fully dedicated to lubricant business
- Production facility in Belgium / India / Russia
- Worldwide Distributor / Agent network



Avi-Oil

Share Holding



Largest petroleum company in India
Maharatna PSU
One of the largest in Asia
35000 marketing touch points
Turnover – Rs 328,744 cr

- Refineries
- Retail stations
- Lubricants
- LPG
- Aviation
- Bitumen
- Kerosene
- Petrochemicals
- Special Products

Mini-Ratna PSU
Turnover – Rs 2100 cr

- Industrial Packaging
- Lubes & Greases
- Chemicals
- Tea
- Tours & travels
- Logistics
- Refinery & Oilfield Services

French MNC – HQ at Paris
Foremost in the area of Defence & Military
Operates in more than 90 countries

Two Business segments – 3 Business units

Defence & Turbine


Complete range of aviation lubricants with international approvals for :

- Defence forces
- Oil & Gas
- Power generation
- MROs
- OEMs

Commercial Aviation


- MROs
- OEMs
- Airlines
- Airframers

Automotive & Industry


- Synthetic ester base stocks sold to the lubricant producers
- High performance finished lubricants for severe to very severe applications
- Biodegradable lubricants formulated with high quality synthetic esters
- Biodegradable dielectric fluids

Manufacturing facility - BELGIUM

A highly performing & flexible tool to match market requirements

Synthetic Esters production

3 production lines (10 and 50 m3 reactors)

- One new production line started mid-2011

Lubricant blending

4 lines (from 1 to 250 m3 blending capacity)

Grease production

2 lines (0,5 and 2 tons batch capacity)

Packaging

(from 0,5 L to 20 m3 bulk)

ISO 9001 – ISO 14001

Manufacturing Facility - INDIA

AVI-Oil Blending Plant

AVI-Oil
Ester
manufacturing
plant

Dedicated to innovation, process efficiency, quality improvements & customer support

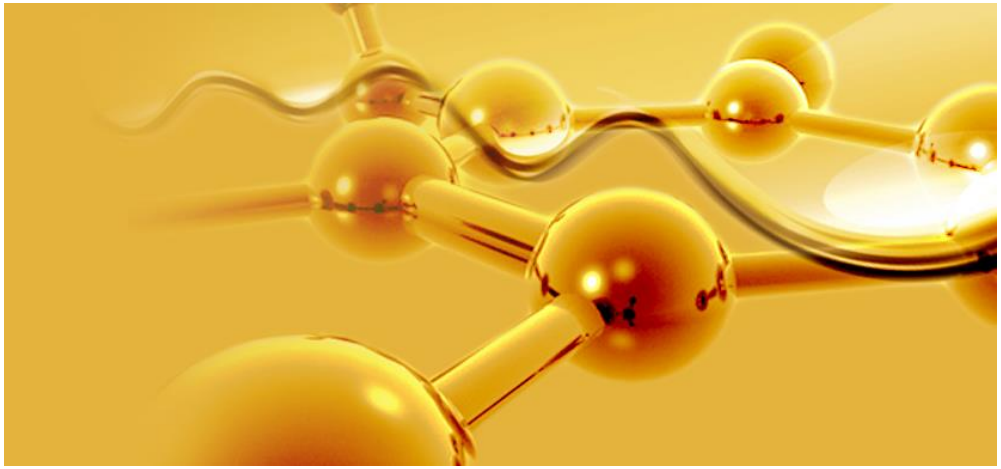
(High skilled teams, research expertise, pilots & analytical resources)

- Be the long term leader in specialty lubricants
- Develop innovative technologies in ester base stocks and additives
- Support our customers in their innovation & development

France

India

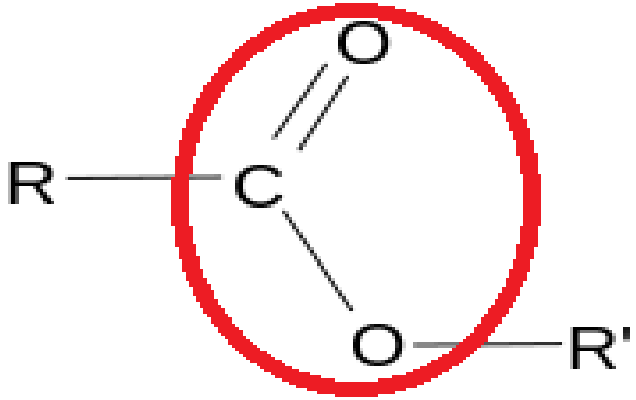
2 – SYNTHETIC ESTER - Chemistry



Definition

- Definition :

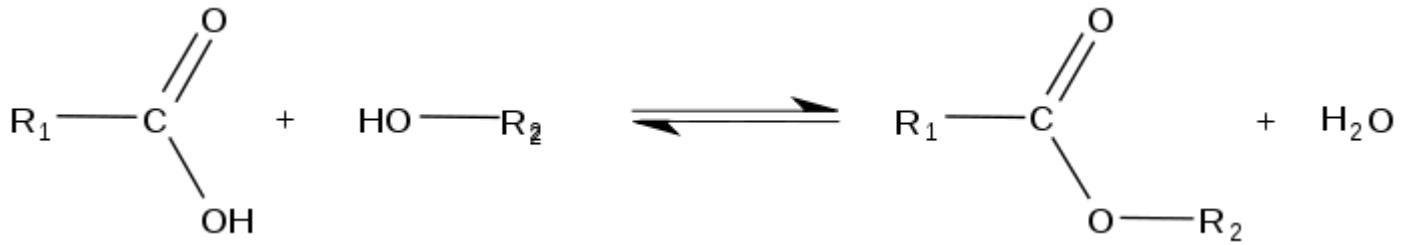
Esters are a family of chemicals that have the below structure in common：



They are naturally found in vegetable oils or animal fats, but they can be synthesized by chemical reaction.

Chemical reaction

- Chemical synthesis of esters : direct synthesis

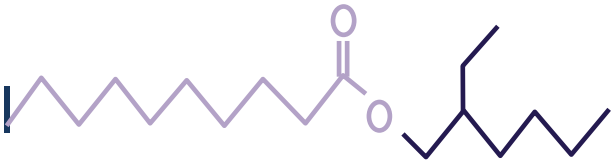


Acid + Alcohol **Ester + Water**

Different ester types

- **Monoesters (MOE)**

  Reaction of monoacid on mono alcohol



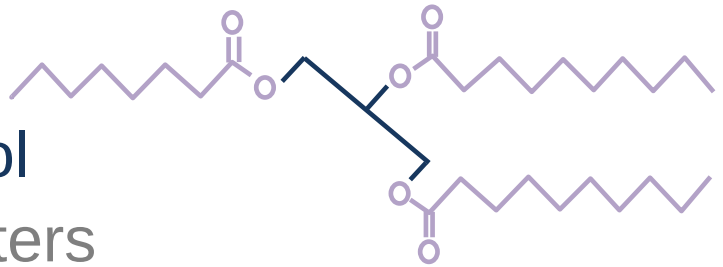
- **Diesters of Diacids (DIE)**

  Reaction of mono alcohol(s) on diacid

- **Polyol esters (POE)**

  Reaction on mono acid(s) on polyol

  Ex : glycol esters, glycerol esters

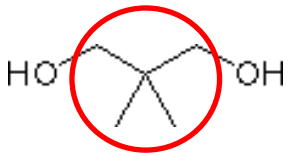


Different ester types

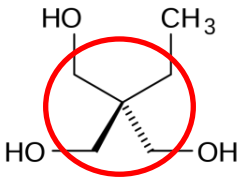
- **Neopolyol esters (NPE)**

Reaction of monoacid(s) on neopolyol

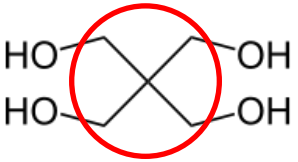
NPG



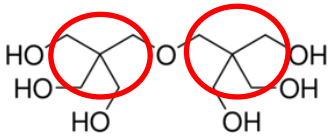
TMP

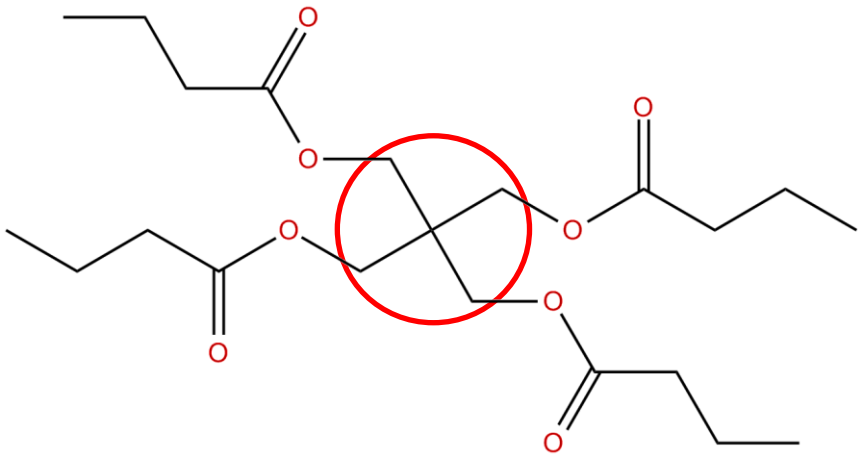


MPE



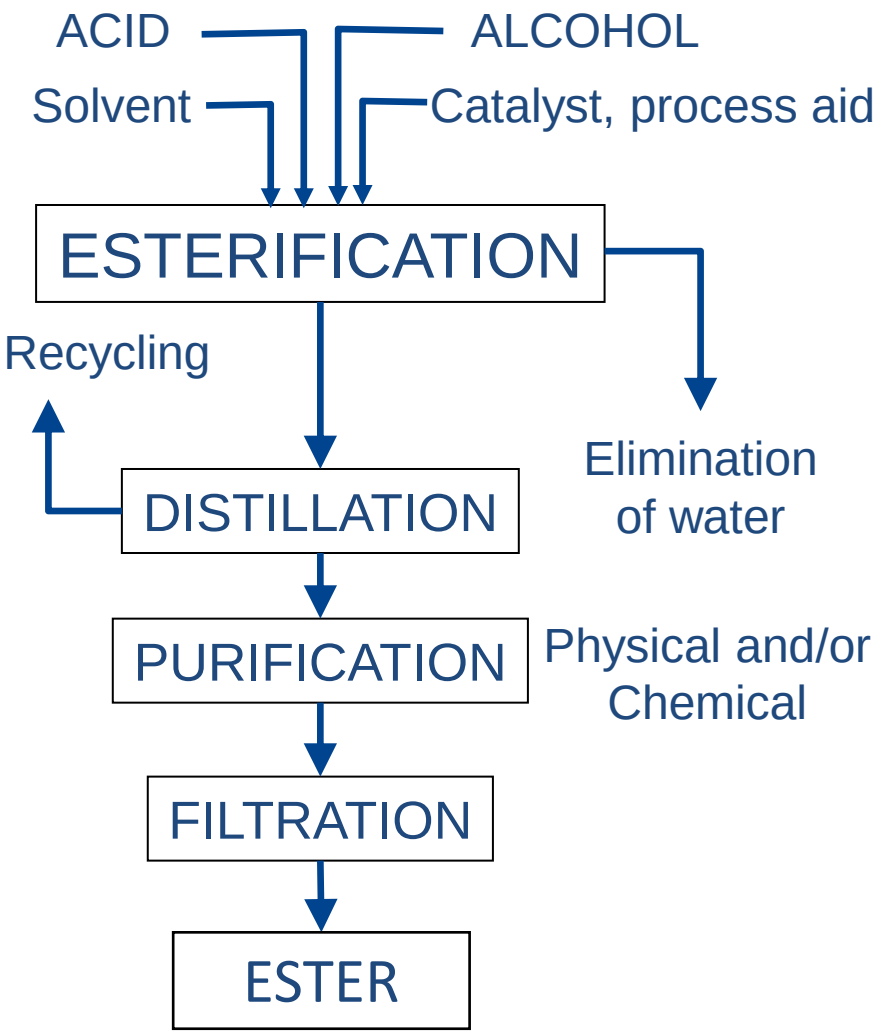
DPE





✓ **NPEs all have the « neo » structure in common**

Ester synthesis - manufacturing



Nyco (Belgium) and Avi-Oil (India) use the same processes and technologies

3 – SYNTHETIC ESTER – Dielectric Fluids

Existing standards

Product	Naphthenic oils	Silicone oils	Vegetable oils	Synthetic esters
Europe	IEC 60296	IEC 60836	--	IEC 61099
USA	ASTM D 3487	ASTM D 4652	ASTM D 6871	--
India				**IS 16081**

General characteristics

Characteristic	Unit	Synthetic ester	Veg. oil	Mineral oil	Silicone	Method
Density at 20°C	kg/dm^3	0.97	0.92	0.88	0.96	ISO 12185
Thermal expansion factor	°C^{-1}	0.0007	0.0007	0.0007	0.0009	--
Kinematic viscosity 100°C 40°C -20°C	mm²/s	 5.15 26.4 1250	 8.3 35 2600 (1)	 2.6 10 270	 15 40 200	ISO 3104
Pour point	°C	-50	-30	-45	-70	ISO 3016
Acid value	mg KOH/g	0.02	0.08	0.03	0.01	ISO 6618
Dielectric dissipation factor 90°C and 50Hz	-	 0.02	 0.08	 0.001	 0.01	IEC 60247
Breakdown voltage	kV	>60	50	30 to 70	50	IEC 60156
Relative permittivity at 20°C	--	3.0	3.1	2.2	2.7	IEC 60247
Thermal conductivity	W/m°K	0.12	0.17	0.13	0.12	ASTM D 2717

(1) Instability

Synthetics esters are a good compromise without weaknesses

Fire safety

- Fire and safety classifications, IEC 61100 :

Fire point classification (ISO 2592)

Class O	< 300°C
Class K	> 300°C
Class L	No measurable fire point

Heat of combustion (ASTM D 240)

Class 1	> 42 MJ/kg
Class 2	<42 MJ/kg and >32 MJ/kg
Class 3	< 32 MJ/kg

Fire safety

Characteristic	Unit	Synthetic ester	Vegetable oil	Mineral oil	Silicone oil	Method
Flash point PM	°C	265	305	150	285	ISO 2719
Flash point COC	°C	275	330	168	328	ISO 2592
Fire point COC	°C	312	360	172	360	ISO 2592
Auto ignition temperature	°C	436	440	~300	440	ASTM D 2155
Heat of combustion	MJ/kg	31.8	~40	~46	28-32	ASTM D 240
IEC 61100 classification	--	K3	K2	O1	K3	--

Only synthetic esters and silicone oils meet K3 classification of IEC 61100.

Vegetable oils have high fire point but have high heat of combustion too.

Thermo-oxidation resistance

Dielectric fluids have been tested against different oxidation and corrosion test methods :

1 / IEC 61125 Method C : based on the IEC 61099 requirements

2 / ASTM D4636 : Corrosiveness and Oxidation Stability test, for Hydraulic Oils, Aircraft Turbine Engine Lubricants, and Other Highly Refined Oils

3 / ASTM D943 : Oxidation Stability of Steam Turbine Oils, “Dry TOST” is a widely used method for comparison of a lubricating oil's ability to resist oxidation

Thermo-oxidation resistance

IEC 61125 method C : oxidation stability for unused fluids under accelerated conditions

- Conditions:
  - Temperature: 120°C
  - Duration: 164 h, 500 h
  - Air flow: 0.15 l/h
  - Metal: Cu
  - Oil quantity: 25 g
- Results :
  - Acid number
  - Deposits

Thermo-oxidation resistance

- Oxidation corrosion IEC 61125 results

Characteristic	Duration Hrs	Synthetic ester	Vegetable oil	Mineral oil	Silicone oil	Limit IEC 61099
Acid number mgKOH/g	0	0.02	0.07	0.03	0.01	--
	164	0.09	2.84	0.40	0.01	Max 0.3
	500	0.20	ND	1.1	0.01	--
	800	0.23	ND	1.29	0.01	--
Deposit	164	0.005	0.5	0.10	0.01	Max. 0.01
	500	0.005	ND	0.14	0.01	--
	800	0.003	ND	0.17	0.02	--
Appearance After 800 hrs			**N/A; Product Become Solid Between 164 h and 500 h**			

Synthetic esters and silicone oils show an exceptional resistance to oxidation

Thermo-oxidation resistance

- Comments on IEC 61125 test

  - Synthetic esters and silicone oil demonstrated an exceptional resistance to thermo-oxidation. Both products are able to run at high temperatures for long periods without degradation.
  - Vegetable oils do not comply with the constraints of IEC 61125 test.
  - Mineral oil generate a lot of deposits already after 164 h

Thermo-oxidation resistance

ASTM D 4636 (Ox-Cor test)

- Conditions :
  - Temperatures: 121°C and 150°C
  - Duration: 168 hours
  - Air flow: 5 l/h
  - Metal: Steel, Al, Cu, Cd, Mg
  - Oil quantity: 200 cm^3
- Results :
  - Acid number : oil is checked for viscosity changes as a result of oxidation reactions.
  - Loss in metal mass : corrosiveness of the oil (and microscopic examination of metal surface)
  - Deposits

Thermo-oxidation resistance

- Oxidation corrosion ASTM D 4636 results.

		Synthetic ester		Vegetable oil		Naphthenic oil		Silicone oil	
Temperature °C		**121**	**150**	**121**	**150**	**121**	**150**	**121**	**150**
Δ acid number	mg KOH/g	0.00	0.04	(1)	ND	0.11	1.9	0.02	0.04
Δ KV 40°C	%	0.20	0.50	(1)	ND	2.4	15.5	0.3	4.1
Deposit	mg/ 100 cm²	0.0	0.0	(1)	ND	11	735	0.3	8.5
Δ w steel	mg/cm²	0.0	0.0	(1)	ND	0.0	0.0	0.0	0.0
Δ w Copper	mg/cm²	0.0	0.0	(1)	ND	0.0	0.0	0.0	0.0
Δ w Cadmium	mg/cm²	0.0	0.0	(1)	ND	0.0	0.4	0.0	0.0
Δ w Aluminium	mg/cm²	0.0	0.0	(1)	ND	0.0	0.0	0.0	0.0
Δ w Magnesium	mg/cm²	0.0	0.0	(1)	ND	0.0	0.0	0.0	0.0

(1) Impossible to make analysis; product became solid before 72 h at 121°C.

Thermo-oxidation resistance

- Comments on ASTM D 4636 test
  - Synthetic esters and silicone oil exhibit best resistance to oxidation and corrosion in this test.
  - Vegetable oils did not stand high temperatures for long time (solid after 72h).
  - Conditions were too severe for mineral oil. High acidity and high viscosity increase and deposit formation.

ASTM D 943 : Dry TOST

- Conditions :

  - Temperature: 95°C
  - Duration: 500 h et 1000 h
  - Oxygen flow: 10 l/h
  - Metal: Iron, Copper
  - Oil quantity: 450 cm^3

- Results :

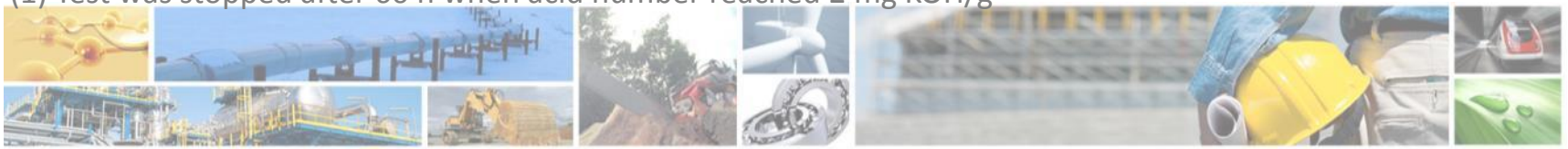
  - Total Acid Number (TAN) : time to value of 2 mgKOH/g

Thermo-oxidation resistance

- Dry tost ASTM D 943 - results

Characteristic	Duration hours	Synthetic ester	Vegetable oil	Mineral oil	Silicone oil	Method
TAN (mg KOH/g)	0	0.01	0.08	0.01	0.01	ASTM D 664
	500	0.01	(1)	0.20	-	
	1000	0.02	(1)	0.20	0.01	
KV 40°C (mm^2/s)	0	21.9	(1)	9.65	41.50	ASTM D 445
	500	21.9	(1)	10.0	-	
	1000	21.9	(1)	9.97	42.20	
Dielectric dissipation factor at 90°C	0	0.006	(1)	0.0007	0.001	IEC 60247
	500	0.031	(1)	0.011	-	
	1000	0.132	(1)	0.036	0.002	
Breakdown voltage (kV)	0	83	(1)	63	55	IEC 60156
	500	76	(1)	75	-	
	1000	62	(1)	53	54	
Appearance	0	limpid	(1)	limpid	limpid	Visual
	500	limpid	(1)	Hazy	-	
	1000	limpid	(1)	deposit	Limpid	

(1) Test was stopped after 60 h when acid number reached 2 mg KOH/g



Thermo-oxidation resistance

- Comments on ASTM D 943 test

  - Synthetic esters and silicone oil showed best stability.
  - Mineral oil showed good resistance to oxidation although deposits were evidenced in long-term conditions.
  - Dielectric properties of silicone oil and mineral oil were stable.
  - DDF of synthetic ester increased after 1000 h but stayed within the requirements of IEC 61203 (maintenance guide for ester for transformers).
  - Vegetable oil showed high level of acidity after very short period of test (60h).

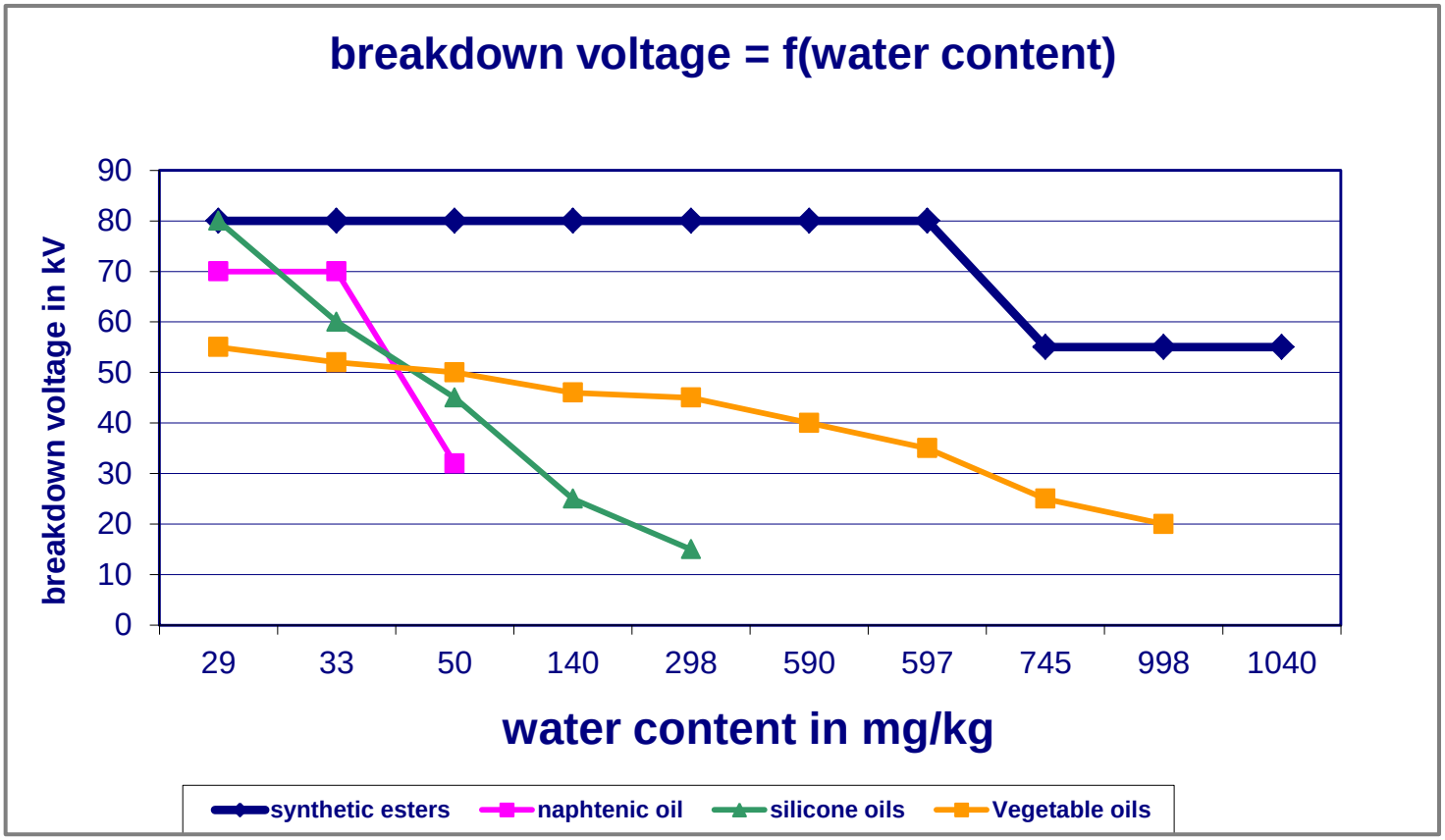
Thermo-oxidation resistance

Thermo-oxidation properties – conclusions :

Synthetic esters and silicone oils demonstrated best resistance to oxidation and corrosion in harsh conditions. They resisted high temperatures and presented long life time within the specifications. Mineral oil performed well at medium temperatures. Vegetable oil has a poor thermal stability due to the presence of unsaturated fats (double bond) in its chemical structure that weakens the molecule.

Water influence

- Breakdown voltage = f (water content)



Water influence

- Water influence – conclusions :

  – Due to their structures, synthetic esters and vegetable oils absorb water. Once absorbed, water is not free but “inactive”. Functionally, water links to ester molecules by hydrogen bonds and Van der Walls links. Synthetic esters and vegetable oils can absorb a high level of water without loss of dielectric breakdown voltage.

  – This ability allows them to “protect” insulating paper; the consequence is an improvement of transformer lifetime without power loss. This property can be very useful when retrofilling; dehydrating insulating paper extends operating lifetime of ageing transformers.

Ecological criteria

Several criteria have been screened to answer the request :

- Ultimate biodegradability
- Water hazard (test on daphnia, algae, and fish)
- Renewable raw material contents
- Toxicity of components
- Hazard to health, no risk phrase on material safety data sheet

Ecological criteria

European Ecolabel

3 of the 7 criteria to get the label are :

Characteristic	Unit	Synthetic ester	Vegetable oil	Mineral oil	Silicone oil	Ecolabel Limits (1)
Ultimate biodegradability (OECD 301 B)	%	**72 – 84 (3)**	**>80**	**<30**	**0-5**	**>60**
Aquatic toxicity - Algae (OECD 201) - Daphnia (OECD 202) - Fish (OECD 203)	mg/l	>1000 >1000 >1000	>1000 >1000 >1000	>1000 >1000 >100	(2)	>100 >100 >100
Renewable carbon content	%	**52 – 78 (3)**	**100**	**0**	**0**	**>50**

(1) Requirement for hydraulic fluids

(2) Is not considered harmful to aquatic organisms

(3) Nyco proposes 3 differents products within these limits

Ecological criteria

Umwelt Bundes Amt – German Agency for Environment

- To protect water, the Federal Water Act (Article 19g) requires that substances used in such installations possibly in contact with water must be tested and classified for their water-hazardous properties. Classification is carried out on the basis of the Administrative Regulation (Verwaltungssvorschrift wassergefährdende Stoffe = VwVwS) of 17 May 1999 (amended in 27 July 2005). There are three water hazard classes (WGK):

  1: low hazard to water
  2: hazard to water
  3: severe hazard to water

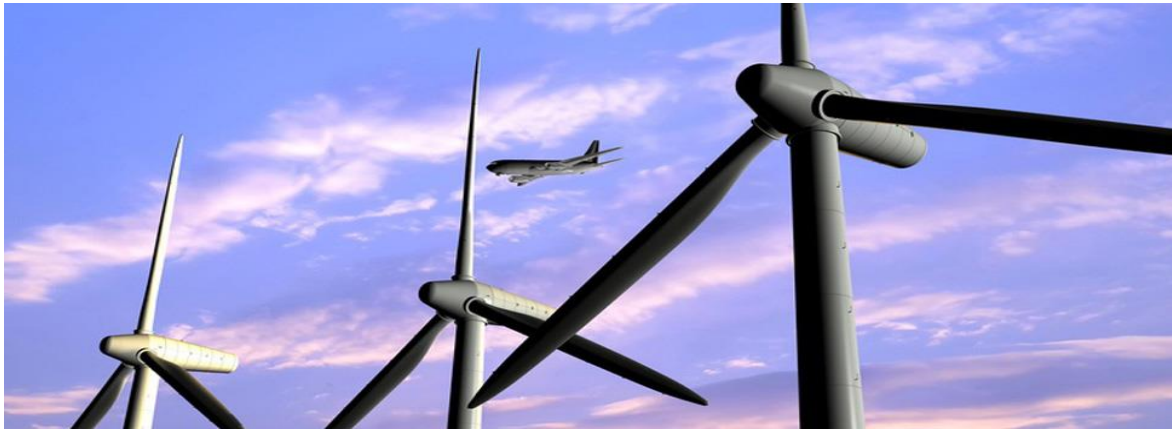
Not hazardous product are classified : NWG

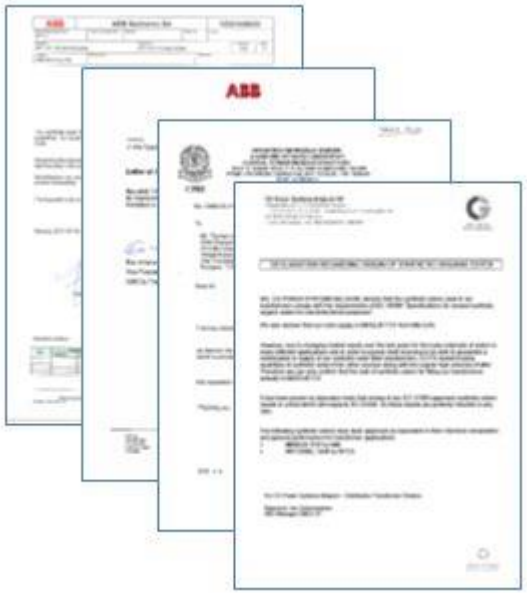
Characteristic	Unit	Synthetic ester	Vegetable oil	Mineral oil	Silicone oil
UBA ranking	--	**NWG**	**NWG**	**WGK 1**	**WGK 1**

Ecological criteria

- Ecological criteria – conclusions :
  - Synthetic esters and vegetable oils have the best environmental friendly profile.
  - Both products meet European Ecolabel and federal environment agency of Germany requirements.

4 - APPLICATIONS





Current applications

- Rail:
  - Traction / Sidetrack
  - Underground
- Wind turbines
- Distribution:
  - Indoor
  - Close to, or in building
  - Factory
  - Outdoor
  - Tunnel
- Marine
- Petroleum platforms
- Power transformer

Chemical answers to special constraints

Nycodiel 1244

IS 16081 - IEC 61099

Higher biodegradability and higher renewable carbon content

Nycodiel 1255

IS 16081 - IEC 61099

Higher fire point

Nycodiel 1233

Low viscosity at very low temperature

High renewable carbon content

High safety requirements vs mineral oil

Nycodiel 1244, Nycodiel 1255 and Nycodiel 1233 are all biodegradable

Chemical answers to special constraints

General characteristics

Characteristic	Unit	Nycodiel 1233	Nycodiel 1244	Nycodiel 1255	Method
Density at 20°C	kg/dm³	0.95	0.98	0.97	ISO 12185
Thermal expansion factor	°C⁻¹	0.0007	0.0007	0.0007	--
Kinematic viscosity 100°C 40°C -20°C -50°C	mm²/s	 3.51 16.1 **400** **11500**	 4.6 22.0 **650**	 5.15 26.4 1250	ISO 3104
Pour point	°C	<-66	-45	-50	ISO 3016
Acid value	mg KOH/g	0.02	0.02	0.02	ISO 6618
Flash point	°C	241	250	255	ISO 2719
Fire point	°C	**284**	304	**310**	ISO 2592
Water content	mg/kg	30	32	30	IEC 60814
Dielectric dissipation factor 90°C and 50Hz	-	0.01	0.02	0.02	IEC 60247
Breakdown voltage	kV	65	>60	>60	IEC 60156
DC resistivity at 90°C	GΩ x m	3.1	7.5	10	IEC 60247

Chemical answers to special constraints

Ecological characteristics

Characteristic	Unit	Nycodiel 1233	Nycodiel 1244	Nycodiel 1255
Ultimate biodegradability (OECD 301 B)	%	79	**84**	72
Aquatic toxicity - Algae (OECD 201) - Daphnia (OECD 202) - Fish (OECD 203)	mg/l	 >1000 >1000 >1000	 >1000 >1000 >1000	 >1000 >1000 >1000
Renewable carbon content	%	**79**	**79**	61
UBA ranking	--	NWG	NWG	NWG
Ecolabel potentiality	--	YES	YES	YES

Fire safety characteristics IEC 61100

IS 16081 - IEC 61099 :
- Flash point : 250° C min
- Fire point : 300 °C min

Characteristic	Unit	Nycodiel 1233	Nycodiel 1244	Nycodiel 1255
Flash point PM	°C	241	255	265
Flash point COC	°C	248	262	275
Fire point COC	°C	284	304	312
Heat of combustion	MJ/kg	32	30.6	31.8
IEC 61100 classification	--	03	K3	K3

Chemical answers to special constraints

Thermal-oxidation characteristics
IEC 61125 method C

Characteristic	Unit	Nycodiel 1233	Nycodiel 1244	Nycodiel 1255
Oxidation 164 h **Acid Number** **Deposit/Sludge**	 mg KOH/g %	 0.09 0.004	 0.08 0.007	 0.09 0.005
Oxidation 800 h **Acid Number** **Deposit/Sludge**	 mg KOH/g %	 0.23 0.005	 0.23 0.005	 0.23 0.003

IS 16081 - IEC 61099 (after 164h)
- Acid number : 0,3 mg KOH/g max
- Sludge : 0,01 % mass max

Synthetic esters in India

- Growing number of damaged/aged transformers that generates interruptions of power supply (ex : failures during festive season – Vanarasi* Dec 2012)
- Prevent transformer explosions and fires in location close to population due to overloads or short-circuits (ex : Uphaar June 1997, Hyderabad* May 2012)
- Environmental protection with biodegradable insulating fluid solutions for transformers close to landscape and sea
  - Traction transformer, sidetrack transformer
  - Wind turbine transformer
  - Distribution transformer (pole mounted, pad mounted)
- Development of compacter transformers, same applications as above

*The Times of India - www.timesofindia.indiatimes.com

Conclusion and perspectives

- Main properties of synthetic esters are :
  - **Environmental friendly**,
  - **Very stable at high temperatures**
  - **Safe** : high fire point in respect to viscosities and low inferior heating power,
  - **Good moisture tolerance**
  - **Advantageous properties at low temperatures**

- Design of synthetic esters is flexible, and therefore they can answer many specific technical demands. This flexibility will allow to design the transformers with wider perspectives and answer new challenges.

Synthetic esters offer the best compromise
for a maximum of requirements

THANK YOU