

PROVIPLAST® PLS GREEN

An innovative way to use epoxidized fatty acid alkyl esters as primary plasticizers for PVC



Proviron[®]

A human and ecological approach to chemistry

PROVIPLAST® PLS GREEN : Introduction



- Partnership between Petrom and Proviron
- Introduction on the European market
- Bio-based plasticisers based on green resources
- No direct competition with feed and food resources

Proviplast® PLS Green 5
Proviplast® PLS Green 8

Iso-amyl epoxy stearate
2-ethylhexyl epoxy stearate

Biobased content
100 %
68 %

MW: 365
MW: 407



Petrom – Petroquímica Mogi das Cruzes S.A.

History:

1953 Start of phthalic anhydride production

1964 Start of plasticiser production

1970 Start of fumaric acid production

1998 Formation of Petrom (MBO)

- Production of plasticisers (>100kt)
- 200 FTE

Incorporation of bio-based products:
Iso-amyl alcohol, and more recently PLS Green



Proviron

- Process Engineering and Environment
- Belgium based Company
- Independent Chemical Company
- Founded in 1977

3 Production sites (Belgium and US)
Sales office in China

- 150m€ turnover (2012)
- 300 FTE

Proviron[®]

Proviron[®]



Proviron

**Niche
Plasticisers**

**Polymer Additives
Water Borne Systems
Feed Additives
Functional Chemicals
Bio Energy**

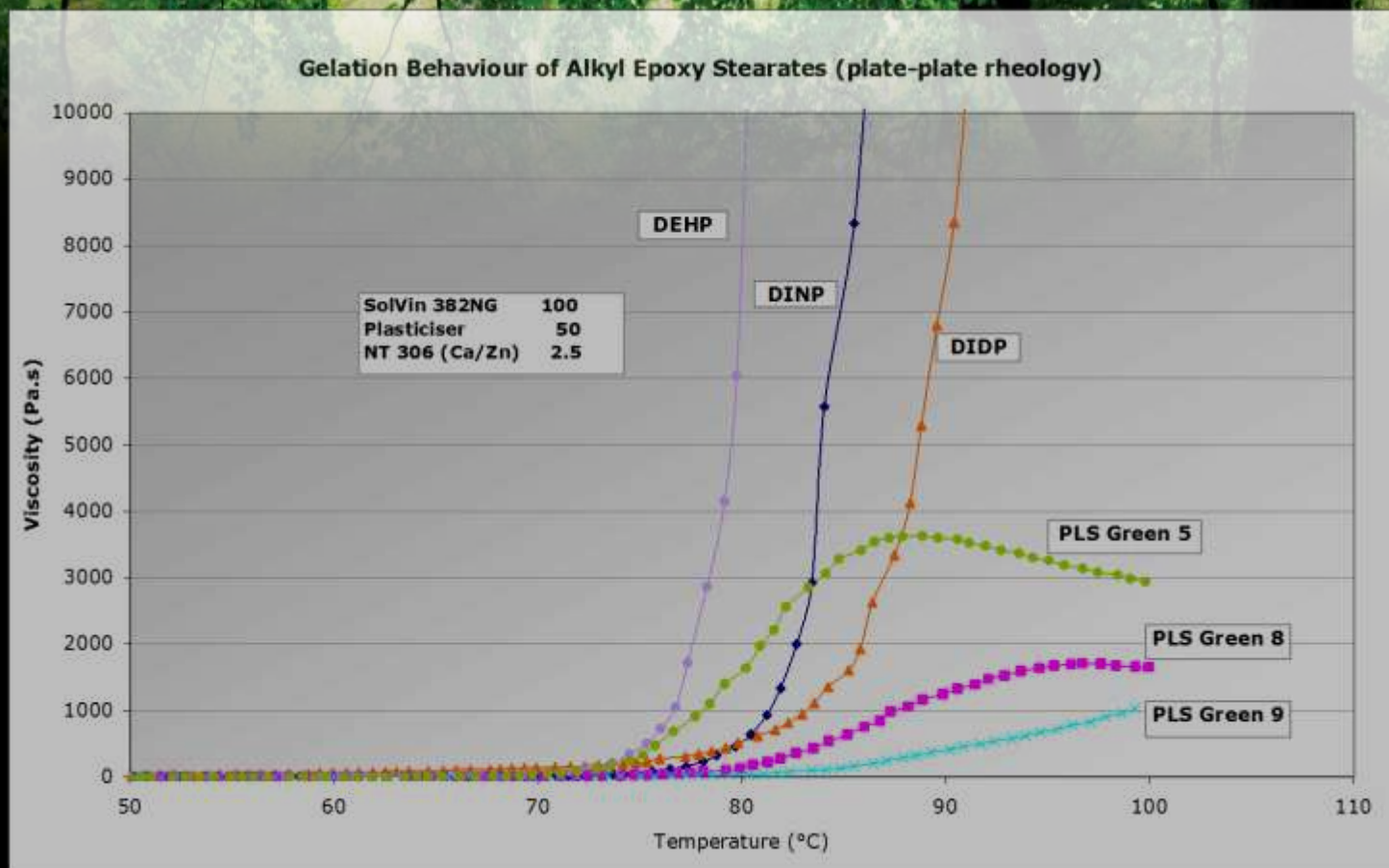
**Specialty
Esters**

Surfactants

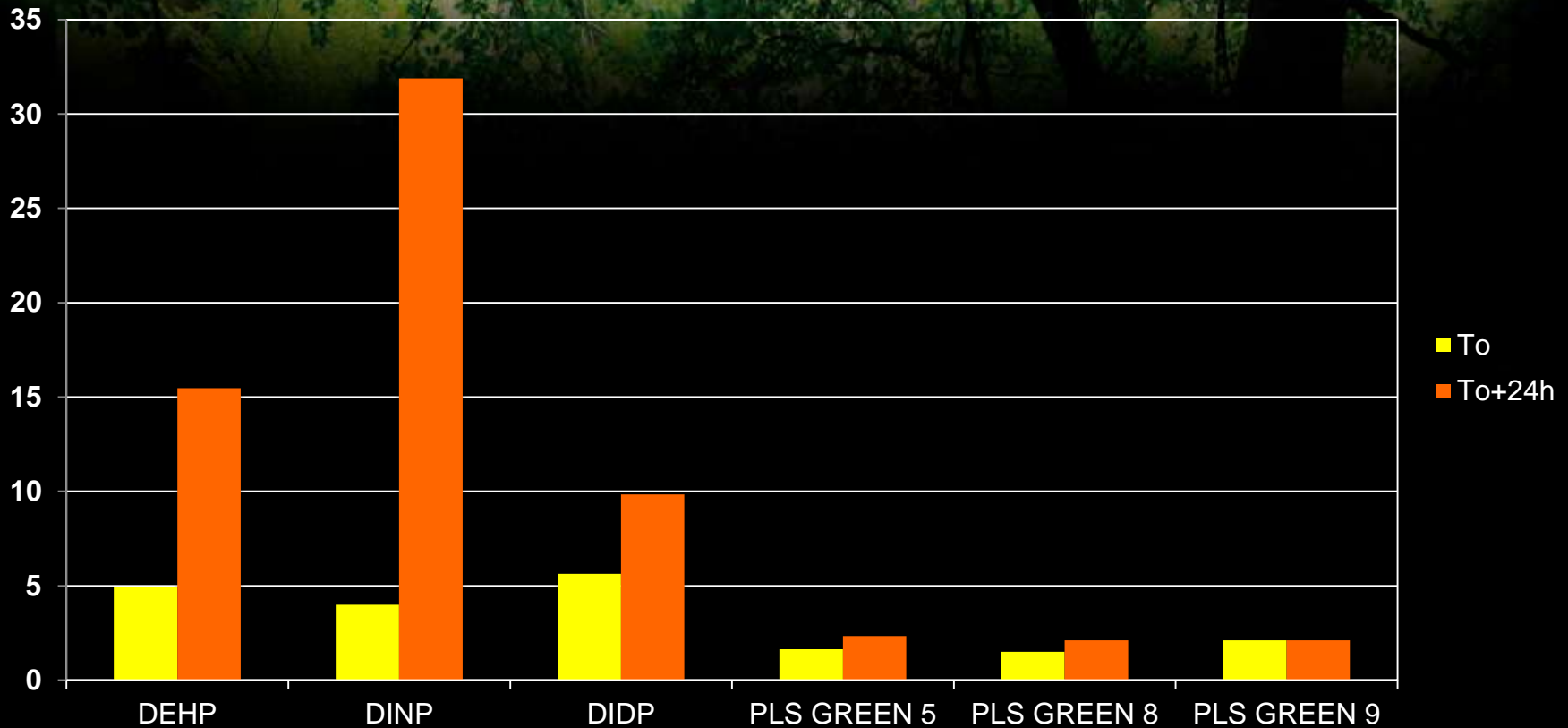
- **Customer oriented approach**
- **Joint development programmes**
- **Close follow-up of trials**
- **Technical advise**
- **Tailor made solutions**
- **Focus on biobased raw materials**
- **Work under confidentiality**

Focus on **three business lines** and **five markets**

Gelation behaviour Transparent Paste PVC

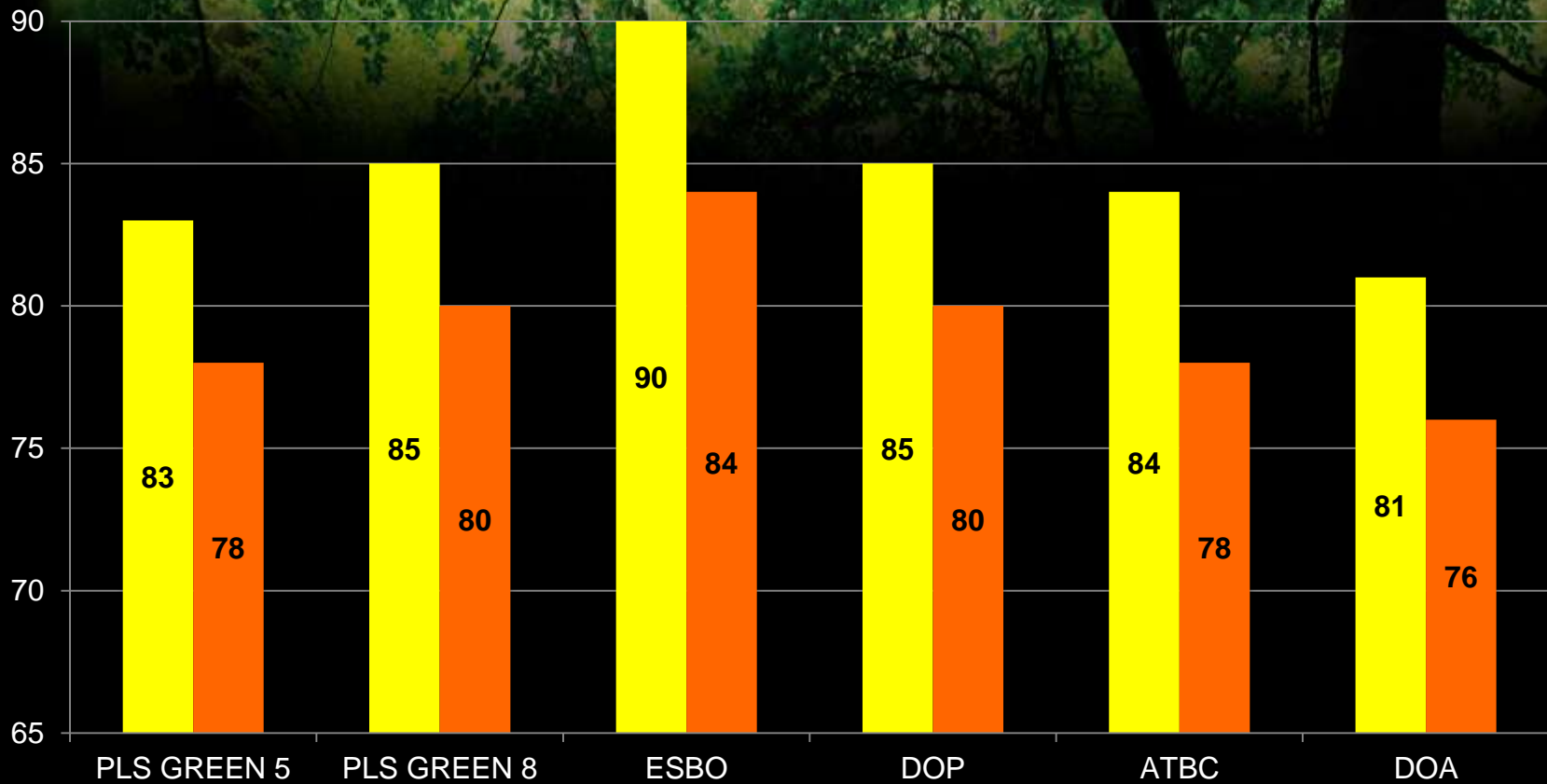


Rheology and paste aging (viscosity Pa.s)

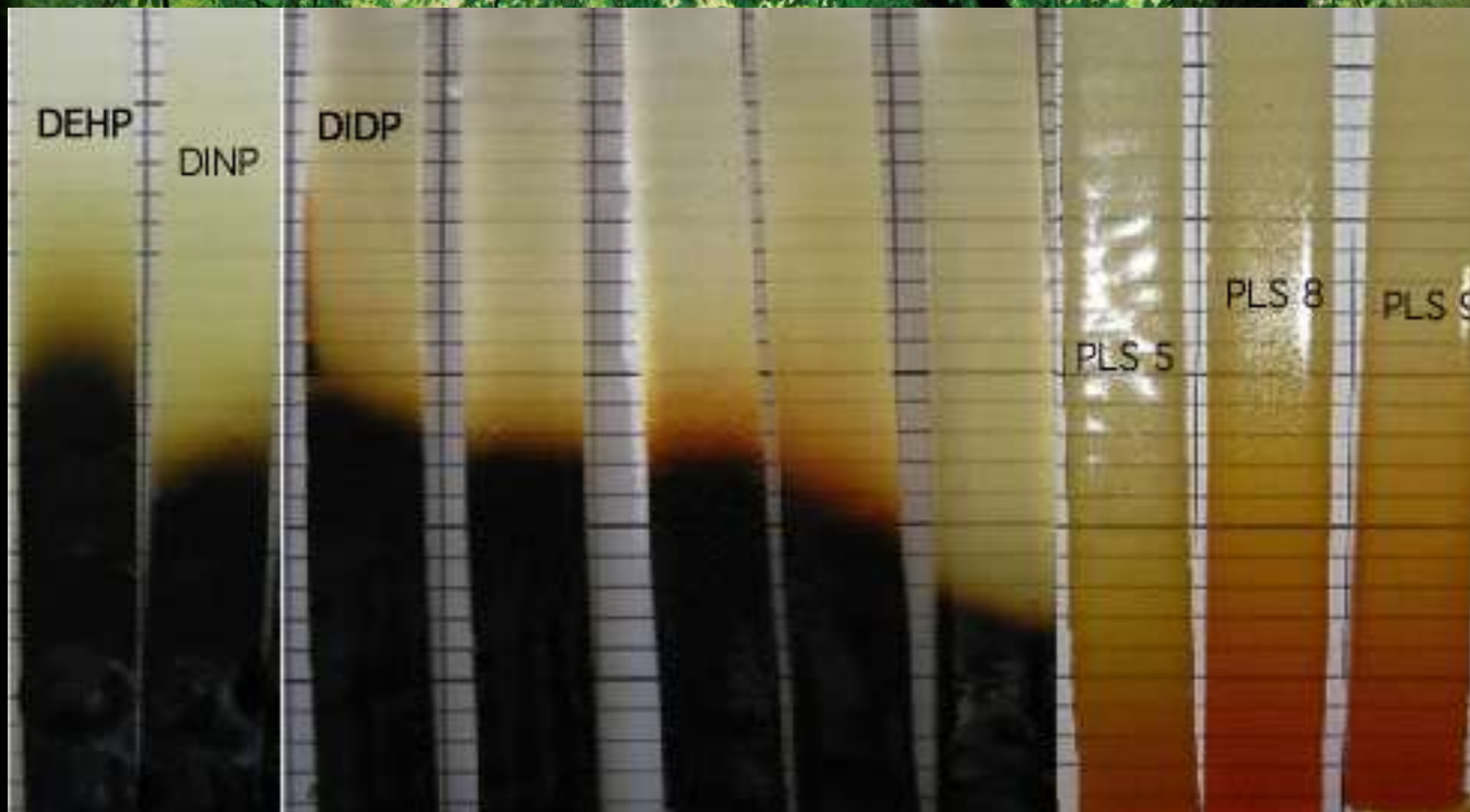


Plasticiser efficiency (Shore A hardness)

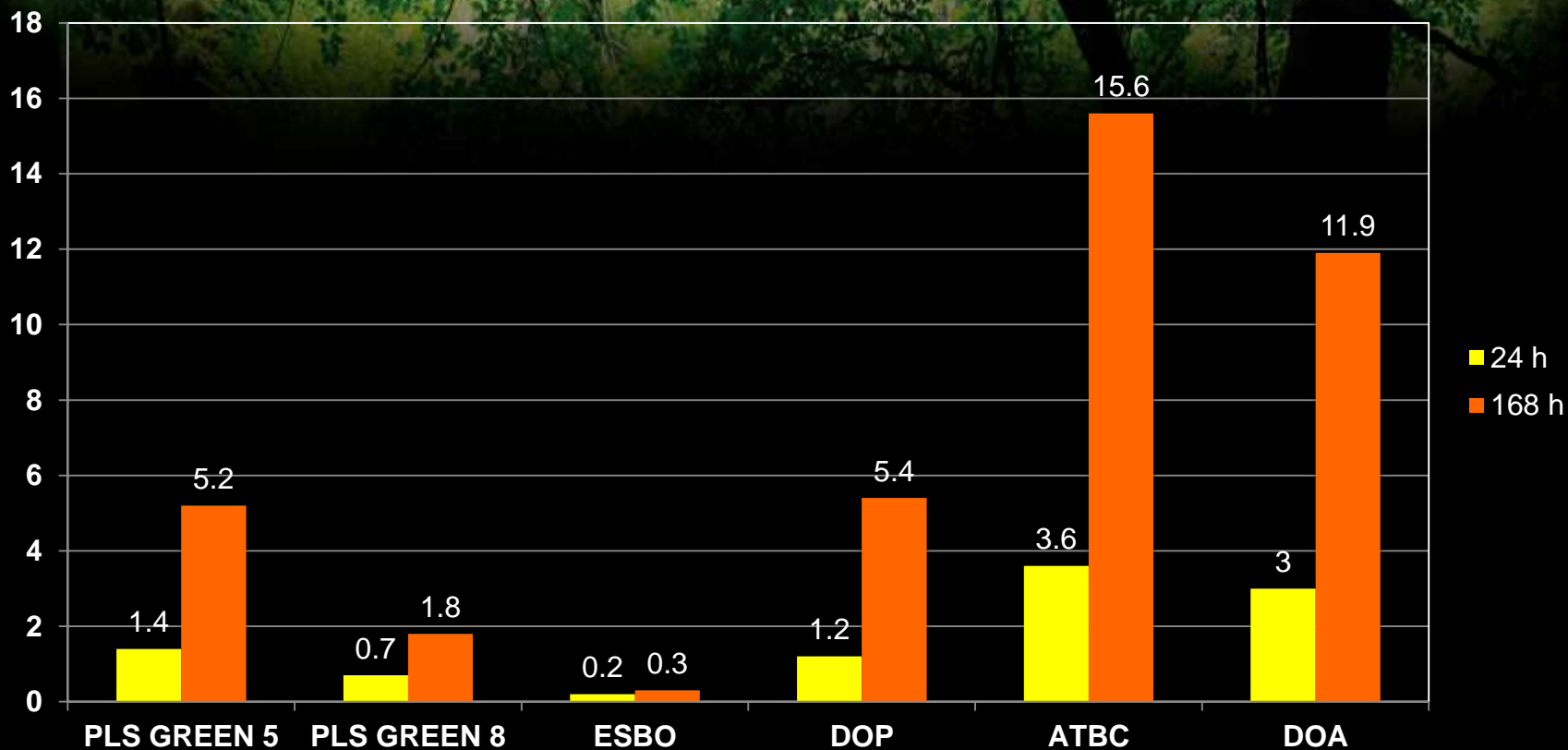
■ Immediate ■ After 15 seconds



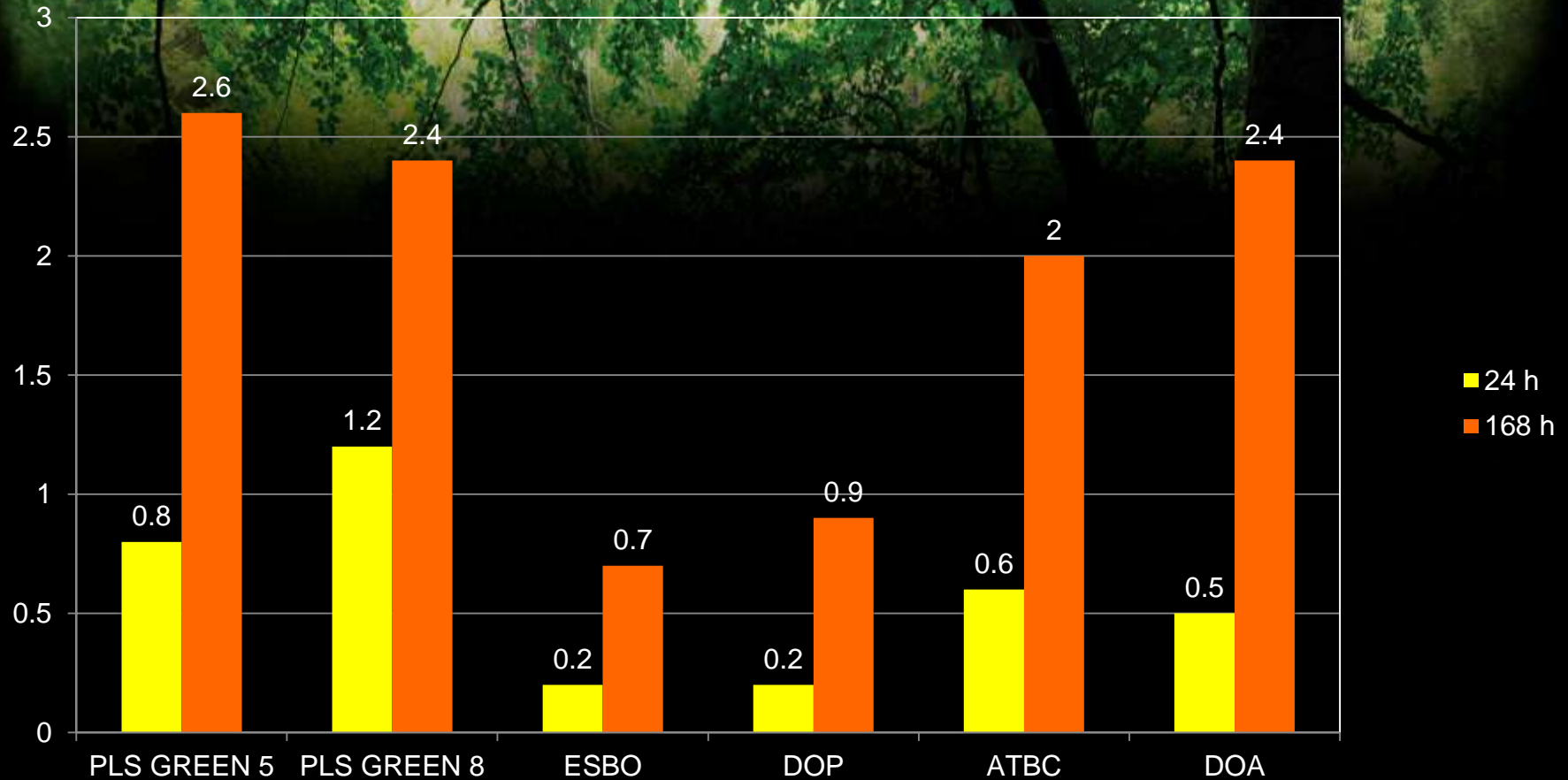
Thermal stability transparent paste PVC 50phr



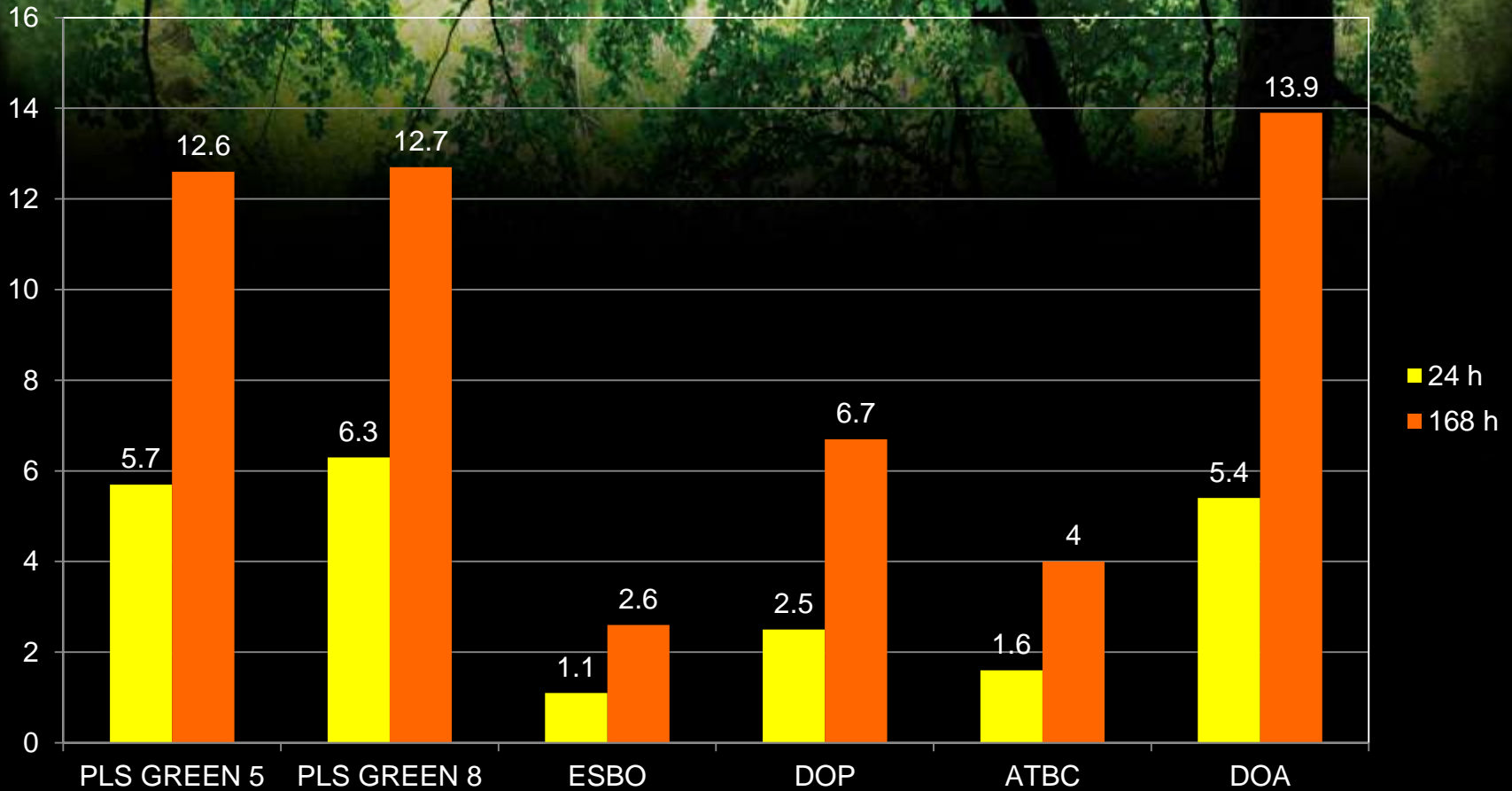
Mass loss at 105°C (ASTM 2115)



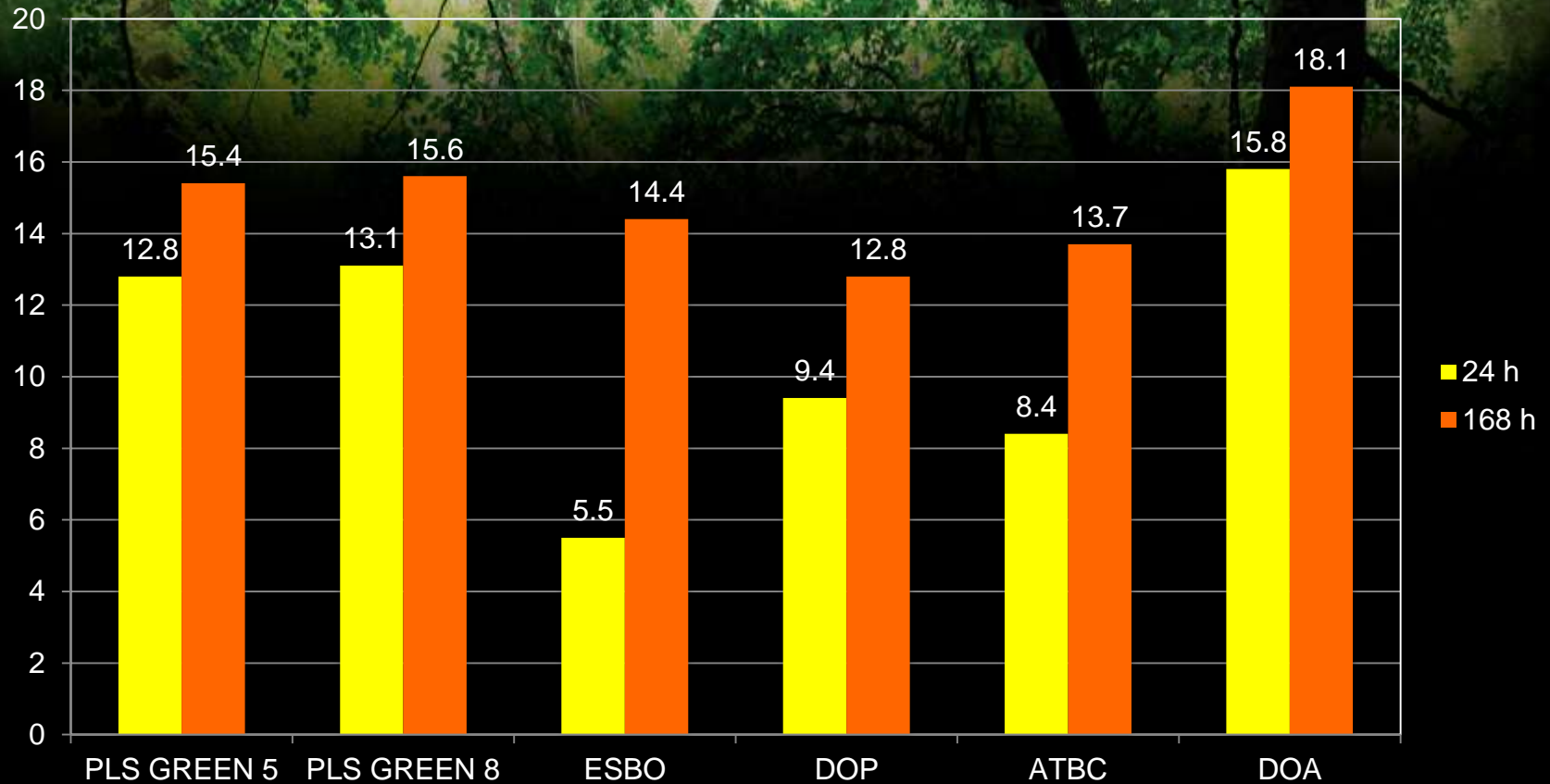
Extraction tests ASTM D1239 Soapy water 40°C (%)



Extraction tests ASTM D1239 Vegetable oil 40°C (%)

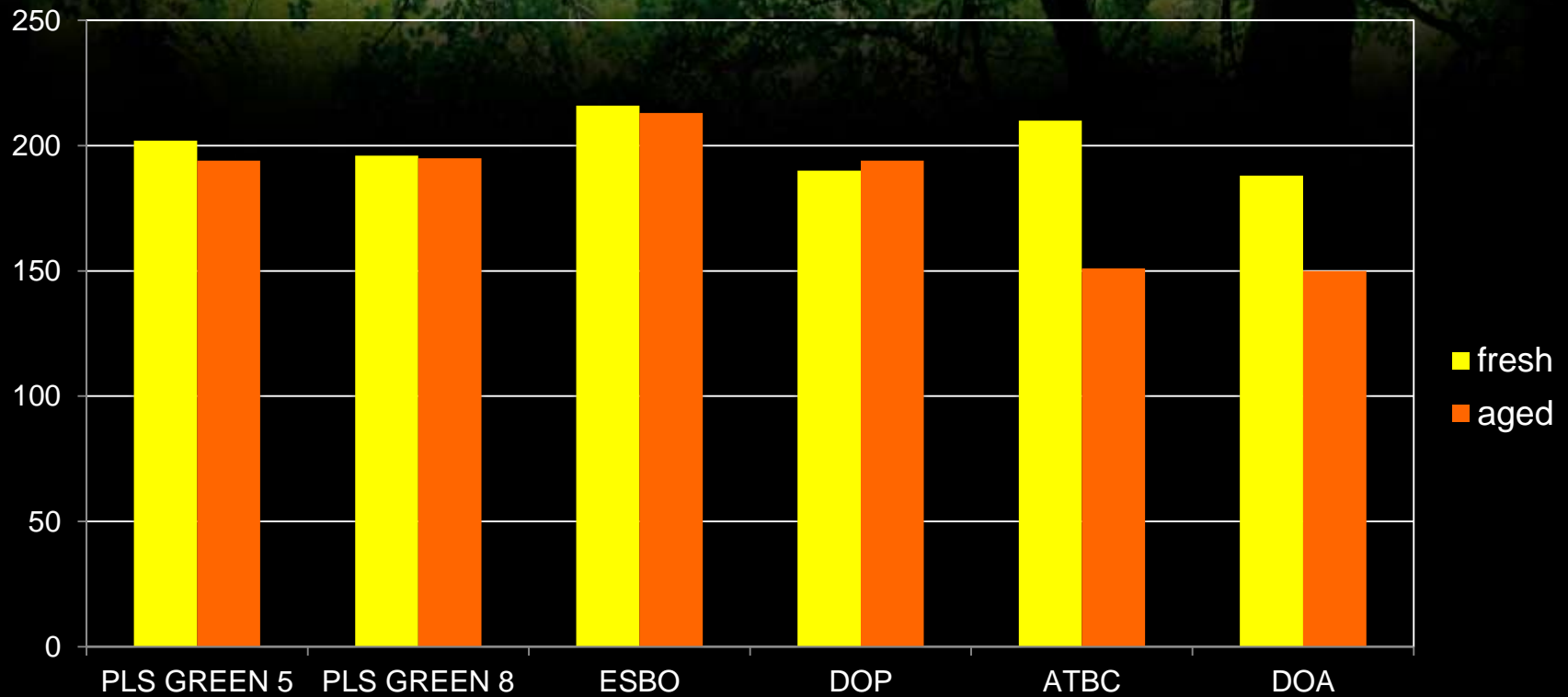


Extraction tests ASTM D1239 Heptane 40°C (%)



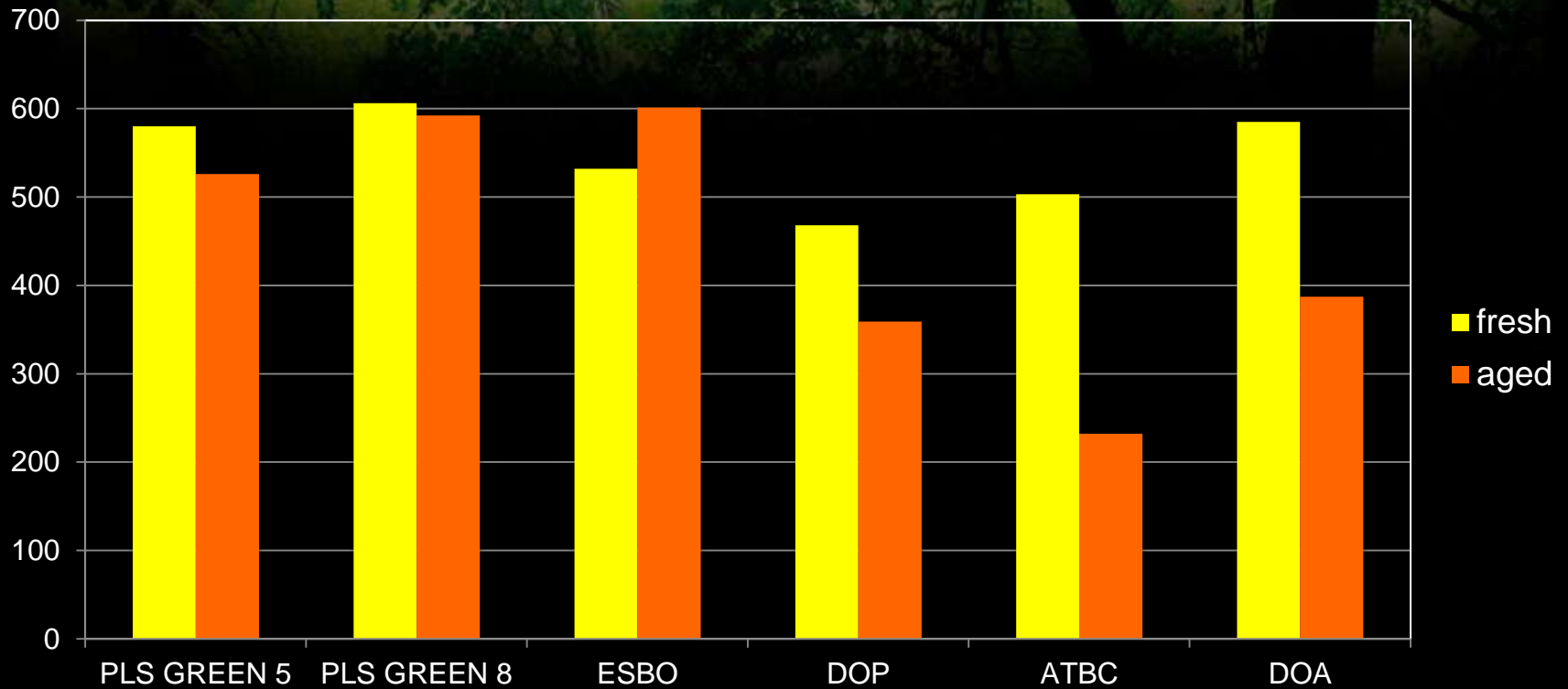
Mechanical properties and ageing

Tensile strenght (N)



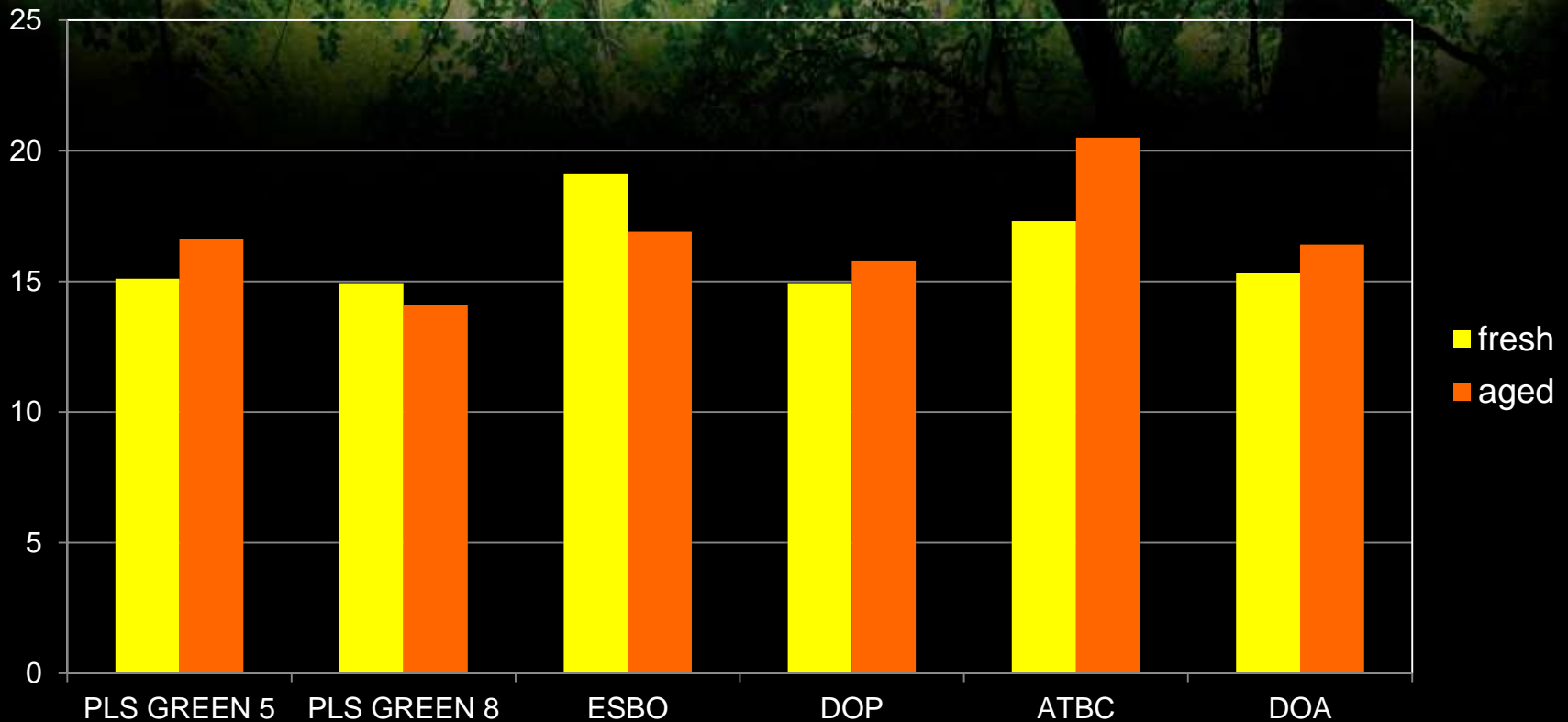
Mechanical properties and ageing

Strain at break (%)



Mechanical properties and ageing

Stress at break (Mpa)



Proviplast® PLS Green Evaluation Summary (Solvay)

TRANSPARANT PASTE PVC SUMMARY

Plasticiser	Rheology	P. ageing	Gelation	Air Release	T. Stability	Colour	Transp	Gloss	W Loss	Score
DEHP	0/-	+	+	0	0	0	0/-	0	--	-1
DINP	0	0	0	0	0	0	0	0	0	0
DIDP	0/-	+	-	0/+	0	0	0/-	0/-	+	0
DEHA	+	+	0	+	0	0	0	0/-	---	-1
PLS GREEN 5	+	++	--	++	+++	-	-	0	-	3
PLS GREEN 8	+	++	--	+	++	-	-	0/+	0	2,5
PLS GREEN 9	+	++	--	-	++	-	-	0/+	+	1,5

FOAMY PASTE PVC SUMMARY

Plasticiser	Rheology	P. ageing	Color	Density	Exp Rate	Cell Quality	Score
DEHP	0/-	0	0/+	0	-	0	-1
DINP	0	0	0	0	0	0	0
DIDP	0/+	-	0/+	0/-	0/-	0	-1
DEHA	++	0	0/-	0/+	0/+	0/-	1,5
PLS GREEN 5	+	0	-	0/+	+	0	1,5
PLS GREEN 8	+	0	-	0/+	+	-	0,5
PLE GREEN 9	+	0	-	+	++	-	2

Commercial examples of the use of Proviplast® PLS Green

Experiences – Uses – Product Replacement - Limitations – Advantages

- 1. Proviplast® PLS Green in artificial leather**
- 2. Phthalate free textile coatings**
- 3. Food wrapping films**

CASE 1: Duvinil: artificial leather



- Proviplast® PLS Green 8 in artificial leather
- Coated high quality materials for sportshoes
- Replacement of DEHP in phthalate-free applications
- 30 % of total production phthalate free

- PVC plastisol application
- 1:1 replacement
- 70 phr loading



CASE 1: Duvinil: artificial leather

“PROJETO FTALATO FREE”

- Project started in November 2011 (pilot run)
- Approved for use in January 2012
- Large scale production started March 2012

2 routes for phthalate free

1. polyurethane (complete plasticiser free)
Non-recyclable / more production waste
Very expensive
Toxic chemicals / safety risks

2. Phthalate free plasticiser
Cheaper
DOA, DOTP, PLS Green 5, 8 and 9 tested
PLS Green 8 best choice



CASE 1: Duvinil: artificial leather



ADVANTAGES PROVIPLAST® PLS GREEN 8

- Same plasticiser efficiency as DEHP / same surface properties
- No exudation (humidity / temperature) / no smell
- Less fumes in production compared to DOP
- No need for a PVC / PU top coating
- No problems with adhesion / printing on the artificial leather surface
- Better siliconated paper release and reuse (50% more)
- Better overall economics

CASE 2: Cipatex

- Coating, adhesives, synthetic laminates, calendering and coagulated substrates based on PVC and PU
- Applications in automotive, graphical, footwear,
- Specialised in post-treatment (coating, embossing, printing, laminating, ...)
- Extensive development center
- Search for phthalate free, more sustainability,
- Total cost of products



CASE 2: Cipatex



Project phthalate-free plasticiser for coated materials

- Until 2009, DOP was the standard plasticiser
- Then changed to DINP
- In 2011 question from customers for phthalate free material
- Different products tested for both standard and foam layer
→ 70% DOTP, DINCH[®] and 30% PLS Green 9
- Formulation tested, approved and in use for already 2 years

CASE 2: Cipatex

Experience with PLS Green

- No exudation
 - Good paste ageing, very good thermal stability
 - No influence on printing and adhesion properties
 - Higher amounts of PLS Green 9 give some cloudiness
-
- Current tests to increase PLS Green 9 to 50% based on experience with the product.
 - Current tests to use PLS Green 5 and PLS Green 8



CASE 3: Goodfilm



- Producer of PVC stretch film
- Produces 150 kilometer / day
- Different food applications

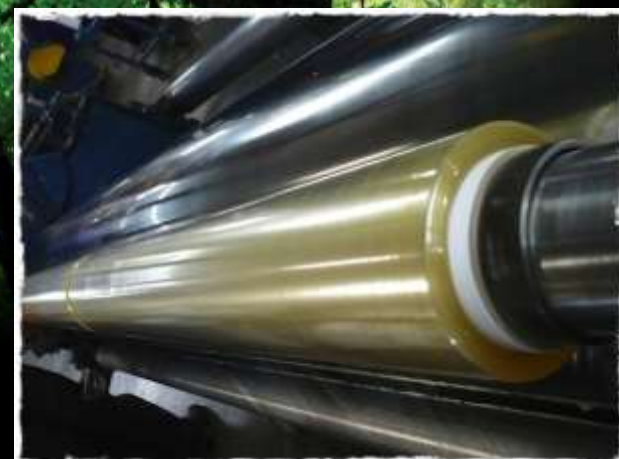


Bio-based phthalate-free formulation

- PVC resin with 40 phr plasticiser
 - 55% epoxidized methyl soyate
 - 45% PLS Green 5
- Anti-fogging aid
- ESBO
- Lubricant



CASE 3: Goodfilm



Experience with PLS Green:

- **PLS Green is a replacement for Unimoll AGF (bio-based product)**
- **PLS Green gives a lower total cost**
- **Color and transparency are better**
- **Film used for refrigerated and room temperature applications**

Conclusions – Proviplast® PLS Green

- Functions as a **primary plasticiser**
- Well suited for **low viscosity plastisol** formulations
- **High bio-based content** (100% for Proviplast® PLS Green 5)
- **Excellent photo-thermal stability**
- Good properties at low temperature, better than GP phthalates

- **Proven applications**
 - Artificial leather
 - PVC laminates
 - Toys and highly flexible objects
 - Coated materials
 - Food-wrapping films

Our commitment

- **To promote and support the product in different applications**
- **We will provide all the needed technical information**
- **Improve product characteristics if needed**
- **Help customers in technical development and recipe transition**
- **Apply for Reach and all needed approvals**

Acknowledgements

- **THANKS TO**

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PROVIRON Functional Chemicals

Oudenburgsesteenweg 100

8400 Oostende, Belgium

[+3259562100](tel:+3259562100)

marc.labbe@proviron.com (R&D)

peter.vanelslander@proviron.com (sales)

PETROM

Petroquimica Mogi das Cruzes S/A

Rod. Dom Paulo Rolim Loureiro

08766-500 – Mogi das Cruzes, SP – Br

[+551147987600](tel:+551147987600)

petrom@petrom.com.br