ATELIER INTERNATIONAL DE DIAGNOSTIQUE DE L’INDUSTRIE DES RÉSINEUX DE SECONDE TRANSFORMATION

“LA COLOPHANE ET SON AVENIR DANS LE DOMAINE DU SUDOE”

BORDEAUX (France), OCTOBRE 2012
What is Rosin?

Rosin is a solid form of natural resin obtained from conifers and mainly pine trees.
Rosin Sources

- **GUM:** Tapping the Oleoresin of Living Pine Trees

- **Tall Oil Rosin (TOR):** By-product of Kraft Pulping Process

- **Stumpwood:** Extraction/Special Processing of Oleoresin from Stumps
**Rosin composition**

Rosin is mainly composed (>90%) of resin acids with similar basic structures

![Chemical structure of Abietic Acid]

- **C–OH Carboxylic Acid**
- **= Unsaturation**
- **Ring Size & Structure**
Two common families of resin acids:

- **Abietane skeletal class:**
  - Abietic
  - Neoabietic
  - Levopimaric
  - Palustric
  - Dehydroabietic

- **Pimarane skeletal class:**
  - Pimaric
  - Isopimanic
  - Sandaracopimaric
Rosin, as natural resin, has a variable composition depending on:

- **Origin of the Rosin** (sources)
- **Types of the trees** (species)
- **Location of the trees** (geographical area)
# Typical composition of resin acids in rosin by SOURCES

<table>
<thead>
<tr>
<th>Resin Acid</th>
<th>Gum rosin</th>
<th>Tall Oil rosin</th>
<th>Wood rosin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Abietic</strong></td>
<td>32-37</td>
<td>40-45</td>
<td>25-35</td>
</tr>
<tr>
<td><strong>Palustric/Levopimaric</strong></td>
<td>18-23</td>
<td>5-10</td>
<td>5-10</td>
</tr>
<tr>
<td><strong>Neoabietic</strong></td>
<td>15-20</td>
<td>1-6</td>
<td>5-15</td>
</tr>
<tr>
<td><strong>Dehydroabietic</strong></td>
<td>8-10</td>
<td>27-32</td>
<td>20-25</td>
</tr>
<tr>
<td><strong>Pimaric</strong></td>
<td>7-12</td>
<td>5-10</td>
<td>3-5</td>
</tr>
<tr>
<td><strong>Isopimaric</strong></td>
<td>6-11</td>
<td>4-9</td>
<td>2-6</td>
</tr>
<tr>
<td><strong>Sandarcopimaric</strong></td>
<td>1-3</td>
<td>&lt;2</td>
<td>1-3</td>
</tr>
</tbody>
</table>
### Principal resin acids of gum rosin by *species*

<table>
<thead>
<tr>
<th>Species (origin)</th>
<th>P. pinaster (France)</th>
<th>P. halepensis (Greece)</th>
<th>P. sylvestris (Russia)</th>
<th>P. massoniana (China)</th>
<th>P. elliotti (Brazil)</th>
<th>P. merkusii (Indonesia)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abietic</td>
<td>35</td>
<td>45</td>
<td>35</td>
<td>39</td>
<td>37</td>
<td>28</td>
</tr>
<tr>
<td>Isopimaric</td>
<td>10</td>
<td>11</td>
<td>7</td>
<td>2</td>
<td>17</td>
<td>16</td>
</tr>
<tr>
<td>Neoabietic</td>
<td>15</td>
<td>13</td>
<td>15</td>
<td>16</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>Palustric/Levopimaric</td>
<td>20</td>
<td>23</td>
<td>23</td>
<td>25</td>
<td>15</td>
<td>27</td>
</tr>
<tr>
<td>Dehydroabietic</td>
<td>9</td>
<td>5</td>
<td>10</td>
<td>7</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>Pimaric</td>
<td>10</td>
<td>9</td>
<td>10</td>
<td>10</td>
<td>5</td>
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<td>Communic</td>
<td></td>
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<td></td>
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<td></td>
<td>4</td>
</tr>
<tr>
<td>Mercusic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>11</td>
</tr>
</tbody>
</table>
Principal resin acids of gum rosin from *P. pinaster* by geographical area

<table>
<thead>
<tr>
<th>Resin acid (%)</th>
<th>P. pinaster tree location</th>
<th>France</th>
<th>Portugal</th>
<th>Spain</th>
<th>USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abietic</td>
<td></td>
<td>35</td>
<td>34</td>
<td>26</td>
<td>14</td>
</tr>
<tr>
<td>Isopimaric</td>
<td></td>
<td>10</td>
<td>7</td>
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</tr>
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<td></td>
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<td>21</td>
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<td>Dehydroabietic</td>
<td></td>
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<td>6</td>
<td>4</td>
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<td>Pimic</td>
<td></td>
<td>10</td>
<td>8</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>Sandarocopimaric</td>
<td></td>
<td>2</td>
<td>2</td>
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</tr>
</tbody>
</table>
Rosin is not an homogenous substance

<table>
<thead>
<tr>
<th>Typical physical and chemical properties of rosin by sources</th>
<th>Gum rosin</th>
<th>Tall Oil rosin</th>
<th>Wood rosin</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acid number</strong></td>
<td>164</td>
<td>167</td>
<td>166</td>
</tr>
<tr>
<td><strong>Saponification index</strong></td>
<td>172</td>
<td>174</td>
<td>172</td>
</tr>
<tr>
<td><strong>Unsaponifiable matter</strong></td>
<td>8%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td><strong>Fatty acids</strong></td>
<td>-</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td><strong>Color, U.S. rosin grade</strong></td>
<td>WW</td>
<td>WG</td>
<td>WG</td>
</tr>
<tr>
<td><strong>Softening point (R&amp;B)</strong></td>
<td>76 ºC</td>
<td>77 ºC</td>
<td>76 ºC</td>
</tr>
<tr>
<td><strong>Refractive index</strong></td>
<td>1.541</td>
<td>1.540</td>
<td>1.545</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>1.07</td>
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<td>1.07</td>
</tr>
</tbody>
</table>
### Typical physical and chemical properties of gum rosin

<table>
<thead>
<tr>
<th>Typical physical and chemical properties of gum rosin by types</th>
<th>Clear types</th>
<th>Middle types</th>
<th>Dark types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid number</td>
<td>165-171</td>
<td>160-170</td>
<td>155-163</td>
</tr>
<tr>
<td>Saponification index</td>
<td>171-177</td>
<td>170-176</td>
<td>165-174</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
<td>4.3%-5.5%</td>
<td>5.3%-8%</td>
<td>7%-10%</td>
</tr>
<tr>
<td>Color, U.S. rosin grade</td>
<td>XC-WW</td>
<td>WG-I</td>
<td>H-D</td>
</tr>
<tr>
<td>Softening point (R&amp;B)</td>
<td>76 ºC</td>
<td>77 ºC</td>
<td>76 ºC</td>
</tr>
<tr>
<td>Ashes</td>
<td>0.041-0.02%</td>
<td>0.041-0.02%</td>
<td>0.01-0.17%</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.541</td>
<td>1.540</td>
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</tr>
<tr>
<td>Density</td>
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</tr>
</tbody>
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Rosin Color
Why Rosin Derivatives?

Not suitable rosin properties:

- Low softening point (70 - 80°C)
- Oxidation trend
- High acidity ($I_a = 155 - 170$)
- Crystallization trend
- Low viscosity
- Quite dark color
- High solvent retention
- Other
**Oxydation test**

*(21 Kg. of pressure of $O_2$ for 7 days)*

% Weight Increase

- Gum Rosin
- Dismutated Rosin
- Glycerol ester
- Pentaester

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**Time**

1 day 2 day 3 day 4 day 5 day 6 day 7 day
Heat stability test

(Color evolution at 170 °C)

Color Gardner

- Gum Rosin
- Dismutated Rosin
- Glycerol ester
- Pentaester

Time

0 h. 12 h. 24 h.
Rosin Chemistry

Abietic Acid

- $\text{C} - \text{OH}$ Carboxylic Acid
- $= \text{Unsaturation}$
- Ring Size & Structure
Rosin Reactivity

**Reaction of Double Bonds:**
- Adduction
- Hydrogenation
- Disproportionation
- Polymerization
- Etc.

**Reaction of Carboxylic Acid:**
- Esterification
- Salt Formation (*Soaps, Resinates*)
- Phenolic modified rosins
- Etc.
Rosin Resins Uses

Chemical Division

- Soaps
- Resinates
- Polymerization emulsifier (synthetic rubbers)
- Paper sizing
- Adhesives
- Printing inks
- Paints and varnishes
- Chewin gum
- Depilating waxes
- Road marking
- Paints and varnishes
- Adhesives
- Chewin gum
- Esterification
- Hydrogenation
- Direct use
- Phosphorus emulsifier
- Sealing wax
- Insulating tackifier
- Water-proofing
- Depilating waxes
- Polymers
- Maleic modified resins
- Rosin adduct
- Dismutation
- Lacquers
- Enamels
- Varnishes
- Printing inks
- Alkyd resins
- Paper sizing
- Printing inks
- Alkyd resins
- Adhesives (labels, tapes)
- Fungicides
- Anti-corrosion agents
Rosin Resins Industrial Applications
Rosin good or poor?
It depends on the particular industrial use

some examples:

Brazilian rosin (P. elliottii) is suitable for depilatory waxes

Indonesian rosin (P. merkusii) is suitable for inks

Chinese rosin (P. massoniana) is suitable for adhesives

SUDOE rosin (P. pinaster) is suitable for most uses (versatile)
EU Rosin Production  (Forecast 2012)
Gum Rosin + Tall-Oil Rosin = 147,500 MT

UE Gum Rosin Production = 22,500 MT. (15.3 %)
UE TOR production = 125,000 MT. (84.7 %)
EU Rosin demand  (Forecast 2012)
Gum Rosin + Tall-Oil Rosin = 325,000 MT

UE  Gum Rosin market= 190,000 MT. (58.5 %)
UE  TOR market = 135,000 MT. (41.5 %)
**EU Rosin Balance** (Production vs. Demand)

Deficit = -177,500 MT

EU Deficit of Gum Rosin = -167,500 MT (94.4%)
EU Deficit of TOR = -10,000 MT (5.6%)
European Rosin market by applications
Gum Rosin + Tall-Oil Rosin = 325,000 MT

Source: PCA International Conference, Boston September 2012
European Rosin Adhesives and Sealants market
Gum Rosin + Tall-Oil Rosin = 130,000 MT
Average annual market growth: 4-5%

Source: PCA International Conference, Boston September 2012
European Rosin Printing Inks market
Gum Rosin + Tall-Oil Rosin = 100.000 MT
Average annual market growth: 3-3.5%

Source: PCA International Conference, Boston September 2012
Rosin Resins are not alone

Pine trees

Pine tapping → Crude Gum → Distillation

Chips-wood

Sulfate turpentine → Kraft Process → Black liquor

Kraft Process

Gum turpentine → Gum Rosin → Distillation → Tall Oil Rosin

Cracking Process

Feedstock (Nafta, etc.) → By-products of fractionations lines C5, C9, DCPD

Hydrocarbon Resins

Terpene Resins

Rosin Resins
Global Resin Production (Forecast 2012)

Total world resin production = 2,430,000 MT
- Rosin resins = 1,300,000 MT.
- Hydrocarbon resins = 1,050,000 MT.
- Terpene resins = 80,000 MT.

Source: PCA International Conference, Boston September 2012
Global Resin Trend

- Moderate growth production of hydrocarbon resins (2%)
- Slightly more sharper growth production of rosin resins (3%)
- Stable production of terpene resins (0%)

Source: PCA International Conference, Boston September 2012
Rosin Resin Trend

Gum Rosin
- Production is closely linked to the market price and the increase in living standards (labor costs).
- Moderate growth of production in the short term (3%) and increased market demand as a renewable raw material.
- Long term limited availability of crude gum rosin (Eucaliptus vs. Pinus, salary increases, etc.)

Tall Oil,
- Production limited by the unavailability of crude tall-oil, linked to the price of energy (biodiesel production).
- Stable production in the short and medium term and longer-term shortages.

Wood Rosin
Sharp decline of wood rosin production in the long term. Small and irrelevant proportion of total rosin production.
World Rosin Resin Trend

- Moderate growth of Gum Rosin production in the coming years (3% p.y.), but high risk of decline in the longer term.
- TOR production expected to remain flat because production of softwood kraft pulp also will be flat in the long term.
- Market demand for Rosin Resins 4 to 5% p.y., leaded by emerging countries (China, India, Brazil, etc.)
- At longer term Trend, demand for Rosin Resins will exceed the offer.

Higher prices and limited availability in the future
Rosin resins advantages

- Rosin market demands the more and more for ecological, biological and green products.

- Current economy requires development of products from renewable resources for sustainable industrial activities.

- Development of friendly environmental products (pine chemicals industry helps to preserve pine forests and reduce carbon footprint).

Clear advantage of Rosin resins over Hydrocarbon resins
Conclusions

- Pine chemical industry in EU has a growing raw material demand, limited only by supply difficulties. This limited availability of rosin and turpentine will probably increase in near future.

- The geographic pine forest area of SUST-FOREST (Portugal, Spain and France), has enough resources to meet their own industrial needs.

- Pine chemical industry is sustainable and environmentally friendly.

- Pine chemical industry generates economic, social and environmental benefits.
Aujourd'hui est de bon sens d'encourager le gemmage dans le domaine du SUDOE

merci beaucoup!