La industria de la colofonia y aguarrás en Europa
Origines de la térébenthine

Essence de papeterie
- Production mondiale 120 - 140 000 t / an
- Co produit de la fabrication du papier

Essence térébenthine
- Production mondiale 130 - 150 000 t / an
- Co produit de la production de colophane
Qualité de la térébenthine

**Essence de papeterie**
- Mise en œuvre complexe
- Désulfuration obligatoire

**Essence térébenthine**
- Directement utilisable
- 95 % de la térébenthine valorisable
Essence de papeterie

Amerique du nord; 61%
Europe; 27%
Amerique Latine; 6%
Asie et Pacifique; 4%
Autres; 2%
Essence de térebenthine

- Chine: 74%
- Brésil: 9%
- Indonésie: 7%
- Mexique: 2%
- Inde: 4%
- Argentine: 1%
- Nepal: 1%
- Autres: 2%
USAGES PRINCIPAUX
(Tonnes de terpènes)

- Pine Oil: 70000
- Resines: 120000
- Parfums et Aromes: 100000
- Camphre: 20000
- Autres: 20000
USAGES PRINCIPAUX

Resines
- Produites principalement à partir d’essence de papeterie
- Adhesifs, chewing gum, pneumatiques

Pine oil
- A partir d’essence papeterie (US) ou de térébenthine (China)
- Détergents

Camphre
- Produit avec alpha pinene de térébenthine
- Désinfectant, Temples en Inde
Gemmage

Résine

Industrie

Térébenthine

Colophane
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.
Two common families of resin acids:

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

- **Pimarane skeletal class:**
  - Pimaric
  - Isopimaric
  - Sandarocopimaric
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>Resin acid (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<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>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Communic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
<td></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>P. pinaster tree location</th>
<th>Resin acid (%)</th>
<th>P. pinaster France</th>
<th>P. Pinaster Portugal</th>
<th>P. Pinaster Spain</th>
<th>P. pinaster USA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abietic</td>
<td>35</td>
<td>34</td>
<td>26</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Isopimmaric</td>
<td>10</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Neoabietic</td>
<td>15</td>
<td>19</td>
<td>27</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Palustric/Levopimmaric</td>
<td>20</td>
<td>21</td>
<td>22</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>Dehydroabietic</td>
<td>9</td>
<td>9</td>
<td>6</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Pimaric</td>
<td>10</td>
<td>8</td>
<td>9</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Sandarocopimmaric</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</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>Acid number</td>
<td>164</td>
<td>167</td>
<td>166</td>
</tr>
<tr>
<td>Saponification index</td>
<td>172</td>
<td>174</td>
<td>172</td>
</tr>
<tr>
<td>Unsaponifiable matter</td>
<td>8%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>-</td>
<td>&lt;5</td>
<td>-</td>
</tr>
<tr>
<td>Color, U.S. rosin grade</td>
<td>WW</td>
<td>WG</td>
<td>WG</td>
</tr>
<tr>
<td>Softening point (R&amp;B)</td>
<td>76 °C</td>
<td>77 °C</td>
<td>76 °C</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.541</td>
<td>1.540</td>
<td>1.545</td>
</tr>
<tr>
<td>Density</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Rosin Color
## Typical physical and chemical properties of gum rosin

<table>
<thead>
<tr>
<th>Typical physical and chemical properties of rosin by sources</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><strong>XC-WW</strong></td>
<td><strong>WG-I</strong></td>
<td><strong>H-D</strong></td>
</tr>
<tr>
<td>Softening point (R&amp;B)</td>
<td>76 °C</td>
<td>77 °C</td>
<td>76 °C</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>
<td>1.545</td>
</tr>
<tr>
<td>Density</td>
<td>1.07</td>
<td>1.07</td>
<td>1.07</td>
</tr>
</tbody>
</table>
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

![Graph showing weight increase over time for different substances.](image)
**Heat stability test**

*(Color evolution at 170 °C)*

Color Gardner

- **Gum Rosin**
- **Dismutated Rosin**
- **Glycerol ester**
- **Pentaester**

<table>
<thead>
<tr>
<th>Time</th>
<th>0 h.</th>
<th>12 h.</th>
<th>24 h.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Color Gardner</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Rosin Chemistry

Abietic Acid

- C–OH Carboxylic Acid
- = 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

- **SOAPS RESINATES POLYMERIZATION EMULSIFIER (SYNTHETIC RUBBERS) PAPER SIZING**
- **ADHESIVES PRINTING INKS PAINTS AND VARNISHES CHEWING GUM DEPILATING WAXES ROAD MARKING**
- **PAINTS AND VARNISHES ADHESIVES CHEWING GUM**
- **PHOSPHORUS EMULSIFIER SEALING WAX INSULATING TACKIFIER WATER PROOFING DEPILATING WAXES**
- **VARNISHES ADHESIVES INKS THERMOPLASTICS**
- **SAPONIFICATION**
- **ESTERIFICATION**
- **HYDROGENATION**
- **DIRECT USE**
- **POLYMERATION**
- **ROSAZINC**
- **DISMUTATION**
- **MALEIC MODIFIED RESINS**
- **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
      - Gum turpentine
      - Gum Rosin
        - Terpene Resins
        - Rosin Resins

- Chips-wood
  - Kraft Process
    - Black liquor
      - Sulfate turpentine
        - Soap
          - Acidulation
            - CTO
              - Distillation
                - Tall Oil Rosin

Petrochemical

- Feedstock (Nafta, etc.)
  - Craking Process
    - By-products of fractionations lines C5, C9, DCPD
      - Hydrocarbon 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.
  Long term limited availability of crude gum rosin (Eucaliptus vs. Pinus)

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.
Diagnostic du secteur industriel de la résine et produits dérivés dans le monde et en Europe