



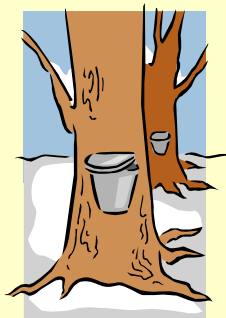
***ATELIER INTERNATIONAL DE  
DIAGNOSTIQUE DE L'INDUSTRIE DES  
RÉSINEUX DE SECONDE  
TRANSFORMATION***  
***“LA COLOPHANE ET SON AVENIR  
DANS LE DOMAINE DU SUDOE”***  
***BORDEAUX (France), OCTOBRE 2012***



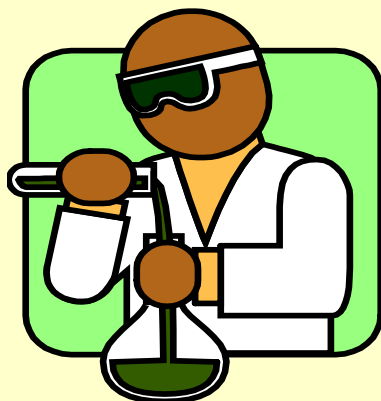
## ***What is Rosin?***

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

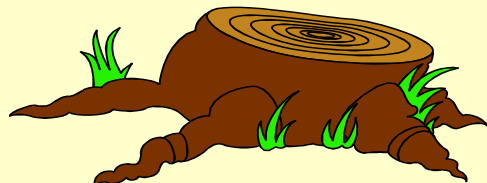
# ***Rosin Sources***



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



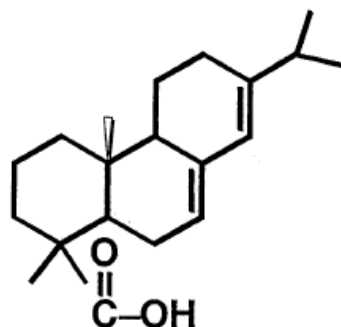
- ***Tall Oil Rosin (TOR):***  
*By-product of Kraft Pulping Process*



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

# ***Rosin composition***

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

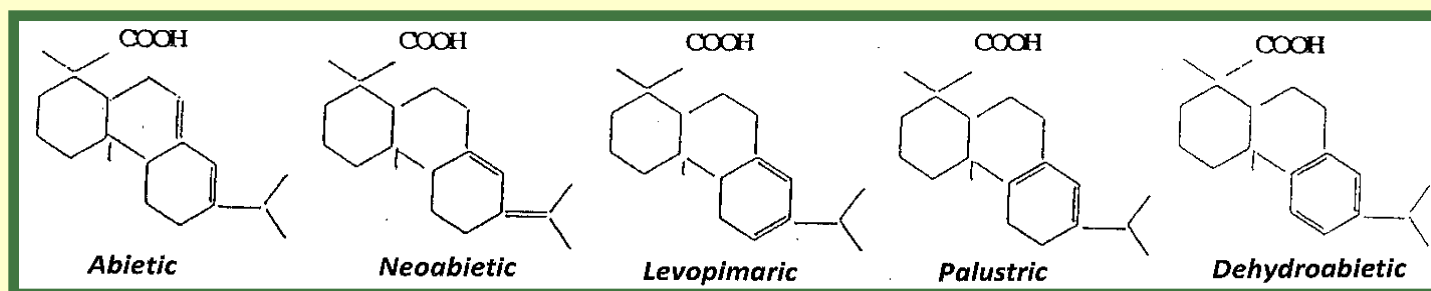


Abietic Acid

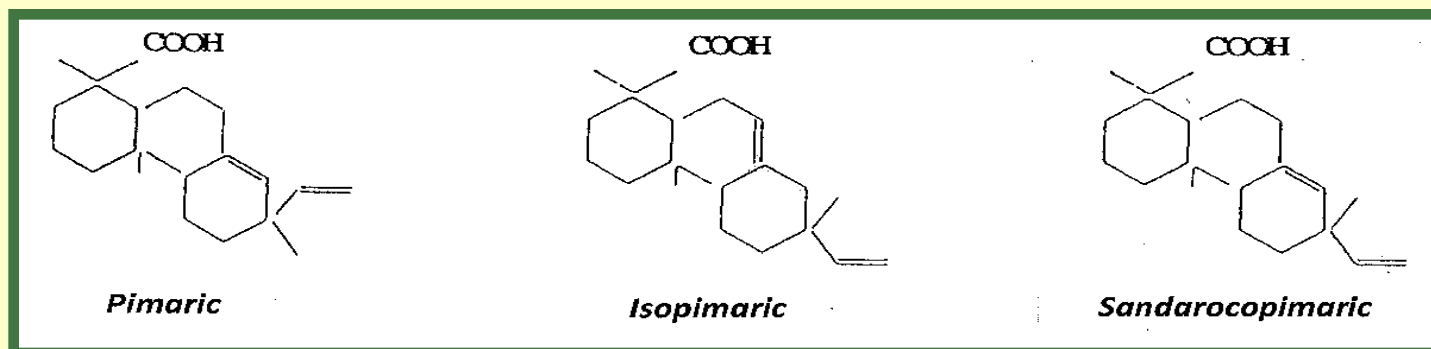
- $\text{C}-\text{OH}$  Carboxylic Acid
- = Unsaturation
- Ring Size & Structure

# ***Two common families of resin acids:***

## ● ***Abietane skeletal class:***



## ● ***Pimarane skeletal class:***



# ***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***

| <b><i>Resin Acid</i></b><br><i>(% of acid fraction)</i> | <b><i>Gum<br/>rosin</i></b> | <b><i>Tall Oil<br/>rosin</i></b> | <b><i>Wood<br/>rosin</i></b> |
|---|-----------------------------|----------------------------------|------------------------------|
| <b><i>Abietic</i></b>                                   | <b><i>32-37</i></b>         | <b><i>40-45</i></b>              | <b><i>25-35</i></b>          |
| <b><i>Palustric/Levopimaric</i></b>                     | <b><i>18-23</i></b>         | <b><i>5-10</i></b>               | <b><i>5-10</i></b>           |
| <b><i>Neoabietic</i></b>                                | <b><i>15-20</i></b>         | <b><i>1-6</i></b>                | <b><i>5-15</i></b>           |
| <b><i>Dehydroabietic</i></b>                            | <b><i>8-10</i></b>          | <b><i>27-32</i></b>              | <b><i>20-25</i></b>          |
| <b><i>Pimaric</i></b>                                   | <b><i>7-12</i></b>          | <b><i>5-10</i></b>               | <b><i>3-5</i></b>            |
| <b><i>Isopimaric</i></b>                                | <b><i>6-11</i></b>          | <b><i>4-9</i></b>                | <b><i>2-6</i></b>            |
| <b><i>Sandarcopimaric</i></b>                           | <b><i>1-3</i></b>           | <b><i>&lt;2</i></b>              | <b><i>1-3</i></b>            |

## ***Principal resin acids of gum rosin by species***

| <b>Species<br/>(origin)</b>       | <b><i>P. pinaster</i><br/>(France)</b> | <b><i>P. halepensis</i><br/>(Greece)</b> | <b><i>P. sylvestris</i><br/>(Russia)</b> | <b><i>P. massoniana</i><br/>(China)</b> | <b><i>P. elliotti</i><br/>(Brazil)</b> | <b><i>P. merkusii</i><br/>(Indonesia)</b> |
|-----------------------------------|--|--|--|---|--|---|
| <b>Resin acid (%)</b>             |  |  |  |   |  |   |
| <b>Abietic</b>                    | <b>35</b>                              | <b>45</b>                                | <b>35</b>                                | <b>39</b>                               | <b>37</b>                              | <b>28</b>                                 |
| <b>Isopimaric</b>                 | <b>10</b>                              | <b>11</b>                                | <b>7</b>                                 | <b>2</b>                                | <b>17</b>                              | <b>16</b>                                 |
| <b>Neoabietic</b>                 | <b>15</b>                              | <b>13</b>                                | <b>15</b>                                | <b>16</b>                               | <b>16</b>                              | <b>5</b>                                  |
| <b>Palustric/<br/>Levopimaric</b> | <b>20</b>                              | <b>23</b>                                | <b>23</b>                                | <b>25</b>                               | <b>15</b>                              | <b>27</b>                                 |
| <b>Dehydroabietic</b>             | <b>9</b>                               | <b>5</b>                                 | <b>10</b>                                | <b>7</b>                                | <b>5</b>                               | <b>4</b>                                  |
| <b>Pimaric</b>                    | <b>10</b>                              |  | <b>9</b>                                 | <b>10</b>                               | <b>5</b>                               |   |
| <b>Communic</b>                   |  |  |  |   | <b>4</b>                               |   |
| <b>Mercusic</b>                   |  |  |  |   |  | <b>11</b>                                 |



# ***Principal resin acids of gum rosin from *P. pinaster* by geographical area***

| <i><b>P. pinaster<br/>tree location</b></i> | <i><b>P. pinaster<br/>France</b></i> | <i><b>P. Pinaster<br/>Portugal</b></i> | <i><b>P. Pinaster<br/>Spain</b></i> | <i><b>P. pinaster<br/>USA</b></i> |
|---|--------------------------------------|--|-------------------------------------|-----------------------------------|
| <i><b>Resin acid (%)</b></i>                |                                      |  |                                     |                                   |
| <i><b>Abietic</b></i>                       | <b>35</b>                            | <b>34</b>                              | <b>26</b>                           | <b>14</b>                         |
| <i><b>Isopimaric</b></i>                    | <b>10</b>                            | <b>7</b>                               | <b>5</b>                            | <b>12</b>                         |
| <i><b>Neoabietic</b></i>                    | <b>15</b>                            | <b>19</b>                              | <b>27</b>                           | <b>18</b>                         |
| <i><b>Palustric/<br/>Levopimaric</b></i>    | <b>20</b>                            | <b>21</b>                              | <b>22</b>                           | <b>39</b>                         |
| <i><b>Dehydroabietic</b></i>                | <b>9</b>                             | <b>9</b>                               | <b>6</b>                            | <b>4</b>                          |
| <i><b>Pimaric</b></i>                       | <b>10</b>                            | <b>8</b>                               | <b>9</b>                            | <b>8</b>                          |
| <i><b>Sandarocopimaric</b></i>              | <b>2</b>                             | <b>2</b>                               | <b>2</b>                            | <b>2</b>                          |
























## ***Rosin is not an homogenous substance***

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

## ***Typical physical and chemical properties of gum rosin***

| <b><i>Typical physical and chemical properties of gum rosin by types</i></b> | <b><i>Clear types</i></b> | <b><i>Middle types</i></b> | <b><i>Dark types</i></b> |
|--|---------------------------|----------------------------|--------------------------|
| <b><i>Acid number</i></b>  | <b><i>165-171</i></b>     | <b><i>160-170</i></b>      | <b><i>155-163</i></b>    |
| <b><i>Saponification index</i></b>   | <b><i>171-177</i></b>     | <b><i>170-176</i></b>      | <b><i>165-174</i></b>    |
| <b><i>Unsaponifiable matter</i></b>  | <b><i>4.3%-5.5%</i></b>   | <b><i>5.3%-8%</i></b>      | <b><i>7%-10%</i></b>     |
| <b><i>Color, U.S. rosin grade</i></b>  | <b><i>XC-WW</i></b>       | <b><i>WG-I</i></b>         | <b><i>H-D</i></b>        |
| <b><i>Softening point (R&amp;B)</i></b>                                      | <b><i>76 °C</i></b>       | <b><i>77 °C</i></b>        | <b><i>76 °C</i></b>      |
| <b><i>Ashes</i></b>  | <b><i>0.041-0.02%</i></b> | <b><i>0.041-0.02%</i></b>  | <b><i>0.01-0.17%</i></b> |
| <b><i>Refractive index</i></b>   | <b><i>1.541</i></b>       | <b><i>1.540</i></b>        | <b><i>1.545</i></b>      |
| <b><i>Density</i></b>  | <b><i>1.07</i></b>        | <b><i>1.07</i></b>         | <b><i>1.07</i></b>       |

# ***Rosin Color***

| U.S. Official<br>Rosin Standards |   | Gardner<br>Color Standards  |   | U.S. Official<br>Rosin Standards |
|----------------------------------|---|---|---|----------------------------------|
| XC                               |    |  3   | 18    | D                                |
| XB                               |    |  4   | 17    | E                                |
| XA                               |    |  5   | 16    | F                                |
| X                                |    |  6   | 15    |                                  |
|                                  |   |   | 14    |                                  |
| WW                               |   |  7  | 13    | G                                |
| WG                               |  |   | 12   | H                                |
| N                                |  |  8 | 11  | I                                |
|                                  |   |  9 | 10  | M                                |

# ***Why Rosin Derivatives?***

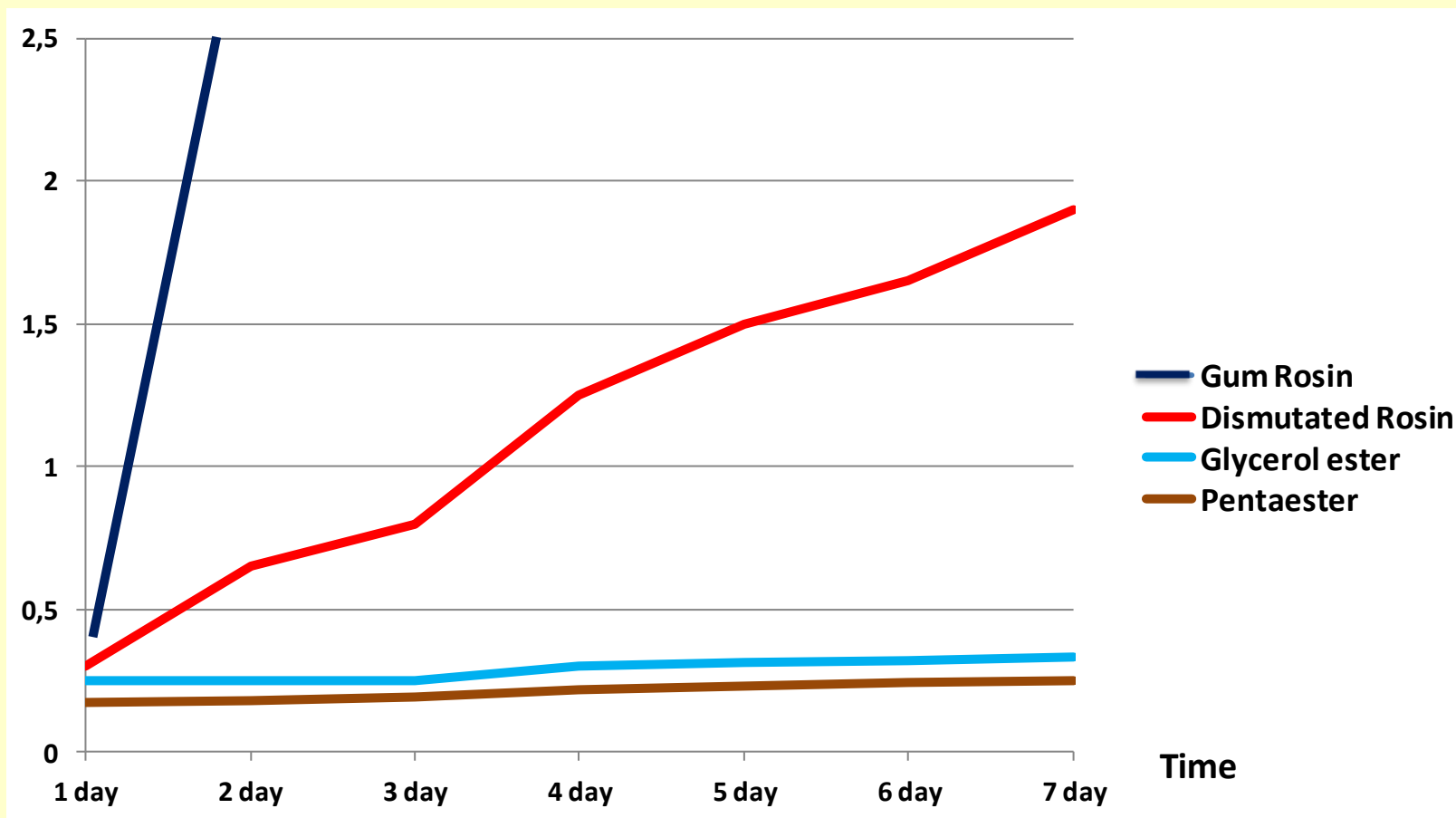
***Not suitable rosin properties:***

- ***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<sub>2</sub> for 7 days)

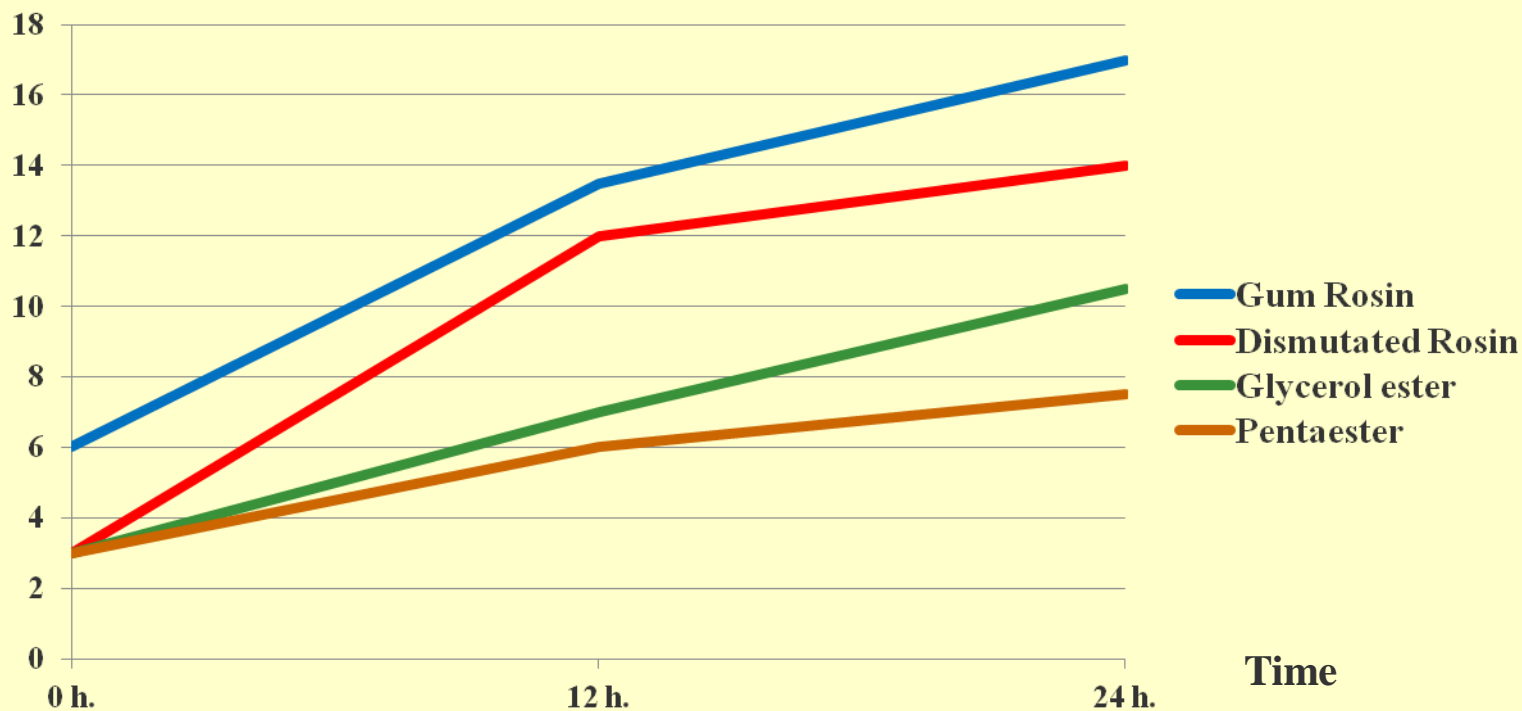
% Weight Increase



# *Heat stability test*

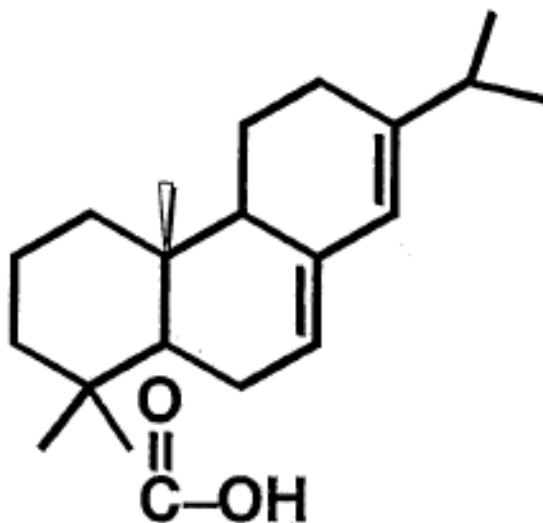
*(Color evolution at 170 °C)*

Color Gardner





# ***Rosin Chemistry***



Abietic Acid

- $\text{C}=\text{O}$  Carboxylic Acid
- = Unsaturation
- Ring Size & Structure

# ***Rosin Reactivity***

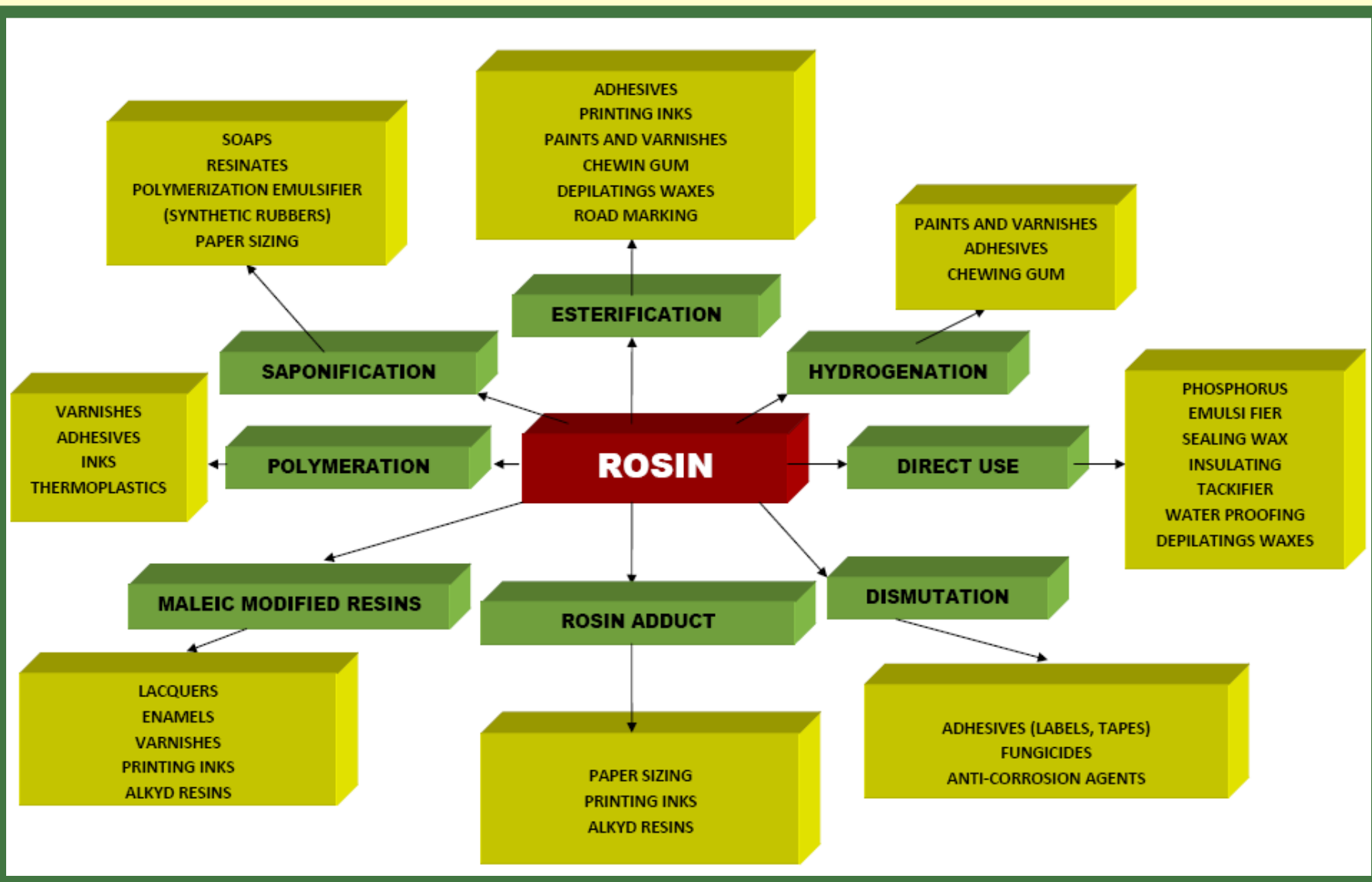
## ■ ***Reaction of Double Bonds:***

- *Adduction*
- *Hydrogenation*
- *Disproportionation*
- *Polymerization*
- *Etc.*

## ■ ***Reaction of Carboxylic Acid:***

- *Esterification*
- *Salt Formation (Soaps, Resinates)*
- *Phenolic modified rosins*
- *Etc.*

# ***Rosin Resins Uses***





# ***Rosin Resins Industrial Applications***



la unión resinera española, s.a.

**CHEMICAL DIVISION**





## ***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***

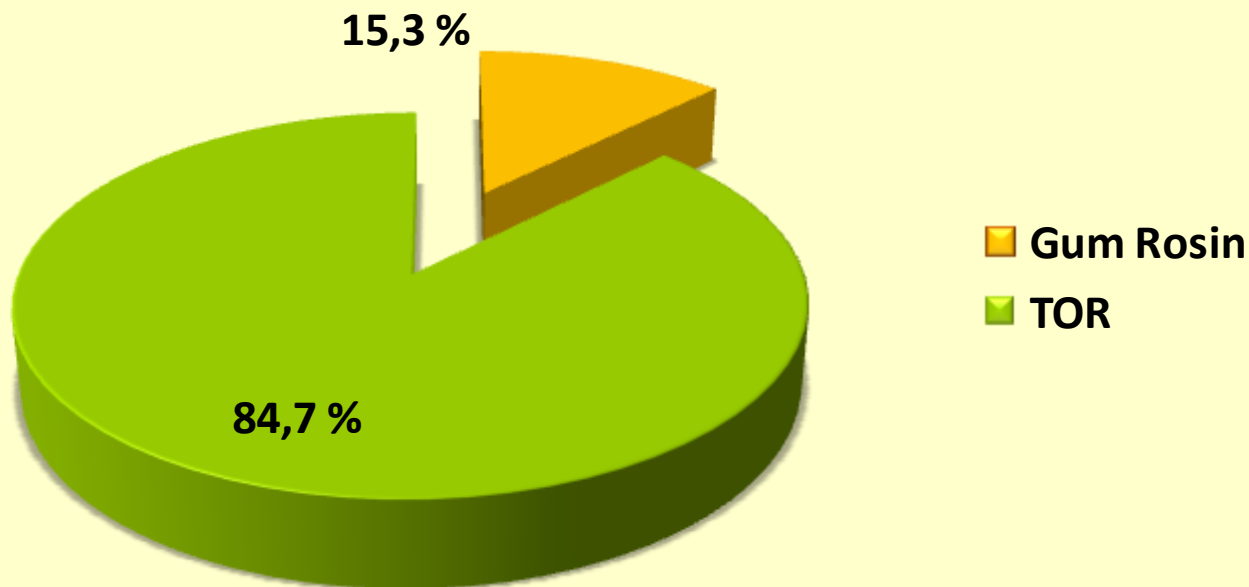
***SUDOE rosin (P. pinaster) is suitable for most uses (versatile)***

## ***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%)**

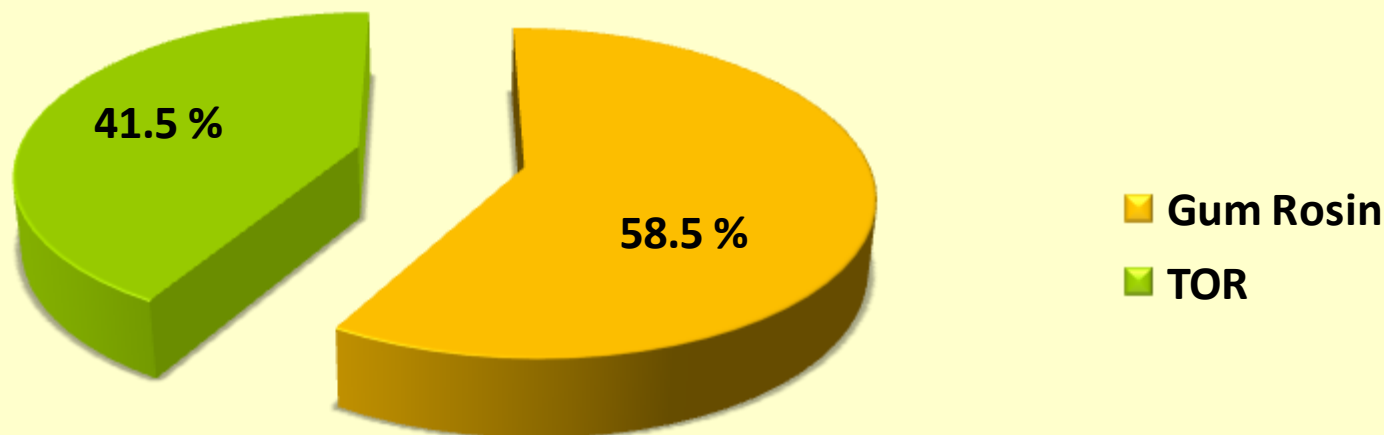


## ***EU Rosin demand (Forecast 2012)***

***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%)**



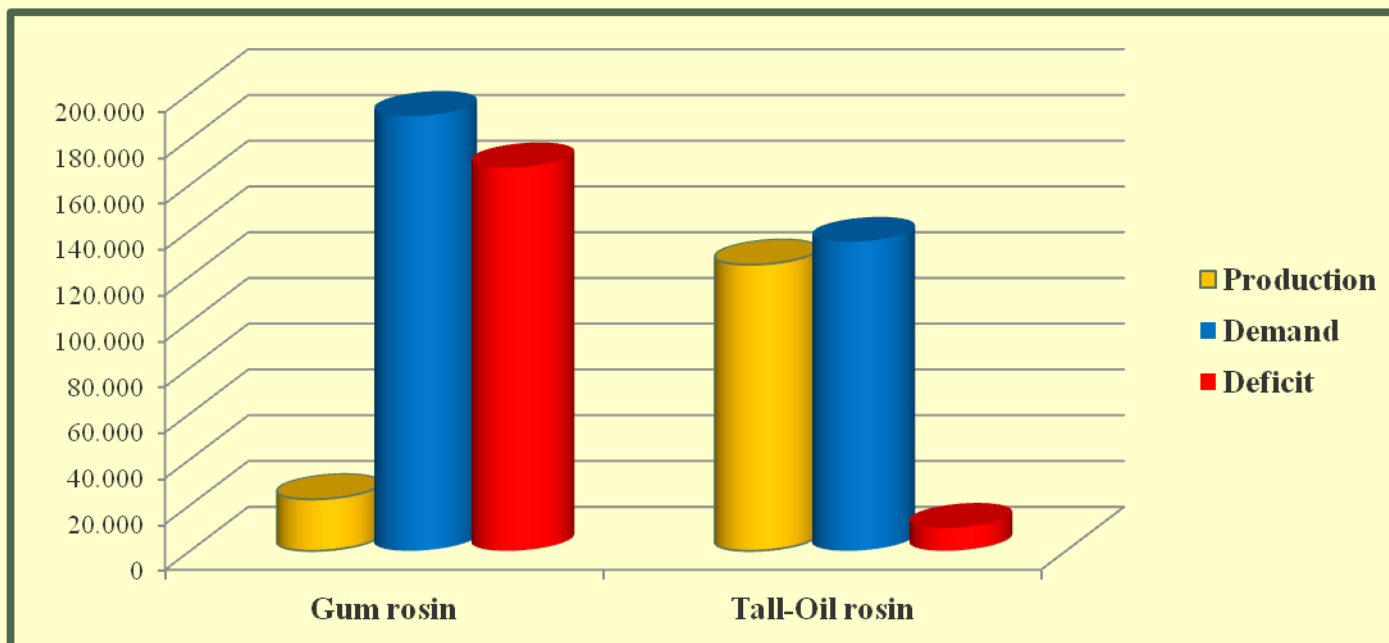


# ***EU Rosin Balance*** (Production vs. Demand)

**Deficit = - 177,500 MT**

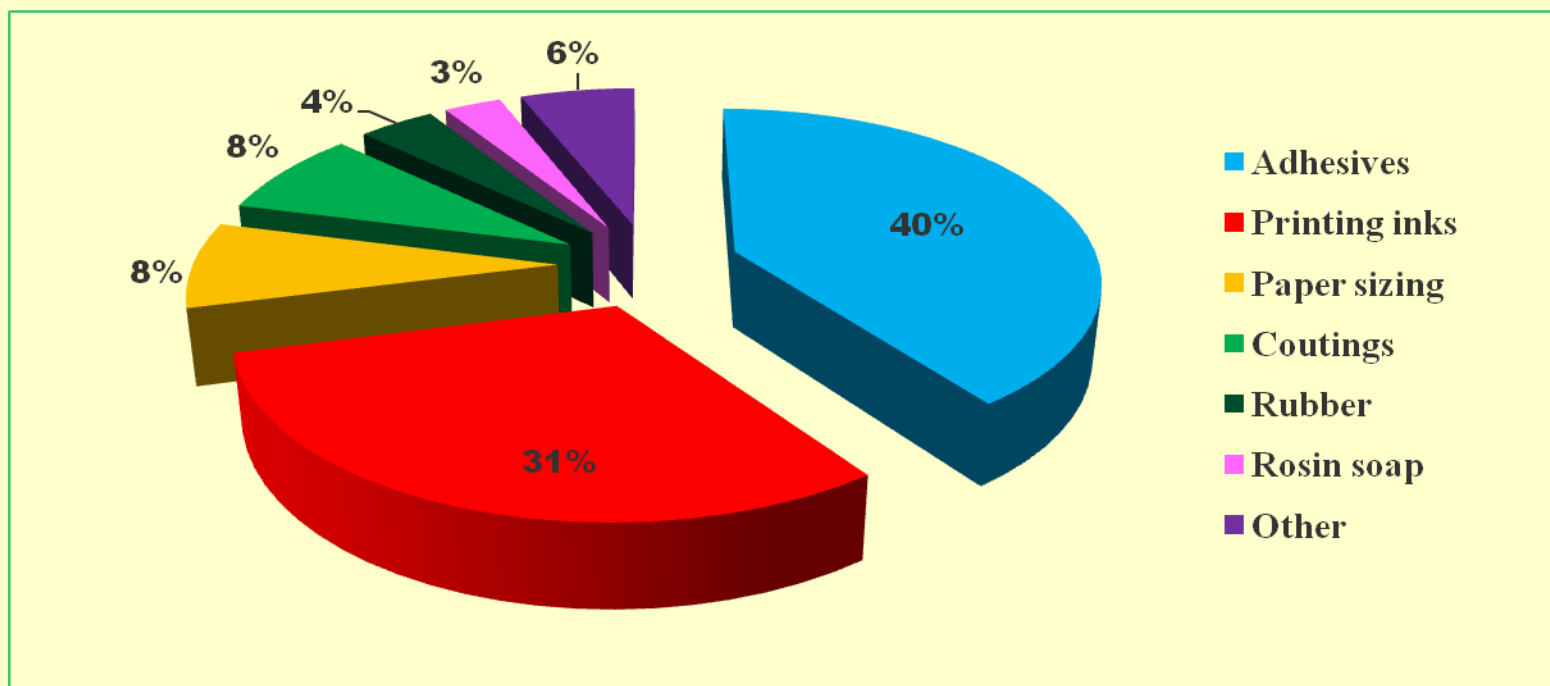
**EU Deficit of Gum Rosin = - 167,500 MT. (94.4%)**

**EU Deficit of TOR = - 10,000 MT. (5.6 %)**



# *European Rosin market by applications*

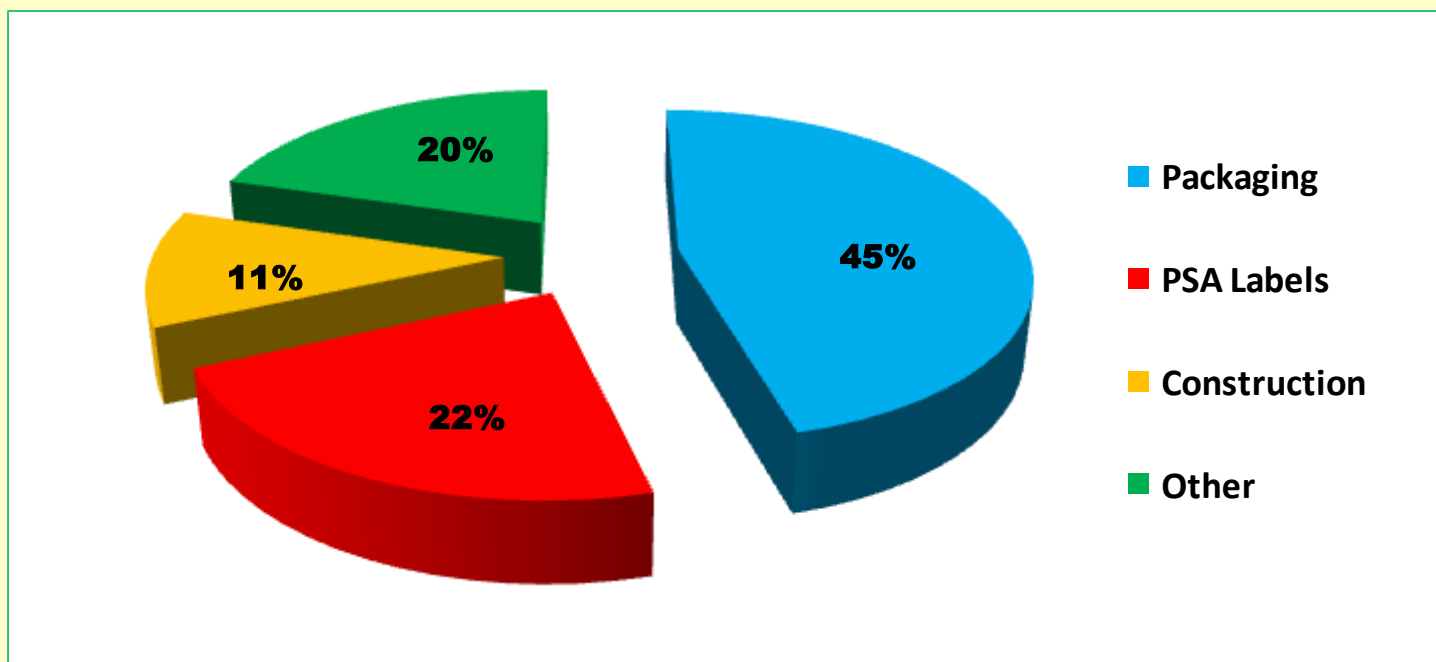
## *Gum Rosin + Tall-Oil Rosin = 325.000 MT*



## *European Rosin Adhesives and Sealants market*

*Gum Rosin + Tall-Oil Rosin = 130.000 MT*

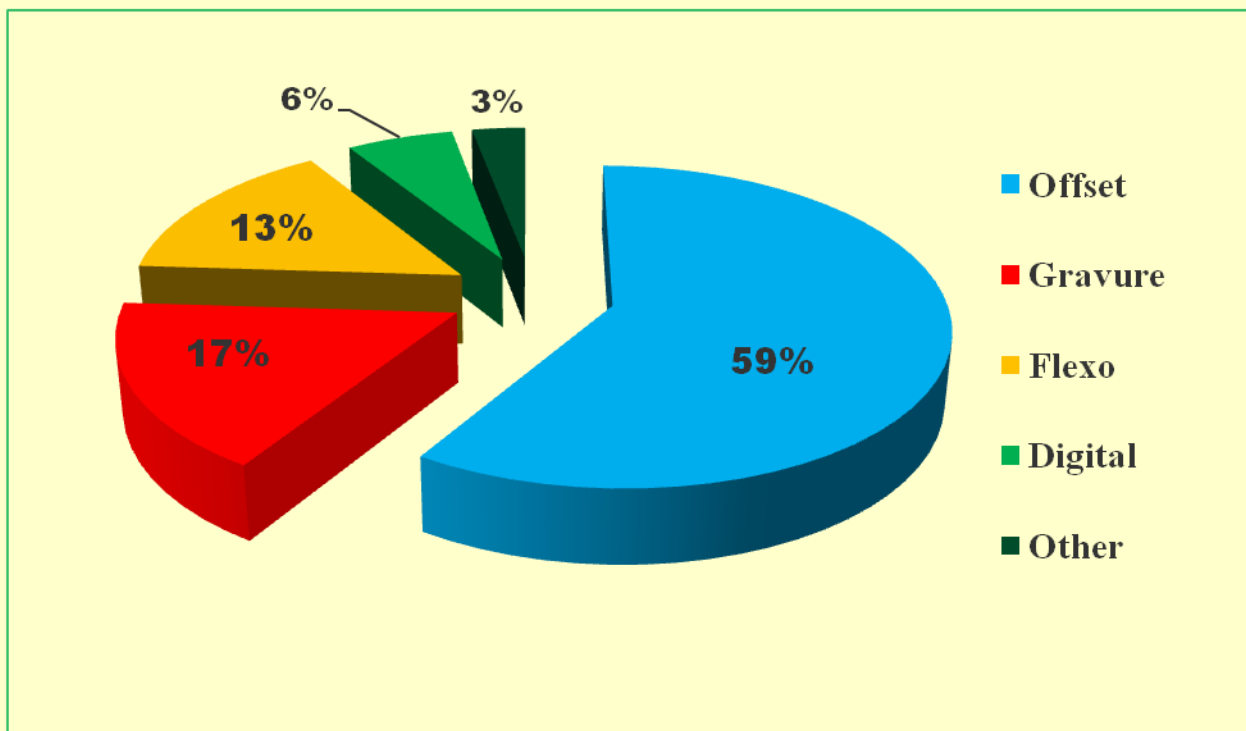
*Average annual market growth : 4-5%*



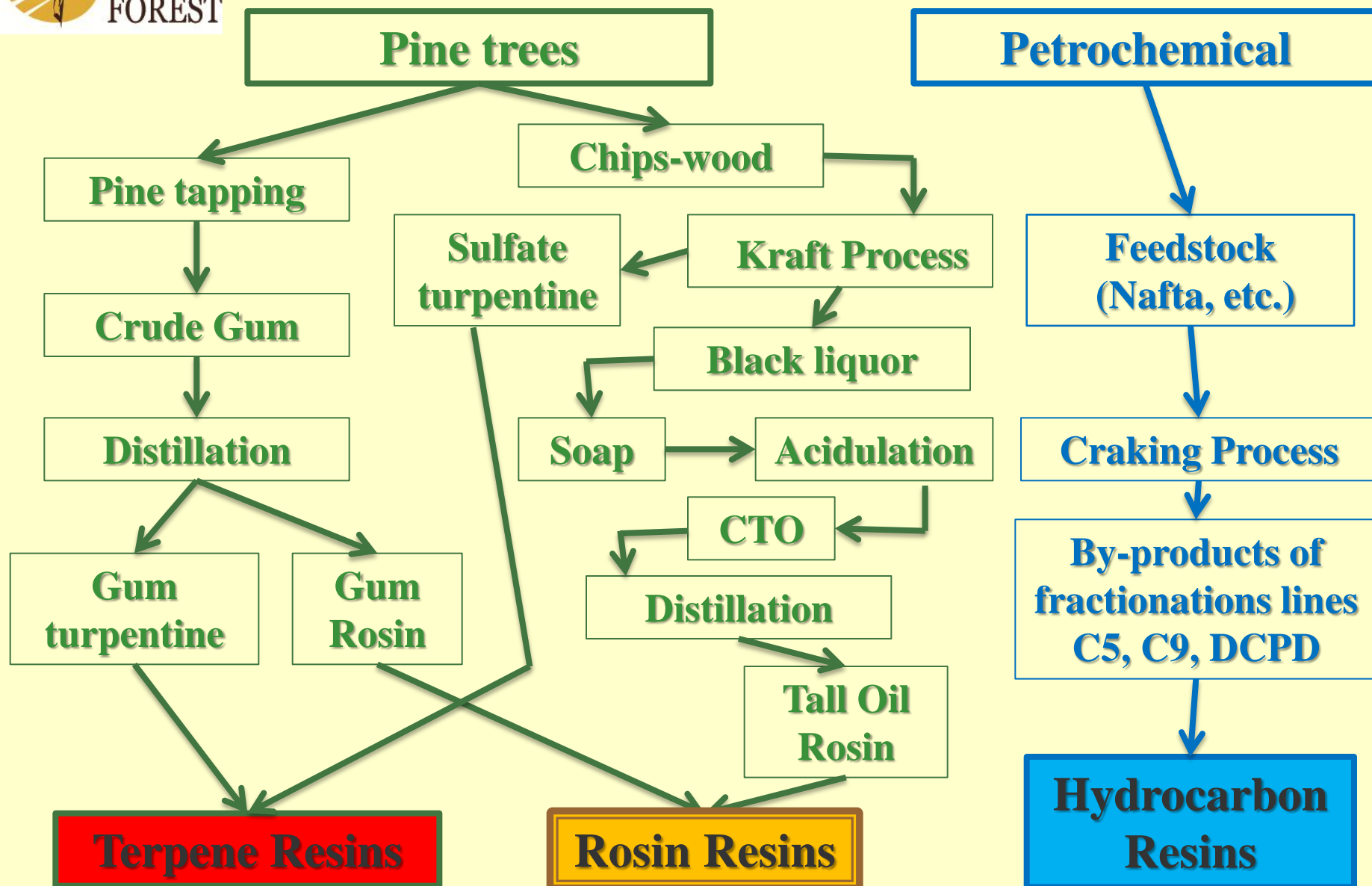
## *European Rosin Printing Inks market*

*Gum Rosin + Tall-Oil Rosin = 100.000 MT*

*Average annual market growth : 3-3,5%*



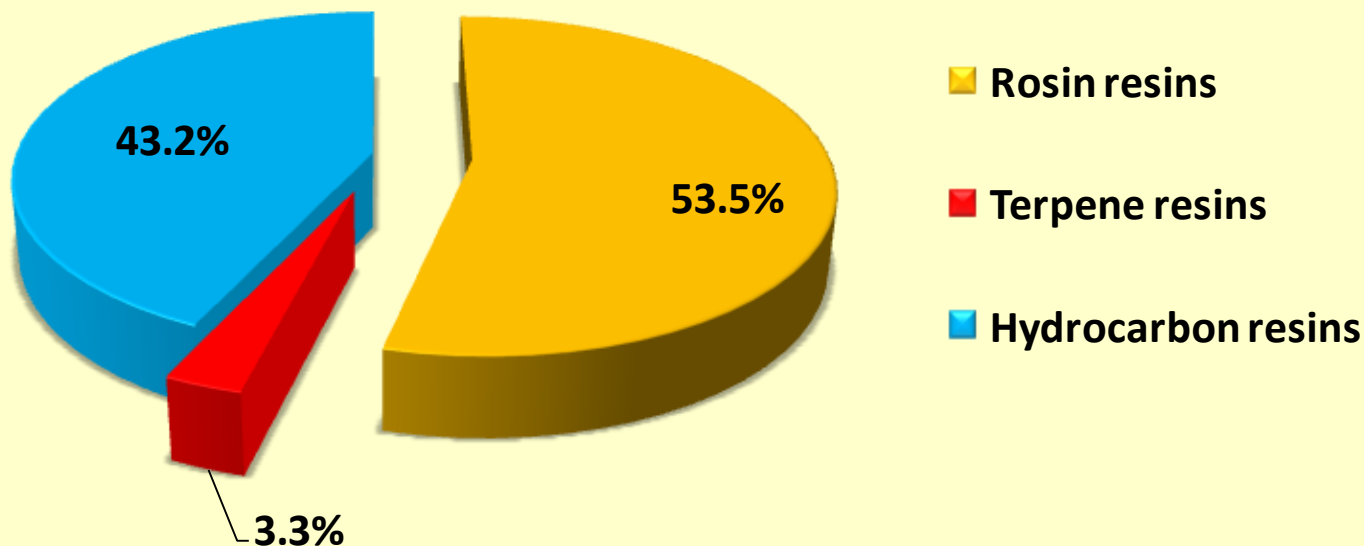
# ***Rosin Resins are not alone***



## *Global Resin Production (Forecast 2012)*

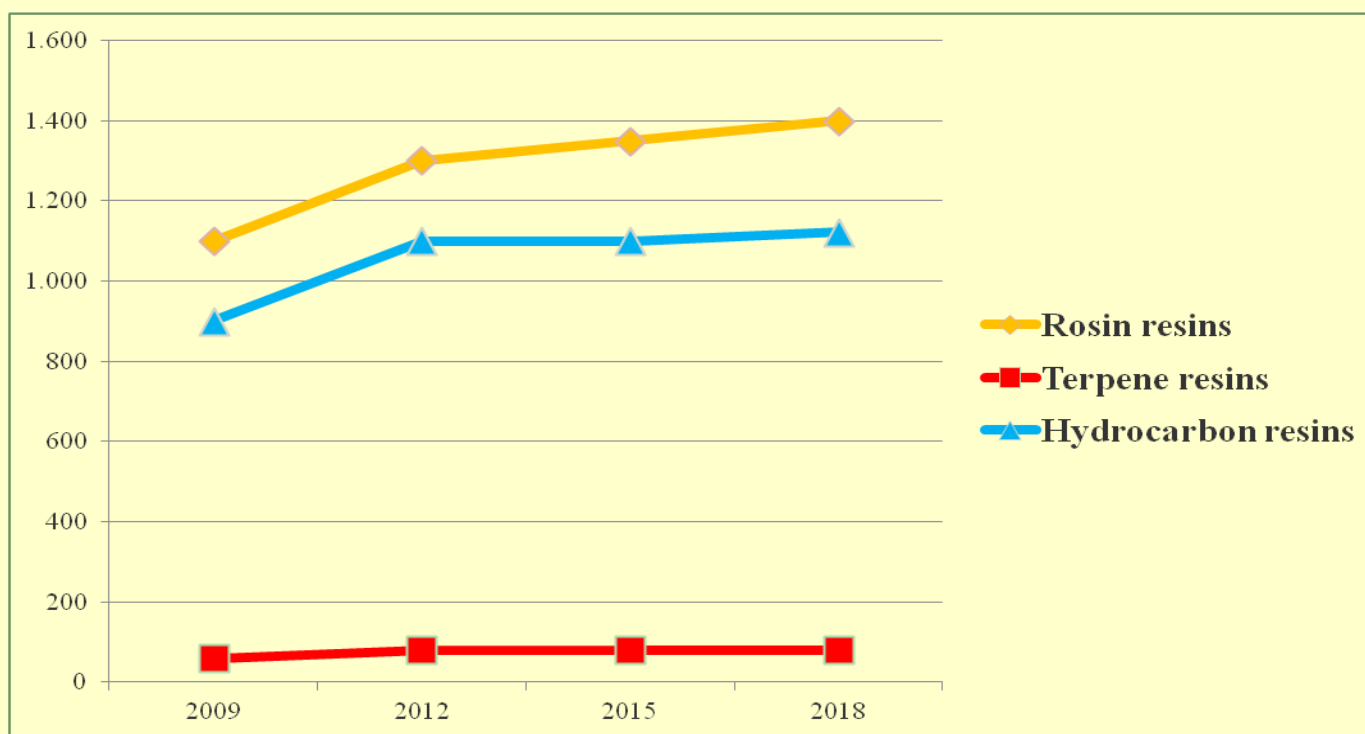
**Total world resin production = 2,430,000 MT**

- Rosin resins = 1,300,000 MT.
- Hydrocarbon resins = 1,050,000 MT.
- Terpene resins = 80,000 MT.



# 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%) →

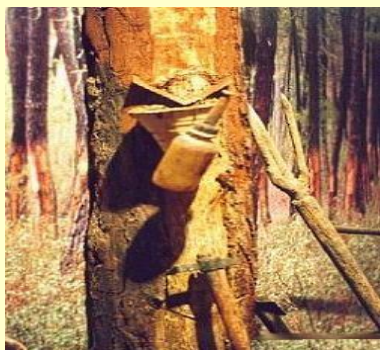


Source: PCA International Conference, Boston September 2012



# ***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***

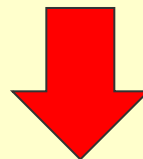
- Moderate growth of Gum Rosin production in the coming years (3% p.y.), but high risk of decline in the longer term.
- TOR production expected to remain flat because production of softwood kraft pulp also will be flat in the long term.
- Market demand for Rosin Resins 4 to 5 % p. y., leaded by emerging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