

DISPROPORTIONATION OF ROSIN FROM *PINUS ELLIOTTI*: OBTENTION OF EMULSIFIER FOR POLYMERIZATION

Mônica Zucolotto, Edmundo Cidade da Rocha and Maria Luiza A. von Holleben\*  
 Instituto de Química, UFRGS - Cx. P. 15003 - 91501-970 - Porto Alegre - RS

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The pulverized, molten or solubilized, rosin from *Pinus elliotti* was disproportionated by using S, NaI, S and I<sub>2</sub> or Pd/C as catalysts. The disproportionated rosin was saponified in aqueous or alcoholic KOH solution. The quality control of the resulting soaps revealed that disproportionation in the presence of Pd/C and of S and I<sub>2</sub> yields potassium abietate and dehydroabietate ratio in accordance to the industrial specifications, thus being adequate for use as emulsifiers.

**Keywords:** rosin; emulsifier; polymerization.

## INTRODUCTION

Rosin is a solid resinous material obtained from the oleoresin or stump wood of various *Pinus* species. It is a complex mixture of monocarboxylic acids of alkylated hydrophenanthrene nuclei, known as resin acids. These constituents are subdivided into two types: the abietic-type acids and the pimaric-type acids<sup>1</sup>.

The process of disproportionation of a rosin consists in the removal of hydrogen from abietic acids (I-IV) to form the aromatic nucleus of the dehydroabietic acid (V)<sup>1</sup>.

The carboxyl group of disproportionated rosin reacts with sodium or potassium hydroxides to form rosin soaps, which are used as emulsifiers in the manufacture of synthetic rubber latex, particularly of the butadiene-styrene copolymers<sup>1</sup>.

The known processes for the disproportionation of rosin consist in heating the resin with a catalyst, for example, S<sup>2</sup>, N-lithium ethylenediamine<sup>3</sup>, Pd/C<sup>4a-c</sup>, Pd, Co, Ni, Pt<sup>5</sup>, metal iodides<sup>6</sup>, arylthiols<sup>7</sup>, I<sub>2</sub><sup>8</sup> or S and I<sub>2</sub><sup>8</sup>. However, it is found that the known treatment of oleoresins leads to different results, depending on the botanical origins of the pines from

which they are obtained, methods of collection, methods and products used for the purification before distillation, and also, on the distillation process employed. It is also found that the geographic localization might have influence on the rosin composition for the same species<sup>8</sup>.

The present work reports a study on catalyst efficiency in rosin disproportionation of *Pinus elliotti* rosin originated from Rio Grande do Sul - Brasil, and compares the results with disproportionation of *Pinus maritima* rosin from France<sup>8</sup>.

## EXPERIMENTAL

## General Procedure

The molten rosin and the catalyst were heated in a two-neck round bottom flask equipped with a reflux condenser and a thermometer. The mixture was heated in an oil bath with vigorous magnetic stirring (see Table 1). After a reaction period varying from 30 min to 4h, the cooled mass was dissolved in light petroleum and the catalyst removed by filtration.

After evaporating the solvent the disproportionated rosin (1g) was saponified by treatment with aqueous or alcoholic 4M KOH solution (10 ml) at reflux temperature<sup>9</sup>.

The acid number of a saponified disproportionated rosin was determined by titration using 0,1N KOH solution<sup>10</sup>.

The amount of potassium abietate and potassium dehydroabietate present in the disproportionated rosin was determined by ultraviolet spectroscopy on a DMS 80 Intralab spectrometer using ethanol as a solvent<sup>11</sup>.

## RESULTS AND DISCUSSION

An important use of disproportionated rosin is in the form of the sodium or potassium soap, as an emulsifier in the production of butadiene-styrene copolymers<sup>1,12</sup>. The major requirement for a disproportionated rosin for this purpose is abietic acid content not exceeding 1% by weight and dehydroabietic acid content at least 50%<sup>8</sup>. The extent of rosin disproportionation can be determined with the aid of ultraviolet spectroscopy. A typical analysis for the various types of acids in a disproportionated rosin shows only two changes, the disappearance of the two double bonds of abietic-type acids, and the increase in dehydroabietic acid<sup>12</sup>. Moreover, the requirement for an emulsifier to be used in the manufacture of synthetic rubber latex is an acid number not exceeding 13 mg KOH/g<sup>13</sup>.

In this work, analyses were performed on disproportionated

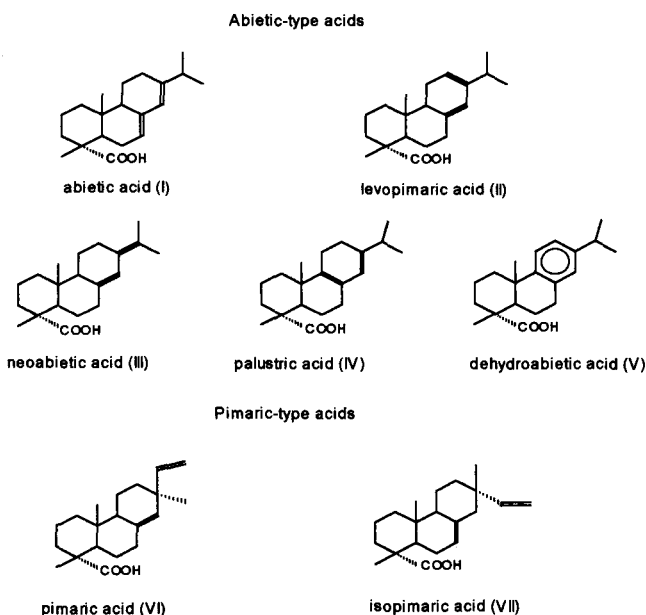


Figure 1. Structure of typical resin acids.

**Table 1.** Results of rosin disproportionation.

| No. | ROSIN (g)        | CATALYST (g)                    | REACTION TIME (hours) | % POTASSIUM DEHYDROABIETATE | % POTASSIUM ABIETATE | Acid NUMBER (mg KOH/g) |
|-----|------------------|---------------------------------|-----------------------|-----------------------------|----------------------|------------------------|
| 1   | 6.0 <sup>a</sup> | S<br>(0.68)                     | 3.0                   | 5.5                         | 7.9                  | zero                   |
| 2   | 6.0 <sup>a</sup> | NaI<br>(0.04)                   | 3.0                   | 38.8                        | 15.5                 | zero                   |
| 3   | 0.8 <sup>b</sup> | I <sub>2</sub><br>(0.74)        | 0.5                   | 28.1                        | 5.5                  | zero                   |
| 4   | 20 <sup>c</sup>  | S+I <sub>2</sub><br>(1.0+0.2)   | 4.0                   | 32.7                        | 4.5                  | 6.9                    |
| 5   | 10 <sup>a</sup>  | Pd/C<br>(0.5)                   | 4.0                   | 59.5                        | zero                 | zero                   |
| 6   | 20 <sup>a</sup>  | S+I <sub>2</sub><br>(0.64+0.18) | 4.0                   | 55.8                        | 0.2                  | zero                   |

a: at 200°C; b: at reflux of benzene (60 ml); c: at reflux of xylol (50 ml).

rosin in the form of the potassium salt and the results are shown in Table 1.

Thus, the rosin disproportionation in the presence of Pd/C (No.5) or S and I<sub>2</sub> (No.6), as presented in Table 1, shows abietic acid and dehydroabietic acid content according to the industrial specifications, being therefore adequate for use as emulsifiers.

The rosin disproportionation was also observed with benzene or xylol as solvents, using I<sub>2</sub> or S and I<sub>2</sub> as a catalyst.

The S + I<sub>2</sub> catalyst was used by Desalbres and Pouydebat to disproportionate *Pinus maritima* rosin<sup>8</sup>. They obtained 57% of dehydroabietic acid (V) and 0.2% of abietic acid (I) when xylol was used as a solvent. The same reaction carried out without any solvent gives 53.3% of V and 0.8% of I. The comparison of these results with those showed in Table 1 (No. 4 and 6) confirms the statement by these authors that the geographic and/or botanical origin of rosin might have influence on the efficiency of the method.

On the other hand, the yields of abietic acid and dehydroabietic acid in No. 1 to 4 (Table 1) might be improved by extending the reaction time and/or modifying the amount of catalyst.

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