

- [54] **REFINING OF FATTY ACIDS**
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[58] **Field of Search**..... **260/104, 97.7**

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[57] **ABSTRACT**

A method of refining impure fatty acids and fatty acid blends by removing impurities including sulphur containing impurities, boiling range of which is close and/or overlapping with the boiling range of the fatty acids and fatty acid blends.

10 Claims, No Drawings

REFINING OF FATTY ACIDS

This invention relates to removing impurities including sulfur containing impurities from fatty acids and blends of fatty acids.

The object of the present invention relates to removing of impurities the boiling range of which is close and/or overlapping with the boiling point of the fatty acid to be purified or with the boiling range of the fatty acid blends from which the impurities are to be removed.

The basic features of my invention are (1) to convert the fatty acids to their diol or polyol esters thus making them less volatile and (2) to remove the unesterified impurities by distillation under vacuum. After the impurities are removed, the esters can be converted to free fatty acids by hydrolysis or saponification. Moreover, the quality of the esters can be improved by other refining methods known to those skilled in the art; e.g. alkali refining or treatment with bleaching clays. The diol or polyol esters can also be converted by generally known methods to other derivatives of fatty acids; e.g. fatty alcohols, fatty amides, fatty nitriles and fatty amines.

Fatty acids and fatty acid blends which can be refined according to this invention are natural and synthetic essentially aliphatic carboxyl acids containing from 6 to 22 carbon atoms in each molecule.

An important source of commercial fatty and rosin acids is a material known as tall oil. Crude tall oil is obtained as a byproduct from manufacturing or wood pulp according to the sulfate or Kraft process. It is a dark brown viscous liquid or semisolid and generally consists of 18 carbon atom fatty acids, rosin acids, unsaponifiable materials, a smaller amount of 16 carbon atom fatty acids and still smaller amounts of other carboxylic acids. Crude tall oil contains also some unidentified sulfur compounds which are largely responsible for the unpleasant odor and limited utility of crude tall oil. The present invention is directed to a method for removing the sulfur containing impurities in order to produce a crude tall oil product having a high acid number.

The most practiced process for refining of crude tall oil is fractionated distillation under vacuum. By this process it is customary to obtain the following fractions which are listed in the order of increasing ranges of boiling temperatures.

1. Light ends or tall oil heads.
2. Tall oil fatty acids.
3. Distilled tall oil.
4. Tall oil rosin
5. Tall oil pitch.

Fractionated distillation under vacuum as presently practiced by a number of commercial plants is aimed at removing the unsaponifiable and other undesirable materials as tall oil heads (light ends) and bottoms (tall oil pitch) fractions and at separating of fatty acids from rosin acids. Thus, Fraction No. 2 is a relatively pure blend of mainly 18 carbon atom unsaturated fatty acids. Fraction No. 3 is a blend of fatty and rosin acids relatively free from unsaponifiable material and other impurities, and Fraction No. 4 is a relatively pure blend of different rosin acids, while most of the undesirable impurities are concentrated in Fractions No. 1 and No. 5. A problem with Fraction No. 1 is associated with the fact that the boiling range of a substantial amount of the lower boiling impurities and 16 carbon atom fatty

acids overlap and is also close to the boiling range of 18 carbon atom fatty acids. Consequently, to obtain a good quality fatty acid fraction (Fraction No. 2), all 16 carbon atom fatty acids and a sizable amount of 18 carbon atom fatty acids have to be removed with Fraction No. 1 (tall oil heads fraction) which usually amounts to 10 – 15 percent by weight of the crude tall oil charged to the vacuum distillation columns. This tall oil heads fraction normally consists of from 50 – 85 percent of fatty acids containing 14 to 18 carbon atoms but is of very low value and utility because of the undesirable impurities especially sulfur containing compounds. For instance, it is not practical to upgrade the tall oil heads fraction by processes involving catalytic hydrogenation because the sulfur compounds tend to poison the commonly used hydrogenation catalysts.

An advantage of the present invention as shown in Example No. 1 is that low sulfur content fatty acids which are also low in unsaponifiable materials can be obtained from tall oil heads fraction by practicing the teaching of this invention. Moreover, it is also shown that the refined propylene glycol diester of tall oil heads fatty acids can be converted to a fatty acid nitrile and that this nitrile can be catalytically hydrogenated to obtain a primary fatty amine. Such a conversion is not possible of unrefined tall oil heads because of the excessive amount of sulfur present.

Another fatty acid blend which contains also branched chain acids and fatty acids having six member carbon ring structures in their molecules is so-called "Monomer Acid" which is obtained as a by-product from clay catalyzed polymerization of unsaturated carboxylic acids. This Monomer Acid is the lower boiling fraction which is removed, usually under vacuum in a thin film evaporator, from the blend of polymerized unsaturated fatty acids leaving the residue which consists of mainly dimerized fatty acids and is called "Dimer Acid." The Monomer Acid is high in unsaponifiable material and contains some sulfur compounds and other impurities.

It is shown in Example No. 2 that the teachings of my invention can be used to refine this Monomer Acid.

The examples are presented to illustrate the invention and to teach its practice to those skilled in the art but are not intended to limit the scope of the invention.

EXAMPLE NO. 1

Commercial tall oil heads having an acid number of 153 were esterified with an equivalent amount plus 10 percent excess of propylene glycol by distilling out the water of reaction at 480°F. to make propylene glycol diester. The unsaponifiable material was stripped from the crude propylene glycol diester by subjecting 1117.3 grams of it to vacuum distillation at 480°F. and 1.2 mm Hg. absolute. 356 grams of distillate and 742 grams of residue were obtained in this manner.

A part of the residue was saponified by boiling with a NaOH solution in water. After saponification, the soap solution was acidified with diluted sulfuric acid, the oily fatty acid layer separated, washed with water, dried and distilled under vacuum at 480°F. and 1 mm Hg. absolute. The analyses of the fractions were as follows:

Material	Acid No.	Sulfur Content ppm
Starting tall oil heads	153	788
Distillate—Unsaponifiable material stripped from propylene glycol diester	29	1783
Residue—Tall oil heads fatty acids after removal of unsaponifiables, saponification and distillation	205	37

Another part of the residue (tall oil heads/propylene glycol diester) was converted to a nitrile by adding 0.5 percent of zinc oxide and sparging it with anhydrous ammonia at 560°F. until the acid number of the material decreased to 3.4.

The crude nitrile was distilled under vacuum (428°F., 2mm Hg. absolute.) which resulted in a distilled nitrile having an acid no. of 0.3.

The distilled nitrile was mixed with 0.75 percent of chromium promoted Raney nickel catalyst and hydrogenated in a Parr autoclave under 40 psi ammonia and 600 psi. of hydrogen and at 175°F. The amine number of the crude hydrogenated product was 206. The amine number of the same product but distilled under vacuum at 480°F. and 2mm Hg. absolute was 220.

EXAMPLE NO. 2

This example was carried out with a commercial product called AZ Monomer Acid. This product is manufactured and marketed by AZ Products Inc. It is obtained from clay catalyzed polymerization of unsaturated 18 carbon atom fatty acid and consists of mainly monomer fatty acids. 644 grams of AZ Monomer Acid, having an acid number of 174 were esterified with 71.3 grams of glycerine at 480°F. until the acid number decreased to 4.5. The impurities were removed from the above triglyceride by exposing it to vacuum distillation at 530°F. and 1.5 mm Hg. absolute. The residual ester was saponified and the fatty acids obtained distilled at 390°F. and 1.7 mm Hg. absolute. The fatty acids refined in this manner had an acid number of 201.

I claim:

1. A method of refining impure fatty acids containing 6 to 22 carbon atoms comprising the steps of decreasing the volatility of said fatty acids by esterifying said fatty acids with hydroxyl containing organic com-

pounds selected from the group consisting of ethylene glycol, propylene glycol, glycerine, sorbitol, mannitol, pentaerythritol, neopentyl glycol, hexylene glycol butane diol, diethylene glycol, dipropylene glycol, ethylene oxide and propylene oxide, distilling out the unesterified compounds under vacuum and recovering purified fatty acids from the residue.

2. A method as defined in claim 1, wherein said recovery step includes recovering esters of said purified fatty acids from the residue.

3. A method as defined in claim 1, wherein said recovery step includes recovering the free fatty acids of said purified fatty acids from the residue.

4. A method as defined in claim 1, including the additional step of converting the purified fatty acids to fatty nitriles.

5. A method as defined in claim 2, including the additional steps of converting the purified fatty acid esters to fatty nitriles and catalytically hydrogenating the fatty nitriles to the corresponding amines.

6. A method of refining tall oil heads fatty acids, containing more than 100 p.p.m. sulfur comprising the steps of decreasing the volatility of said tall oil heads fatty acids by esterifying said tall heads fatty acids with hydroxyl containing organic compounds selected from the group consisting of ethylene glycol, propylene glycol, glycerine, sorbitol, mannitol, pentaerythritol, neopentyl glycol, hexylene glycol, butane diol, diethylene glycol, dipropylene glycol, ethylene oxide and propylene oxide, distilling out the unesterified compounds under vacuum and recovering purified tall oil heads fatty acids containing less than 50 p.p.m. sulfur from the residue.

7. A method as defined in claim 6, wherein said recovery step includes recovering esters of said purified tall oil heads fatty acids from the residue.

8. A method as defined in claim 6, wherein said recovery step includes recovering free fatty acids of said purified tall oil heads fatty acids.

9. A method as defined in claim 6, including the additional step of converting the purified tall oil heads fatty acids to tall oil heads fatty nitriles.

10. A method as defined in claim 7, including the additional steps of converting the purified tall oil heads fatty acids esters to fatty nitriles and catalytically hydrogenating the fatty nitriles to their corresponding amines.

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