

TALL OIL PRODUCTION AND PROCESSING

Tall oil is a mixture of mainly acidic compounds found, like turpentine, in pine trees and obtained as a by-product of the pulp and paper industry. It is used as a resin in many different industries, including mining, paper manufacture, paint manufacture and synthetic rubber manufacture.

It is extracted at the pulp and paper mill, and undergoes the first two processing steps there.

Step 1 - Extraction of tall oil soap

The "black liquor" from the paper making process is concentrated and left to settle. The top layer is known as "tall oil soap", and is skimmed off. The rest is recycled for further use in paper making.

Step2 - Production of crude tall oil

The tall oil soap is reacted with acid to form crude tall oil. The following reaction occurs:



The acids formed from this reaction, along with small quantities of other compounds of similar volatility, make up the crude tall oil.

All crude tall oil produced in New Zealand is then sent to a plant in Mt. Maunganui to complete processing.

Step 3 - Crude tall oil distillation

The oil is distilled into five components with different boiling points: heads (which boils first), then fatty acids, distilled tall oil (a mixture of fatty and resin acids), resin acids (collectively known as rosin) and pitch (the residue). All of these can be used in various industries as is, but some of the rosin is also further processed on site.

Step 4 - Production of rosin paper size

"Paper size" is the substance that stops all paper from behaving like blotting paper. It is produced by reacting rosin with maleic or fumaric acid and then KOH, and mixing the resulting compound with water.

All stages of the process are monitored by the laboratory to ensure quality is consistent. Various measures are also in place to ensure safety, as tall oil is highly flammable (and in its soap form is slippery as well).

INTRODUCTION

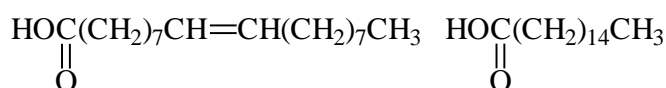
Tall oil is one of the two commercially important by-products of the paper making process, the other being turpentine (see article). It is produced by coniferous trees, and put to a wide variety of end uses. In the fuel crisis much research was done into the use of tall oil as an alternative fuel, and hormones were developed that made young trees produce 5 to 10 times their normal tall oil yield.

Composition

Tall oil, also known as 'tallol' or 'liquid resin', has three major components: resin acids, fatty acids and unsaponifiables (also known as "neutral compounds"). A typical composition of tall oil from the Kinleith Mill in Tokoroa is 49% resin acids, 32% fatty acids and 19% unsaponifiables.

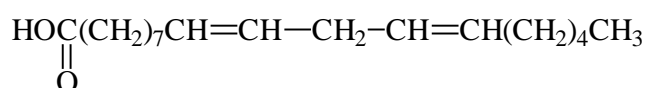
Fatty acids

These are the long chain monocarboxylic acids which make up fats and oils (see "edible fats and oils" article), and are found in both hardwoods and softwoods. The main fatty acids in tall oil are oleic, linoleic and palmitic acids.



oleic acid

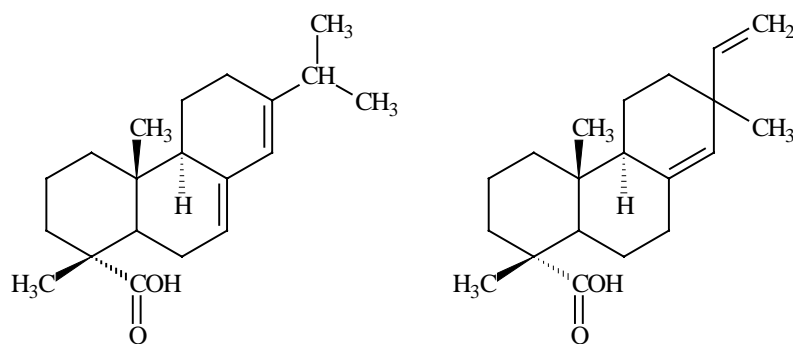
palmitic



linoleic acid

Resin acids

Resin acids are a mixture of organic acids derived from oxidation and polymerisation reactions of terpenes that are found in softwoods, hardwoods and conifers. The main resin acid in tall oil is abietic acid, but abietic acid derivatives and other acids such as pimaric acid are also found in noticeable quantities.

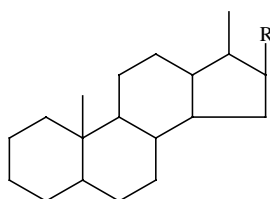


abietic acid

pimaric acid

Unsaponifiables

These are neutral compounds which do not react with sodium hydroxide to form salts, and thus cannot be turned into "soap". These compounds include hydrocarbons, higher alcohols and sterols. Sterols are steroids incorporating a hydroxy group. Steroids are compounds of the general form given below:

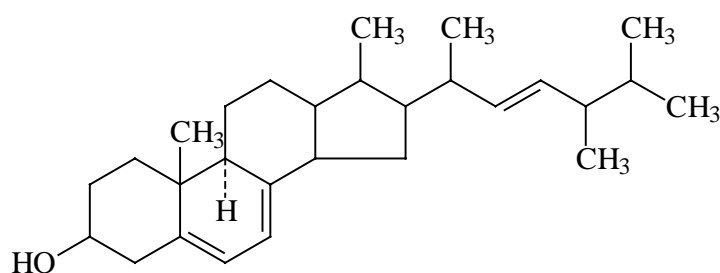


They have no present use in industry, so large proportions in tall oil are not desirable.

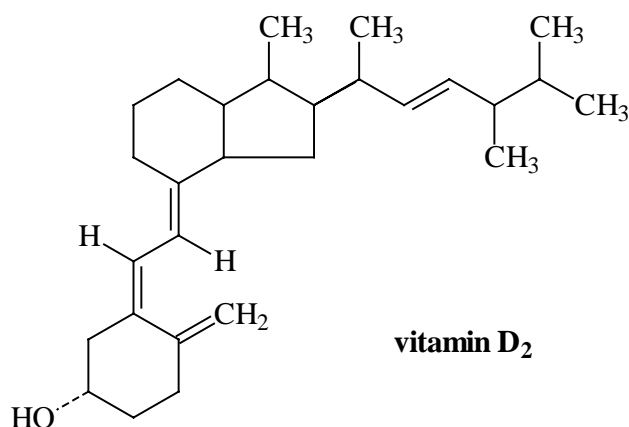
Uses

Tall oil itself has a variety of uses in industry. It is used as a frothing agent in the flotation process for reclaiming low grade copper-, lead- and zinc-bearing ores, and as a solvent or wetting agent in a variety of textile and synthetic fibre manufacturing processes. The distilled fatty acids are used in soaps, detergents and disinfectants and as a base for lubricating greases, textile oils, cutting oils and metal polishes. They are also used as drying agents in paint, although synthetic substances are becoming widely used (see article). The fatty acids are unsaturated and on exposure to air undergo autoxidation and polymerisation to form resin-like materials which form a tough protective coating. Resin acids are used in rubber polymerisation and compounding, as size to impart water resistance to paper (see below), and in adhesives and printing inks. Resin acids are the major component of a substance known as rosin, which is used by musicians to improve the grip of bows used for string instruments.

One of the common sterols found in the unsaponifiable portion of tall oil is ergosterol, a compound which forms a number of products, including vitamin D₂ (caloiferol), on irradiation with ultraviolet light. If a suitable process to carry out this reaction commercially is found then the unsaponifiable fraction of tall oil may also have a use in the future.



ergosterol



vitamin D₂

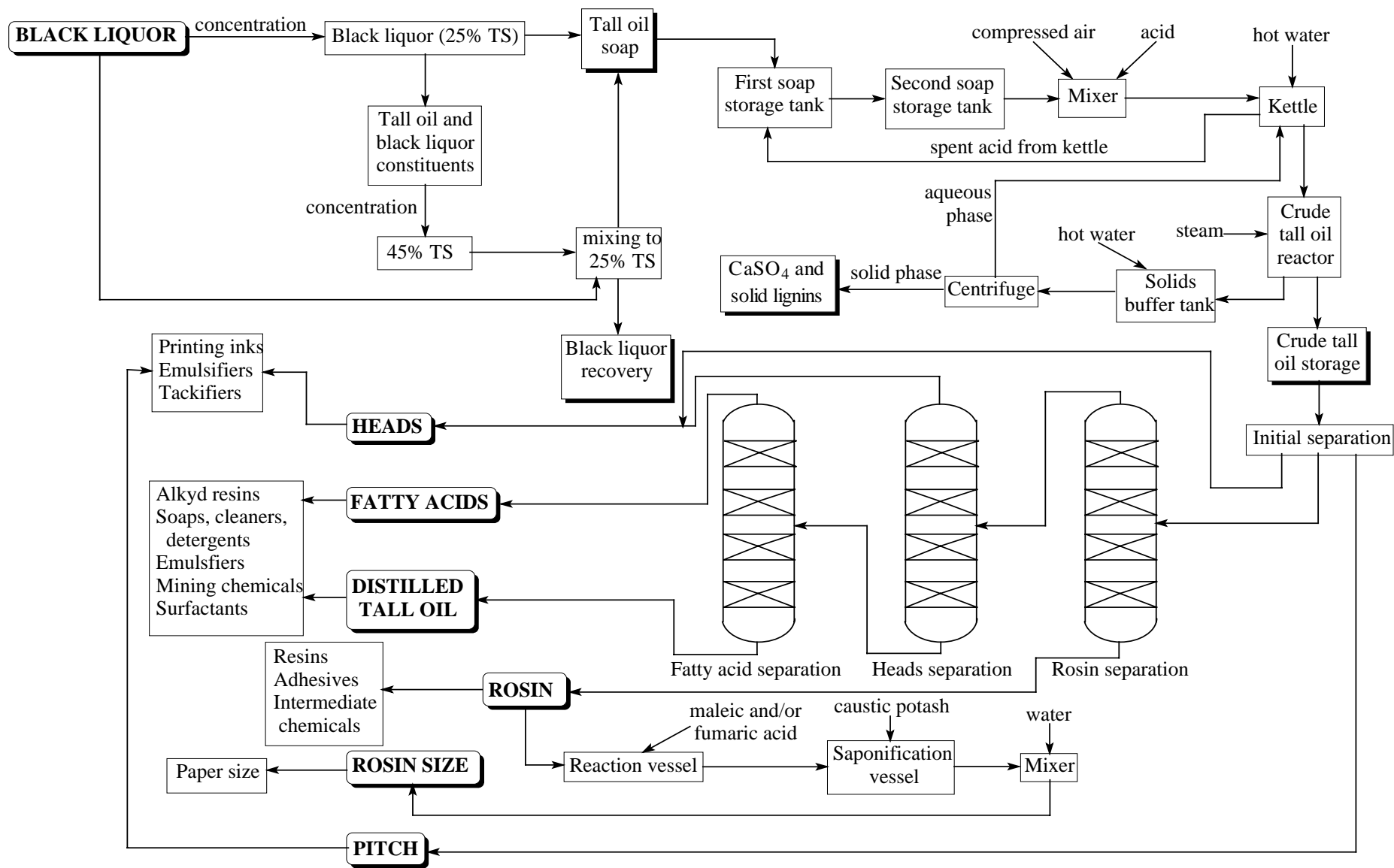


Figure 1 - The tall oil process

EXTRACTION AND PROCESSING OF TALL OIL

Tall oil, as has already been stated, is a by-product of the pulp and paper industry. It is produced on two sites: crude tall oil is extracted by kraft wood pulping mills, and then this crude is processed off-site. Until 1983 it was sent overseas, mostly to Japan, for processing. In 1980 work began on a plant in New Zealand to process this oil, and in 1983 Pine Chemicals Ltd. (which also process turpentine) began operation. All New Zealand and a small quantity of Australian crude tall oil is now processed in Mt. Maunganui by this company - now known as Eka Chemicals (NZ) Ltd.

The entire extraction and processing procedure is summarised in **Figure 1**.

Step 1 - Extraction of Tall Oil Soap

"Black liquor" from kraft pulping (see article) contains sodium salts of tall oil ("tall oil soap"), sodium lignates and excess NaOH, Na₂S and Na₂SO₄. The initial concentration of the black liquor is 15% TS¹, with a tall oil concentration of 1.35 g per 100 g total solids. The solubility of tall oil soap varies with TS value: up to 25% TS the tall oil soap solubility gradually decreases, due to a common ion effect caused by the Na⁺ ions; above 25% the concentrated lignates cause it to become more soluble, and the increasing viscosity slows down the rate of separation of the soap on top of the liquor from which it is skimmed off. For this reason the soap is skimmed off when the liquor is 25% TS.

The weak liquor from the digester is evaporated to 25% TS and then passed to the skim tank where the soap is skimmed off. The underflow from this tank is concentrated by evaporation to 45% and some is mixed with more weak liquor to give 25% TS again. The soap from this is taken off from a second skimming tank from which the underflow goes to the recovery boilers for recycling. This underflow contains about 0.58 g / 100g TS of tall oil which is lost. All the above processes take place at elevated temperatures (60-100°C) in order to keep all components as fluid as possible and thus able to be pumped.

Step 2 - Production of Crude Tall Oil

The crude tall oil soap passes from the pulp mill into the first soap storage tank where it is washed with spent acid (see below). It is then pumped to a second soap storage tank where it remains until there is enough tall oil soap for a 'cook', and approximately once a day a measured amount of this soap is placed in the reaction kettle (made of monel or high-nickel steel). At this stage the soap contains a number of impurities, principally sodium lignates, and inorganic components from the black liquor (NaOH, Na₂S and some Ca²⁺ from the slaking process).

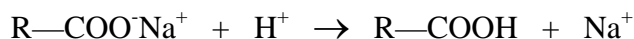
After being heated to boiling by steam injection the concentrated sulphuric acid is added to the soap. The heat of dilution of the acid helps attain the desired temperature. The acid is added to the soap so that there is never an excess of acid. The reaction mixture is constantly heated by steam and agitated by stirrers to give uniform acid concentration. The mixture is 'cooked' for almost two hours until the desired pH (about 4.0) is attained, and then left to

¹The concentration of the various solids in the liquor is calculated as "total solids" (TS). These solids are tall oil soap, sodium lignates, NaOH, Na₂S and Na₂SO₄.

settle overnight. The corrosiveness of the sulphuric acid means that all metal pipes etc. must be made of stainless steel.

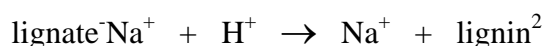
The principle reactions occurring are as follows.

Tall oil



This is the most important reaction occurring. Here the ionic soap is converted into a carboxylic acid and thus an oil. This reaction applies to both fatty and resin acids and ensures that these are present in essentially molecular form in the oil.

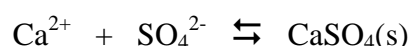
Lignins



This acidulation also causes the sodium lignates present in the soap to be precipitated. During the settling, these form an emulsion between the aqueous and oil phases.

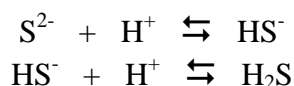
Calcium ions

The calcium present in the soap forms a precipitate with the sulphate ions provided by the acid, which falls to the bottom of the tank during the settling period as follows:



Sulphide ions

In the alkaline black liquor and tall oil soap, sulphide ions are present in appreciable concentrations. On acidification, the majority of these would be protonated to form H₂S:



Some, at least, of this H₂S comes off the reaction mixture. Therefore, there is an ever present danger from H₂S fumes in the tall oil plant.

The mixture is left overnight to settle, and then the various phases (crude tall oil, lignin emulsion and aqueous phase) are removed using a variable position pump. The phases are treated as follows:

- The crude tall oil is pumped to hot storage, from where it is transported to Mt. Maunganui for further processing.
- The lignin emulsion layer, which contains dissolved tall oil, is recycled to extract the oil. It is pumped along with the calcium sulphate and lignin solids slurry at the bottom of the reaction kettle to a buffer tank where it is mixed with hot water. From there it passes to a centrifuge feed tank and thence to a centrifuge (after having been

²Lignin is composed of complex polymers containing many aromatic groups.

steam heated). Here the CaSO_4 is removed and dumped along with the solid lignins. The rest is pumped back into the reaction kettle to mix with the next batch of soap, as it is not pure enough to be sent straight to tall oil storage.

- The aqueous phase is the spent acid mentioned earlier. It is used for the washing of the incoming tall oil in the first storage tank, and it eventually passes to the recovery boilers. It contains sodium ions, sulphide ions, sulphate ions and bisulphate ions, and some soap and lignin.

The normal yield is about 15-20 kg of tall oil per tonne of air-dried pulp, but for slow-growing species up to 100 kg can be obtained.

Factors affecting quality of CTO

Wood type has an obvious bearing on the quality of tall oil - different woods produce different proportions of resin acids, fatty acids and unsaponifiables, and a different total amount of oil. In general, older and slower growing trees produce more resin acids (since they have more heartwood).

The conditions under which the acidification is carried out has a bearing on the quality of the oil. Acid number (a measure of the quantity of resin and fatty acids in the oil) may drop due to decarboxylation or esterification, both of which are favoured by the presence of strong acid. Polymerisation, which only reduces the acid number when it occurs through the carboxylate groups, is also favoured by concentrated sulphuric acid. This in itself does not reduce acid number (unless polymerisation is carried out through the carboxylate group as in proteins), but does make the oil more viscous and increases the proportion of oil in the lignin emulsion. These factors mean that using H_2SO_4 as the acidifying agent lowers the quality of the oil. However the only practical alternative would be boric acid ($\text{B}(\text{OH})_3$), which is a suitable weaker acid, but it is expensive and interferes with the paper making process. For this reason H_2SO_4 is still used. In default of a suitably cheap and practical weak acid, it has been found that dilution of the soap, before acidification, in the ratio of 8 parts soap to 1 part water, produces significant yield improvement and requires less mixing and less acid to reach the desired pH.

Tall oil is used by living wood cells (as well as bacteria, fungi etc.) as a source of energy. This means that the trees should be processed as soon as possible after felling to ensure the maximum possible yield of oil is obtained.

The oil storage time and temperature have an influence on the quality of the tall oil. Temperatures above 60°C favour the formation of esters between the acids and the various alcohols (sterols, higher alcohols) present in the unsaponifiable part of the oil. The longer the oil is left, the further this esterification proceeds. A storage temperature of 55°C (used at Kinleith) prevents the oil from solidifying while allowing an acceptable low rate of degradation.

Step 3 - Crude Tall Oil Distillation

The crude tall oil is a mixture of fatty acids and resin acids along with various other materials such as unsaponifiables. The single most important characterisation parameter for tall oil is its acid number, which for the New Zealand product averages around 150 to 155. Given the acid number and concentration of one of the major acid types, then the concentration of the

other can be estimated by a simple calculation. General practise is to analyse for acid number and resin acids, then to calculate the fatty acid content by the formula:

$$FA = \frac{AN - 1.55RA - 1.8OA}{1.986}$$

where: FA = fatty acid concentration

AN = acid number

RA = resin acid concentration

OA = oxi acid concentration

all on a dry basis.

This formula is based on the fact that pure fatty acids have an average acid number of 198.6 whilst pure resin acids have an average acid number of 185.5. The oxi acids are a species which give repeatable analytical results and which are a useful parameter to measure and to correlate performance with, but whose existence and nature is under question.

On average, New Zealand crude tall oil is about 45% resin acids and 32% fatty acids. The fatty acids are generally more volatile than the resin acids and hence these two products can be separated to a large degree by distillation. The impurities also have volatility differences so that they too can be distilled off first (the light ends) or left behind as residues at the end of distillation. There are, however, some overlaps in volatility so that perfect separation is not possible. The heavier fatty acids and the lighter resin acids cannot be separated by distillation alone and hence there is an intermediate distillation cut called DTO (distilled tall oil) which consists of about 30% resin acids, 65% fatty acids and perhaps 5% of other substances. A distillation of CTO therefore yields effectively five streams or cuts. For a typical New Zealand crude the yields from a distillation might approximate to:

- Heads 10%
- Fatty acids 20%
- DTO 5%
- Resin acids 40%
- Residues (Pitch) 25%

In theory, the distillation could be effected on a batch basis with four cuts taken off at increasing temperature of the still, and a residue left behind. In practice the distillation is carried out as a continuous operation comprising the following five separation stages.

Dehydration

Removal of water and volailes from the crude tall oil feedstock yielding a heads stream.

Depitching

Removal of nonvolatile materials from the crude tall oil to provide a residue stream and to minimise operating problems in subsequent stages.

Rosin separation

Recovery of rosin as the bottoms product in the first distillation column which is about 40 m tall by 1.5 m diameter.

Heads separation

Removal of impurities (heads) from the overheads coming from the rosin column prior to recovering the fatty acids. These heads are the top product from the second distillation column of about 30 m tall by 0.6 m diameter.

Fatty acid separation

Recovery of high grade fatty acids as top product and distilled tall oil as bottoms in the last distillation column. This column is about 40 m tall by 0.9 m diameter.

Each column has a feed and top and bottom offtakes, providing two fractions from each stage of the distillation process. The higher volatility materials will gravitate to the top fraction and the lower volatility substances to the bottom. One fraction from each stage provides the feed to the next stage whilst the other fraction yields either a product or a recycle or residue stream.

Heat is provided to the columns using hot oil fed to reboilers on the bottoms streams whilst some heat is recovered using condensers on the tops streams. The columns are operated under partial reflux to increase the driving force for separation and there is also provision for recycling material from later stages back to earlier units to attain a more precise distillation cut.

The major processing feature of the distillation is that the tall oil and its products are very sensitive to heat. Excessive temperature or holding at temperature for long periods of time will cause degradation and subsequent loss of product, or at least a discoloured product. This is countered by the use of very high vacuum for all the distillation columns and Luwa thin film wiped evaporators as the reboilers. These measures minimise the operating temperatures experienced by the fluids and the time to which they are exposed to heat. The high vacuum operation also helps in the distillation by exaggerating the relative volatility differences between the components, whilst also minimising the thermal energy requirements of the process.

The net result of the distillation process is the production of three main products: fatty acids, DTO and rosin, plus some quantities of residue (pitch) and a Heads stream. There is a reasonable market for the fatty acids and DTO, but a poor market for rosin. The main value of rosin is that it can be used to manufacture rosin size and a variety of other specialty substances such as rosin oils and tackifiers. In preparation of those rosin based products, proportions of DTO, pitch and heads can also be utilised to maximise the saleable product recovered from the CTO. Any pitch and heads which cannot be incorporated into saleable products can be used as a fuel in the tall oil plant itself.

Step 4 - Production of Rosin Paper Size

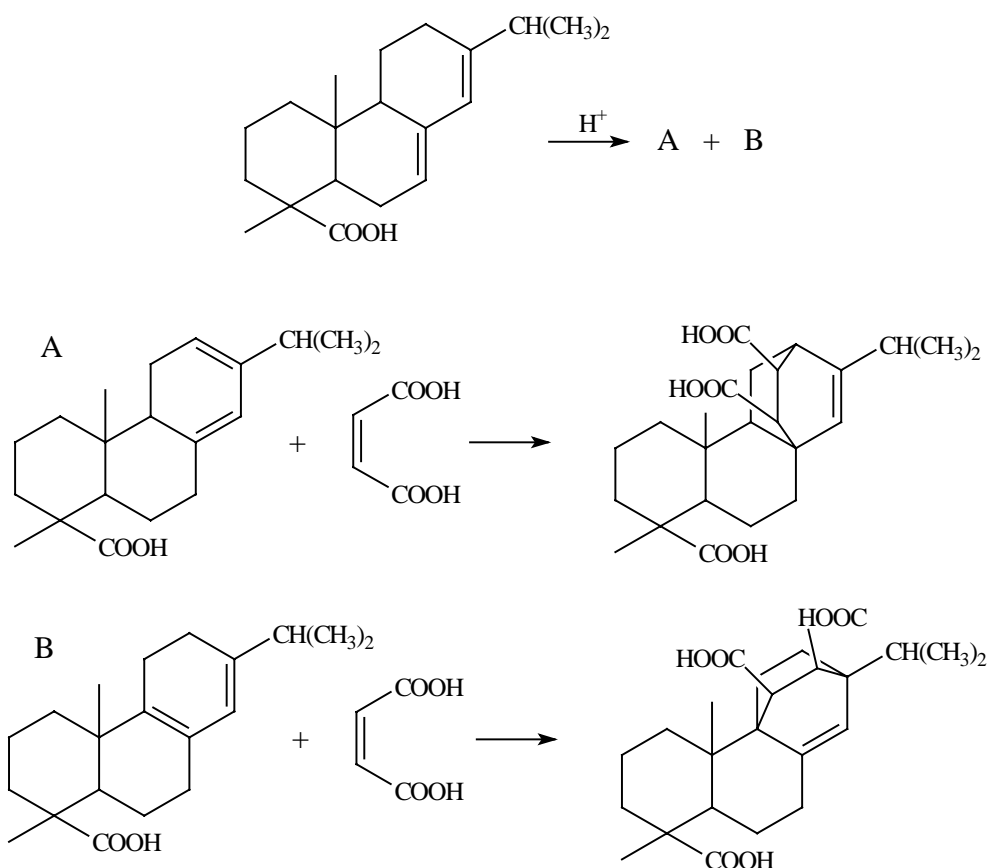
"Paper size" is a material applied to paper to make the surface less absorbent to ink. Without sizing the paper would tend to act as a blotting paper and would be useless for printing or writing. Large quantities of size used to be imported, mainly from Japan, until the Pine Chemicals plant was commissioned.

The plant makes sizes by reacting rosin from the CTO distillation with maleic and/or fumaric acid (*cis*- and *trans*- $\text{HO}_2\text{C}-\text{CH}=\text{CH}-\text{CO}_2\text{H}$ respectively) to give a fortified rosin which has a much higher softening point. The fortified rosin is then saponified, with caustic potash, and mixed with water to give soap of either 50% or 70% wt. of saponified rosin to make size.

Several different grades of size can be produced by varying the recipe with the water content of the finished product.

The size operation is a batch process requiring about 10 hours to complete the process. It has two steps, as outlined above, which are carried out in separate vessels and the sequencing and loading of correct quantities is assisted by the use of computer control.

The chemistry of these processes involves a tautomeric rearrangement of the main component of rosin, abietic acid, on treatment with maleic acid to give isomers in which both double bonds are in the same ring. These then undergo a Diels-Alder reaction. Saponification will give the potassium salts.



PLANT SAFETY

There are four main hazards that workers have to be aware of during the extraction and processing of tall oil. These are H_2S fumes, the slipperiness of the soap, the flammability of the oil, and the corrosive nature of the strong mineral acids being handled. The measures taken to minimise the hazard due to oil flammability are described below.

Flammability

Many of the materials handled in the processing of turpentine and tall oil are classed as dangerous goods class 3a or 3b (flammable liquids) and the design and operation of the plant is governed by the requirements of the appropriate dangerous goods regulations. These specify such matters as the area classification for electrical equipment, restriction of ignition

sources, spacing and siting of vessels and vents, compounding and fire protection/fighting equipment.

With the operation of the distillation columns under high vacuum, there is always the possibility of a small leak allowing air to be drawn into the system and thus creating a flammable mixture inside the vessels. To counter the possibility of fire or explosion inside the vessels there are elaborate leak detection systems which are coupled to a nitrogen flood system. If the vacuum integrity is broken, then the columns are automatically flooded with nitrogen so that ignition is not possible. There is also a manual emergency shut down and nitrogen flood system.

THE ROLE OF THE LABORATORY

The laboratory is involved exclusively in quality control. The measures used at the pulp mills are described below.

The quality of the tall oil is monitored by using the acid number. This is a measure of the total acid (i.e. fatty and resin acids, so long as there is no excess of sulphuric acid) content of the crude tall oil. It is determined by ordinary titration with KOH, and is expressed as mg KOH/g sample. This is a sufficiently good measure of the quality of the oil for those at Kinleith, but the users of the oil have more sophisticated procedures.

The non-saponifiables are obtained from aqueous solution of the saponifiables by solvent extraction. The acids are analysed for by acidification of the solution, causing the acids to precipitate, followed by solvent extraction and then quantitative gas chromatographic analysis.

Written by Heather Wansbrough as a combination of two articles from edition one by P.J. Hooker and L.E. Fotherby (1977 Chemistry 100 students) and by Malcolm Rough, Senior Process Engineer, KRTA Ltd. respectively, with updated information provided by Stuart Cooney (Eka Chemicals) and with reference to:

Grant, Roger and Grant, Claire; *Grant and Hockh's Chemical Dictionary (5th ed.)*; McGraw-Hill Book Company; 1987