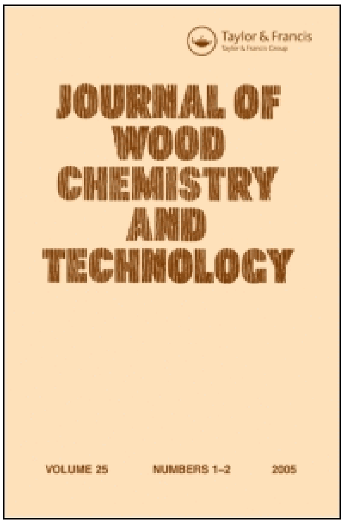
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

Separation of Tall Oil Head Fraction Into Fatty Acids and Unsaponifiables

A. Koebner[a]
[a] The Retreat, Cumbria, England

To cite this Article Koebner, A.(1983) 'Separation of Tall Oil Head Fraction Into Fatty Acids and Unsaponifiables', Journal of Wood Chemistry and Technology, 3: 4, 413 — 420
To link to this Article: DOI: 10.1080/02773818308085172
URL: http://dx.doi.org/10.1080/02773818308085172

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 3(4), 413-420 (1983)

SEPARATION OF TALL OIL HEAD FRACTION INTO FATTY ACIDS AND UNSAPONIFIABLES

A. Koebner,
The Retreat,
St. Bees,
Cumbria.
CA27 OBY
England.

ABSTRACT

A method is described which permits ready and complete separation of the unsaponifiable constituents from the fatty acids contained in the tall oil head fraction. The fatty acids are converted to zinc soaps which are essentially non-volatile and surprisingly heat stable. They form a low viscosity, homogeneous solution in the unsaponifiable components. The latter are then removed by distillation in vacuo leaving zinc soaps as a low melting residue. These soaps are readily decomposed by mineral or organic acids to fatty acids and an aqueous solution of the appropriate zinc salt which is re-cycled for further preparations of zinc soaps.

INTRODUCTION

In the production of fatty and rosin acids from crude tall oil by fractional distillation two by-products arise which have as yet not found any economic utilisation. Tall oil pitch represents some 20% of the crude tall oil processed and whilst a considerable body of literature exists on its genesis and composition, there are few prospects to achieve a worthwhile procedure to isolate even some of the individual components or group of components from the intricate mixture of naturally occurring materials

0277-3813/83/0304-0413$3.50/0

and those which result from chemical and physical changes suffered during the rather severe conditions of the separation process.

The other by-product fraction, tall oil heads, represents up to 10% of the tall oil processed. This fraction contains relatively volatile unsaponifiable constituents such as saturated and unsaturated hydrocarbons, ketones and some of the alcohols present in the original crude tall oil which have not suffered esterification with fatty and rosin acids during the first total distillation stage. According to the procedure adopted, this head fraction contains 50 - 75% fatty acids and 25 - 50% unsaponifiables. It is often found desirable to leave a larger proportion of fatty acids in this fraction to avoid high reflux ratios and, rather, re-run this fraction separately to recover more of the fatty acid values. However, because the unsaponifiables boil within the range of tall oil fatty acids, a complete physical separation is impossible and a mixture of equal parts of fatty acids and unsaponifiable matter must be accepted.

A GLC-analysis of a typical tall oil head fraction of US origin, (Hercules Inc) Table 1, shows that with the exception of a high palmitic acid content, the remainder of the fatty acid composition closely resembles TOFA.

TABLE 1.

Fatty Acid Composition of a Tall Oil Head Fraction (USA) by GLC-Analysis

Acids (less than 16 carbon atoms)	8.5%
Palmitic acid	35.9%
Palmitoleic acid	8.5%
Stearic acid	1.0%
Oleic acid	23.1%
Linoleic acid	17.8%
Linoleic acid (cis-8, trans-11)	0.4%
Linoleic acid (trans 8, trans-11)	0.4%
Unidentified unsat. acids	2.9%
Eiccosanoic acid	0.1%

Experiments have shown that an excellent grade of palmitic acid can be obtained from a tall oil head fraction freed from unsaponifiables by pressing at room temperature, by solvent crystallisation and by fractional distillation. But even without a separation of the saturated from the unsaturated component fatty acids, unsap.-free tall oil head fraction acids can be used for many purposes where stable, light coloured fatty acids are employed. If a slightly higher cloud point would be found acceptable, they may also be blended back into the main stream TOFA.

Many attempts have been made, and reported, to separate the tall oil head fraction into its two components: Fatty acids and unsaponifiable matter. These have usually failed because the resultant product was not pure enough or the cost of processing proved to be too high for economic utilisation. Other proposals were found unacceptable because the processes could not be scaled up.

In two US patents (1) (2) it has been suggested that the fatty acids contained in the head fraction should be saponified with a caustic alkali, either in the presence or in almost complete absence of water, the latter to avoid foaming during the drying stage of the resultant soaps. Both proposals, however, involve heterogeneous mixtures of sodium soaps and unsap. components which, even at temperatures in the region of 260 - 280°C., form viscous masses. Their extremely poor heat transfer characteristics severely hinder the process of distilling off the unsaponifiables. Below 260°C. anhydrous sodium soaps set readily to intractable masses which dissolve only very slowly, even in hot water. It has, therefore, been proposed (2) that the dissolution and the splitting of the soaps take place in a special glass lined pressure vessel capable of withstanding 600 p.s.i. internal pressure. The disadvantages of such methods lie in the high temperatures and alkalinity which may lead to degradation, particularly of the unsaturated acids, the intractability of the reaction medium and the special plant requirements.

DISCUSSION AND RESULTS

The concept of modifying the fatty acids chemically by employing the carboxylic function for conversion to an almost non-volatile species remains valid. Esterification with higher alcohols or polyhydroxylic compounds, such as glycerol, leads to mixtures of esters from which the relatively volatile unsaponifiables can be stripped. However, saponification of the stripped esters to acids and the recovery of the alcohols appear too cumbersome and uneconomic. Alcoholysis of the stripped partial glycerides with methanol provide an excellent route to methyl esters, but their uses in industry would be much more limited than that of the parent acids.

Whilst the soaps formed from alkali metal hydroxides are high melting and insoluble in the unsaponifiable constituents of tall oil heads, it was found that lead and zinc soaps fulfil both the preconditions for easy removal of the unsaps by distillation. They are readily soluble in the unsaponifiables and form low viscosity solutions at temperatures as low as 50°C. Zinc soaps freed from unsap. matter are also low melting (about 75°C.) and as they do not hydrate in water may be readily decomposed by mineral acids to fatty acids and metal salts.

Because of the inherent toxicity of lead compounds development work was concentrated upon the use of zinc. The zinc soaps in this case, always accompanied by the unsap. components of the tall oil head fraction, are readily and conveniently prepared in a number of ways:

1. React tall oil heads with solid zinc oxide, hydroxide, basic carbonate or carbonate in a ratio of 2 mols fatty acid to 1 mol zinc compound by heating at 100 - 160°C. with stirring for one half to one hour until all water or water and carbon dioxide, liberated by the zinc soap formation, has been removed. A clear, low viscosity solution of zinc soaps in unsap. matter is thus obtained. This is suitable for further processing.

2. An aqueous emulsion of sodium soaps and unsap. matter is prepared by warming 1 part of tall oil heads with 3 parts of water with stirring to 75°C. and adding 5 N caustic soda solution until a pH of 9 is reached. The amount of alkali required may be calculated from the AV of the head fraction. With continued stirring and maintaining the temperature, nearly saturated zinc salt solution, such as chloride, sulphate etc. is then introduced. By a rapid process of double decomposition the water insoluble zinc soaps are precipitated and form an oily upper phase which can be readily separated from the aqueous solution of the appropriate sodium salt. The organic layer is then dehydrated by heating before further processing.

3. A particularly attractive procedure is the use of zinc acetate in the preparation of zinc soaps. When (as under 1.) the tall oil forerun fraction is heated from 100 to 160°C. with the equivalent amount of solid zinc acetate tri-hydrate,acetic acid and water distils and can be recovered almost quantitatively. This procedure requires 1 - 2 hours. This distillate can be used at a later stage to decompose the zinc soaps freed from unsap. matter. In this stage free fatty acids and a new saturated aqueous solution of zinc acetate are obtained as easily separable phases. The metal acetate solution may be re-cycled to form further zinc soaps. This variation allows the process to be operated without by-product inorganic salts which may cause environmental problems in their disposal.

From the mixture of zinc soaps and unsap. constituents thus obtained the latter can be readily stripped by vacuum distillation. Complete removal of unsaps. is achieved at temperatures in the range of 200 - 225°C. and vacua from 1 - 10mm Hg. It was found to be particularly advantageous to use live steam injection to expedite the stripping. Unsap. contamination in the fatty acids can be reduced to the 1% level.

In contrast to the high melting point and viscosity of alkali metal soaps, zinc soaps, due to their low melting point and viscosity, can be readily handled and pumped. The use of zinc soaps rather than alkali metal soaps also overcomes one of the greatest disadvantages associated with the splitting of aqueous sodium soaps. When brought into contact with hot dilute mineral acids these soaps hydrate rather than decompose, forming gelatinous masses which resist even treatment with open steam for many hours before finally breaking down to fatty acids. Obviously, such processing conditions are highly corrosive and foaming adds a further problem during this operation. The decomposition of zinc soaps on the other hand, proceeds almost instantaneously at 95°C. when mineral acid or acetic acid is slowly added to a stirred two-phase mixture of molten zinc soaps and water. This easy decomposition permits the use of stoichiometric proportions of the reactants without the local build-up of high acid concentrations. The reaction can be controlled by pH measurement of the aqueous phase. As zinc soaps are completely insoluble in water, no foaming problems are encountered.

As zinc soaps are not "salted out" of aqueous solution by high electrolyte concentrations, as is the case with sodium soaps, it is possible to reduce the aqueous phase of the splitting stage to achieve near saturation in respect of the salt being formed. This is a considerable advantage when the resultant solution has to be treated either for disposal or recovery. Reference has already been made to the recycle of zinc acetate. It is obviously beneficial here to reduce the amount of water which has to be removed by distillation prior to the reuse of zinc acetate.

The recovered acids are somewhat discoloured but can be readily purified by distillation or, if desired, by fractionation. Total distillation on a laboratory scale yields a very pale coloured product, free from the characteristic odour which might indicate its origin, in 95% yield. This is also the yield over the process as a whole. The relatively mild conditions do not bring about any change in the fatty acid distribution from the crude head fraction to the finished product. The small distillation residue observed is probably due to some polymerisation under the rather unfavourable batch distillation conditions employed and is no larger than that encountered during the distillation of similar highly unsaturated fatty acids. If it were found possible, as previously suggested, to blend the forerun fatty acids, once they have been freed from the contaminating unsap. matter, with the main TOFA-fraction, the crude acids from the zinc treatment step could be introduced into the appropriate stage of the main tall oil separation process, thus saving a separate distillation stage.

Traditionally, low value tall oil fractions such as pitch or the head fraction have been used as fuel, often after being blended together to reduce viscosity and setting points. Whilst attempts have been made to isolate some of the interesting compounds or groups of compounds from the very complex mixture of tall oil heads unsaponifiables, nothing of real interest has as yet been achieved. The ready availability of the unsaponifiable fraction from the zinc process which occurs as a pale amber coloured oil, might provide some future stimulus for further investigations. The author has shown that by addition of maleic anhydride (3) to some of the highly unsaturated species contained in the unsaps., complex acids are obtained with properties which may make them suitable for the preparation of paper sizes. Obviously, the heat value of the unsap. fraction is by no means diminished by the recovery of the fatty acids, and the residue may yet continue to serve as fuel.

The process described in this paper has previously been published. (4)

ACKNOWLEDGEMENT

The author wishes to express his thanks to the Principal and Staff of the West Cumbria College, Whitehaven, England for providing facilities and help in carrying out this work.

REFERENCES

1. T. Harada and T. Yumoto, U.S. Patent 3,887,537, June 3, 1975 (Japan Synthetic Rubber Company).
2. D. E. Leavens, C. F. Phillips, Jr., U.S. Patent 4,064,117, December 20, 1977 (Sylvachem Corporation).
3. A. Koebner, U.S. Patent 4,019,921, April 26, 1977.
4. A. Koebner, U.S. Patent 4,151,160, April 24, 1979.