Handbook on Tall Oil Rosin Production, Processing and Utilization
<table>
<thead>
<tr>
<th>Code:</th>
<th>ENI247</th>
</tr>
</thead>
<tbody>
<tr>
<td>Format:</td>
<td>Paperback</td>
</tr>
<tr>
<td>Indian Price:</td>
<td>1575</td>
</tr>
<tr>
<td>US Price:</td>
<td>150</td>
</tr>
<tr>
<td>Pages:</td>
<td>480</td>
</tr>
<tr>
<td>ISBN:</td>
<td>9788178331515</td>
</tr>
<tr>
<td>Publisher:</td>
<td>Pacific Business Press Inc.</td>
</tr>
<tr>
<td></td>
<td>Asia</td>
</tr>
</tbody>
</table>
Tall oil, a by-product of kraft pulping of pine wood, is formed by acidifying black liquor soap skimmings. It consists of resin acids or rosin, fatty acids, and neutrals. Crude tall oil is an excellent source of rosin and tall oil fatty acid, an industrial-grade oleic and linoleic acid blend. The bulk of the neutrals, largely esters of fatty acids, sterols, resin and wax alcohols, and hydrocarbons, boil at either lower or higher temperatures than the boiling range of the fatty and resin acids.

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 widely used. The fatty acids are unsaturated and on exposure to air undergo autoxidation and polymerization to form resin-like materials which form a tough protective coating. Resin acids are used in rubber polymerization and compounding, as size to impart water resistance to paper, 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.

The book contains production details of different products like recovery of crude tall oil, Composition and properties of crude tall oil, Lab. Scale fractional vacuum distillation, tall oil soap acidulation, purification of sulphate soap, hydrodynamic separation of CTO, dimerization of tall oil fatty acid, black liquor soap recovery methods, tall oil in asphalt products and petroleum uses, tall oil in liquid soaps, tall oil in rubber, paper and printing inks etc. This book is very useful for scientists, scholars, consultants and technical institutions.

Content:
1. INTRODUCTION
Introduction to Tall Oil
History of Tall Oil
Production Process for Tall Oil
Recovery of Tall Oil
Composition and Properties of Tall Oil
Crude Tall Oil
Analysis and Testing of Tall Oil Products
Applications of Tall Oil
2. RECOVERY OF TALL OIL
The Chemistry of Tall Oil Fatty and Rosin Acids
Chemical Composition of Tall Oil Fatty Acids
General Reactions of Tall Oil Fatty Acids
Reactions Involving the Carboxyl Group
Chemical Composition of Tall Oil Rosin
Dimer Acids Manufacture and Feedstock
3. COMPOSITION AND PROPERTIES OF CRUDE TALL OIL
Tall Oil Production and Laboratory Analyses at the Factories
Studies on the Precursors of Indian Tall Oil
Analytical Studies on the Composition of Crude Tall Oil
Experimental
Testing of Tall Oil with Standard Methods
Fractionation of Samples
Crude Tall Oil Recovery from Sulfate Soap
Separation of Free Acids and Neutrals
Preferential Esterification
Saponification
Methylation and Silylation
Thin-Layer Chromatography (TLC)
Preparative Argentation TLC
Gas Chromatography (GC)
Gas Chromatography-Mass Spectrometry (GC-MS)
Results and Discussion
Testing of Tall Oil with Standard Methods
Group Fractionations
Studies on the Composition and Component Distribution
Fatty Acids
Saturated Fatty Acids
Monoenoic Fatty Acids
Dienoic Fatty Acids
Trienoic Fatty Acids
Tetraenoic Fatty Acids
Conjugated Fatty Acids
Esterified Acids
Resin Acids
Neutral Components
Gr. 1 Phytosterols
Gr. 2 Monoterpenoid alcohols
Diterpene Abietic and Pimaric Type Alcohols
Fatty Alcohols
Triterpene Alcohols
Gr. 3
Gr. 4
Gr. 5
Gr. 6 Oxosteroids
Gr. 7 Dimethoxy Stilbenes
Gr. 8 Resin Acid Methyl Esters
Gr. 9 Diterpene Aldehydes
Gr. 10 Esters of Fatty Acids with Diterpene Alcohols
Gr. 11 Esters of Fatty Acids with Fatty Alcohols
Gr. 12 Esters of Fatty Acids with Sterols and Triterpene Alcohols
Gr. 13 Hydrocarbons
Sesquiterpene Hydrocarbons
Diterpene Hydrocarbons
Typical Features of Indian Tall Oil
General Properties
Component Distribution
Factors Influencing the Properties and Composition of Crude Tall Oil
Wood Species
Geographical Location (Climate)
Roundwood and Chip Storage
Other Factors
4. CHEMICAL CHANGES DURING STORAGE OF CRUDE TALL OIL
Experimental
Results and Discussion
Drop in Acid Number
Esterification
Thermal and Acid Isomerization of Resin Acids
General
Results from Laboratory Storage
Crystallization
Changes in the Composition of Conjugated Fatty Acids
Aspects of the Storage of Turkish Crude Tall Oil
5. LABORATORY-SCALE FRACTIONAL VACUUM DISTILLATION
Experimental
Still
Charges
Procedure
Analytical Procedures
Results and Discussion
Composition of the Distillates
Distribution of Tall Oil Constituents in the Distillates
Fatty Acids
Esterified Acids
Resin Acids
Neutrals
Sesquiterpene Hydrocarbons
Diterpene Hydrocarbons
Hydrocarbons from Decarboxylation of Resin Acids
Diterpene Aldehydes
Pinosylvin Dimethyl Ether
Diterpene Alcohols
Resin Acid Methyl Esters
Fatty Alcohols
Dehydrated Sterols
Sterols
Triterpene Alcohols
Esters
Unidentified Components
Composition of the Pitches
Components Not Eluted on GC
Volatilities of Tall Oil Constituents with Special Reference to Fatty and Resin Acids
General
Observations on the Laboratory Distillation
Brief Critique on the Laboratory Distillation
Conclusions
6. OZONOLYSIS AND EPOXIDATION OF METHYL MALEOPIMARATE
Results and Discussion
Ozonolysis and Epoxidation of Methyl Maleopimarate (lb) and Other Related Compounds
Structural Assignment to 4a
Absolute Configuration of 4b
Structure of the Anhydride 6
Structure of the Epoxy Anhydride 5
Reaction of Peroxytrifluoroacetic with Bicyclo[2.2.2]oct-5-ene-endo-cis-2,3-dicarboxylic Anhydride (8)
Structural Assignment to 9
Structure of the Hydroxy Lactone 10
Experimental
Ozonolysis of Methyl Maleopinamate (lb). Isolation of 4b, 5, and 6
Preparation of the Tetramethyl Ester of 6
Preparation of 5 by Direct Epoxidation of lb
Preparation of 20
Reaction of 21 with Peroxytrifluoroacetic Acid. Preparation of 22
Reaction of Peroxytrifluoroacetic Acid with Olefin 8. Preparation of 5,6-Endo-epoxy-bicyclo[2.2.2]octane-
cis-2,3-dicarboxylie Anhydride 9
Epoxidation of Olefin 8 with m-Chloroperbenzoic Acid. Preparation of Hydroxy Lactone 10
Preparation of 35 and 36 from 10
Preparation of 37 and 38
Preparation of Bromo Lactonic Acid 39 from the Olefinic Anhydride 8
Preparation of the Bromohydrin 41 of Dimethyl Ester 37
Preparation of 40, the C2 Epimer of 39
Discussion of Results
The Benzogulnone Adduct of Levopimaric Acid (XXVIII)
The Dimethyl Acetyleneidcarboxylate Adduct of Levopinaric Acid
Other Adducts of Levoplmaric Acid
7. TALL OIL SOAP ACIDULATION
Batch Process
Semi-Batch Process
Continuous Decanting Process
Centrifuge Process
8. RETROFITTING A TALL OIL ACIDULATION PLANT
9. PURIFICATION OF SULPHATE SOAP
10. HYDRODYNAMIC SEPARATION OF CTO
11. REFINING OF TALL OIL BY COLUMN LIQUID-LIQUID EXTRACTION
Introduction
The Pilot Plant at the Technical Research Centre of Finland
Trials with Mixed Pine-Birch Soap
Trials with Other Tall Oil Products
Conclusions
12. DIMERIZATION OF TALL OIL FATTY ACID
13. TALL OIL SOAP ACIDULATION AND SULFUR BALANCE PROBLEMS IN KRAFT MILLS
Soap Acidulation
Spent Acid Disposal
Sulfur Losses
Soda Losses
Sulfur Balance
Replace H2SO4 with DGE
Sewering DGE
Modified C102 Production Technology
Concluding Remarks
14. BLACK LIQUOR SOAP RECOVERY METHODS
Woodstorage
Digestion and Washing
Soap Recovery in the Weak Liquor System
Soak Skimmer Design and Operation
Air Injection to Improve Recovery
Influence of Hardwood Liquor on Soap Recovery
Heavy Liquor Soap Recovery
Soap Decanter Design and Operation
Monitoring Soap Recovery Efficiency
Summary
15. CONTROLLING POLLUTION IN A LUWA TALL OIL DISTILLATION PLANT
Sources of Effluents from CTO Facilities
Processes for the Distillation of Crude Tall Oil
The Luwa CTO Distillation Process
Effluents from the Luwa CTO Distillation Process
Minimizing Effluents in CTO Distillation Plants
16. ADVANCED POLLUTION CONTROL TECHNOLOGY IN THE STEAM DISTILLATION OF TALL OIL
Corrosion & Materials of Construction
Reboiler Design
Tower Internals
Stability
Conclusion
17. NEW SEPARATION TECHNOLOGY FOR DISTILLED TALL OIL
Introduction
Sorbex Process Outline
Simulated Moving Bed
Experimental Results
Conclusions
18. CARBON DIOXIDE PROCESS
Introduction
Discussion
19. FINNISH EXPERIENCE IN TALL OIL PITCH AS ASPHALT SUBSTITUTE
Background
Tall Oil Pitch - Renewable Natural Resource
Pitches in Asphalt and Pavement Characteristics
Mixing and Laying of the Pavements in Field Experiments
Wear Tests in Laboratory and On Field Show Improved Tendency
Asphalt Paving Contracts in 1988
Prejudices Disappear - The Future Is Open
20. USES OF TALL OIL
Tall Oil Products in Surface Coatings
Tall Oil in Alkyd Resins
Tall Oil Formulations in Alkyd Resins
Short Oil Baking Alkyd - Solvent Process Properties
Short Oil Baking Alkyd - Fusion Process
Medium Oil Alkyd-Fusion Process
Long Oil Alkyd - Fusion Process
Rosin Modified Alkyd-Fusion Process
Glycerine Ester
Maleic Modified Ester
Distilled Tall Oil Epoxy Ester
Other Uses for Tall Oil Products
Tall Oil in the Plasticizer Field
Tall Oil Plasticizers
Esterification of Tall Oil for Plasticizers
Tall Oil in Adhesives and Linoleum Cement
Tall Oil in Rubber Based Adhesives
Tall Oil in Hot-Melt Adhesives
Tall Oil Products in Linoleum Cements

21. TALL OIL IN ASPHALT PRODUCTS AND PETROLEUM USES
Tall Oil in Asphalt
Roads
Soil Treatments
Roofing
Adhesives
Antistripping Agents
Plasticizers
Miscellaneous
Tall Oil in Petroleum Applications
Oil and Gas Well Fracturing
Drilling Muds
Demulsification Agents
Corrosion Inhibitors
Catalyst
Lubricating Oil Additives

22. TALL OIL IN LIQUID SOAPS
Tall Oil in Disinfectants
Tall Oil in Synthetic Detergents and Wetting Agents
Syndet Types
Syndet Products
Tall Oil in Biodegradable Detergents

23. TALL OIL IN FLOTATION COLLECTORS AND CORE OILS
Tall Oil in Flotation Collectors
Flotation Collectors
Flotation Applications
Tall Oil in Core Oils

24. TALL OIL IN RUBBER
Styrene-Butadiene Rubber
Cold SBR Formulation (SBR 1500 Series)
Hot SBR Formulation (SBR 1000 Series)
Cold High Solids SBR 2105 Latex Formulation (SBR 2100 Series)
Hot SBR Latex Formulation (SBR 2000 Series Type II)
Foam Rubber
25.TALL OIL IN PAPER SIZE
Papermaking Process
Rosin Sizing Materials
Forms of Size Available
Paste Size
Dry Size
Methods of Preparing Liquid Size
Cooking Process
Emulsion Process
Bewoid Process
Delthirna Process
Internal and External Sizing
Effect of Wet Strength Resins and Paper Coating Resins on Sizing
Sizing of Nonconventional Paper
Testing of Sizing
Water Resistance of Paper and Paperboard-T433 M-44 (Dry Indicator Method)
Water Immersion Test of Paperboard-T491 SU-63
Water Absorption of Paperboard-T492 SM-60
Water Absorptiveness of Nonbibulous Paper and Paperboard- T441M-60 (Cobb Test)
Degree of Curl and Sizing of Paper-T466 M-52
Ink Penetration Test
Fotosize Penetration Test-Lactic Acid Test
26.TALL OIL IN PRINTING INK
Typographic Printing and Typographic Inks
Heat-Set Inks
Steam-Set Inks
Newsprint Inks
Lithographic Printing and Lithographic Inks
Intaglio or Gravure Printing and Gravure Inks
Silk-Screen Printing Inks
Overprint Varnishes
Bag Inks
27.MISCELLANEOUS APPLICATIONS OF TALL OIL
Tall Oil Fatty Acids for Chemical Intermediates
Polymerized Fatty Acids
Azelaic and Pelargonic Acids
Tall Oil in Coprecipitated Barium Salts
Tall Oil in Defoamers
   TALL OIL IN PIGMENT DISPERSANTS

Sample Chapter:
Recovery of Tall Oil

The Chemistry of Tall Oil Fatty and Rosin Acids

Fatty acids and rosin acids are large and important groups of organic acids occurring in nature—the fatty acids usually in combination with glycerol or sterols in the form of esters. During the kraft process of making pulp, most of the esters present in the wood are saponified with the formation of soaps of sodium salts of the fatty and rosin acids. Acidulation of these soaps yields crude tall oil, from which fatty acids and rosins are obtained by fractional distillation.

Chemical Composition of Tall Oil Fatty Acids

Tall oil fatty acids are composed of carbon, hydrogen, and oxygen. The carbon atoms are linked together in the fatty acid molecule in the form of a long chain. At one end of the chain is an acidic or carboxyl group (COOH) which characterizes all carboxylic acids, both aliphatic and aromatic. Practically of the fatty acids present in crude tall oil have a straight chain and contain an even number of carbon atoms. However, small amounts of branched-chain and odd-numbered acids have recently been reported. The tall oil fatty acids consist chiefly of oleic and linoleic acids. Palmitic acid, which is the main component of the saturated fatty acids in tall oil, is almost completely removed as a heads product in the fractionation process. Rosin acids present in crude tall oil are almost completely absent in high-grade tall oil fatty acids. Higher molecular weight fatty acids also present in crude tall oil are removed in the pitch fraction. The typical composition of tall oil fatty acids is given in Table 1. The physical properties of the major tall oil fatty acids are given in Table 2. The neutral material in tall oil fatty acids consists mainly of dimethoxystilbene and abietene type hydrocarbons, which are essentially free of functional groups.

Dimer Acids Manufacture and Feedstock

In present-day commercial practice, dimer acids are prepared by the thermal condensation of unsaturated fatty acids, usually catalyzed by small amounts of montmorillonite clay. These manufacturing procedures are described in a number of patents, like detail the effect of reaction temperatures, pressures, clay content and type and other reaction variables. Another, and overwhelmingly important, variable is the unsaturated fatty acid used as feedstock for dimer production. The published literature describes the use of starting materials (both free fatty acids and alkyl esters) which are rich in polyunsaturates such as those derived from drying and semi-drying vegetable and marine oils linoleic and linolenic acid and their higher-molecular-weight homologues. The literature also describes the use of monounsaturated fatty acids such as oleic acid and its isomers, erucic acid, undecylenic acid, and other monounsaturated fatty acids. The principal feedstock for production of dimer acids, from the outset of commercial production, has been tall oil fatty acids, the cheapest unsaturated fatty acid available. This raw material is produced by the high-vacuum fractionation of tall oil, which, is the generic name for the products derived from the black liquor residue of the kraft pulping process. A typical analysis of commercial grade tall oil shown in Table 3.

Carbon Dioxide Process

Introduction

A major source of sulfur in kraft mills that have crude tall oil acidification plants is the sodium sulfate brine. As kraft mills reduce their emissions, less sulfur is lost, and the sulfur input to the kraft mill must be reduced to maintain targeted sulfidity levels. The carbon dioxide process was developed as an approach to reducing the sulfate brine generated by the crude tall oil acidification plant. A pilot plant was constructed and run continuously for two weeks in 1975 to demonstrate the process. This initial work and subsequent work done in the laboratory and pilot plant at Westvaco form the basis of this paper.

Discussion

Chemistry. In sulfuric acid acidification, the tall oil soap is converted to crude tall oil (CTO) via an essentially irreversible and quantitative reaction:
2 RCOO-Na\(^+\) + H\(_2\)SO\(_4\) \(\rightarrow\) 2 RCOOH + Na\(_2\)SO\(_4\) \((1)\)

CTO Soap + Sulfuric Acid \(\rightarrow\) CTO Sulfate

In the carbon dioxide process, the inorganic acid is carbonic acid formed by the reversible reaction of carbon dioxide and water:

\[ \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \] \((2)\)

Carbon Dioxide + Water \(\rightarrow\) Carbonic Acid

The process flows for a plant which would produce 100 tons of CTO per day are shown in Table 1. These flows are based upon 40% replacement of the inorganic acid in a normal sulfuric acid process with carbon dioxide. The low-solids sodium bicarbonate stream is significant and is discussed later.

The major costs and savings of implementing the carbon dioxide process on an existing sulfuric acid process are listed in Table 2. The cost of purchased carbon dioxide could be reduced substantially by installing an absorption process to recover carbon dioxide from lime kiln stacks, but this would increase capital cost and increase the operating complexity. Carbon dioxide application will reduce the sulfuric acid consumption by at least 40% and also reduce the sodium hydroxide required to neutralize the sulfate brine by at least 40% since the sulfate brine stream is reduced proportionally. The extra dilution water contained in the bicarbonate brine must be evaporated if the sodium is to be retained in the kraft system; alternatively the bicarbonate brine may replace an existing water stream in the kraft system as discussed below and not add cost to the process. The capital required for a system shown in Figure 2 capable of producing 100 tons of CTO per day is estimated to be $1.5 million, although this would vary significantly with the preparation, tankage and piping required at each individual site. The depreciation of this capital is a significant fraction of the costs as shown in Table 2. The assumption is made that the operator running the crude plant could operate the carbon dioxide process and that no extra labor is required. Electricity and steam costs of running the plant are small and are not included in Table 2.

As shown in Table 2, the incremental cost of a carbon dioxide process is relatively low; the process would not be implemented unless changes were mandated as a result of the sulfidity levels being too high in a kraft system. When compared to other alternatives such as dumping sulfate into the waste treatment system and not recovering the sodium, the incremental cost of the carbon dioxide system is favorable.

**Bicarbonate Brine Disposition.** A problem which must be addressed before a carbon dioxide process can be implemented is finding a "home" for the dilute sodium bicarbonate brine stream. Two alternatives that have been considered are shown in figure 3. The bicarbonate brine could displace wash water in the lime mud washing system. The sodium thus would be recovered in the white liquor. But washing efficiency and foaming tendency from dissolved organics are concerns which must be assessed. However, the level of these organics is very low, and no foaming tendency has been noticed in laboratory and pilot work. A second alternative is to put the bicarbonate brine directly into the dissolving tank for the smelt where foam would not be a concern. Neither alternative is envisioned to benefit the operation to which the bicarbonate brine is added; the overall benefit would be keeping sodium in the kraft mill system.

**Black Liquor Soap Recovery Methods**

The recovery of black liquor, and the conversion and the sale of the tall oil products make a significant contribution to the profitability of mill sites for Union Camp Corporation. This discussion will concern itself with recovery methods at southern kraft pulp mills in Savannah, Georgia and Montgomery, Alabama.

**Woodstorage**

At both mills a relatively small wood inventory is maintained. Roundwood is inventoried in the field, and tall oil losses during storage are limited to less than about 10% as estimated by Cowart, Tate, and Churchill. The mills maintain wood inventories primarily in outside chip storage facilities. Additional tall oil losses...
resulting from outside chip storage are less than 1% as per Thornburg. Chips are removed from the pile on a last in, first out basis as per Springer.

**Digestion and Washing**

In Savannah the pulp is washed on drum washers. Soap losses on the washers vary from eight to twelve pounds per air dry ton of pulp produced. There is no attempt made to segregate the liquors of the different species of pulps prior to evaporation to improve soap recovery. No semi-chemical hardwood pulp is currently produced in Savannah.

In Montgomery hardwood and pine liquors are evaporated separately so that in the event that semi-chemical pulp is produced in the hardwood digesters, soap losses could be minimized.

**Soap Recovery in the Weak Liquor System**

In Savannah, the wash plant weak liquor is filtered and drops into the first of several weak liquor storage tanks placed in series. The foam produced is directed through a Lundberg Foam Concentrator and the concentrated (broken) foam is then directed to a tall foam tower in which the weight of the broken foam is used to densify it. This densified broken foam is then directed to the soap decanter where the broken foam and the liquor separate. The density of the broken foam varies from 3 to 5.5 lbs./gallon. The other tanks in the series are soaped once to twice per week by filling the tanks and overflowing the soap through the broken foam system to the soap decanter. Approximately 25% of the total mill soap recovery is accomplished in this manner.

In the Montgomery, Alabama mill the filtered weak liquor is directed to weak liquor tanks for each of the evaporator trains. These weak liquor tanks operate in parallel. The weak liquor tanks are soaped daily by overflowing the soap and foam into an inverted cone collector. This soap and foam is then sent to the soap decanter where the liquor is drained off. The solids content of the liquor being fed to weak liquor storage from the washers is 14 to 15%. Heavy liquor from the evaporator discharge is recirculated to increase the feed solids to the evaporator.

**Soak Skimmer Design and Operation**

**Principle of Operation - Stokes' Law:** For soap recovery by gravity separation, as occurs in skim tanks, the soap particles must agglomerate into particles considerably larger than micelles as reported by Pon'Kina. However these particles agglomerate rapidly as was reported by Bolger and Hopfenberg and that on standing for a short while, the agglomerates normally have rise velocities of about 5 to 20 feet per hour. The agglomerated soap particles separate from the black liquor according to Stokes. Since Stokes' Law only applies in the laminar flow regime at Reynold's numbers less than 1 it is necessary that turbulence in a skim tank be avoided if at all possible. Down-ward flow conditions should also be minimized. Further consideration of the Stokes' Law equation indicates that by increasing the density of the black liquor through increased solids, the rise rate should be increased. By decreasing the density of the soap particles such as through air injection the rise rate may be increased. Increasing the particle diameter size could occur as a result of agglomeration resulting from increased settling time, and also air injection or perhaps by chemical additives to agglomerate the particles. Decreasing the viscosity of the liquor through increasing the liquor temperature should assist the particles to separate. However, viscosity is increased by increased solids at a given temperature and therefore a minimum solubility exists in the region of 22 to 28% solids. As is indicated in Table 1, all of Union Camp's soap skimmers operate in this region. Studies have been carried out on our No. 7 Soap Skimmer in Savannah where the feed solids to the soap skimmer were changed from 22% to 27% in the liquor feed, however, no appreciable change in tall oil residual content of the skimmed liquor was observed. This is not surprising since the studies performed to determine the effect of liquor solids on soap solubility were performed under static conditions and the turbulence generated in an operating soap skimmer would be such that liquor density effects would be negated. Furthermore, the difference between liquor density and soap density increased about 33% but this was largely offset by a
30% increase in liquor viscosity.

**Skim Tank Design:** As has been pointed out by Dusenbury the design of a soap skimmer should be based upon the rise rate of the soap in that skimmer. In the Savannah Mill, the soap rise rates have been measured to be in excess of 80 feet per hour. Although these rise rates are much in excess of those normally reported, it would appear that they also vary widely in the absence of air injection and therefore may explain wide variations in soap skimmer performance. Despite these very high soap rise rates. No. 7 Skimmer has shown very poor soap recovery unless assisted by air flotation. The reason for this poor performance is skim tank design. No. 7 Soak Skimmer is very deep and tends to be rather turbulent. Much of this turbulence is related to its circular shape.

Of the eight skim tanks operating in the Savannah and Montgomery mills, four of the skimmers are rectangular in shape and four of the skimmers are circular in shape. The rectangular skimmers as a whole have a much smaller residence time than the circular skimmers, however, their performance in the absence of air injection is as good as or better than the performance of two of the circular skimmers. The most efficient skimmer is No. 3 Skimmer in Montgomery which is a circular skimmer. It is effective in that it essentially models a rectangular soap skimmer by the use of a spiral baffling arrangement.

**Skim Tank Baffling:** The baffling arrangement has been found to be very important in skim tank operation because of its effect on turbulence and soap particle "short circuiting." This is evidenced by the performance of No. 4 and No. 5 Skimmers in Savannah. With reference to Table 1, it is apparent that both skimmers although they are similar in size, shape, and liquor residence time, the increased turbulence caused by the baffling in No. 4 Skimmer results in a higher product liquor tall oil residual than No. 5 Skimmer. The baffling on No. 4 Soap Skimmer creates an over and under flow pattern and results in excessive turbulence which reduces the efficiency of the skimmer.

No. 7 Skimmer in Savannah is a circular skimmer. It was originally baffled as shown in Figure 1A. No. 7 Skimmer experienced very poor performance as evidenced by high outlet tall oil residuals in the product liquor and this was due to excessive turbulence generated by the baffles. By replacing the baffles with a single mid-feather baffle, as in Figure 1B, the tall oil residuals in the product liquor were reduced.

The No. 1 Circular Skimmer in the Montgomery, Alabama Mill is inefficient for its size. This skimmer is concentrically baffled as in Figure 1A and this baffling also tends to produce excessive turbulence and therefore soap particle short circuiting in the outlet liquor. However, it is a more efficient skimmer than No. 7 Soap Skimmer in Savannah was when it was baffled in the same way. This is because No. 1 Skimmer in Montgomery is more shallow and has a longer residence time. The most efficient baffling for a circular skimmer is that observed on No. 2 and No. 3 Soap Skimmers in Montgomery, Alabama.

**Liquor Entry Point:** Short circuiting of the soap particles to the outlet liquor from the skimmer may also be reduced by carefully positioning the inlet liquor level. A study was performed on No. 7 Soap Skimmer in Savannah, in which liquor entry points were located at four foot intervals down the side of the skim tank. Initially the liquor was introduced at the top most entry point and the skimmer outlet tall oil residual was noted. When the liquor entry point was lowered four feet, a significant increase in the outlet tall oil residual was noted as in Table 3. This finding is consistent with the skimmer design parameters as proposed by Dusenbury in that it minimizes the distance which a soap particle must travel to reach the surface of the skim tank. A similar effect may be created if the existing liquor entry point is near the bottom of the skimmer by providing the liquor entering the skimmer with an updraft.

**Influence of Soap-Liquor Interface Position:** It has been proposed that skimmers ought to operate with a thick soap pad, to insulate the skimmer, minimize the liquor carry-over with the soap, and to densify the soap collected. On rectangular skimmers, this practice has led to an increased tall oil residual in the skimmer output liquor. In the Savannah Mill, rectangular skimmers are operated so as to maintain a small
liquor interface at the discharge end of the soap skimmer. This minimizes the losses of the soap particles from the bottom of the soap bed due to suction effects at the skimmer discharge pump. These results are summarized in Table 2. The thermal loss in the skimmer resulting from operating with a small liquor interface is very small and reduces the total evaporator capacity less than 1%.

A similar dependence of the outlet liquor tall oil residual on the soap-liquor interface position has been noted on No. 7 Soap Skimmer as is illustrated in Figure 4. It is generally not necessary for an operator to adjust the skimmer level to control the soap liquor interface more often than once/shift on any of the skimmers.

Miscellaneous Applications of Tall Oil
Tall Oil Fatty Acids for Chemical Intermediates
The nature and ratio of the fatty acids comprising tall oil fatty acids, as well as the non-fatty content, governs the behavior and properties of derived products. Commercial advantages other than low cost for tall oil fatty acids and their derivatives must arise from the properties due to the special nature and combinations of the constituents. The use of tall oil fatty acids, containing at least 90 percent fatty acids, is preferred for preparation of intermediates. (Rude tall oil or tall oil products can be used if it is known that the rosin or other nonfatty acid components do not unfavorably affect the use of the intermediates. For example, crude tall oil (25 percent or more rosin acid content) has been satisfactorily used in the preparation of rigid urethane foam to effect lower costs.

Good quality tall oil fatty acid is unique in containing a high content of oleic and linoleic acids with little or no linolenic or other highly unsaturated acids. It also has a low content (about 3 percent) of saturated acids, chiefly palmitic acid. Oleic acid is present to the extent of about 48 to 52 percent and linoleic acid to the extent of about 43 to 48 percent (37 to 42 percent nonconjugated; 6 percent conjugated). Rosin acid content may be less than 1 percent and neutrals content is usually less than 2 percent.

Tall oil fatty acids, like other unsaturated fatty acids, can be reacted at the carboxyl group and at the unsaturated linkages, or at both points. As noted earlier for tall oil fatty acids, the varieties and uses of intermediates obtainable from tall oil fatty acids are so numerous that a comprehensive coverage is impractical.

Reactions at the carboxyl group to form soaps and esters have been considered elsewhere, as have reactions at the unsaturated linkages to form sulfation or sulfonation compounds. Additional reactions that can be carried out at the carboxyl group include formation of amides, nitrites, amines, and quaternary ammonium compounds. Alcohols are also obtainable. All of these products can be hydrogenated at the double bonds to obtain the saturated forms. A wide range of derivatives is thus available as with fatty acids from other sources.

Applications include use of the cationic amine and quaternary ammonium compounds in the flotation and textile fields. Condensates of tall oil fatty acids with alkylol amines find use in detergents and emulsifiers. Fatty amines and their salts derived from tall oil have been proposed for many uses such as for flotation agents, corrosion inhibitors, antistatic agents, wetting and dispersing agents, and lubricants. Stabilized tall oil nitriles and amines, substantially free of rosin acids, are the subject of patents with suggested uses in disinfectants, detergents, etc.

Polyethoxylated fatty acids have been proposed as dispersing agents, pesticide wetting agents, etc. Polyethoxylated acids derived from tall oil fatty acids having 4 percent and 70 percent rosin acid contents are included in commercial offerings.

In all cases, practical use must be dependent on special properties offering advantages over corresponding derivatives of fatty acids from other sources. Hydrogenation of tall oil fatty acids supplies the C18 saturated, stearic acid, with very little C16 palmitic or other acids being present.

Polymerized Fatty Acids
The unsaturated nature of tall oil fatty acids permits their use as a suitable source for the commercial polymerized fatty acids. These are obtained by polymerization of unsaturated fatty acids under conditions minimizing degradation. The polymerized fatty acids consist of dimer (C36) and trimer (C54) acids. They are sometimes referred to as dilinoleic and polymeric fatty acids. Such acids have found wide use in industry and a large number of patents for their use have been issued. In the polymerization of the unsaturated fatty acids, some monobasic acids are formed, which are characterized by some double-bond shifting, skeletal rearrangement and cis-trans isomerization. An excellent review article on dimerization is available.

The polymeric acids undergo most of the reactions of polybasic acids in general. Among the more important commercial derivatives are the polyamide products obtained by reacting the polymeric acids with polyamines. These polyamides are of solid and liquid types. Solid polyamide resins based on polymerized fatty acids have a variety of end uses including vehicles for printing inks, in formulation of hot-melt adhesives, as organic solders for side-seam sealants of cans, in preparation of thixotropic paint vehicles, as antisagging agents for paints, in resinous systems for paper coating, and as wax modifiers. Liquid polyamides are used primarily as epoxy resin curing agents and the epoxy resin-polyamide resin systems are used in surface coatings, structural adhesives and sealants, tough castings, structural laminates, and auto-body solders.

Azelaic and Pelargonic Acids
The presence of unsaturation in tall oil fatty acids permits application of the oxidative cleavage reaction to form shorter chain dibasic and monobasic acids. Although cleavage can be effected by chromic acid, nitric acid, etc., ozone is now used in commercial practice to obtain the dibasic azelaic acid and the monobasic pelargonic acid. Here again, industrial utility depends on the nature of the fatty acids being such as to confer useful properties on the products. A favorable factor for use of tall oil fatty acids for preparing dibasic and monobasic acids is the low content of saturated fatty acids compared to the relatively large amount of palmitic and stearic acids in most of the commercially available grades of oleic acid. Relatively low cost is another advantage. The high linoleic acid content of tall oil fatty acids, however, results in high chemical cost and more fragmentation products than is the case when using oleic acid as the feedstock.

The resulting odd carbon C9 dibasic azelaic acid and C9 monobasic pelargonic acid have many uses and numerous patents have been issued. Azelaic acid is especially valuable as a building block for polymers, plasticizers, and lubricant compounds. Pelargonic acid finds most of its outlets in the manufacture of lubricants, plasticizers, flotation agents, perfume bases, fungistats, and wetting compounds.

Tall Oil in Coprecipitated Barium Salts
Calcium or barium tallates can be employed in the preparation of toluidine reds. The pigment is treated with a tall oil fatty acid having an acid number 196, 97.6 percent fatty acid, and 0.9 to 1.3 percent free rosin acids. The tall oil fatty acid is in the form of calcium or barium salts, up to 25 percent by weight of the pigment. A solution of the calcium or barium chloride is added to the sodium tallate, and a precipitate of the tallate is obtained. The surface of the pigment particles is then changed.

Lithol reds and maroons constitute one of the most widely used groups of organic colors. This is due to their relatively low cost, wide range of color, and good color strength. Lithols are prepared by diazotizing Tobias acid and coupling it with b-napthol in the presence of sodium hydroxide. This gives the relatively insoluble sodium lithol. The barium, calcium, or strontium lithols are obtained by reacting the sodium lithol with suitable salts of the other metals. The differences in color of the lithols depends chiefly on the metal used for precipitation. The sodium lithols are light yellow reds, barium lithols are medium reds, and the calcium lithols are deep reds to maroons. The strontium lithols range in color between the barium and calcium lithols.

Lithols are available in both nonrosinated and rosinated forms. Rosination, a special case of surface
treatment for the particles, is accomplished during manufacture of the pigment by insolubilizing alkali rosinate simultaneously with the dyestuff. The rosinated types may contain 15 to 30 percent of metallic rosinate. Rosinated lithols are more brilliant in color, more transparent, produce greater gloss in printing inks, and are more readily dispersed in vehicles than are the nonrosinated types. Also, they have higher oil absorption and tend to produce a thixotropic consistency.

**Tall Oil in Defoamers**

Foams, in one form or another, are frequently encountered in chemical technology. Sometimes their presence heralds difficulties in process and equipment operation. Reaction vessels, gas-liquid contactors, and stirred tanks in general are frequently troubled with foam buildup.

One of the chemical processes most troubled with foaming is the fermentation industry. Here, large batches of liquid medium containing surface-active substances, and usually finely divided solids as well, are sparged with great volumes of air. Foaming is rapid and generally persistent, since conditions are very favorable for foam production.

A foam can be destroyed if its films are subjected to sufficiently great stresses. If the foam's "elasticity" is unable to counteract these stresses, the resultant strains cause rupture and breakdown of the foam structure. In essence, methods of foam destruction are based on the reversal of those factors that contribute to foam stability. By reversing or inhibiting the natural stabilizing influences in the foam, it can be caused to collapse.

Antifoam agents (defoamers) constitute one of the most effective and widely used means of foam control. They offer the advantage of rapid and reasonable lasting action with high specific activity requiring only small amounts of antifoam agents.

Antifoam agents are themselves surface-active. Their specific feature is a very rapid decrease in surface tension with concentration. When dropped or sprayed on to an existing stable foam, they cause extreme and rapid local variations in surface tension. Since their surface activity is greater than that of other substances, they concentrate at bubble film interfaces and force the liquid away. The film, so thinned, is weakened and breaks.

Foam formation is not just a matter of low surface tension alone. Antifoam agents produce low surface tensions but do not readily produce stable foams themselves. Chemical foam control is an essentially competitive process. The defoamers monopolize the surface layer but do not support foam formation. In doing so they keep away other surface-active agents that can produce persistent foams.

Antifoaming agents comprising a condensate of 6 moles of ethylene oxide and 1 mole of tall oil fatty acids can be employed in the aqueous nutrient fermentation media used in the manufacture of yeast. No toxic effects can be observed, either microscopically or by filtration performance, and no off-odor can be detected after washing.

Condensates of ethylene oxide with products containing abietic acid, e.g., rosin, rosin oil, or tall oil, have been cited in the patent literature as suitable foam-inhibiting agents for nutrient media for yeast and molds, penicillin, and streptomycin. Ratios of 0.76 to 6.0 moles of ethylene oxide per mole of abietic acid give most satisfactory results.

In the manufacture of phosphoric acid by the wet-process, foaming problems invariably occur, especially when the process is operated at high production rate. In this case, a 4 percent rosin tall oil acid can be used very effectively as a defoamer.

To inhibit the production of foam in the reaction between soda ash and mineral acids, especially in the preparation of NaH2PO4 from Na2CO3 and 85 percent H3PO4, refined or purified tall oil (50-600 ppm by wt.) is added to the Na2CO3 (dry or in a slurry). Tall oil is introduced in a continuous process into the mixing vessel in an amount to provide 10-800 ppm of the soda ash. The tall oil reduces the foam by more than half.
The papermaking industry is particularly concerned with combating foam troubles. Foams or bubbles of gas in paper stock cause many difficulties in the papermaking system and in the final product. In addition to detrimental effects on stock pumping, drainage on the wire, sheet formation, and internal sizing, foam may collect resin particles occurring naturally in the pulp and cause pitch trouble. Foam troubles may also occur in pigment coating of paper, surface-sizing solutions, and black-liquor recovery.

Antifoams may be added directly to the stock close to the point where foam is most troublesome, or they may be sprayed in the form of a fine, dilute emulsion onto the stock on the paper-machine wire. Fatty acids and fatty acid esters, amides of fatty acids, and metallic soaps of fatty acids are some of the foam inhibitors used by the paper industry. Usually between 0.01 and 1.0 percent defoaming agent is required on the basis of the air-dry pulp.

Products useful as defoamers for paper-mill Whitewater can be prepared as follows: 5.1 parts acid refined tall oil, 11.9 parts polyethylene glycol (600) monooleate, and 63 parts paraffin oil are mixed at room temperature. To this are added 20 parts diethylene glycol monooleate and the mixture is heated to 75°C (177°F) until clear.

Another formulation can be made by mixing 10.2 parts acid refined tall oil, 6.8 parts polyethylene glycol (400) monoester of coconut fatty acids, and 63 parts paraffin oil. To this is added 20 parts of diethylene glycol monooleate and the mixture heated to 75°C (177°F) until clear.

Effective foam-suppressing compositions, which are nontoxic and applicable in a wide range of foaming media, can be prepared from tall oil pitch. The pitch is subjected to countercurrent fractionation with propane at 54°-104°C (130°-220°F) and 550 to 575 psi. The pitch is separated into a sterol-rich raffinate and a tarry residue. The raffinate phase is saponified with alcoholic alkali to liberate combined sterols, which are then crystallized and filtered from the mixture. The filtrate is acidified to release the acids present, and the alcohol is recovered by distillation. The alcohol-free filtrate is washed with water to removal residual acid. The resultant liquid product, which is the active defoamer, contains 20 to 45 percent fatty acids, 20 to 50 percent rosin acids, and 15 to 30 percent neutral material.