

this information, and much of the data used in this paper has been obtained from them. While individual uses are many, they can be classified into two main divisions: as a raw material for numerous surfaetants, *e.g.,* soaps, asphalt additives, lubricants, flotation chemicals, fat chemicals, etc. ; and as a drying oil component in the manufacture of core oils, linoleum, oil cloth, floor tile, driers, paints, varnishes, printing inks, etc.

In some of these uses the mixture of rosin and fatty acids serves as a superior raw material to either one or the other; and it is to be expected that a substantial quantity of the whole oil, either in the crude or its refined form, will continue to be used.

The percentage of the total production of crude oil used as such will undoubtedly diminish, and the future will find increasing amounts being separated into its component parts, *i.e,* low-boiling unsaponifiable, saturated acids, oleic and linoleic acids, solid rosin, sterols, and pitch.

Until 1955 about two-thirds of the refined tall oil sold were acid-refined. In 1955 distilled tall oil increased to half the total, and now we find more than 80% of the refined tail oil is fractionally distilled.

Obviously the future of the tall oiI industry is tied up directly with the sulphate pulp industry. The average yield of tall oiI varies from mill to mill, both because of the source of the pine and the effectiveness of their recovery methods. It is generally accepted that about *90* lbs. of crude tall oil can be produced with each ton of pulp made. Not all mills achieve this yield, but, in general, good practice will produce this amount from average pine.

Using these figures, we find it would be possible to produce one billion lbs. of tall oil for the year 1958. Estimates for the future show that by 1970 or 1975 we can expect a production of about 1,550,000,000 lbs. of tall oil. The amount of fatty acid that can be produced from this volume is greater than the present fatty acid production from all sources. When one realizes that not only can these acids replace the unsaturated acids of soybean, cottonseed, red oil, and the like but also that they can readily be hydrogenated to stearic acid, it is easily understood that this produetion will have a great impact on the fatty acid industry. Even by-products, such as the palmitic acid, become a sizeable quantity when we talk of amounts of this nature. Three per cent of 1,550,000,000 lbs. is a sizeable quantity of palmitie acid if it is recovered.

Tall oil is truly a unique and valuable material and is growing in available supplies, in new refineries, in new uses, and new products.

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Production Methods for the Manufacture of Crude Tall Oil and Its Subsequent *Processing*

E. O. BARNES, Union Bag-Camp Paper Corporation, Savannah, Georgia; R. H. POTTS, Armour and Company, Chicago, Illinois; and F. B. WHITE, Foster Wheeler Corporation, New York, New York

V ARIOUS SPECIES of pine trees contain varying **kraft** pulping operation the pine chips **are** amounts of fatty acids and rosin acids. In the cooked at a relatively high temperature with a strong alkali. In addition to its primary purpose of dissolving the lignin which holds the cellulose fibers together, this cooking operation also saponifies the fatty acids and the rosin. These soaps in turn are washed out of the pulp along' with the dissolved lignin and sent back through the chemical recovery operation. In this the spent or black liquor which contains the dissolved fatty and rosin soaps is passed through multipleeffect evaporators for concentrating the black liquor to a point where it may be burned in special highpressure boilers for recovery of the inorganic chemicals and the production of steam. When the black

liquor reaches a concentration of 20 to 23% solids during evaporation, it is sent through soap skimmers where the major portion of this soap salts out, rises to the surface, and is skimmed off. This material is termed "blaek liquor skimmings" and is the starting material for the manufacture and subsequent processing of crude tall oil.

Production of crude tall oil involves the acidulation of black liquor skimmings or soaps with sulfuric acid at an elevated temperature. The actual mechanics of this production of crude tall oil has been the subject of considerable study, which has resulted in the development of several processes for the conversion of the skimmings to crude tall oil.

Basically the production methods for crude tall oil may be divided into two major classes: a) those which

utilize gravity to separate the brine and lignin from the crude tall oil, and b) those which depend on centrifugal force for the separation. There are, of course, a number of variations of each of these processes. A variation of the latter method is the use of batch acidulation equipment, followed by centrifugation for the separation of the brine and lignin from the crude tall oil.

Gravity Separation Processes

In the gravity separation processes the acidulation is normally carried out in lead and acid-proof-brick lined vats. There have been reports that money may be used in this application. Necessary agitation may be provided by top-entering turbine type of agitators or by the use of sparge steam alone. If agitators are used, it is also necessary to have the cooking tanks equipped with means for heating. Usually either coils or sparge nozzles of corrosion-resistant material are used.

A sample of the skimmings to be acidulated is titrated with acid to a pH of 4.0 to determine the amount of sulfuric acid required. Because of problems associated with obtaining representative samples of skimmings it is the usual practice to use approximately 5% in excess of the calculated amount. The sulfuric acid (usually 60° or 66° Bé) together with sufficient water or spent brine (from a previous cook) is charged to the cooking vat. Agitation and heating are started, and the skimmings are fed to the vat. As soon as the mixture is thoroughly mixed and the temperature reaches approximately 200 to 210° F. the "break" occurs, *i.e.,* enough of the skimmings are converted to crude tall oil to form an oil phase. Heating and agitation are continued for 15 to 20 min. after the "break" to insure complete acidulation of all skimmings.

Following this, heating and agitation are stopped and the contents of the "cooker" are allowed to settle. Upon settling, three layers are present in the "cooker." The bottom is a spent-brine layer, which should contain about 20% salt cake and 1% sulfuric acid. This is either returned directly to the pulp mill or pumped to a tank for neutralization with soda ash or other alkali and then pumped to the pulp mill for recovery of the salt cake.

The top layer is the crude tall oil, which contains 3% to 4% moisture in the form of spent brine and also approximately 2% solid lignin. This layer may be pumped to intermediate storage for further settling. Here most of the residual moisture and lignin settle out and are discarded or returned to the cooking vat for recovery of the oil content. Following this settling, the crude oil contains between 1% to $1\frac{1}{2}\%$ moisture and is ready for use.

The middle layer in the cooking vat is the lignin layer and contains about 60% solid lignin, 20% moisture, and 20% crude tall oil. In an operation of this type the lignin layer may be washed out of the cooking yat with a high-pressure water stream and sent to the sewer.

The flow diagram of the process described above is shown in Figure 1.

Centrifugal Separation Processes

There are at least two processes utilizing the principles of continuous acidulation, followed by centrifugal separation. One of these is described elsewhere in this symposium (1). Another employs the flow diagram shown in Figure 2 (2).

The soap is pumped through a manually adjusted feed control to an acidulation mixer. Prior to its introduction into the mixer, the soap is diluted by means of a mixture of a solution of a selected treating agent and hot water, which is metered directly into the soap line through a mixing tee. This treatment is utilized both to reduce the viscosity of the soap and also to permit the treating agent to contact the lignin and emulsified soap present in the soap skimmings. The latter action has been found to be quite critical to the success of the process in conditioning the soap for acidulation and subsequent separation.

The diluted soap stream is piped into the bottom of a vertical acidulation mixer, which provides for the continuous mixing of the soap with dilute sulfuric acid. The latter is fed into the bottom section of the mixer and is prepared by metering concentrated sulfuric acid into a cold water stream and by passing the solution through a cooler before entry into the mixer. The soap skimmings are acidulated, producing a mixture of crude tall oil, lignin, and spent acid. This stream, discharging from the top of the mixer, passes a self-cleaning screen, which is utilized to remove a small amount of fibrous solids present in the feed so as to prevent plugging the centrifugal separator.

The screened stream drops to a catch tank where live steam is used to increase its temperature from approximately 160 to 200° F. Into this tank are fed two additional streams: metered hot water to reduce the density of the spent acid and recycled spent acid.

The hot mixture of tall oil, lignin, and spent acid together with some sulfate salts is fed to the centrifugal separator. The centrifuge utilizes nozzles in the periphery of the bowl to discharge continuously any

heavy solids, mainly lignin. Its design has been altered substantially from standard units to permit the separation of the tall oil and spent acid without the plugging that would require a shut-down for cleaning.

The centrifuge discharges three streams: a light phase consisting of separated crude tall oil, a heavy phase or ring dam discharge containing lignin and spent acid, and a nozzle discharge composed of spent acid together with a small amount of fine solids. The ring dam discharge together with the nozzle discharge from the centrifuge drops to a compartmented tank. A separation of the lignin and spent acid occurs; clear spent acid is recycled back to the centrifuge feed tank. The remaining spent acid together with the lignin phase is discharged over a weir in the compartmented tank and is pumped back to the mill for recovery. The separated crude tall oil from the centrifuge is pumped from a catch tank to a settling storage tank for removal of additional moisture before being pumped to storage.

Published data on the continuous process indicate excellent yields without problems associated with disposal of a lignin. The resulting crude is very high in acid value and contains a minimum amount of lignin.

Crude Tall Oil Product

The American crude tall oil is primarily a mixture of fatty acids and rosin acids and may contain from 35 to 65% rosin, depending upon the geographic source and species of pine used for pulping. In addition to these fatty acids and rosin acids, the crude tall oil contains about 5 to 8% of what we term *"un*saponifiables," composed principally of sterols, hydrocarbons, and higher alcohols. Yields of crude tall oil are normally expected to be in the neighborhood of 2%, based upon the dry weight of the pine wood pulped. In some regions it may be as high as $3\frac{1}{2}\%$. While these yields appear low, it must be remembered that the production of kraft from pine is a tremendous business and in 1957 a total of approximately 320,000 tons of crude tall oil were produced.

l~ractional Distillation of Tall Oil

This portion of the paper will be presented in sections: preparation and storage of crude tall oil, dehydration of feed stock, fractional distillation, and storage of products. In general, reference will be to a plant which fractionally distills crude tall oil to produce stable, light-colored fatty acids and rosin. It was engineered and constructed for the Union Bag-Camp Paper Corporation by the Foster Wheeler Corporation under license from Armour and Company.

Preparation and Storage of Crude Tall Oil. Proper preparation of crude tall oil before it enters the distillation system has an important effect upon the distillation process. The "cleaner" the feedstock, the higher will be the recovery of desirable end-products. Absence of free inorganic acid will result in reduced rates of corrosion. Unchanging feed analysis will aid the still man to control operating conditions to give end-products of uniform quality.

Good results in a fractional distillation system depend more than a little on the facilities available in the area of raw-material storage. This is well known to fatty acid producers with distillation systems and is attributable to the dependence of good still-operation upon the continuity of uniform conditions.

For example, if raw material storage tanks are too small, the still operation may suffer when changing from one feed tank to another unless the stock in each tank is identical. This is not always possible when raw materials are constantly being shipped into the plant from different locations.

Another recommendation, again to insure maximum feedstock uniformity, calls for the use of tank mixers. Without these, settling and sedimentation in the feed tanks would make it necessary for the still to handle a constantly varying feed. Consequently operating conditions in the still would have to be changed intermittently to compensate for this varying feed. Such varying conditions are not conducive to the production of high-purity products expected from a top-notch tall oil fractional-distillation plant.

In addition to feed-stock uniformity it is beneficial to maintain constant temperature in the feed tank. A changing feed temperature would make it necessary to adjust other stock temperatures farther down the line, which again would make more difficult the production of high-purity products.

Heating of feed in storage can be accomplished by use of an external system in which crude tall oil is circulated through a shell and tube steam-heated exchanger. This is schematically shown in our flow sheet, Figure 3. With such a system it would also be

helpful to provide some heat locally in the feed tank adjacent to the outlet nozzle leading to the circulating pump. The latter supplementary heat is needed in case of a protracted shut-down of the circulating pump.

Construction of the crude storage tanks may be of carbon steel without running into serious corrosion if a protective coating is used in the vapor space. However it is recommended that feed tank temperatures do not exceed 160°F.

Dehydration of Feed Stock. Reference to the flow sheet shows that we recommend dehydration of feed stock prior to distillation. This may be accomplished by heating the feed to about 185°F. under barometric condenser vacuum and by providing adequate vapor release area for dissolved and occluded water on trays or in sprays. Flashing will take place and leave a feed containing no more than 0.2% moisture.

Dehydration has two important beneficial effects. First, the removal of moisture eliminates the possibility of slugs of water being evaporated into steam at a point in the distillation system where such would be harmful. For example, a sudden flashing of water into steam in the feed heaters, following the dehydrator, would increase sharply the pressure drop in the feed line to the distillation towers. This would cause a decrease in output of the feed pump until the flow-controller could take hold to readjust the flow. However no ordinary flow-controller can cope with sudden pressure-drop changes which result from flashing slugs of water. Second, the removal of moisture in the dehydrator reduces fouling of heat transfer surfaces downstream in the system. This comes about since the water present in crude tall oil, either in suspension or in solution, always contains some inorganic salts, such as sodium sulfate. (These salts come from the acidification of tall oil soap to form crude tall oil.)

If the water is not removed from the feed stock in a dehydrator, where the salts coming out of solution can be handled easily as a suspension, evaporation will inevitably take place in the heaters which precede the distillation towers. Where this evaporation takes place in the heaters, salts dissolved in the water are deposited on the heater tubes, thereby reducing greatly their capacity for heat transfer. In time this fouling will make necessary a shut-down of the heater to permit cleaning.

Fractional Distillation. The plant operates in a blocked operation, that is, rosin and fatty acid intermediate are made during a portion of the cycle. A switch is then made to run the fatty acid intermediate back through the distillation system to produce high-quality fatty acid. The reason for choosing blocked operation over a completely continuous process was two-fold. In the first place the plant could be built for a lower initial cost, and secondly it could be expanded into a much larger installation by adding a second tower to permit continuous operation as the business expanded.

The dehydrated feed stock is heated by pumping through a heat exchanger and a feed heater, where it is brought up to approximately 500° F. It then is flashed-distilled under high vacuum in a Dowtherm 1 heated flasher and stripping tower in the presence of steam. The flash distillation takes place so quickly that degradation of heat-sensitive constituents in the crude tall oil is minimized in spite of the relatively high temperature. Pitch is removed from the base of the stripping tower after it has been thoroughly steam-stripped of its volatile products. Overhead vapor from the tower, consisting of rosin, fatty acids, and some unsaponifiables, leaves the stripping tower to enter the main fraetionating tower.

This consists of a large number of bubble plates, a reboiler in the base, and a series of condensing trays at the top. The tower's main function is to separate rosin from fatty acids, and the rosin, stripped of its fatty acid content, leaves the base of the tower and requires no further processing. On its way to storage it is cooled by a heat exchanger in which the feed stock is partially preheated. Intermediate fatty acids containing a small amount of rosin are distilled and collected for further processing, and odor-containing, low-boiling impurities are removed from the very top of the tower.

The design of equipment for condensing fatty acid vapors requires close attention. The presence of the saturated fatty acids which have high melting-points tend to foul conventional condensers. There are patents covering the use of internal condensing systems, and these are widely used.

A problem which requires careful consideration is the cooling of rosin leaving the fractionation tower. This normally leaves the tower at a temperature range of 480 to 525°F. If put directly in drums for storage, the rosin will pick up oxygen from the air, and, as a result, the product is considerably degraded. It is therefore necessary to cool it down to approximately 350° F. Use of a simple heat-exchanger, using water at normal temperatures as a cooling medium, will result in plugging quite quickly. It is necessary instead to use other means of cooling the rosin, such as heating the feed stock or circulating a coolant at high temperature. It is a corollary that all pipe lines used for handling rosin must be either steam-traced and insulated or else jacketed and insulated; all valves in the rosin lines must be jacketed.

The flow diagram for the second-stage operation is practically the same as for the first stage, but in this case the intermediate fatty acid fraction containing some rosin is fed directly to the distillation tower, after being brought up to distillation temperature by the use of the Dowtherm preheater. The bottomsproduct from the distillation tower is in this case a fraction containing about 30% rosin acid, which may be sold as distilled tall oil. The main product is taken off near the top of the tower and is a distilled fatty acid of high purity. At the top an overhead product is withdrawn, consisting of unsaponifiables and lowerboiling fatty acids. This cut also contains the saturated acids, principally palmitic.

Typical product specifications which may be expected are shown in Tables I and II.

In addition to the production of high grade fatty acids and rosin, the separation of these two materials necessarily carries with it the production of other secondary products. Tall oil pitch, which comprises roughly 10 to 20% of the crude tall oil fed to the distillation process, finds use in asphalt emulsions and similar products. Care must be taken in a distillation to keep the pitch to a minimum although at the same time degradation of the pitch because of heat and/or residence time can result in dark rosin products and, in some cases, dark fatty acid products.

¹Dowtherm is a registered trade mark of the Dow Chemical Company.

By the same token, failure to produce an optimum amount of pitch may result in the decreased production of rosin and fatty acids, and both products may have characteristics somewhat different from the characteristics ordinarily expected of such materials. Heads and odor-cut products are also obtained.

TABLE 1I

These should be kept to a minimum. However failure to remove the optimum amount will result in increased unsaponifiables and saturated fatty acids in the fatty acid product.

The production of rosin containing 3% or less fatty acids and the production of fatty acids containing 1% or less rosin acids necessarily carry along the production of a small amount of distilled tall oil. This oil contains fatty acids and rosin acids which boil in the same range so that separation is either impossible or ineffectual. These components may result from degradation of the fatty acids and rosin acids during the distillation operation, or they may have originally been present in the crude tall oil. There is evidence to support both theories. Regardless of the source of these components, it is necessary to remove them as a separate stream; otherwise the rosin product will eontain an excessive amount of fatty acids, which will render it unfit for certain uses, and the fatty acids will contain an excessive amount of rosin acids.

Based upon a feed containing 50% rosin, 42% fatty acid, and 8% unsaponifiables, approximate recovery may be expected as indicated in Table III.

It is natural that distillation has become the preferred method of separation for it has been in use as a means of purifying fats for many years. It is an economical and successful method, but it has presented and perhaps ahvays will present many problems to test the ingenuity of chemists and chemical engineers because, at the temperatures required for vaporization, fatty acids are thermally unstable. Care must be taken if high yields and products of good quality are to be obtained. When fatty acids are subjected to high temperature, they decompose; the extent of decomposition is a function of time and temperature. Usually the first step is one of anhydride formation, with the loss of one mol of water

TABLE III

${\bf Pitch}.\hspace{1cm} \begin{minipage}{1.5cm} \begin{tabular}{l} \hline \textbf{Pitch} & \textbf{Pitch} & \textbf{Pitch} \\ \hline \textbf{Pitch} & \textbf{Pitch} & \textbf{Pitch} \\ \hline \end{tabular} \end{minipage} }$	

from two mols of fatty acids. As the temperature increases, ketones and hydrocarbons are formed, with a loss of $CO₂$. Unsaturated fatty acids condense to form nonvolatile polymers, resulting in high residue losses. To prevent thermal decomposition during distillation, combinations of injected steam and reduced pressures are used. Distillation temperatures of about 250° C. (482°F.) are desirable, and it is also beneficial to use some direct steam, regardless of the pressure, because a small amount of water helps to repress anhydride formation.

The decision as to the type of column to be used for the separation of crude tall oil into fatty acids and rosin acids must, of course, be predicated upon the individual requirements of the processing and the availability of the various utilities. Regardless of the type of column used, it is quite important that care be exercised to eliminate air leakage, to keep the residence time at high temperature to an absolute minimum, and to utilize those materials of construction necessary to prevent corrosion and color pick-up in the product. In most cases Type 316 stainless steel with a minimum molybdenum content of 2.5% is preferred for this service. For the most severe services there are those who prefer Type 317 stainless steel with a minimum molybdenum content of 3.0%.

Storage of Products. Product storage must be designed to minimize day-to-day problems confronting a producer. Such problems relate to balancing production with sales, minimizing maintenance and unnecessary labor in the storage area, darkening of products, and uniformity of product quality.

The first is primarily a management decision, finally to be made when operating procedures have been standardized. However it is up to the plant supervisor to see that he has adequate storage for both raw materials and products to satisfy the requirements of his sales department without the need to face unreasonable production schedules. Careful consideration of this factor is necessary before the plants is constructed.

Second, to minmize maintenance costs in the product-storage area, attention should be paid to the materials of construction of the tankage and its related piping'. Aluminum or an 18-8 stainless steel will do very well and are recommended.

Heating of lines and provision to blow them clean with inert gas also will be helpful to minimize maintenanee work in the storage area. Lines containing materials which may harden or solidify at atmospheric temperatures are best kept warm to prevent freezing. There is always the possibility, particularly when handling rosin, that a frozen line must be dismantled to thaw and free it effectively.

Third, the tendency of fatty materials to darken on standing is well known. To combat this tendency, tankage and piping should be constructed of materials which have little or no effect upon product color. Aluminum and 18-8 stainless steel arc both recommended for this purpose. Similarly tank ears and drums should be lined with a protective coating to prevent iron pick-up and consequent darkening.

Oxygen in the air will hasten the darkening of distilled products. Therefore it is desirable to exclude atmospheric air from the storage tanks. This is done with a blanket of dry inert gas, supplied by

compressing and drying the combustion products of a gas or oil burner. Distribution of this gas to each storage tank may be controlled by flow orifices which limit the flow to each tank. The same inert gas system should be used to purge tank ears before loading.

Last, uniformity of product quality may be improved by providing good agitation in the storage tanks. This is particularly useful in the case of relatively large storage tanks, which are capable of holding several weeks' to several months' production.

The use of these procedures helps to insure a product in storage of much the same quality as that produced in the distillation columns.

Summary

The source of crude tall oil and methods to produce the oil have been described. These include acidulation of sulfate pulp, black liquor skimmings, and gravity settling as well as centrifugal means of separation to reduce the ligniu content of the product.

Subsequent processing of the crude tall oil into fraetionated fatty acids and rosin has been outlined with suggestions for consideration in all stages of the distillation section of the plant.

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The Nomenclature of Tal Oil Fatty Acids and Their Derivatives

EDWARD H. SHEERS and BENJAMIN D. BERKMAN,

American Cyanamid Company, Stanford, Connecticut

consists of a mixture of C₁₈ unsaturated fatty acids, rosin acids, and relatively small amounts ALL OIL, a by-product of the Kraft paper industry, consists of a mixture of C_{18} unsaturated fatty of saturated fatty acids, and unsaponifiables. Vacuum fractionation yields predominantly a fatty acid fraction and a rosin fraction; the saturated fatty acids and unsaponifiables are either almost completely removed in the overhead fraction or remain in the residue, which is called tall oil pitch.

We are concerned in this paper with the nomenclature of the fatty acid fraction and its derivatives. Although there is some geographical and seasonal variation in the ratio of fatty to rosin acid content, American tall oil fatty acid fractions can generally be considered to be a 1:1 mixture of octadecenoic (oleie) and octadecadienoic (linoleie) acids. Thus this fraction has an over-all unsaturation of 1.5 double bonds per molecule. It is this simplicity and consistency of composition which makes the tall oil fatty acid fraction different from most other natural sourcederived fatty acids. Most others have at least three major constituents (Table I).

We believe therefore that for certain purposes it would be both desirable and possible to name this

TABLE I Major Components of Fatty Acid Fractions Derived
from Natural Sources ^a

Acid	Coconut oil	Cotton- seed oil	Soybean oil	Ta11 oil
	18			
		21		
Octadecenoic (oleic)		30	33	48
Octadecadienoic (linoleic)		44	51	50

a Percentages less than 5% have been ignored.

fraction, particularly its derivatives, in a manner which would be more indicative of their chemical nature than "tall oil fatty acids."

At present, no system of nomenclature is used consistently in this field. Generally tall oil fatty acids are eith ϵ_1 referred to as such or by trade names. Occasionally the term "TOFA" is used as an abbreviation. Derivatives are also either referred to by trade names or by derivation from "tall oil fatty acids."

As the use of the tall oil fatty acid fraction as a chemical intermediate increases, the need for a systematic nomenclature to describe its derivatives becomes increasingly evident. To many organic chemists the

