Trends

It seems inevitable that marine oils will be further exploited as raw materials for further chemical modification. They form a unique source of long chain fatty acids and alcohols, and it is quite possible that, by separating the oils from different parts of the fish or animal bodies more carefully, products of greatly increased value will result; certainly this is already true of the liver oils. These marine oil products reacted with various chemicals should form intermediates, such as olefins, amines, nitriles, halogenated compounds, and many others which are not available from other fats and oils or from petroleum. Much research work must be done to accomplish the possibilities that exist in this field.

Additional regulation of the fishing industry may be necessary to prevent the extermination of some important species. These must be accompanied by further studies of marine life to learn how to stem or reverse the migration of some fishes away from the coastal areas of this country. The fishing industry is large and marine oil production is an important phase of it. Continued research is destined to make it even more important in the future.

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Tall Oil

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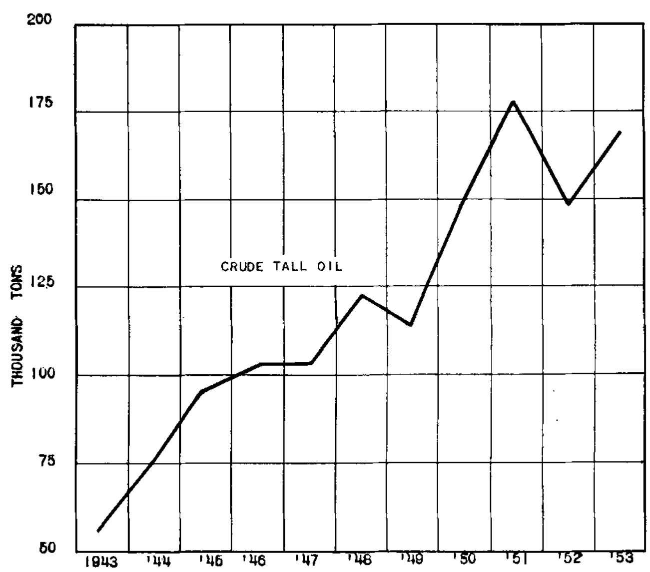
A RELATIVELY new source of inedible fatty acids and of rosin is derived from southern pine. It is tall oil, a mixture of rosin and fatty acids, which is obtained as a by-product in the manufacture of kraft paper by the sulfate process. It is the purpose of this paper to outline the general method used for recovery of tall oil and to review the refining and separation processes which are used in the United States to convert tall oil into more valuable raw materials for the chemical industry. The production of tall oil in America has increased at a rapid rate during the last 10 years, according to figures of the Tall Oil Association (1) shown in Figure 1.

Richard Herrlinger

The fast growth of tall oil production from about 50,000 tons in 1943 to 175,000 tons in 1953 reflects the technological advances achieved during this period by both the producers and the users of tall oil and tall oil products. Processing methods were developed which now allow not only the production of products of higher quality but also the substantially complete separation of tall oil into rosin and fatty acids. The paint and varnish industry, through the use of new polyfunctional alcohols, maleation, and styrenation, has greatly extended the utility of tall oil products in surface coatings. New applications have developed in such fields as detergents and metallic driers.

A major reason for the growth of tall oil production is the economical and stable source of black liquor soap from which tall oil is made. Black liquor soap is derived as a by-product during recovery operations from digester liquors of the sulfate paper process as shown in Figure 2.



PRODUCTION OF CRUDE TALL OIL 1943-53

FIG. 1

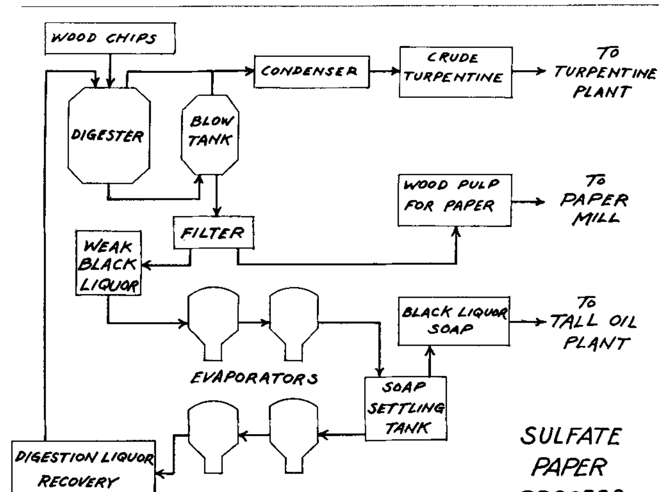


FIG. 2

To produce paper by the sulfate process, chips of pine wood are digested under pressure with a solution of sodium hydroxide and sodium sulfide in order to free the cellulose from lignin and other wood constitutents. Fats, which are present in wood, are hydrolyzed during this process and go into solution as soaps. Rosin and lignin are also converted to soluble sodium salts. Terpenes are volatized with the steam, released from the digesters, and condensed as crude sulfate turpentine, which is also recovered and constitutes another important by-product of the sulfate paper mills.

After the digesting cycle is completed, the charge is blown into a blow-tank, the wood pulp is drained of its digestion liquor, washed in Oliver filters, and further processed into paper. The dilute dark solution, coming from blow-tank and filters, called black liquor, is then concentrated in multiple-effect evaporators.

At some stage during the concentration, usually between the second- and third-effect evaporation, the liquor is allowed to cool in a tank where the sodium salts of the fatty and rosin acids separate as a brown curdy mass, which is called black liquor soap or black liquor soap skimmings. The liquor is concentrated further and is finally burned in a furnace; the valuable alkali is recovered from the ash for re-use in the process.

The black liquor soap is skimmed off and pumped to the crude oil tanks for conversion into tall oil. It contains about 60% solids and yields about 50% crude tall oil on acidification. For each ton of paper pulp produced by the paper mills, 80 to 200 lbs. of black liquor soap or 40 to 100 lbs. of tall oil can be obtained from the recovery liquors. The potential amount of raw material which is available from this source and which is constantly growing can be appreciated by examining the figures for southern states' pulp production as reported by the Tall Oil Association (see Figure 3).

At present only 50% of the available black liquor soap is being recovered so that the present potential is already nearly 300,000 tons of crude tall oil per year. The conversion of black liquor soap to crude tall oil is illustrated in Figure 4.

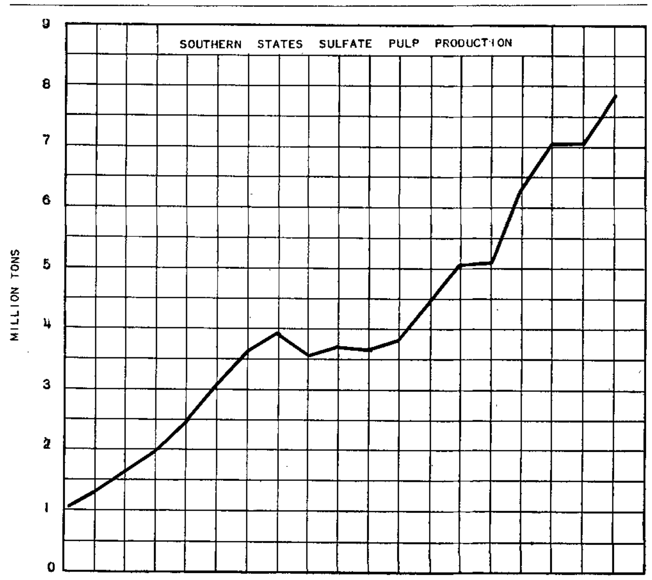
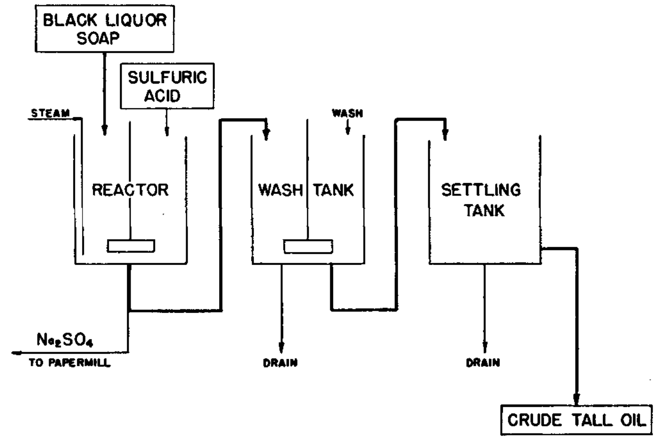


FIG. 3



CRUDE TALL OIL PROCESS

FIG. 4

Black liquor soap and sulfuric acid are reacted in a lead or brick-lined kettle. Live steam is used to cook and agitate the mass. Mechanical agitation may also be used. On settling, the reaction mixture separates into an upper layer of light-brown tall oil and a lower layer of a concentrated solution of sodium sulfate, which also contains water-soluble wood constituents. The sodium sulfate solution is drawn off and returned to the alkali recovery liquors of the paper mill.

The tall oil is then washed with sodium sulfate solution or water to remove free sulfuric acid and finally allowed to settle in storage tanks to reduce the water content to specifications.

TABLE I

Analysis Range of American Crude Tall Oil

Acid No.	153-170
Sapon. No.	167-178
Iodine No. (Wijs)	165-176
Rosin Acids, %	35 - 50
Fatty Acids, %	41 - 59
Unsaponifiables, %	6 - 9
Moisture, %	0.2-1.2

The analysis range and composition of American tall oil is given in Table I. It will be seen that tall oil is essentially a mixture of rosin acids and fatty acids. The composition of the fatty acids in American tall oil has been determined by fractional distillation of the methyl esters and spectrophotometric analysis by Anderson and Wheeler (2) and confirmed in our Stamford Laboratories. It is given in Table II.

The fatty acids consist chiefly of a mixture of oleic and linoleic acids. The saturated acids consist mainly of palmitic acid but include minor quantities of stearic and higher saturated acids. There is also a minor percentage of palmitoleic acid, which is listed as oleic acid, and there are traces of dibasic acids.

The unsaponifiables in tall oil consist mainly of a mixture of hydrocarbons, long-chain alcohols, and

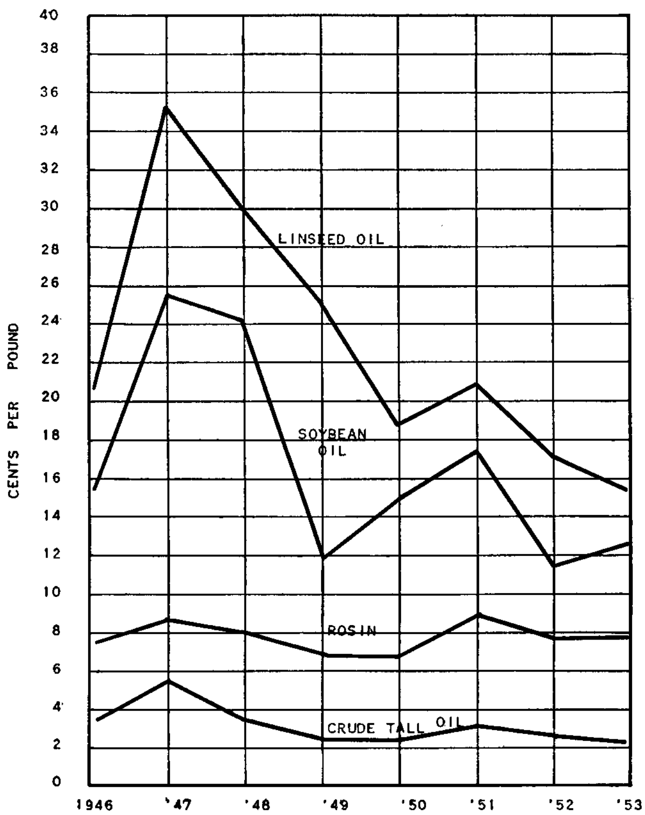
TABLE II

Average Composition of Fatty Acids in American Crude Tall Oil

	Anderson & Wheeler	American Cyanamid Co.
Saturated Fatty Acids, %	7	6
Oleic Acid, %	45	48
Linoleic Acid, %	48	45
Linolenic Acid, %	None	1

sterols, primarily β-sitosterol. The rosin acids of tall oil have been investigated by Harris (3) and found to be substantially the same in composition as the rosin acids found in gum and wood rosins.

Tall oil is therefore a very valuable source of both fatty acids and rosin. Manufacturers who use both materials in products such as paints and varnishes, flotation reagents, linoleum, and core oils have found crude tall oil a low-cost raw material. It has found a large market despite certain deficiencies such as dark color, woody odor, varying rosin content, and difficult handling due to crystallization of the rosin. A dependable supply of black liquor soap has kept the price of crude tall oil fairly steady during the last eight years as seen in Figure 5.



PRICES OF CRUDE TALL OIL LINSEED & SOYBEAN OILS

FIG. 5

This is in contrast to the fluctuating prices for other inedible oils and for rosin during the same period of time. The price of tall oil, as compared to the much higher prices of fatty acids and rosin, has inspired chemists and engineers to upgrade tall oil products and to attempt its separation into rosin and fatty acids.

Since the beginning of this century, when tall oil was first discovered in Sweden, there have been hundreds of patents issued and numerous papers published (4) which give testimony to the imagination and resourcefulness which has been applied to these problems.

Despite the many ingenious schemes which have been proposed and tried, there are only a few processes which have found technical application. Major processes currently practiced in the United States fall into the following three groups:

Process	Products
Acid Refining	Refined tall oil (high viscosity, 35-45% rosin acids)
Distillation	Distilled tall oil (low viscosity, 20-32% rosin acids) Technical abietic acid (crystals, 10% fatty acids) Tall oil pitch
Fractional Distillation (A.) Partial Separation	Tall oil fatty acids (5-20% rosin acids) Distilled tall oil (20-32% rosin acids) Rosin acids concentrate (25-40% fatty acids) Tall oil pitch
(B.) Complete Separation	Tall oil fatty acids (1-1.5% rosin acids) Tall oil rosin (1-3% fatty acids) Tall oil pitch

Acid-refining of tall oil is widely practiced in the United States. Crude tall oil is dissolved in a low-boiling petroleum hydrocarbon and treated with 10-15% concentrated sulfuric acid (5) in a lead-lined tank equipped with cooling coils. The temperature is preferably kept below 30° C. to minimize side reactions. The principal effects are the precipitation of color bodies and unsaponifiables in the form of a heavy black tar and a partial polymerization of the rosin acids. The clear, settled solution is washed first with a sodium chloride solution, then with water, and is finally stripped free from the solvent which is re-used.

The refined oil is lower in unsaponifiables, has a lighter color, better odor, and a much higher viscosity than the original crude tall oil. It has found a large market in surface-coating products, soaps, and detergents.

The most successful methods for purification and separation of tall oil are simple distillation and fractional distillation. Rosin, fatty acids, and low-boiling unsaponifiables have sufficiently different vapor pressures to allow their separation from higher-boiling impurities (pitch) as well as from each other.

Since both rosin and fatty acids are heat-sensitive and their vapor pressures are low, high vacuum or vacuum with the addition of superheated steam is needed to keep the temperature low enough to prevent decomposition. The equipment is therefore specially designed to accomplish the desired results and may range from a still pot or short fractionation tower to a complicated multiple-tower system. Various tower packings and bubble plates are used.

Since tall oil is very corrosive at the high temperatures which are used in tall oil processing (150-300° C.), the finding of suitable materials of construction for towers, heat exchangers, and pumps has been a major problem to tall oil processors. This has now been largely solved by the availability of special corrosion-resisting alloys. Heat for vaporizers and reboilers is usually supplied by Dowtherm, and advantage is taken of heat exchangers to transfer heat from the condensate to the feed.

A typical scheme for simple distillation combined with rosin acids crystallization is shown in Figure 6. In this process crude tall oil is vaporized or flashed under vacuum into a short column or still pot, often equipped with some packing or a few plates to allow separation of the more volatile heads and to prevent entrainment.

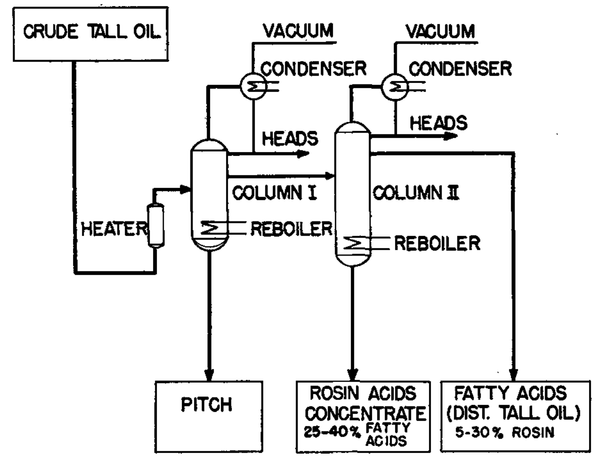
A high-boiling residue, rich in unsaponifiables including sterols, flows as pitch from the bottom of the still while the mixture of rosin and fatty acids distills. The distillate is essentially of the same rosin acid content but of lower unsaponifiables content as the crude tall oil feed. It is passed into water-cooled crystallizers where rosin acids in excess of their solubility crystallize. They are separated by centrifuging. The mother liquor containing about 36% rosin acids is usually redistilled to lower the rosin content and to lighten the color. One still is often used for both distillations.

The rosin content of this type of distilled tall oil is usually held between 28-32%. It is of light color and similar to oil obtained with more elaborate fractionation equipment but contains more unsaponifiables and saturated fatty acids than the fractionated product. The consistency of tall oil pitch depends on the extent of stripping. It may vary from a thick dark-brown oil to a waxy balsam-like mass. The acid number also varies but is usually held between 50-100, depending on the efficiency of the equipment or customers' requirements.

Technical abietic acid is obtained as free-flowing white crystals containing about 10% fatty acids. Because of the large surface area of the crystals, oxidation takes place after a short initiation period, the crystals turn yellow, and their quality decreases unless used within a relatively short time. For this reason some tall oil distillers have modified their equipment to avoid the production of abietic acid. This may be done by the addition of fractionation plates or packing to the distillation tower to allow the separation of rosin and fatty acids into two fractions, one containing less than 30% rosin acids and one high in rosin acids, usually 60-70%.

This type of separation is better accomplished by employing a second fractionation tower which, if equipped with sufficient packing or bubble plates, will also allow the production of fatty acids with a still lower rosin acids content. The scheme for this type of operation, which is also extensively used, is shown in Figure 7.

Depending on the design or operation of the fractionating columns, tall oil fatty acids or distilled tall oil over a range of 5 to 30% rosin acids are obtained from the top of the second column while a rosin acids concentrate containing 60-70% rosin is obtained from the bottom. Tall oil pitch and low-boiling heads are also removed.



TALL OIL PARTIAL FRACTIONATION

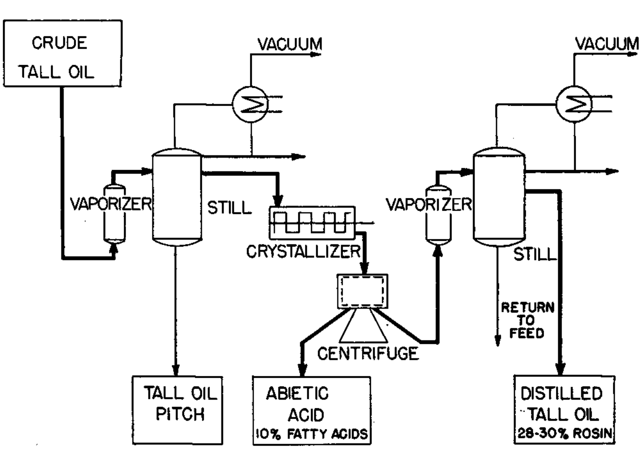
FIG. 7

This system is an advance over simple distillation in that it allows the production of fatty acids with a relatively low rosin content. However this affords only a partial separation because a considerable part of the fatty acids remain with the rosin, which is drawn off as the concentrate.

These rosin acids concentrates have found some use in soaps and alkyd resins. Because they are obtained as thick crystalline slurries, resembling honey, they are hard to handle. One producer has improved handling by controlling the crystallization during the cooling of the rosin acid concentrate fraction so as to produce a mass of very fine crystals resembling maple sugar. Another manufacturer converts the rosin acids concentrates, by chemical treatment, into a thick, non-crystallizing syrup.

The problem of complete separation of tall oil into fatty acids and into hard, vitreous rosin, comparable to gum and wood rosin, was finally solved by a more elaborate fractional distillation process. This process, which was developed in the laboratories of the American Cyanamid Company, employs the newest fractional distillation techniques and equipment design. It achieves the separation of tall oil into fatty acids with a rosin content as low as 1% and into rosin containing as little as 1% fatty acids. This process is carried out on a large scale at the Panama City, Florida, plant of the Arizona Chemical Company, a company jointly owned by the American Cyanamid and International Paper Company.

The scheme for separation of tall oil into rosin and fatty acids is shown in Figure 8. Crude tall oil is vaporized and passed into a fractionating tower to remove high boiling constituents as tall oil pitch. The vapors of fatty acids and rosin acids are passed into a second tower where they are fractionated into fatty acids, containing 3-5% rosin acids, which are removed overhead, and rosin containing 0-3% fatty acids, which is drawn off the bottom of the tower. The over-all recovery as rosin and fatty acids by this process is over 75%. Low-boiling constituents containing color and odor bodies are removed as heads; water vapor and non-condensable gases pass out of the tower. The fatty acids on refractionation yield



TALL OIL DISTILLATION & ROSIN ACIDS CRYSTALLIZATION PROCESS

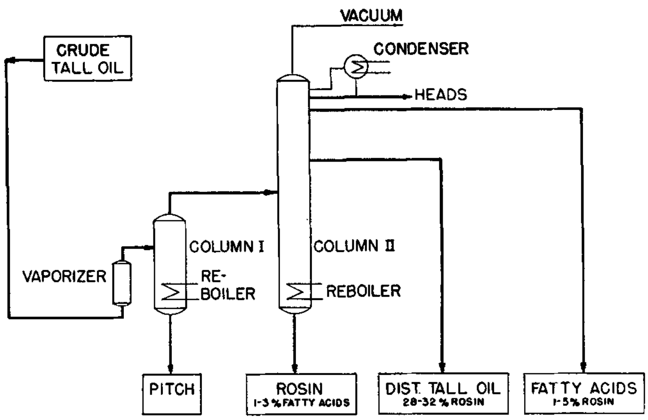
FIG. 6

TABLE III

Analysis of Typical American Tall Oil Products

	Acid-Refined Tall Oil		Distilled Tall Oil	Tech. Abietic Acid	Tall Oil Pitch	Rosin Acids Conc.	Tall Oil Fatty Acids		Tall Oil Rosin
	Low Visc.	High Visc.					Single Fractionation	Refractionation	
Color, Gardner	9+	12	9		18 [a]		9	6+	WW [c]
Acid No.	167	158	190	182	63	178	189	194	168
Sapon. No.	170	162	193	184	110	184	192	196	176
Iodine No. (Wijs)	143	162	164	—	138	—	138	130	—
Rosin Acids, %	40.1	42.0	30.0	89.0	28	62	3.5	1.0	94.5 [b]
Fatty Acids, %	52.7	50.5	68.6	9.5	31	30	92.5	96.8	1.5
Unsaponifiables, %	6.9	7.5	1.4	1.5	33	8	4.0	2.2	4.0
Viscosity, Gardner	X-Y	Z+	D	—	—	—	A	A	—

[a] 10% in benzene.
[b] Includes rosin esters and anhydrides.
[c] U. S. Rosin Standards.



TALL OIL COMPLETE FRACTINATION

FIG. 8

a product with a rosin content of 1-1.5% and an unsaponifiable content of 1.5-2.0%. A fraction containing about 30% rosin is withdrawn from a lower point on the tower as "distilled tall oil."

Table III shows the analysis and composition of high quality products obtainable from the refining and distillation processes described. The pitch obtained in all distillation processes is essentially the same except for acid number and consistency. Fatty acids differ mainly in rosin and unsaponifiable content.

Complete separation has produced fatty acids which, due to their low rosin and unsaponifiable content, have moved into the class of semi-drying oils and fatty acids. Because of their similarity in composition to soya fatty acids, as shown in Table IV, they have found excellent applications in alkyds, soaps, synthetic detergents, and metallic driers.

The rosin obtained by the complete fractionating process has been admitted under the Naval Stores Act (6) as tall oil rosin and is the only rosin derived from tall oil defined under this Act. A comparison with wood and gum rosin is shown in Table V. Tall oil rosin is obtained in very pale color grades, varying from WG to X. It is characterized by a low unsaponifiables content, high softening point, low fatty acid content, and freedom from impurities.

TABLE IV

Comparison of Tall Oil Fatty Acids with Soya Fatty Acids

	Soya Fatty Acids	Tall Oil Fatty Acids
Acid No.	198	194
Sapon. No.	204	196
Iodine No.	132	130
Rosin Acids	—	1.0%
Unsaponifiables	2.3%	2.2%
Fatty Acids	97.7%	96.8%
Composition of Fatty Acids		
Saturated Acids	15 %	2 %
Oleic Acid	27 %	50 %
Linoleic Acid	51 %	48 %
Linolenic Acid	7 %	None

TABLE V

Comparison of Typical Tall Oil Rosin with Pale Grades of Wood and Gum Rosin

	Tall Oil Rosin	Gum Rosin	Wood Rosin
Color Grades	WG-X	WG-X	WG-X
Acid No.	165	165	164
Sapon. No.	173	171	173
Softening Point	78° C.	78° C.	80° C.
Unsaponifiables	3.5%	6.5%	7.0%
Fatty Acids	1.5%	None	None

There are a number of processes which have been proposed but are not commercially practiced, such as extractions with liquid propane or furfural, selective esterification followed by distillation, neutralization, or extraction, selective neutralization, and thermal diffusion. References to numerous articles and patents describing these processes can be found in the literature (4, 7).

There have been a number of excellent reviews on the application of tall oil products, references for which can be found in West's bibliography (4). Other valuable and detailed information on the uses of tall oil products are found in the bulletin, Tall Oil in Industry (1), published by the Tall Oil Association, and in sales literature of producers of tall oil products.

Summary

Tall oil processing is a relatively new and rapidly growing industry. Based on a stable supply of raw material from the kraft paper industry, it provides an important source of rosin and fatty acid products. The processes most generally employed in the United States are acid refining, distillation, and separation by fractional distillation.

Tall oil refining techniques have advanced to the point where fatty acids substantially free from rosin acids and rosin substantially free from fatty acids are produced. With continued growth of the industry and further advances in tall oil technology, products of even greater refinement and wider utility may be expected in the not too distant future.

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