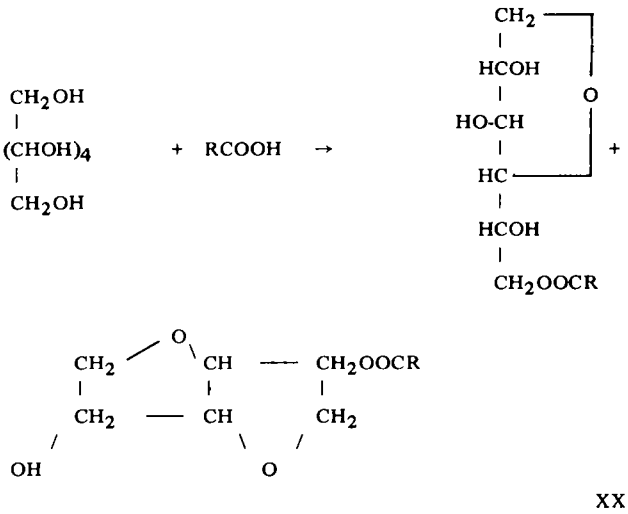
TABLE I

$RCOOH$	$+ {}^-OH$	very → fast	$RCOO^-$	$+ HOH$	XIII
$RCOO^-$	$+ C_2H_4O$	→ slow	$RCOOC_2H_4O^-$		XIV
$RCOOC_2H_4O^-$	$+ RCOOH$	very → fast	$RCOOC_2H_4OH$	$+ RCOO^-$	XV
$RCOOC_2H_4OH$	$+ RCOO^-$	→	$RCOOC_2H_4OOCR$	$+ {}^-OH$	XVI
$-OH$	$+ C_2H_4O$	→	$HOC_2H_4O^-$		XVII
$RCOO(C_2H_4O)_{X-1}^-$	$+ C_2H_4O$	→	$RCOO(C_2H_4O)_X^-$		XVIII
$RCOO(C_2H_4O)_X^-$	$+ RCOO(C_2H_4O)_YH$	⇌	$RCOO(C_2H_4O)_XOCR$	$+ HO(C_2H_4O)^-_Y$	XIX



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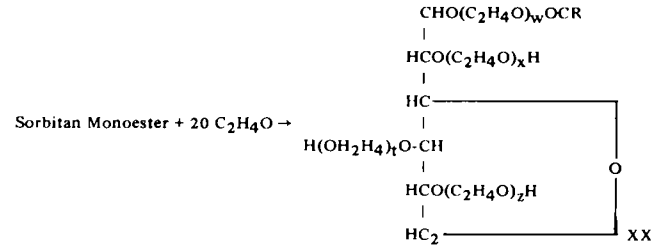
The oxyethylation reaction is conducted under basic conditions which also promotes ester interchange resulting in more or less random addition of ethylene oxide to the hydroxyl groups. Thus, a 20 mole ethoxylate, known commercially as polysorbate 20, can be pictured as a sorbitan monoester with 4 ethylene oxide chains of varying length. The total chain length (w + x + y + x) averages 20 units per molecule. The fatty acid will not only be distributed along these chains, but some ethoxylated sorbitan molecules will also contain 0 or 2 or more fatty acids per molecule. The same type of ethylene oxide chain length and fatty acid distribution will be expected for the other anhydro sorbitol moieties in the product.



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Tall Oil Fatty Acids

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ABSTRACT

About 1949, with the advent of effective fractional distillation, the tall oil industry came of age, and tall oil fatty acids (TOFA), generally any product containing 90% or more fatty acids and 10% or less of rosin, have grown in annual volume ever since, until they amount to 398.8 million pounds annual production in the U.S. in 1978. Crude tall oil is a byproduct of the Kraft process for producing wood pulp from pine wood. Crude tall oil is about 50% fatty acids and 40% rosin acids, the remainder unsaps and residues; actually, a national average recovery of about 1-2% of tall oil is obtained from wood. On a pulp basis, each ton of pulp affords 140-220 pounds black liquor soaps, which yields 70-110 pounds crude tall oil, yielding 30-50 pounds of TOFA. Separative and upgrading technology involves: (a) recovery of the tall oil; (b) acid refining; (c) fractionation of tall oil; and occasionally (d) conversion to derivatives. TOFA of good quality and color of Gardner 2 corresponds to

TABLE I

Fatty Acid Analyses

	Tall Oil (%)	Soya (%)	Linseed (%)
Palmitic and stearic acids	3	5	4
Oleic acid	48	34	5
Linoleic acid and isomers	46	51	62
Linolenic acid	0	4	24
Miscellaneous acids	3	6	5

above 97% fatty acids with the composition of 1.6% palmitic & stearic acid, 49.3% oleic acid, 45.1% linoleic acid, 1.1% miscellaneous acids, 1.2% rosin acids, and 1.7% unsaponifiables.

INTRODUCTION

In the Southern States, pine trees are harvested after twenty-five to thirty years for the Kraft papermaking industry. A valuable byproduct of this process is crude tall oil. In 1905, crude tall oil was isolated in Sweden where it was named "tallolja" which means pine oil. The term tall oil was introduced to avoid confusion with pine oil which is composed mainly of α-terpineol. In the Kraft process, pine wood chips are digested under pressure with alkali. This dissolves fatty acids and rosin acids as sodium soaps, and the fats are saponified, which liberates the cellulose fibers for making pulp. The alkaline washings from the pulp are termed "black liquor," which is partially evaporated so that the sodium soaps of tall oil fatty and rosin separate as "black liquor soap." This product is skimmed off and treated with sulfuric acid to liberate crude tall oil in ca. 1 to 2% yield, based on the weight of the wood. In 1978, the domestic production of crude tall oil exceeded 800,000 tons.

The term tall oil is a misnomer because tall oil is not an oil but is a mixture of roughly equal amounts of fatty acids and rosin acids, plus ca. 7% of neutral materials.

Production Processes

Soon after 1930, distilled tall oil was made commercially. The product was a mixture of fatty acids and rosin; and the rosin content was 20 to 35%. This type of product was in demand as a substitute for drying oils for coatings' use during World War II.

Another process is acid refining, where the crude tall oil is treated with sulfuric acid to improve color and odor. The proportions of fatty acids and rosin acids are largely unchanged during acid refining.

The tall oil industry came of age in 1949 with the advent of effective fractional distillation by the Arizona Chemical Company, a joint venture of American Cyanamid and International Paper. The tall oil fatty acids contained less than 2% of rosin, and the rosin contained less than 3% of fatty acids. Today, much better separations are possible; but, for most applications, it is not necessary to reduce the rosin in tall oil fatty acids below 1%.

In the fractionation process, crude tall oil is first dehydrated, heated, and vaporized, under reduced pressure. Pitch is then removed in a stripping tower, and the remaining vapor is fed into a fractionating column. Rosin is taken off from the bottom of the tower. A fatty acid intermediate is drawn off near the top of the tower, and volatile odor bodies are removed at the top of the tower. Fractionation of the fatty acid intermediate, in either the same or a different column, gives high purity fatty acids, distilled tall oil containing 20 to 40% of rosin and heads.

Composition of Tall Oil Fatty Acids

Good quality American tall oil fatty acids contain at least 97% of fatty acids, and the following data are typical analyses: 97.1% fatty acids, 0.9% rosin acids, 2.0% unsaponifiables (neutrals), Gardner color 3, and acid number 194.

Typical compositions of tall oil fatty acids, soya, and linseed fatty acids are shown in Table I. The absence of linolenic acid in tall oil fatty acids has led to their widespread use in alkyd resin coatings with good resistance to yellowing.

Tall Oil Fractionators

The 1978 capacity of the domestic tall oil fractionators is shown in Table II.

The Pulp Chemicals Association has reported the following statistics for 1978 domestic production and sales: 194,000 tons tall oil fatty acids, 212,000 tons tall oil rosin, and 58,000 tons distilled and acid-refined tall oils.

Uses of Tall Oil Fatty Acids

When the above-mentioned fractionation plants were installed during the period of 1949 to 1958, rosin was the most desired product for use in paper size. In those days, tall oil fatty acids were offered as a lower cost replacement for other unsaturated acids and oils. However, in recent years, the price of tall oil fatty acids has been much less dependent upon soybean oil prices. This is because, as

TABLE II

Capacity for Tall Oil Fractionation
(from Pulp Chemicals Association)

Company	Locations	Tons crude tall oil input
Arizona Chemical Company	Panama City, Florida	105,000
	Spring Hill, Louisiana	45,000
Hercules, Inc.	Franklin, Virginia	65,000
	Hattiesburg, Mississippi	60,000
	Portland, Oregon	30,000
	Savannah, Georgia	65,000
Monsanto-Emery	Nitro, West Virginia	65,000
Reichhold Chemicals, Inc.	Bay Minette, Alabama	36,000
(Newport Division)	Oakdale, Louisiana	60,000
Sylvachem Corporation	Port St. Joe, Florida	100,000
Union Camp Corporation	Savannah, Georgia	105,000
Westvaco Corporation	Charleston, South Carolina	85,000
	De Ridder, Louisiana	55,000
	Total	876,000

shown in Table III, most tall oil fatty acid utilization is now in chemical intermediates where fatty acids are the preferred raw materials.

The intermediate chemicals which account for this rapidly growing share of tall oil fatty acid utilization are the following (A.-E.).

(A.) Dimer Acids. Polymerization of tall oil fatty acids under heat and pressure with a clay catalyst gives a mixture of methyl branched C_{18} monobasic acids, C_{36} dibasic acids (called dimer acids), C_{54} tribasic acids (called trimer acids), plus some higher acids. The products are separated by high vacuum distillation in a thin film.

Hydrogenation of the monobasic acids gives a mixture of stearic acid and a liquid isomer called isostearic acid.

Dimer acids are the highest molecular weight dibasic acids commercially available. They are complex mixtures of isomers, including cyclic structures, with residual carbon-carbon unsaturation. Dimer acids are used mainly in the synthesis of polyamide resins, derived by reaction with various amines. The solid thermoplastic resins are essentially neutral with a wide range of melting points. The lower molecular weight resins are used in solvent-based flexographic printing inks and in thixotropic coatings. The higher molecular weight polyamide resins are used as hot melt adhesives. Liquid polyamide resins with reactive amine groups are used for curing epoxy resins in surface coatings and adhesives. The long chain hydrocarbon structure of dimer acids affords flexibility in the cured resin composition.

Dimer acids are used in the synthesis of polyester resins of improved flexibility; e.g., in oilless alkyds used in coil coatings. Other applications are in hot melt adhesive polyester resins, and in surface coatings based on oil-modified alkyds, epoxy esters or urethanes.

Esters of dimer acids are used in modern industrial lubricants and metal-working compounds to provide both lubrication and rust prevention.

Trimer acids are used as the free acids or as a soap or polyamidoamine in corrosion inhibitors. The polar carboxyl groups are adsorbed onto steel surfaces, and the long chain fatty, hydrophobic part of the trimer acids limits the access of water and other corrosive chemicals. Important applications are in oil well drilling and in petroleum refineries.

(B.) About ten years ago, Hercules started production of oleic and linoleic acids which were obtained by solvent crystallization of tall oil fatty acids. The oleic acid fraction is high quality and one grade, Pamolyn 100-FG, has wide FDA approval for direct food contact. The linoleic acid fraction is further conjugated and used as a replacement for dehydrated castor oil in surface coatings.

(C.) Epoxidized esters of tall oil fatty acids are used as plasticizer-stabilizers for vinyl. The tall oil fatty acid is generally pretreated to remove phenolic impurities, such as dimethoxystilbene, in order to avoid a pink coloration.

TABLE III

Domestic Utilization of Tall Oil Fatty Acids in 1978
(from Pulp Chemicals Association)

	Tons	% of Total
Intermediate chemicals	73,000	49
Surface coatings	34,000	23
Miscellaneous	20,000	13
Surfactants	14,000	9
Flotation	8,000	6
Total	149,000	

(D.) About five years ago, Westvaco pioneered the production of a C_{21} dibasic acid made by the addition of acrylic acid to the linoleic portion of tall oil fatty acids. The unreacted oleic and elaidic acid portions were then stripped off. The two carboxyl groups differ in reactivity and unique surfactants, and other products have been made.

(E.) Low cost byproducts of tall oil fractionation, including heads and pitch, have traditionally been blended together and used in the flotation of phosphate and iron ores. In one stage of the beneficiation process, the fatty acids are used without further processing; but in a subsequent stage, they are used as amidoamine derivatives of the fatty acids.

Union Camp isolates the palmitic acid in tall oil heads by means of solvent crystallization. The purity is sufficiently high for conversion to low odor isopropyl palmitate for use in cosmetics.

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Product Forms and Packaging in the Fatty Acid Industry

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THE FATTY ACIDS INDUSTRY—AN OVERVIEW

Fatty acids, derived from tall oil and fats and oils represent a 1.3 billion pound industry with shipments currently valued at $320 million a year. Twenty-one percent of the fatty acid production is converted into other chemical derivatives by the fatty acids producer. Another 19% is sold on the merchant market to intermediate manufacturers of other chemical derivatives. The remaining 60% of production is sold as free fatty acids for direct use in a wide variety of end uses.

The direct consumption of fatty acids, which represents over 800 million pounds a year, is in such consumer product areas as cosmetics, drugs and pharmaceuticals, and specialty soap and detergents. Fatty acids are also directly consumed in many industrial uses and products including metalworking fluids, oilfield chemicals, paints, plasticizers and plastics.

Chemicals derived from fatty acids amount to 539