A percentage of the isolated acid is obtained and the main reaction is accompanied by side reactions producing undesirable decomposition products.

This process, involving preparation of the fatty acid, its dehydration and subsequent esterification is naturally quite expensive. Work by other investigators has shown that dehydration of the castor oil fatty acid does not necessarily have to be carried out on the fatty acid in a free state, but also on the triglyceride itself. A host of catalysts have been patented for the process, generally of an acidic nature and varying widely in efficiency. However, by the most refined of the modern processes, it has become possible to produce a completely dehydrated castor oil which is free from objectionable decomposition products.

The oil is of great interest for two reasons. First, because of the value of the product.

Carrying as it does two conjugated double bonds in the fatty acid molecule the properties of dehydrated castor oil as it comes to the market today begin to approach those of tung oil for which a substitute has so long been sought. The oil bodies with great rapidity in the varnish kettle. Varnishes prepared from it dry rapidly to hard tough and elastic films which have marked resistance to hot and cold water and alkali solutions. As received the oil dries to a frosted wrinkled film just as tung oil does. That the oil is not identical with tung oil is evident. The fatty acid of tung oil carries three double bonds in comparison with only two for the dehydrated castor oil. The difference in behavior of the two oils is in approximately the same ratio in some respects.

Dehydrated castor oil is a welcome new ingredient to the manufacturer of protective coatings since, while not a direct substitute for tung oil, he is able by its use to replace tung oil in his formulas with less change in the formula than is necessary with any of the other substitute oil which have been offered. A main point of difference between varnishes prepared from tung oils and dehydrated castor oil is the greater softness of film of the dehydrated castor oil varnish. This difference is easily compensated for by the addition of harder resin, preferably synthetic phenolic resin for greater speed of drying.

In much the same manner that tung oil is used to speed drying and to form a firmer film in blends with the slower drying oils dehydrated castor may be used for the same purpose, except that a larger quantity of the castor will be necessary to obtain the same result.

The second point of interest is that the development and use of dehydrated castor oil represents an important step forward in a new field. The product represents an entirely new drying oil not found in nature, but produced by alteration of the structure of a fatty acid molecule by chemical reaction.

The attention being given to the first synthetic oil mentioned and to dehydrated castor oil signifies that the manufacturer of protective coatings is no longer content to accept as the ultimate, oils supplied by nature and to limit himself to the effects he can produce with natural oils. For a long time he has compromised on the undesirable features of the natural drying oils overcoming the shortcomings of one by blending with another. The viewpoint is changing. He now looks for methods whereby he may produce oils of the desired properties by synthesis of the oil molecule and even alteration of the fatty acid itself. This viewpoint opens up the possibility of producing synthetic oils formulated just as is a paint or varnish to serve a specific purpose.

It seems safe to say that in the future more and better synthetic drying oils will make their appearance in the protective coatings industry and that these synthetic oils will surpass in performance the drying oils supplied by nature.

Industrial Utilization of Tall Oil*

by ARTHUR POLLAK

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ABOUT fifteen years ago a confidential questionnaire was circulated among American pulp and paper manufacturers questioning them on the best means for disposing of a troublesome, frothy paste that seemed to settle out of pulp mill waste liquors, plugging pipe lines and clogging equipment. The response concurred remarkably in the opinion that (1) the material was a nuisance, (2) the best way to be rid of it was to burn it up.

Tall oil is derived from these waste liquors of the paper and pulp industry. As first recovered it appears as a brown, frothy paste. When properly treated, it may be consolidated to a more or less homogeneous phase consisting of the sodium soap of tall oil, associated with about 35% of water. This soap may be spray dried or vacuum dried to a powder. The original paste or the consolidated soap may be treated with acids to give crude tall oil. Such crude tall oil may be subjected to one of several refining processes to improve its color or its odor or to separate various constituents.

Most of these processes were first developed in Europe, especially in the Scandinavian countries, where talloel, or tallöl, as it is known there, has been produced since the beginning of this century.

In 1930, when first produced in this country, tall oil was ranked as a fatty acid. Resembling commercial red oil in many of its properties, it was first offered as a substitute for it. Later, as its properties became better known, new uses for tall oil developed. At the present time its most effective advantage for most large users is its extremely low price. Crude tall oil is cheaper than any other organic acid available. Thus in December 1939, the price, in bulk, F. O. B. works, was being quoted at 30 dollars per ton. Tall oil has become well established commercially and merits the serious attention of potential users. The origin, the principal forms, and the properties of tall oil have already been described on previous occasions. Methods for the analysis of tall oil have also been described.

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*Presented in a symposium on the Industrial Applications of Fats & Fatty Acids at the Fall Convention of the American Oil Chemists Society, Chicago, Oct. 1939.

Tall oil contains three groups of substances, fatty acids, rosin acids, and non acids. The fatty acids contain considerable linoleic acid, the rosin acids contain some abietic acid, the non-acids, some phytosterols. Most of the substances present have not yet been identified.

The following table gives typical analyses of American and European tall oils. In all cases the samples analyzed were from commercial deliveries and do not represent samples produced in laboratories.

Tall Oil	Acid No.	Saponification No.	Rosin Acids %	Fatty Acids %	Non-acids Sterols etc.
American — Crude	150-160	160-170	40-45	45-55	6-10
American — Refined	170-180	170-185	34-38	55-60	6-10
Danish — Crude	158-166	173-176	33	54-55	6-7
Danish — Distilled	—	185	12	83	5
Finnish — Distilled	155	173	37	58	5
Swedish — Crude	163	170	44	—	9
Swedish — Distilled	186-189	—	12	82-83	5

Tall oil is the by-product of a stable yet rapidly growing industry, the sulphate pulp industry. The rapid growth of this industry is illustrated by the following statistics.

Year	Sulphate Pulp Made Tons	Per Cent of All Pulp Made
1916	73,000	2.1
1935	1,468,000	29.2
1936	1,795,000	31.5
1937	2,161,000	32.0
1938	2,470,000	44.3

The mounting number of industrial applications for sulphate pulp — making paper bags, boxes, and other shipping containers, assures its continued growth.

Over 80% of this production originates in the southern and southeastern states where in most cases forest reserves are ample for a perpetual supply of rapidly growing, hardy pine wood.

The yield of crude tall oil per ton of pulp varies considerably depending upon the kind of pine wood, the greeness of the wood as used, and upon the details of the processes employed. A reasonable estimate based on published and unpublished data would be that 60 lbs. of crude tall oil per ton of pulp can be collected at most mills without resorting to elaborate and expensive devices for increasing the yield.

Accordingly, 75,000 tons of tall oil is potentially available. Taking into account the steady growth of the sulphate pulp industry, an estimate of 100,000 tons available in a few years is not unreasonable.

For the yearly period April 1937 to April 1938 the Department of Agriculture reported that 10,800 tons of tall oil was produced. American tall oil is now being exported to all parts of the world.

In Sweden, where tall oil has been known since about 1900, production is comparatively more developed. In 1937, 23,700 tons was produced. Finland produced 2,050 tons in 1936. Germany produced only 1,000 tons of tall oil in 1937, there being very few sulphate mills in Germany. Their imports of tall oil have grown rapidly, as the following figures show:

Year	Tons (2000 lbs.)
1935	7,180
1936	12,750
1937	——
1938	20,030

The U. S. S. R. expected to produce 2,000 tons of tall oil in 1937.

While in the case of such a new product the current commercial applications of tall oil cannot suggest its future possibilities, it is of interest to note the present uses. Except as noted, the applications described below refer to commercial uses in the United States.

SOAPS AND SOAP PRODUCTS

Tall oil soaps have excellent emulsifying power and appear to be effective detergents. The soap is very soluble, even in cold water. The viscosity of tall oil soaps is lower than that for most fatty acids. The pH in dilute solutions does not differ from other soaps. Increased soap prices and the advent of soap replacing chemicals have tended to reduce or eliminate altogether the use of soap in many rag washing plants and commercial laundries. Many of these have found the use of tall oil soap effective and inexpensive.

Various branches of the textile industry have also found the use of tall oil soaps economical and effective. Cotton linters are being scoured with tall oil soap. Large tonnages have been consumed in scouring silks and rayons. Wool scouring soaps, dry cleaning soaps, and many textile oils and specialties are being compounded with tall oil as the soap base. Metal cleaning compounds, scrub soaps, garage floor cleaners, and many other cleansers are being marketed.

Where the alkali used is expensive, as when triethanolamine or other amines are used, tall oil is preferable to other fatty acids owing to its comparatively low alkali requirement.

Hard soaps containing up to 25% of tall oil are being made. The objection to using larger amounts is that the soap becomes too soft. By using soap builders, abrasives, or fillers even larger amounts can be used.

FLOTATION CHEMICAL

Tall oil has been applied to the flotation of many oxide minerals such as limestones, phosphate rock, manganese ore. Its effectiveness varies with the manner of its application and the nature of the ore. In some cases it appears preferable to other fatty acids.

PETROLEUM INDUSTRY

The principal application of commercial significance is in the manufacture of cutting oils and greases, especially where sulphurized oils are required. Here tall oil appears to be unique in its property of combining with large amounts of sulphur. When heated to about 350°F sulphur combines readily with tall oil, the viscosity of the product increasing with its sulphur content. Mixed with oils or greases sulphurized tall oil greatly improves their lubricating qualities, especially at high temperatures. Tall oil is also used as the soap base in emulsion type cutting oils and other mineral oil emulsions. In Roumania, tall oil has been reported to be very effective in reducing the water-in-oil emulsions so troublesome at certain oil fields.

PAINT INDUSTRY

Some tall oil has been sold to the paint industry where the glyceryl ester of tall oil is used. The glyceryl ester is readily prepared by heating with about 11% of glycerine. Esterification proceeds in the usual way an acid number of 2 is not difficult to attain. The addition of dryers accelerates drying.

In Germany, in 1935, the Committee for Paint Technique, on investigating tall oil, reported it favorably. Thousands of tons of tall oil are reported to have been consumed there in 1936 in the manufacture of paints and alkyd resins.

SULPHONATED TALL OIL

Tall oil sulphonates readily; in fact it is more reactive than other oils, though, with care, the usual commercial sulphonation produces a satisfactory product. Sulphonated tall oil serves as a substitute for turkey red oil. In Germany it is reported that some plants prefer to dilute with inert oils to reduce the rate of reaction.

ASPHALT EMULSIONS

Large amounts of tall oil are used to make asphalt emulsions. It appears preferable to rosin and other cheap fatty acids for asphalt emulsions of certain specifications.

RUBBER CHEMICALS

Tall oil is being used for softening or curing rubber, replacing stearic acid, cotton seed fatty acids, or hydrogenated fish oils in these processes.

Since the production of tall oil in this country is less than ten years old many promising applications have not yet emerged from the laboratory.

The Preparation and Properties of High Molecular Weight Primary Amines*

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ANY derivative which is classed as a commercial derivative must have useful properties. These are always a function of the chemical and physical properties of the compound in question. In addition to the requirement that the compound or group of compounds be useful, they must also be available in substantial amounts at reasonable prices. This requires that the raw material from which such compounds are prepared must be readily available and that their synthesis from this material be by a commercially practical procedure. In any discussion of fatty acid derivatives it should be borne in mind that the fatty acids fulfill the first of these requirements in that the raw material exists in extremely large quantities. The problem, therefore, of preparing fatty acid derivatives which have commercial significance is to synthesize compounds which have useful properties from the fatty acids by processes which are commercially feasible and practical.

The question of the utilization of fatty acids for the preparation of derivatives which show commerical promise is fundamentally the same as that encountered in any field where one is attempting to utilize a starting material which exists in enormous amounts. Numerous compounds are prepared and their physical and chemical properties studied. From this group of compounds prepared in the laboratory a certain few will appear to possess interesting properties and to have possible commercial applications. A more intensive study is then made of the preparation and properties of such compounds with the view to placing them within the price range of commercial acceptability.

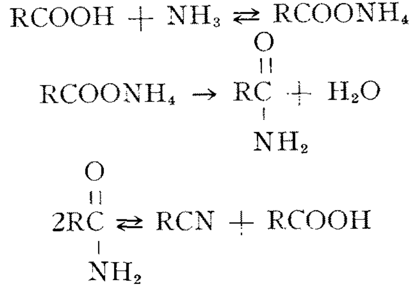
Generally speaking, all fatty acid derivatives have some properties in common which properties have and will continue to influence both research and commercial developments in this field. These properties result from the presence of the long hydrocarbon chain of the fatty acid. The combination of a long hydrocarbon chain attached to a polar group or groups brings about a unique surface chemistry, adsorption phenomena, plasticizing properties, and various other effects which characterize these compounds. The influence of this long chain is illustrated by the difference in properties of sodium acetate and sodium stearate. The long chain imparts to solutions of sodium stearate surface properties, properties of emulsification, etc., which are essentially absent in sodium acetate.

In the time allowed to this talk it is impossible to discuss many of the fatty derivatives. The high molecular weight amines are interesting products which can be prepared from the fatty acids and I wish to discuss briefly their method of preparation, general physical and chemical properties, some of their simple derivatives, and their indicated uses.

The most satisfactory method for the preparation of high molecular weight amines is by the hydrogenation of the corresponding nitriles. Nitriles are formed by passing ammonia gas into a fatty acid held at a temperature somewhat below its boiling point. The mechanism of the reaction is probably represented by the following series of equilibrium.

Figure 1

Equilibria Involved in Nitrile Formation.



$$RCOOH + NH_3 \rightleftarrows RCOONH_4$$

$$RCOONH_4 \rightarrow R\overset{\overset{O}{\|}}{\underset{\underset{NH_2}{|}}{C}} + H_2O$$

$$2R\overset{\overset{O}{\|}}{\underset{\underset{NH_2}{|}}{C}} \rightleftarrows RCN + RCOOH$$

When ammonia is passed into the system continuously this cycle is repeated until the fatty acids are quantitatively converted into nitriles.

The mechanism of the catalytic hydrogenation of nitriles to amines is somewhat complex. The overall reaction is represented as follows:

$$RCN + 2H_2 \rightarrow RCH_2NH_2$$

A high yield of primary amines and a low percentage of secondary amines and other products is desirable. The hydrogenation probably proceeds in stages and a high yield of primary amines requires a very careful selection of the conditions of hydrogenation.

The simplest explanation for the formation of secondary amines is that two molecules of primary amine lose one molecule of ammonia according to the following reaction:

$$2RNH_2 \rightarrow R_2NH + NH_3$$

However, secondary amines may be formed as a primary hydrogenation product under certain conditions. The following equation (see "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts" by Homer Adkins, Page 53) illustrates one possible mechanism for the formation of secondary amines.

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*An address presented at the Fall Convention of The American Oil Chemists' Society, Chicago, Oct. 1939.