Fatty Acids From Pulp Mill Wastes

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Abstract

This paper discusses the new fatty acid-containing product "Tall Oil," which is derived from the waste liquors of the paper industry. The method of preparation, some thoughts on chemical composition, uses, and available supplies are discussed.

THE growing shortage of fats, oils and fatty acids together with the various import restrictions has encouraged many technical investigations of products not heretofore considered. Some of these investigations have led to the commercial production of oils or fatty acids from comparatively little known sources. In this country the paper industry as a source for fatty acids and their derivatives appears to have been ignored until recently. In the manufacture of pulp for making paper, pine wood is rapidly displacing other woods as a paper making raw material. The lower cost of production that results from using pine wood has greatly increased the demand for paper so that increasing quantities of fatty acids will become available.

Pine wood is popularly associated with rosin but rosin by no means is the principal constituent of the fats and resins occurring naturally in pine wood. The relative amount of fatty acids present depends upon the climate, the species and variety of the trees and numerous other factors. Whereas a tree that has been bruised or purposely tapped as in turpentining exudes a fluid containing comparatively little fatty acids an uninjured tree is relatively rich in fatty acids obtained from the sap fluid. It has been found altogether feasible to develop processes whereby fatty and resin acids occurring in the trees are recovered during the process of manufacturing paper from the pine wood.

The wood used in paper manufacture is cut into chips from one-half to one-inch square and about one-eighth inch thick. These chips are then poured into a steel pressure vessel or digester and steamed under pressure with a solution containing caustic soda and other chemicals. After several hours' cooking the contents of the vessel are discharged and the cooked chips freed from the solution. The washed cooked chips disintegrate to a pulp which is then converted to paper. About one-half of the wood dissolves during the cooking process forming a liquid from which the chemicals must be recovered in order to make the process economical enough to operate. The fats and resins originally occurring in the pine wood are saponified and dissolved out during the cooking of the wood chips and are present in the waste liquor as soaps.

The first step in reclaiming or recovering the chemicals from the waste liquor is by evaporation. As the evaporation proceeds the liquor becomes more and more concentrated until the soaps present become insoluble and grain out much as soaps do in a soap kettle on adding salt. These curds which are skimmed off represent the raw material which the process depends on, as will be described.

The crude soap (curds) as first collected occludes considerable amounts of waste liquor and in appearance, is a brown frothy paste. Because of its considerable water content and impurities at this stage it is seldom economical to ship this material without first converting the material to the free acid state. While many processes have been proposed for purifying the soap and using it directly, or for dehydrating the purified soap, very few cases are on record which have proven practical.

Product history indicates that the material was first collected in the Baltic countries of Europe and was then known as liquid rosin in all languages, Swedish, German, French and English. This designation proved misleading or, at least, not sufficiently descriptive. In Germany, it soon became known as tallerl or tallol combining the Swedish word from pine, which is tall with their own word erl meaning oil. To use the strictly correct German, kiefernerel would have been confusing for this means pine oil, a commodity which was already on the market and descriptive of a product entirely different from the product under consideration. Today the material is known as tallerl or tallol in European countries and also the term liquid rosin is occasionally referred to.

When this product was imported into the United States and later when processes mentioning it were quoted in the literature the United States Patent Office accepted the designation of liquid rosin and curiously enough, also permitted a phonetic translation of the half-German tallol into tall oil.

The tall oil imported into the United States soon earned a bad name because importers found the name connoted its source rather than any consideration of quality. The oil varied in color from black to lemon yellow, in consistency from liquid to solid, in odor from very bad to odorless and its chemical composition was anyone's guess. It is therefore no wonder that when one American manufacturer undertook its production and sale considerable antagonism met its early introduction, particularly since prejudice existed in regard to materials of a similar character as imported from the European markets. Today this American manufacturer—one of the largest paper manufacturers in the world—and, incidentally the manufacturer of Oil & Soap on which this is printed—offers the semi-refined tall oil under definite specifications by the name "Liqro." The same manufacturer markets the refined, double distilled material under the name of "Indusoil."

Composition of Tall Oil

Tall oil is said to contain the following classes of compounds:

a. Rosin acids.
b. Fatty acids.
c. Non-acids such as sterols, higher alcohols and other unsaponified material.

The relative proportions of these groups of compounds depend somewhat upon the source of the tall

oil, but even more upon the process of refining. The content of rosin acids will vary from 10-60 per cent, the content of fatty acids from 20-60 per cent and that of the non-acids from as low as 5 per cent to at times over 20 per cent.

Experience has taught that any comparison of tall oil, with the fatty acids present in some of the better known fats or oils, is dangerous. To illustrate what we mean we might consider briefly the term "rosin acids." By rosin acids chemists mean those acids which do not esterify on boiling for a few minutes with methyl or ethyl alcohol in the presence of sulphuric acid. When an analysis for rosin acids in common fats is made we reason that if the fat contains rosin acids, then it must be that rosin has been added, and the presence of rosin means a change in the properties of the soap or soap product. With tall oil, however, the procedure is not so simple. Analysis by the customary method indicate considerable quantities of rosin acids. We find, however, that these rosin acids when isolated do not resemble rosin. It is not very reasonable to conclude, therefore, that the presence of rosin acids in tall oil will imply qualities in its soap products in analogy with rosin in ordinary fats. The crude tall oil undoubtedly contains considerable abietic acid, which is the principal constituent of ordinary rosin. When most of the abietic acid is removed there are still rosin acids present. These rosin acids are liquids at ordinary temperature and do not resemble any grade of rosin. Abietic acid is a solid, melting at about 170° C.

The greatest chemical puzzle in tall oil is that mixture of non-acids, the sterols, higher alcohols and other substances. While many chemists consider these non-acids as unsaponifiable material their results do not always check. If these substances were truly unsaponifiable it should be possible to decant them in dilute soap solutions, but they do not separate out, though they can be extracted by means of solvents. Some investigators claim that the detergent power of other acids is increased by the presence of these non-acids. At any rate, detergency tests indicate that a well refined tall oil is, weight for weight, as effective as red oil. In view of the complex nature of tall oil it can only be suggested to manufacturers who consider its use that it be tried out in a practical test. Analytical data cannot decide the utility of tall oil. Where large scale tests are not feasible, preliminary laboratory experiments, however positive, are best translated into practice by blending the customary fatty acid in use with gradually increasing percentages of tall oil.

Uses of Tall Oil

SOAPS—The use of tall oil for making soaps was one of the first developed. Tall oil was first produced in the Scandinavian countries, in Norway, Sweden and Finland, so that it is not surprising that the greatest progress in its application for soap making is to be noted there first. In the manufacture of soaps, up to 25 per cent of the usual fats can be replaced with tall oil to produce a good grade of hard soap. It is generally reported that when much more than 25 per cent of the fats are so replaced the soap becomes too soft unless chemicals like soda ash are added. Millions of pounds annually are going into the manufacture of soaps. In Finland and Sweden, soft soap made from tall oil is packed in tubes and is widely used. The soap is reported to have excellent lathering and detergent powers.

Textile soaps for scouring silks and woolens as well as the synthetic fibers, dry cleaning soaps and scrub soaps made with tall oil as a base, have proved acceptable all over the world. In this country they have been manufactured and sold for several years.

SOAP BASE EMULSIONS—In the manufacture of soap base emulsions tall oil is used in much the same way as red oil, which it frequently serves to displace. Increasingly, manufacturers of emulsions such as textile oils, polishes and disinfectants and preservatives, find it most economical to adjust their formulae to the use of tall oil. Asphalt and tar emulsions prepared with tall oil are being applied all over the world.

Cutting oils of exceptional stability are made using tall oil. Heated with sulphur, tall oil readily combines with it. This product is very satisfactory as a base for the manufacture of sulphurized cutting oils, widely used for heavy machining.

Sulphonated Tall Oil

It has proved quite practical to sulphonate tall oil to produce the equivalent of a sulphonated fatty acid. Tall oil is rather reactive and to the early experimenters proved difficult to sulphonate. It was found, however, that by proper refrigeration during sulphonation or by dilution with inert oils such as mineral oil, sulphonation proceeds quite smoothly. The product is being applied as a turkey red oil substitute.

Paints

In the last few years the paint industry has become interested in tall oil. Small amounts of tall oil go into the manufacture of driers. Its greatest use is in the manufacture of drying oils. Tall oil is heated with glycerine or other polyhydric alcohols, with which it combines to form esters. These esters have drying properties and serve as substitutes for linseed or other paint oils. In most instances the tall oil product is being blended with the better known drying oils because tall oil drying films tend to be short.

Miscellaneous Applications

A large number of special applications have been made. A number of binding materials are being manufactured using tall oil that has been heated with calcium hydroxide. Core binders containing tall oil are also known. In these instances it has been used either alone or with linseed oil or other drying oils, with rosin oil, pine oil or other softening agents. It has also been combined with molasses, glue, starch, alkali, and so forth, to give cores of the proper physical properties. Tall oil appears to be satisfactory in a great many de-inking and degreasing operations. In the field of flotation reagents tall oil compares favorably with a great many other fatty acids. It has been most successful thus far in the flotation of alkaline earth minerals such as phosphates and calcite.

In view of the recent developments of tall oil, especially in this country, its present use can hardly be considered indicative of its possibilities.

Available Supplies

At the present time the production of paper from pine wood is increasing at a rapid rate and this branch of the paper industry is rapidly concentrating in the southern states in huge mills. Based on data available, it would appear that about six million pounds of crude tall oil is available from the 1937 production of our southern pulp mills. Allowing for a continued increase in production, improvements in recovery process, and considering mills using pine wood in other sections of our country, it is reasonable to estimate that within the next few years one hundred and fifty to two hundred million pounds of tall oil can be produced.