SEPARATION AND PURIFICATION
of the
RESINS IN TALLOL

by

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I. INTRODUCTION

Tallol is a waste product of the paper industry. It is obtained by the acid hydrolysis of the soaps precipitated when the spent cooking liquors from the kraft paper pulp process are subjected to evaporation. These soaps cause considerable trouble in the evaporators by foaming and by coating the evaporator tubes. Because of this, the evaporators have to be shut-down to clean the tubes of these soaps. Naturally, an effort is made to utillize the soaps in order to dispose of them and to make them yield some return.

The hydrolysis of the soaps by a mineral acid such as sulfuric acid produces a mixture composed chiefly of resinous materials and fatty acids. This mixture has been named by various investigators; tallol, tall oil, talloel, liquid rosin, crude fatty acids, Swedish rosin oil and tallol distillate. The term tallol is the most common used in the United States and will be used in this discussion.

The production of tallol for 1937 was estimated by Ward and Vilbrandt to be about 40,000 tons in the

United States. In recent years this figure will be increased to some extent. Much of this crude material is used as a cheap fuel with a value of about six dollars per ton. But after refining, the value can be increased to about eighty dollars per ton. The conversion cost would be about twenty-four dollars per ton.

The uses of crude tallol are limited; its disagreeable color and odor make it undesirable for most commercial purposes. However, when tallol is purified, it is a source of various derivatives made from separated fatty and resin acids. The fatty acids separated from tallol and purified can be used in various ways. They are used in the soap industry for manufacturing soft soaps, liquid soaps, and other toilet preparations. They are suitable for use as bases for lubricating greases, textile oils, cutting oils, metal polishes, and wax polishes. Esterified, they are used as substitutes for linseed oil in paints and varnishes. These fatty acids are now also used as softening agents in rubber in place of oleic and stearic acids and as emulsifying agents in Buna-S. The purified resins are similar to common rosin and can be used in place of rosin. As examples, the resins can be used in plastics, adhesives, paints, varnishes, shoe polishes, linoleum, and in many other ways. The sulfonated product

can be used in place of Turkey-red oil and also as a detergent in the textile industry.

Various methods have been devised for the purification of tallol by separating it into fatty and resin acids. These methods are mainly; distillation, solvent extraction, and chemical means. The chemical means are chlorination, esterification, and sulfonation. As yet, distillation is the commercial method of purification adopted in this country. Objections to this method are corrosion of equipment and losses as carbonaceous material incurred at the high distillation temperatures involved.

The purpose of this research is to investigate the possibility of a commercial method of separating the resin and fatty acids in tallol by solvent extraction and crystallization, and the subsequent purification of the resins.

II. LITERATURE REVIEW

Composition of Tallol

The composition of tallol varies from mill to mill and even with different batches in a given mill. The tallol produced in European countries has somewhat different compositions than that produced in the United States.

Generally, the composition of tallol is reported by investigators as per cent fatty acids, resin acids, and unsaponifiables. As noted from different sources, (9, 10, 12, 25, 44, 46) the composition of tallol is as follows:

Fatty Acids	40-60%
Resin Acids	30-50%
Unsaponifiables	6-12%

The fatty acids are reported to consist mainly of oleic, linoleic, and linolenic acids with small amounts of related acids. It has been found that the average composition of the fatty acids is: (9, 25, 29)

Oleic Acid	15-20%

Linoleic Acid	70-80%
Linolenic Acid	4-6%

Keghel [25] reported that the fatty acids consisted of "talloleic", linolenic, lauric, palmitic, and myristic acids.

The resin acids portion of tallol has been reported to be composed primarily of abietic acid with a small amount of similar acids. [9, 22, 29]

The unsaponifiable matter is considered to be a mixture of sterols such as phytosterol. [9, 25, 36] Schmid [36] has stated that phytosterol may be present in tallol in amounts up to two per cent.

The analysis of tallol may also be given in terms of such properties as acid number, saponification number, and iodine number. A compilation of the analyses of several investigators is given below: [1, 10, 22, 25, 30, 44, 46]

Acid number	120-170
Saponification number	120-185
Iodine number	117-180

The above data for the composition and analysis of tallol has been taken from the various references and is for tallol produced in different countries.

Separation and Purification of Resins

Many methods have been devised and advocated for the purification of tallol. These methods fall into three general classes; distillation, solvent extraction, and chemical treatment. Some of the methods are a combination of two or more of the above processes. A fourth method recently proposed is the crystallization of the resins from a tallol solution using a suitable polar solvent.

The above methods have been used for the purification of tallol and also as a means of separating the resin acids from the fatty acids.

Distillation: This was the earliest method employed for purifying tallol and has been adopted in the country for the purpose of separating the constituents of tallol.

By distillation, tallol can be separated into fractions; or, one purified overhead product can be obtained.

The objections to this method are the poor heat transfer characteristics of tallol, corrosive action of tallol at the high distillation temperatures (200-300°C. under high vacuum), and the losses as carbonaceous material incurred at those temperatures. Distillation must be carried out under very low pressures to prevent cracking

and polymerization with resulting losses as residue. According to Ward, (45) these losses may amount to about twenty-five per cent of the original charge.

Solvent Extraction: The extraction methods of purifying tallol are generally useful for removing color - and odor - bodies from the oil. Some extraction processes have also been devised for the separation of the resin and fatty acids. These methods are usually coupled with chemical treatment to change the solubility of the resinous and fatty acid portions of tallol, thereby making it possible to use two immiscible solvents for selective extraction of these portions.

The color - and odor - bodies in tallol are generally extracted by using two immiscible solvents; one of which selectively dissolves the impurities while the other dissolves the resin and fatty acids.

Segessmann (40) employs the use of various solvents such as ethylene chlorohydrin, alpha-dichlorohydrin, ethylene glycol, etc., to extract the impurities in a tallol solution using a suitable petroleum solvent such as gasoline, petroleum naphtha, or heptane.

McKee and Blengsli (27) describe a process using gasoline and furfural as the solvents. The furfural is used in small portions to remove the undesirable materials.

The gasoline solution may also be treated with activated charcoal or Fuller's earth.

Humphrey (23) uses petroleum naphtha and furfural for the purification of rosin. The furfural is used in small amounts to extract the dark rosin part leaving a refined rosin in the petroleum naphtha solution. After distillation of the solvents from their respective solutions, two grades of rosin are obtained. By this method, it was stated that seven grades of refined rosin can be obtained, G, H, I, K, M, N, and WG by the rosin color scale.

Chemical Treatment: The main chemical methods of purifying tallol are chlorination, esterification, and sulfonation. These methods attempt to separate the resin and fatty acids of tallol by selective chemical action.

1. Chlorination: Chlorination methods have been devised generally for refining tallol without separation of the constituents. (6) The separation of the resin and fatty acids by selective chlorination has been attempted by Crockin (6) without much success.

2. Esterification: Many methods have been devised employing esterification for separating the constituents of tallol. Generally, they attempt to

esterify the fatty acids only and then separate the fatty esters from the resins by distillation or by solvent extraction.

Schultze, (38) Brown and Scott, (3) and others esterify the fatty acids with an alcohol, such as ethyl or methyl alcohol, in the presence of sulfuric acid, and then distill the esters from the solution.

Gayer and Fawkes (17) neutralize the resin acids with a base such as sodium hydroxide before separating the esters and salts by using two immiscible solvents, furfural and a hydrocarbon solvent. The hydrocarbon solvent will dissolve the esters. In another process, Gayer and Fawkes (18) react the resins with zinc oxide to form resinates and separate the two products by distillation.

Segessmann (39) esterifies the fatty acids with a low boiling-point alcohol such as methyl alcohol and the resin acids with a high boiling-point alcohol such as glycerol, and then separates the esters by distillation.

3. Sulfonation: The sulfonation method of purifying tallol has been worked on extensively.

Geigy (19) treats a mixture of tallol and phenol with a sulfonating agent. The product obtained

has been described as a resinous water soluble substance useful in the textile industry.

Chapman (5) attempted the separation of resin and fatty acids by selective sulfonation. He treated the tallol with small amounts of concentrated sulfuric acid and found that the resin and fatty acid portions of tallol could be separated by this method.

Crockin and Vilbrandt (7) have designed a pilot plant for the purification of tallol by the sulfonation method. The product obtained by this method has been described as a limpid straw-colored oil which on standing yields clear abietic acid crystals.

Crystallization: Jenkins (24) has devised a method of separating the resin acids from the fatty acids by dissolving the tallol in a suitable polar solvent containing a considerable amount of water and then crystallizing the resin acids out by any suitable means. The solvents employed were the monomethyl ether of ethylene glycol, diacetone alcohol, or furfural. When furfural was used, the amount of water in the solution was five per cent by weight. The ratio of tallol to solvent was varied but results were obtained with tallol content of fifty per cent or less by weight.

Abietic Acid

Abietic acid is one of the earliest rosin acids isolated and studied. It is the principle constituent of American rosin and the resin acids in tallol. The term "abietic acid" has been used indiscriminately in the literature to describe various rosin acids thought to be individual compounds. Compounds thought to be abietic acid have been reported in the literature with melting points varying from 132°C. to 182°C. and having been named "abietic acid" or "isomers of abietic acid". Later investigators found that many of these compounds were not pure but mixtures of abietic acid and abietic acid derivatives. As an example, Fleck and Palkin (15) have shown that pyro-abietic acid, a so-called "isomer of abietic acid" with a melting point of 173-174°C. is in reality a mixture of three acids similar to abietic acid - dehydroabietic, dihydroabietic, and tetrahydroabietic acids. Their work was substantiated later by Ruzicka, et al. (34) Later, Hasselstrom, et al (20) proved that pin-abietic acid long considered a stereoisomer of abietic acid was a mixture of abietic, dehydroabietic, and dihydroabietic acids.

A search of the literature revealed that there are but two known isomers of abietic acid - one named "abietic acid" and the other named "levo-pimaric acid".

The structures of these two acids were determined by Fieser and Campbell. (14) The structures differ in that abietic acid has its two double bonds in two rings whereas levopimaric acid has the double bonds in the same ring. These structures are pictured below:

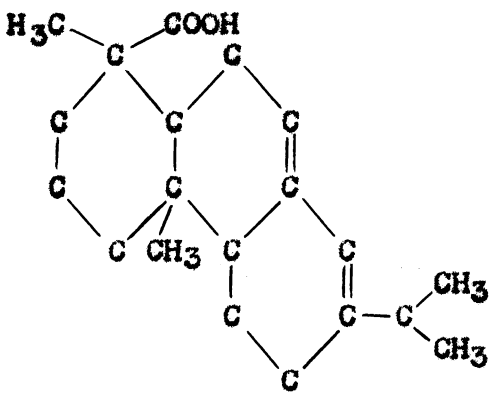


Fig. 1. Abietic Acid

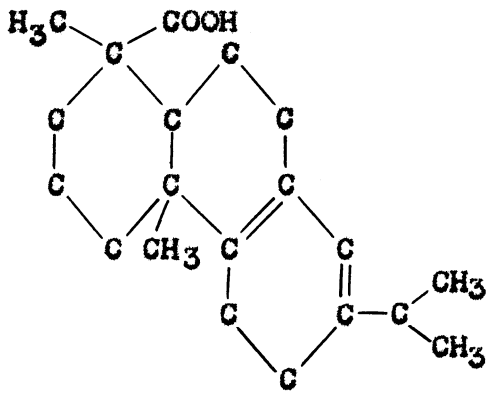


Fig. 2. Levo-pimaric Acid

The above structures for abietic and levo-pimaric acid have been accepted by various investigators.(4, 16, 33, 35)

The physical properties of abietic and levo-pimaric acids differ somewhat. The melting point of abietic acid has been reported in various references(11, 21, 28, 33, 42, 47) to be in the range 153-160°C. Ellington (11) states that abietic acid is not characterized by a sharp melting point but melts over a range of three or four degrees. Abietic acid crystals are described as being thin, transparent, colorless, triangular plates which grow in clusters. (11, 13, 42)

These crystals belong to the monoclinic system [11, 42] and are optically negative. [42]

The melting point of levo-pimaric acid is difficult to determine since levo-pimaric acid can be easily isomerized to abietic acid. [14, 35] According to Bacon and Ruzicka,[2] levo-pimaric acid will isomerize to abietic acid at temperatures near 80°C. Vesterberg [43] determined that levo-pimaric acid crystals belong to the ortho-rhombic system and are optically positive differing from abietic acid crystals in these respects. The crystals grow in rectangular tablets with two axes nearly equal. The melting point has been found to be in the range of 140-150°C. but a sharper melting point could not be obtained. [43]

III. EXPERIMENTAL

Purpose of the Investigation

This research was conducted to determine the possibility of separating the resin acids from the fatty acids in tallol and to purify the resin acids.

Another object of this investigation was to attempt an identification of any resinous products obtained in the course of the investigation.

Plan of Investigation

The plan of this investigation can be devided into three sections as given below:

1. To effect a separation of the resin acids from the fatty acids by the use of furfural and tallol as immiscible solvents to selectively dissolve portions of tallol and then to crystallize the resin acids from the solution.

2. To effect a separation of the resin acids from the fatty acids by using a

furfural - water solution to act as a polar solvent of the tallol and allowing the subsequent crystallization of the resin acids from the solution.

3. To identify any crystals obtained in the course of the investigation by standard methods set up in Shriner and Fuson (41) and/or by methods found in the literature.

Materials

Tallol: The tallol used in this investigation was obtained from the West Virginia Pulp and Paper Company, Industrial Sales Division, New York City, and is currently sold under the name "Ligro".

The composition of thic material as supplied by the company is listed below:

Fatty Acids	48.6 %
Resin Acids	44.1 %
Unsaponifiables	7.3 %
Ash	.24%
Moisture	.02%
Acid Number	166

The material is a dark brown, viscous liquid containing many crystals believed to be rosin crystals. Before using, the tallol was thoroughly mixed to insure a uniform sample.

Petroleum Ether: The petroleum ether used as a solvent in this work was a five pound shipment of analytical reagent grade obtained from the Mallinckrodt Chemical Works, New York. This solvent had a boiling point range of 30-60° Centigrade.

Furfural: The furfural used was obtained from the Chemical Engineering Storeroom and was part of a shipment previously used for extraction. Before using, the furfural was purified by distillation. The product distilled at 158°C. at atmospheric pressure and was a light yellow color.

Methyl Alcohol: The methyl alcohol used was obtained from the Chemical Engineering Storeroom and was part of a shipment obtained from the Phipps and Bird, Inc. of Richmond, Virginia. This alcohol was absolute refined.

Miscellaneous Chemicals: The various reagents used in the identification of the crystals were obtained from the Chemistry Stockroom and were generally of C.P. grade.

Apparatus

Centrifuge: The centrifuge used was a laboratory model obtained from the International Equipment Company, Boston, Mass., through the Fischer Scientific Company, Pittsburgh, Pa. It had a five inch basket and a maximum speed of 3600 R.P.M. The filtering medium used was Whatman No. 2, large sheets, cut to the proper size.

Distillation Apparatus: A standard laboratory vacuum distillation apparatus was set up using a laboratory aspirator as a vacuum pump. The complete apparatus consisted of:

1. One 500 cc. distilling flask.
2. One glass condenser.
3. One 500 cc. round bottom flask.
4. One 1000 cc filter flask.
5. One 10 gallon carboy.
6. One 30 in. mercury manometer.
7. Miscellaneous glass and rubber tubing, rubber sloppers, rings, ringstands, and clamps.
8. One Bunsen burner.

The above items were obtained from the Chemical Engineering Storeroom.

Analytical Balance: The analytical balance was obtained from the Fisher Scientific Company, Pittsburgh, Pa., and used when accurate weighings were necessary.

Beam Balance: A beam balance of the single pan type was used for rough weighings and was obtained from the Chemical Rubber Company, Cleveland, Ohio.

Thermometer: A mercury thermometer graduated in degrees with a range from -10°C. to 360°C. was used for temperature measurements and was obtained from Brothcom, New York.

Miscellaneous Equipment: All other miscellaneous laboratory equipment such as glassware used in this investigation was obtained from the Chemical Engineering Storeroom.

Methods of Procedure

Two methods were attempted in order to separate the resin acids from the fatty acids of tallol. For the sake of clarity, these methods have been named "Furfural - Petroleum Ether" and "Furfural - Water", indicating the solvents used in their respective procedures. The general procedure for each method along with the general procedure for the identification of the crystols is given on the following pages.

Furfural - Petroleum Ether: This method employed the use of furfural and petroleum ether as immiscible solvents to separate the dissolved tallol into two portions. Five runs were made using 250 grams of petroleum ether and 25 grams of tallol in each but varying the ratio of furfural to tallol. These ratios were 1/2-1, 1-1, 1½-1, 2-1, and 3-1. Another run was made using 200 grams of tallol, 1000 grams of petroleum ether, and 100 grams of furfural. This procedure was the same except that two crystallizations were made from the same residue.

The general procedure for the runs is as follows:

1. The tallol is weighed in a 500 cc Erlenmeyer flask and then the weighed amount of petroleum ether is added.

2. The tallol and petroleum ether are thoroughly agitated for about ten minutes. This is sufficient time for solution.

3. The solution is centrifuged to remove insolubles. The amount of insolubles in each case is determined by weighing the filter paper before and after centrifuging.

4. The proper amount of furfural is added to the solution and agitated for approximately 1/2 hour.

5. The furfural and petroleum ether layers are allowed to separate at room temperature of about 26°C. for three days. The flask is stoppered during this time.

6. After having settled, the furfural layer is separated from the petroleum ether layer by decanting the petroleum ether solution. Each solution is then weighed.

7. The petroleum ether is distilled from the solution at atmospheric pressure. The temperature of the solution is not allowed to exceed 120°C.

8. Distillation is further carried out under a 27 in. vacuum. The temperature of the residue is kept below 60°C.

9. The amount of petroleum ether recovered is determined.

10. The residue is weighed, put in a test-

tube, and set aside for crystallization. During this time, the test-tube is stoppered, kept at a room temperature approximately 26°C., and agitated frequently.

11. The residue is then centrifuged to recover the crystals. These crystals are washed in the centrifuge with petroleum ether, dried, and then weighed. To insure sufficient time for crystallization, the residues are not centrifuged until two weeks after crystallization begins. During this time the residue is agitated at intervals.

Furfural - Water: In this method a furfural - water solution is used as a polar solvent to dissolve the tallol and to allow the subsequent crystallization of the resin acids from the solution. Three runs were attempted using 50 grams of tallol and varying the tallol - solvent ratio. These ratios were 1-1, 1-2, and 1-3. The solvent contained 5% of water by weight.

The procedure for this method is given below:

1. The solvent is made up by weighing the proper amounts of furfural and water

and then thoroughly mixing them to dissolve the water.

2. Tallol is weighed in a 250 cc Erlenmeyer flask and the weighed amount of solvent is added.

3. The solvent and tallol are agitated for 30 minutes and then centrifuged to clarify the solution.

4. The solution was then set aside at a room temperature of about 26°C. for crystallization.

Identification of the Crystals: The identification of the crystals was carried out by the standard methods of Shriner and Fuson (41) and Mulliken (28). It is not deemed necessary to include a detailed description of the methods of identification used in the general method of procedure, but the tests used will be described as used in the "Results."

The general procedure for identifying the crystals was as follows:

1. The solubility class of the crystals was determined by dissolving the crystals in various solvents.

2. Using various classification reagents, the functional groups of the crystals was determined.

3. The melting point of the crystals was found by the capillary tube method.

4. An approximation of the molecular weight was made by the depression of melting point method using camphor as the solvent and by determining the Neutral Equivalent of the crystals.

5. A survey of the literature was made and a derivative was prepared. The procedure for making the derivative will be given in the "Results".

6. Pertinant crystallographic data was obtained by studying the crystals with the naked eye and by using a petrographic microscope.

Data and Results

Furfural - Petroleum Ether: The data for the five runs using 25 grams of tallol and for the run using 200 grams of tallol is tabulated in Table 1.

The insolubles obtained when centrifuging the petroleum - ether - tallol solution were a dark brown color. This material was readily soluble in furfural imparting a dark brown color to the solution.

When distilling the petroleum ether, the receiving flask was emptied of solvent before applying a vacuum. No solvent was collected under vacuum distillation conditions since the atmospheric temperature of about 26°C. was sufficient to vaporize any solvent at the low pressure of the distillation.

TABLE I. Data for Furfural-Petroleum Ether Runs

Run	1	2	3	4	5	6
Furfural to Tallol (ratio)	½-1	1-1	1½-1	2-1	3-1	½-1
Wgt. Pet. Ether (gms)	250	250	250	250	250	1000
Wgt. Tallol (gms)	25	25	25	25	25	200
Wgt. Insolubles (gms)	1.4	1.7	1.3	1.4	1.5	13.7
Insolubles (%)	5.6	6.8	5.2	5.6	6.0	6.9
Wgt. Furfural (gms)	12.5	25	37.5	50	75	100
Wgt. Pet. Ether Layer (gms)	258.8	252.9	278.3	244.6	269.6	1122.3
Wgt. Furfural Layer (gms)	10.3	21.9	33.8	46.5	68.4	89.0
Furfural Loss (% Initial Wgt.)	17.6	12.4	9.85	7.00	8.8	11.0
Pet. Ether Recovered (gms)	201.6	195.8	218.5	184.9	207.0	878.2
Pet. Ether Loss (% Initial Wgt.)	19.4	21.6	12.6	25.6	17.2	21.8
Wgt. Residue (gms)	26.8	26.9	26.1	25.7	30.5	218.5
Residue Gain (% Tallol Wgt.)	7.2	7.6	4.4	2.8	22.0	9.3
Residue Color	dk.red-br.	dk.red-br.	red-br.	red-br.	amber	dk.red-br.
Wgt. Crystal (gms)	1.5	.95	.70	.45	.25	11.6
Crystals (Initial Sample, %)	6.0	3.8	2.8	1.8	1.0	5.8
Wgt. Crystals (2nd Crystn. gms)	-	-	-	-	-	6.2
Crystals (2nd Crystn, %)	-	-	-	-	-	3.1
Crystals (Total, %)	-	-	-	-	-	8.9

All crystals obtained were finer than 30 mesh, U. S. Standard Sieve, and were a white color with a faint yellowish tinge.

Furfural - Water: No quantitative data was obtained for this method since the runs made failed to crystallize. In approximately three months time, no crystals were evident in any of the solutions. The solutions were not viscous but very fluid.

An attempt was made to induce crystallization by chilling. The 1-1 furfural to tallol ratio solution was immersed for three days in a constant temperature bath at 2°C. Although the solution became more viscous, no crystals appeared in the solution.

It was also tried to distill part of the solvent from the solution. This was also a failure since the furfural polmerized at the distillation temperature of about 158°C.

Identification of the Crystals: The crystals were identified by the standard procedures set up by Shriner and Fuson [41] and with the help of sundry data found in the literature.

1. Solubility Class: The solubility class of the crystals was determined by attempting to dissolve some of the powdered crystals in various solvents. The solvents and results are listed below:

Water (distilled)	insoluble
Sodium hydroxide (5% aq. sol.)	soluble

Sodium bicarbonate (5% aq. sol.)	soluble
Hydrochloric acid (5% aq. sol.)	insoluble
Sulfuric acid (98%)	soluble
Phosphoric acid (85%)	insoluble

This placed the crystals in the solubility class A-1 which contains most of the acidic compounds.

2. Functional Groups: By means of reactions with various classification reagents, the functional groups of the crystals were determined.

Some of the powdered crystals was shaken with bromine in carbon tetrachloride solution and with a 2% water-potassium permanganate solution with the following results.

Carbon tetrachloride - - -	discharge of color, no evolution of gas
Potassium permanganate - -	discharge of color

This would indicate unsaturated linkage in the molecule of the crystals.

Tests were attempted with the following reagents: Tollen's Reagent, Schiff's Reagent, Fehling's solution, phenylhydrazine, and iodic acid. No reaction was evident with any of these solutions indicating the absence of such groups as alcohol, aldehyde, ketone, pheolic, or aniline derivative.

3. Melting Point: The melting point of the crystals was determined by the standard capillary tube method using glycerine as the liquid bath. The melting point range was 155-159°C. Three grams of the crystals were purified by recrystallization from methyl alcohol. The procedure was to dissolve the crystals in 25 cc. of alcohol, filter the solution, and then allow the alcohol to evaporate slowly at about 26°C. In three days the crystals were filtered, dried, and weighed. The weight of the crystals obtained was 1.4 grams. The melting point of these crystals was determined and found to be 155°-159°C. The melting point of a mixture of purified and impure crystals was determined and found to be 155°-159°C. also.

4. Molecular Weight: An approximation of the molecular weight of the crystals was made by the Neutral Equivalent method and by the molar freezing point depression method. The Neutral Equivalent was determined by titrating a 0.499 gram sample of the crystals dissolved in 50 cc. of methyl alcohol with 3.7 cc. of a 0.441 normal aqueous solution of potassium hydroxide. The Neutral Equivalent was calculated by the formula:

$$N.E. = \frac{\text{Wgt. of sample} \times 1000}{\text{Vol. of Alkali (cc.)} \times \text{Normality Factor}}$$

Substituting in the formula:

$$N.E. = \frac{0.499 \times 1000}{3.7 \times 0.441} = 306$$

Since the molecular weight of a compound is equal to the N.E. times the number of acidic groups in the molecule and assuming one acid group in the molecule of the crystals, the molecular weight of the crystals would be 306.

The molecular weight was also determined by melting 4.0 grams of pure camphor and 0.4 grams of the crystals together, cooling the melt, and powdering the mixture. The melting points of pure camphor and of the mixture was determined and found to be 173-177°C. and 160-163°C. respectively. The average freezing point depression was 13.5°C. The molecular weight was calculated from the formula:

$$M.W. = \frac{39.7 \times w \times 1000}{D \times G}$$

where:

39.7 is the molar depression of camphor

w is the weight of the crystals

G is the weight of camphor

and D is the depression in melting point.

Substituting the values in the equation:

$$M.W. = \frac{39.7 \times 0.4 \times 1000}{13.5 \times 4.0} = 296$$

5. Crystallographic Data: The crystals previously obtained by recrystallization from alcohol (page 28) were studied with the naked eye and with the petrographic microscope. These studies were made by Professor P. S. Dear of the Virginia Polytechnic Institute Ceramic Department. The crystals appeared to be thin, transparent, triangular shaped plates. These plates, some nearly 0.5 centimeters long, grew in clusters. They were entirely colorless. By use of the petrographic microscope, it was determined that the crystals were biaxial, optically negative, and had an optic angle of about 55 degrees. (8) From the shape of the crystals and the above data, it was concluded that the crystals belonged to the monoclinic system.(8) Confirmation of this conclusion by the measurement of the interfinal angles was not possible since the microscope used did not have a universal stage.

6. Derivatives: Two derivatives were made of the crystals following the procedure of Steele. (42) The general procedure is to dissolve the crystals in methyl alcohol and then neutralize the solution with alcoholic sodium hydroxide solution using phenolphthalein as an indicator. this solution is then poured, while mixing, into a water solution of cobalt chloride or manganese sulfate. The precipitate which forms is filtered, washed with water,

and then dried in a vacuum at 80 to 90°C. The quantities of materials used were as follows:

3 grams of crystals

30 cc. of methyl alcohol

6 grams of the cobalt chloride

or manganese sulfate

and 100 cc. of distilled water.

The cobalt derivative was a lavender color and melted in the range 195-242°C. The manganese derivative was a faint pink color and melted at 252-276°C. The colors correspond to those recorded by Steele but no melting points were recorded so substantiation of the melting point data was not possible. The melting point of the two derivatives made are presented here as a matter of record for future investigations. The high melting point ranges indicate that the derivatives are impure or are amorphous compounds.

The author wished to make the hydroxy derivative of the crystals but the lack of selerium dioxide prevented this.

IV. DISCUSSION

Furfural-Water

No data was obtainable for this method since it was not successful in separating the resin acids from the fatty acids of tallol. It may be that this method would work if tallol to solvent ratios other than the ones employed in this investigation were used in further studies of this method. Different methods of inducing crystallization might be necessary to attain success by this method.

Furfural-Petroleum Ether

From the data it can be seen that the method of using furfural and petroleum ether as immiscible solvents of tallol is fairly successful in separating the resin acids (abietic acid) from the fatty acids of tallol.

Yields: The maximum yield of crystals based on the weight of the original tallol sample was 6.0% by one crystallization. But assuming that the maximum amount of resin acids in tallol is about 50%, the actual yield of

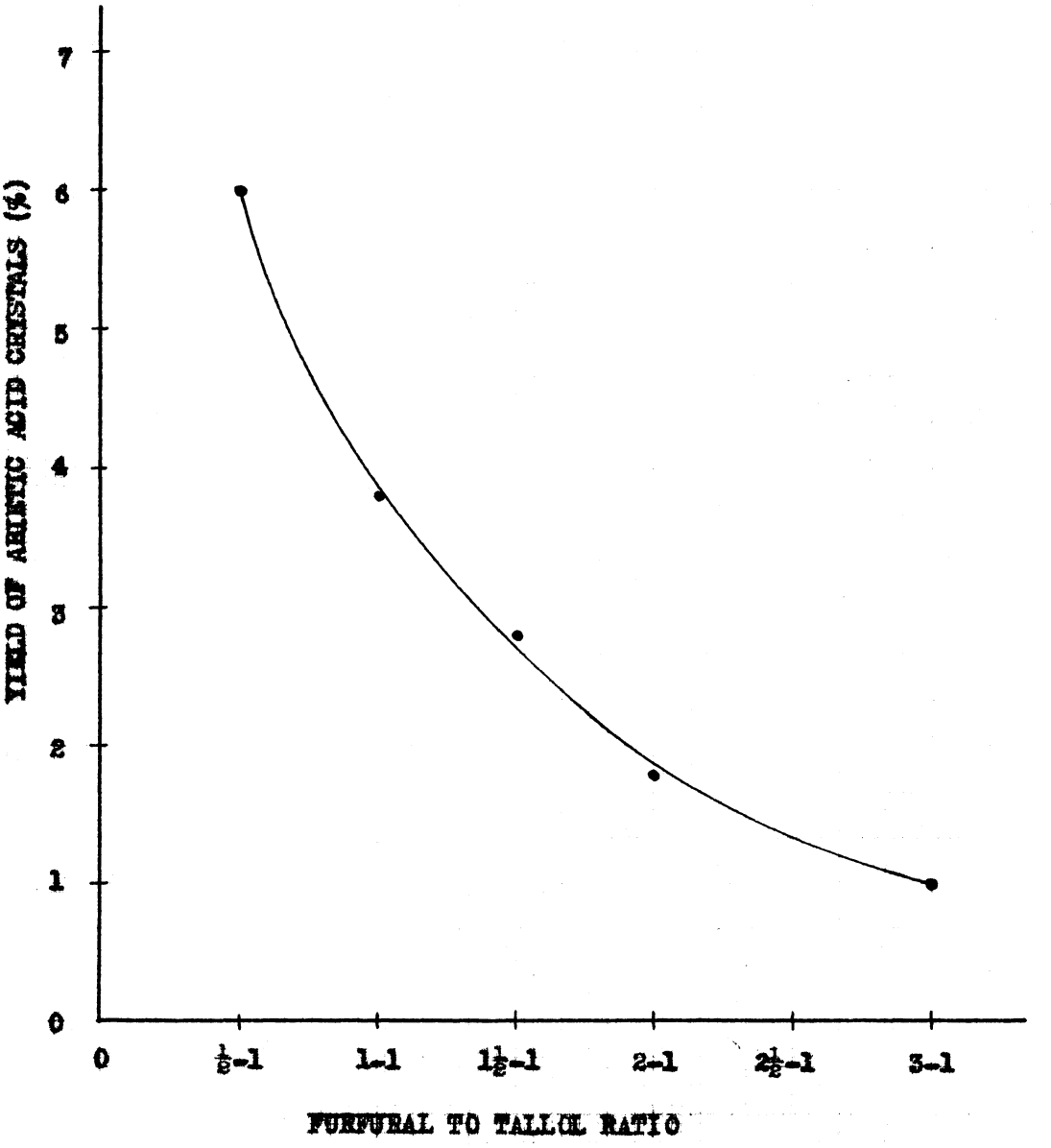
resin acids by this method is calculated as 12%. It is shown that by a second crystallization of the residue, the yield based on the sample weight can be increased to 8.9%, and the actual yield becomes 17.8%. With this yield it may be possible to adapt this process for commercial purposes; or, after more study of the problem, the yield may be increased by increasing the number of crystallizations.

Graph No. I. (page 34) of the furfural to tallol ratios effect on the yield of crystals obtained shows that as less furfural is used more crystals are obtained. This can be explained that some furfural dissolves in the petroleum ether solution and is not completely removed by distillation. This residual furfural probably hinders the crystallization thereby lowering the yield. Table I. shows that in each case there is a loss of weight in the furfural layer while there is a gain in the residue. This can be attributed to the dissolving of the furfural in the petroleum ether solution.

Crystal Appearance: The crystals obtained after centrifuging the residues were white and opaque as seen by the naked eye. Under the microscope they appeared colorless and transparent. The crystals grown in alcohol were colorless and transparent to the eye. The reason

GRAPH No. I

Effect of Furfural to Tallol Ratios
on the
Yield of Abietic Acid Crystals from Tallol



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that the original crystals appeared opaque is probably because they were not single crystals but small aggregates of crystals. The heterogeneous arrangement of the crystals in the aggregates would allow the reflection of light simulating opaqueness.

Identification of the Crystals

In the opinion of the author, the crystals can be identified as abietic acid crystals. It has been shown that the crystals belong to the A-1 solubility class which contains most acidic compounds. The bromine and permanganate tests indicate unsaturated linkage in the compound. The negative results obtained with Tollen's Reagent, Schiff's Reagent, Fehling's solution, phenylhydrazine, and iodic acid preclude the absence of such functional groups as alcohol, aldehyde, ketone, phenol, or aniline derivatives. From these reactions it may be concluded that the compound is an acid with unsaturated linkages.

The only compound listed by Heilbron [21] and Mulliken [28] as an unsaturated acid with a melting point range of 155-159°C., a Neutral Equivalent of approximately 306, and a molecular weight of about 296 is abietic acid. Abietic acid has reported melting points in the range 153-160°C. and a molecular weight of 302. The crystals have

been described as thin, colorless, transparent, triangular shaped plates growing in clusters, which is also a description of abietic acid crystals as recorded in the literature. (11, 13, 42) The derivatives made correspond to Steele's (42) cobalt and manganese abietates in color although no melting point data was obtainable to substantiate this data.

Abietic acid has one isomer, levo-pimaric acid. The crystals cannot be levo-pimaric acid crystals for the following reasons:

1. Levo-pimaric acid can be isomerized to abietic acid at about 80°C. Since distillation was carried out above this temperature it can be concluded that any levo-pimaric acid present would be converted to abietic acid.

2. Levo-pimaric acid crystals belong to the orthorhombic system. (43) The crystals from tallol and also abietic acid are in the monoclinic system. (8, 11, 42)

3. Levo-pimaric acid crystals are optically positive (43) whereas the crystals from tallol and abietic acid crystals are optically negative. (8, 42)

4. Levo-pimaric acid crystals are rectangular shaped prisms (43) but the crystals from tallol and abietic acid crystals are triangular shaped prisms. (11, 43, 42)

Recommendations

The following recommendations are suggested for future study.

1. Make additional runs by the furfural-water method using different solvent to tallol ratios than used by the author.

2. Determination of the optimum furfural to tallol ratio by making more runs and using furfural to tallol ratios larger and smaller than those used by the author.

3. Determination of the optimum petroleum ether to tallol ratio by making more runs and varying the amount of petroleum ether used while keeping the tallol and furfural amounts constant.

4. Determination of the optimum number of crystallizations necessary for increasing the yields of abietic acid crystals. This would probably necessitate the use of larger tallol samples than used by the author so that several recrystallizations of the same residue can be made.

5. Determination of the commercial feasibility of furfural-petroleum ether method by large scale development of the process.

6. Identification of the materials dissolved in the furfural layer.

7. Improve on the identification of the crystals by making, purifying, and determining the properties of a more suitable derivative than those made by the author. A suggested derivative would be hydroxyabietic acid which has been identified with recorded data in the literature.

Limitations

Only a limited investigation was attempted by the author to effect separation of resin acids from fatty acids in tallol by the furfural-water as a polar solvent method.

This study has not been complete in determining the commercial possibility of the furfural-petroleum ether process for separating abietic acid from tallol. Further work will be necessary before definite conclusions can be drawn.

The crystallographic data determined by Prof. Dear was not complete since the microscope used did not have a universal stage with which to measure the inter-facial angles.

V. CONCLUSIONS

The following conclusions can be drawn from the results of this investigation:

1. Using furfural to tallol ratios of 1/2-1 up to 3-1 by weight and a petroleum ether to tallol ratio of 10-1 by weight, crystals were obtained from tallol with these solvents acting as immiscible solvents and the subsequent crystallization of the compound from the residue left after the removal of the petroleum ether by distillation.

2. The crystals obtained by this method are identified as abietic acid crystals having a melting point of 155-159°C., the appearance of thin, transparent, triangular shaped prisms, in the monoclinic system, biaxial, optically negative, and having an optic axis of about 55 degrees.

3. In the furfural to tallol ratio range of 1/2-1 up to 3-1, the yields of crystals were

inversely proportional to the furfural to tallol ratio, varying from 6.0% to 1.0%.

4. With a furfural to tallol ratio of 1/2-1, an increase in the yield from 5.8% to 8.9% was obtained by a second crystallization of the residue.

5. No separation of resin acids and fatty acids can be made by the furfural-water method using solvent to tallol ratios of 1-1, 2-1, and 3-1 and attempting to induce crystallization by chilling to 2°C. for 72 hours or by distillation of about 50% of the solvent.

VI. SUMMARY

The investigation was undertaken to effect a separation of the resin acids from the fatty acids of tallol a waste product of the paper industry.

The furfural-water and furfural-petroleum ether methods were investigated. In the first method, a 5% solution of water in furfural by weight was used as a polar solvent with solvent to tallol ratios of 1-1, 2-1, and 3-1 by weight and attempting to induce crystallization by allowing the solution to stand at a temperature of about 26°C., chilling the solution to 2°C. for about 72 hours, and distilling about 50% of the solvent from the solution. No crystallization was evident in any of the solutions.

In the second method, solutions of tallol and petroleum ether were agitated with furfural. The petroleum ether to tallol ratio was 10-1 by weight, and the furfural to tallol ratios were 1/2-1, 1-1, 1-1/2 - 1, 2-1, and 3-1 by weight. After agitation the solutions were allowed to stand at approximately 26°C., and then the two layers formed were separated by decantation. The petroleum ether layers

were distilled, and the residues allowed to stand at about 26°C. Crystals appeared in three days and were recovered by centrifuging the residues.

These crystals with yields varying between 1.0% and 6.0% were identified by their melting point of 155-159°C., molecular weight determination as approximately 306, reactions with various reagents, and pertinent crystallographic data.

VII. BIBLIOGRAPHY

1. Alberti, B. Constants of Tall Oil. Seifensieder - Ztg. 55, 58-9 (1928). Original not seen. (C.A. 22, 1865 (1928)

2. Bacon, R. G. R. and Ruzicka, L. Levopimaric Acid. Chem. & Ind. 14, 546 (1936)

3. Brown, C. R. and Scott, A. T. Treatment of Tall Oil Acids. U. S. Pat. 2,294,446 (1942)

4. Brown, R. F., Bachman, S. J., and Miller, S. J. The Irradiation of Abietic Acid with Ultraviolet Rays. J. Am. Chem. Soc. 65, 623-6 (1943)

5. Chapman, P. E. Separation of Rosin and Fatty Acids from Tall Oil by Selective Sulfonation. Unpublished Thesis. V. P. I. Library, Blacksburg, Va.

6. Crockin, J. M. Separation of Rosin and Fatty Acids from Tall Oil by Selective Chlorination. Unpublished Thesis. V. P. I. Library, Blacksburg, Va.

7. Crockin, J. M. and Vilbrandt, F. C. Design of a Commercial Plant for the Purification of Tall Oil. Va. J. Sci. 2, 201 (1941)

8. Dear, P. S. Private Communication. Blacksburg, Va. 1945

9. Dittmer, M. Tall Oil, a Byproduct of the Sulfate Pulp Manufacture. Z. Angew. Chem. 39, 262-9 (1926) Original not seen. (C.A. 20, 2072 (1926)

10. Duesburg, K. Tall Oil. Seifensieder - Ztg. 52, 873-4 (1925). Original not seen. (C. A. 20, 514 (1926)

11. Ellington, E. O. Abietic Acid and Some Its Salts. J. Am. Chem. Soc. 36, 325 (1944)

12. Ellis, C. "The Chemistry of Synthetic Resins". Vol. I, p. 754-7. Reinhold Publishing Corp., New York, 1935.

13. ibid. p. 766

14. Fieser, L. F. and Campbell, W. P. Concerning Dehydroabietic Acid and the Structure of Pine Resin Acids. J. Am. Chem. Soc. 60, 159 (1938)

15. Fleck, E. E. and Palkin, S. On the Nature of Pyroabietic Acids. J. Am.

Chem. Soc. 60, 921 (1938)

16. Fleck, E. E. and Palkin, S. Lactonization of Dihydro-l-abietic and Dihydro-l-pimaric Acids. J. Am. Chem. Soc. 61, 3197 (1939)

17. Goyer, F. H. and Fawkes, C. E. Separating Fatty Acids from Resin Acids. U. S. Pat. 2,166,812 (1939).

18. Goyer, F. H. and Fawkes, C. E. Separating Fatty Acids from Resin Acids Contained in Tall Oil. U. S. Pat. 2,288,947 (1943)

19. Geigy, J. R. Sulfonated Derivatives of Tall Oil. Swiss Pat. 156,113 (1931). Original not seen. (C.A. 27, 1212 (1933).

20. Hasselstrom, T., McPherson, J. P., and Hopkins, S. The Identity of the Resin Acids. Paper Trade J. 110, No. 4, 41-3 (1940). Original not seen. (C.A. 34, 2386 (1940)

21. Heilbron, I. M. "Dictionary of Organic Compounds", Vol. I, p. 1, Oxford University Press, New York, 1934.

22. Hubscher, J. Swidish Rosin Oil. Seifensieder - Ztg. 48, 231-2 (1921).

Original not seen. (C.A. 15, 2177 (1921)

23. Humphrey, I. W. Solvent Refining of Wood Rosin. Ind. Engr. Chem. 35, 1062-7 (1943)

24. Jenkins, J. D. Separating Resin Acids from Tall Oil. U. S. Pat. 2,352,547 (1944)

25. deKeghel, M. Composition and Utilization of Tallol. Rev. Chim. Ind. 35, 170-3, 202-6 (1926). Original not seen. (C.A. 21, 1354 (1927).

26. Martin, R. W. Refining Rosin, Rosin Esters, Rosin Alcohols, and Esters of Rosin Alcohols. U. S. Pat. 2,306,455 (1942).

27. McKee, R. H. and Blengsli, H. L. Refining Tall Oil. Paper Trade J. 103, No. 14, 33-4 (1936). Original not seen. (C.A. 30, 8613 (1936).

28. Mulliken, S. P. "Identification of Pure Organic Compounds". Vol. I, p. 63 John Wiley and Sons, Inc., New York, 1914.

29. Niesen, H. The Chemistry of Tall Oil. Fette u. Seifen, 47, 296-300 (1940). Original not seen. (C.A. 35, 3470 (1941).

30. Poppe, G. and Othmer, D. F. Tall Oil. Ind. Engr. Chem., 36, 430-434 (1944).

31. Pollak, A. Industrial Utilization of Tall Oil. Oil and Soap 17, 87-9 (1940). Original not seen. (C.A. 34, 3492 (1940)

32. Reinert, B. Tall Oil as a Varnish Material. Farbe. u. Lack, 461-2 (1936). Original not seen. (C.A. 31, 5603 (1937).

33. Ruzicka, L. and Sternback, L. Origin and Degradation of Tetrahydroxyabietic Acid. Helv. Chim. Acta, 21, 565-83 (1938). Original not seen. (C.A. 32, 7044 (1938).

34. Ruzicka, L., Bacon, R. G. R., Sternback, H., and Waldmann, H. So-Called Pyro-abietic. Acid Helv. Chim. Acta, 21, 591-7 (1938).

35. Sandermann, W. Constitution of l-Pimaric Acid. Ber. 74B, 154-61 (1941).

36. Schmid, W. "Liquid Rosin" and Its Possible Uses. Papier-Fabr. 29, Tech.-Wisc. Teil 1-4 (1931). Original not seen. (C.A. 25, 3165 (1931).

37. Schmid, W. Tall Oil and Its Possible Uses. Farben-Chemiker 2, 306-10 (1931).

Original not seen. (C.A. 25, 5582 (1931).

38. Segessemann, E. Treating Tall Oil. U. S. Pat. 2,199,653 (1940).

40. Segessemann, E. Refining Tall Oil. U. S. Pat. 2,275,186 (1942).

41. Shriner, R. L. and Fuson, R. C. "Identification of Organic Compounds". 2nd ed., John Wiley and Sons, Inc., New York, (1940).

42. Steele, L. L. Abietic Acid and Certain Metal Abietates. J. Am. Chem. Soc. 44, 1333 (1922).

43. Vesterberg, A. Levo-pimaric Acid. Ber. 20, 3248 (1887).

44. Wallach, J. A. Fatty Acids from Pine Wood, Soap 13, 31-3, 73 (1937). Original not seen. (C.A. 31, 3313 (1937).

45. Ward, L. E. Design Characteristics for By-Product Fatty Acid Recovery. Unpublished Thesis, V.P.I. Library, Blacksburg, Virginia (1937).

46. Ward, L. E. and Vilbrandt, F. C. Corrosion Characteristics in Distillation of Fatty Acids. V.P.I. Engr. Exp. Sta. Bull. 30, 4 (1937).

47. Weinhous, H. and Mucke, K. The Chemistry of the Oleoresinc. Ber. 75B, 1830-40 (1942).

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