THE ESTERIFICATION OF TALL OIL TO OBTAIN DRYING OIL CHARACTERISTICS

by

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I INTRODUCTION

The shortage of suitable drying oils during the past few years has served to emphasize the need for the development of suitable products which could be used as substitutes for drying oils. The larger portion of oils now used in the United States are imported from foreign sources; specifically the Argentine supplies the linseed oil market. There are very few synthetic drying oils used at the present time. Quite a bit of work has been done to produce synthetic paints using certain resins in place of drying oils, but these new products are not as satisfactory as oil base paints and varnishes. The need therefore exists for the production of a domestic drying oil or a product that has all of the characteristics of a drying oil. This would solve the problem now faced by the paint and varnish industry of obtaining a domestic source of drying oils.

During the past few years investigations have been carried out to determine the possibilities of incorporating drying oil characteristics in tall oil, a by-product of the sulphate pulp and paper industry. Until recently it was regarded as a waste product and was either disposed of or burned for its heat content. The tall oil is separated and recovered from the black liquor during the black liquor recovery process. During evaporation of the black liquor soaps are formed which tend to corrode the evaporating equipment and reduce efficiency. These soaps are drawn off as they form during the evaporation, and are acidified with excess mineral acids to remove the tall oil. In addition to the tall oil they contain mercaptans, lignin, sterols, higher alcohols, and rosins.

Tall oil contains some of the basic requirements of a drying oil and the possibility exists that it could be converted into a suitable drying oil substitute. To be a satisfactory drying oil an oil should have a sufficient number of unsaturated conjugated ethenoid linkages in the form of unsaturated esters of unsaturated fatty acids: tall oil contains enough of these unsaturated linkages in the form of the free unsaturated fatty acids. The problem is to successfully convert these acids into their unsaturated esters.

The object of this investigation is to obtain drying oil characteristics in tall oil by esterifying it with a polyhydroxic alcohol, pentaerythritol, using activated aluminum oxide as a catalyst.

II LITERATURE REVIEW

Tall oil was originally regarded as a waste product, and presented a problem in waste disposal. Before 1939 the price of tall oil was about six dollars a ton. After 1939 many new uses were found for tall oil and the demand for it increased many times. The price has risen to a present day quotation of one hundred and twenty dollars a ton, and the product is now being used in industries that had little use for it heretofore.

Yields and Quantities. The yield of crude tall oil per ton of pulp varies widely depending upon the type pulp used, greeness of the wood, and the process used.(32) Some tall oil is lost in the black liquor recovery process, and in the separation of the tall oil from the soaps formed in the evaporators. A conservative estimate based on available data is that approximately sixty pounds of tall oil can be obtained from each ton of wood pulp.(32) Some sources estimate that the yield is as high as 250 pounds for Northern pine, and one hundred pounds for Southern pine.(20) At this time over one hundred and twenty-five thousand tons of tall oil are potentially available based on the fact that nearly five million tons of pulp were made during 1944.(32) Actual production of tall oil in 1938 was ten thousand tons.(8)

Composition of Tall Oil. Tall oil is defined(3) as the natural mixture of rosin acids related to abietic acid, and of fatty acids related to oleic acid, together with monacidic bodies, which is the product of the acidification of the skimmings from the black liquor of the alkaline pulp industry. The analysis of higher fatty acids has not been developed sufficiently to give the exact composition of tall oil, and the tall oil changes composition from batch to batch. In view of these factors the composition of tall oil is usually reported as, (a) fatty acids, (b) rosin acids, and (c) unsaponifiables. These factors vary widely in analyses. These analyses are shown in Tables I and II. The best work done to date indicates that the composition of the three major components is as follows:(32)

(a) Fatty acids: principally unsaturated 18 carbon acids such as oleic, linoleic, and linolenic acid.

(b) Rosin acids: Those acids which do not esterify with methyl or ethyl alcohol after boiling for several minutes in the presence of sulfuric acid. Undoubtedly contains abietic acid.

(c) Unsaponifiables: Sterols, higher alcohols, and other substances which can not be saponified.

Table I

CRUDE TALL OILS

From Various Domestic Sources. (31)(32)

Source	Rosin Acids %	Fatty Acids %	Sterols, Higher Alcohols %
A	38	54	8.4
B	39	52	8.5
C	40	54	7.2
D	42	54	6.7
E	42	39	18.1
F	44	50	7.5
G	45	47	7.5
H	47	46	7.8
I	51	43	8.6
J	56	37	7.0
K	58	36	6.5

Table II

Variations in Analyses. (26)(31)

Property	Crude Tall Oil		Refined Tall Oil	
	Ref.30	Ref.26	Ref.30	Ref.26
Acid Number	120-130	145-175	145-175	165-185
Sapon. Number	120-130	145-175	150-170	165-185
Rosin Acid No.		40-120		10-80
Iodine Number		120-150	100-11	100-150
Fatty Acids %	17-25	25-60	43-50	40-90
Rosin Acids %	45-65	20-60	38-45	5-40
Sterols, Higher Alcohols, etc. %	20-30	6-20	13-18	3-15

Drying Oils. A drying oil is an oil used in paints and varnishes to form the hard, protective coating produced when paints and varnishes are applied to a surface in a thin coating. Morrell and Wood(25) define a drying oil as an oil that possesses to a marked degree the ability to absorb oxygen from the air and change to a hard, elastic, tough substance when exposed in a thin surface.

Because of these properties drying oils are used mainly in the paint and varnish industries, linoleum industry, and in the printing ink industry. The most important drying oils now in use are linseed oil, tung oil, perilla oil, and oiticica oil.(11) The major portion of these oils is imported from foreign sources as shown in Table III. The factory consumption of the primary animal and vegetable fats is shown in Table IV.

The physical constants as well as the composition of these oils vary greatly. These are indicated in Table V. The constants of linseed oil, the most widely used drying oil, are generally accepted as a guide for determining whether or not oils will be acceptable as drying oils. The requirements for linseed oil as established by the American Society for Testing Materials(3) are given in Table VI.

The fact that most drying oils are imported(21)(11) causes the supply to vary with the state of international affairs. To offset this, attempts have been made to find a domestic source. Attempts have been made to convert soya bean oil, cottonseed oil, and castor oil into drying oils. Numerous attempts have been made to determine the value of tobacco seed oil as a drying oil.(2)(12) Many attempts have been made to use tall oil as a drying oil substitute.(4)(9)(10)(15)(16)(18)(23)(27)(1)(28)(29)(14) With the development of improved methods of obtaining the desired unsaturated fatty acids from tall oil and other nondrying oils, a domestic source of drying oils could be developed for future use.

Table III

Drying Oils and Oil Seeds Imported Into The United States (lbs)(1)

Year	Linseed	Tung Oil	Perilla Oil and its Equiv. of Seed	Oiticica Oil
1935	274532000	120058817	73357413	
1936	269647500	134829995	119287951	2892137
1937	533724615	174884803	43664481	3631147
1938	292522297	107455674	31821654	5300899
1939	305176000	78717634	53451620	18866689

Table IV

Factory Consumption of Primary Animal & Vegetable Fats in 1941(21) (In thousands of Pounds)

Oil	Soap	Paint & Varnish	Linoleum	Inks	Total
Linseed	2278	373745	110236	23547	539362
Tung		48825	1896	2960	54008
Perilla		5408	340	831	7024
Soya Bean	24737	41594	7666	250	463686
Castor	1976	44240	1295	760	89920

Table V

Physical Constants and Composition of Drying Oils(21)						
Oil	Sapon. No.	Iodine No.	% Unsapon.	% Oleic Acid	% Linoleic Acid	% Linolenic Acid
Linseed	188-196	170-204	.5-1.7	9.6	42.6	38.1
Castor	176-187	81-91	.3-1.0	7.2	3.6	
Perilla	187-197	193-208	.4-1.5	3.9	44.3	44.2
Oiticica	186-195	139-155	.4-1.0	8.0	8.0	
Soya Bean	189-195	120-141	.2-1.5	33.7	52.0	2.3
Tung	189-195	160-175	.4-1.1	14.9		

Table VI

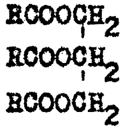
Requirements For Linseed Oil(19)		
Physical Property	Maximum	Minimum
Acid Number	5.5	
Saponification Number	195.0	189
Iodine Number		177
Unsaponifiable Material	1.5%	

Requirements of a Drying Oil. An oil must meet certain requirements to be classified as a drying oil. When applied to a surface in a thin coating and exposed to air, it must possess the marked ability to absorb oxygen from the atmosphere and then change into a tough, hard, elastic film.(25) It must contain a sufficient number of unsaturated, conjugated ethenoid linkages, and polybranched molecules capable of expanding indefinitely in any direction.(5) The unsaturated linkages are present in the form of the esters of the unsaturated fatty acids. These linkages are the reactive centers at which oxidation supposedly takes place, and are illustrated as follows:(9)

$$-\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\overset{H}{C}-$$

Linseed oil which is regarded as a typical drying oil contains the glyceride esters of oleic acid, linoleic acid, and linolenic acid. These compounds contain one, two, and three unsaturated ethenoid linkages respectively.

It has been determined that only those polybranched molecules containing more than two branches form good films.(9)(22) The esters formed from alcohols having less than two hydroxyl groups do not have good film forming qualities.(21) It has also been determined that the films are formed by the esters of the unsaturated fatty acids.(25) The glyceride esters in linseed oil are those of an alcohol containing three hydroxyl radicals and contain three branches. This is illustrated as follows:

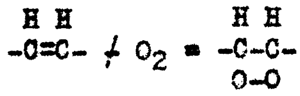


$$\begin{array}{l} RCOOCH_2 \\ \quad\;\; | \\ RCOOCH_2 \\ \quad\;\; | \\ RCOOCH_2 \end{array}$$

<u>Mechanism of Drying</u>. Drying has been defined by Bradley(5) as the conversion of a two dimensional type of structure into a three dimensional type of structure. Conant(6) defines it as the chemical change in which the unsaturated linkages absorb oxygen and then polymerize. Krumbhaar(22) defines it as the formation of a film by the oxidation of the oil and the polymerisation of the products of oxidation. Actually very little is known about the mechanism of drying in spite of the many investigations that have been made into the subject. The generally accepted theory is that oxidation takes place at the unsaturated linkages and that polymerization of the resulting compounds takes place. However, this theory does not completely answer the

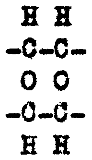
question of what takes place when a drying oil dries. There are many arguments for and against the theory.

It has been found that the oxidation of the oils takes place very slowly at first due to the presence of anti-oxidants. As soon as these are destroyed oxidation proceeds rapidly. Kirschenbauer(21) and Morrell and Wood(25) report that a molecule of oxygen is added at each double bond leading to the formation of peroxides in the following manner:



$$\begin{array}{c} H\ H \\ -C=C- \end{array} + O_2 = \begin{array}{c} H\ H \\ -C-C- \\ O-O \end{array}$$

This causes an increase in the weight of the compound. These peroxides break down into monoxides(25) and apparently polymerize in the following manner:



$$\begin{array}{c} H\ H \\ -C-C- \\ O\ \ O \\ -C-C- \\ H\ H \end{array}$$

This polymerization is defined by Conant(6) as the combining of two or more identical molecules to form a compound of greater molecular weight. Groggins(13) defines polymerization as the agglomeration of molecules to form products that have a molecular weight that is equal to the sum of the molecular weights of the reacting substances. The reactants are usually those with a large degree of unsaturation. Cheronis(7) defines polymerization as the chemical union of a number of similar molecules to form a single complex molecule of high molecular weight. In order for organic molecules to react some type of reactivity must exist or must be induced. Consequently, the saturated compounds do not polymerize. The greater the degree of unsaturation the more easily polymerization takes place. Those molecules having conjugated unsaturated linkages will polymerize better than those with consecutive unsaturated linkages. Actually, this polymerization is the combination of the poly-branched molecules to form the film desired of drying oils.

Esterification. Esterification is the name applied to the reaction occuring between an acid and an alcohol. The products of this reaction are an ester and water. In making a drying oil it is necessary to esterify the unsaturated acid with a higher alcohol such as pentaerythritol since a compound with three or more branches is necessary to form a three dimensional type structure.(5) Attempts have been made to esterify the higher unsaturated fatty acids with polyhydroxic alcohols to form synthetic drying oils.(5)(9)(16)(17)(18)(23)(27)(28)(29)(32) The majority of these attempts have met with only fair success. Esterification becomes more difficult as the size of the reacting molecules becomes larger. The saturated groups tend to retard esterification. In order to increase the rate and degree of esterification catalysts are sometimes used.(24) Sulfuric acid, phosphoric acid, zinc, and aluminum salts have been used in previous work.(9)(16)(17)(27) Attempts have also been made to increase yields by using gases such as nitrogen and carbon dioxide to form inert atmospheres in the reaction vessel in order to prevent oxidation.(9)

Determination of Drying Characteristics. In order to test for drying characteristics and qualities the drying time should be observed and the iodine number, saponification number, and acid number of the oil should be determined.

Drying Time. The method recommended by the A.S.T.M.(3) for determining the time required for drying is to spread the sample on a glass plate and after two hours test the film at intervals by touching with the finger tip.

The time required for the film to reach a point where it no longer adheres to the finger is the drying time.

Iodine Number. The iodine number will be determined by the Wijs or Hanus method as approved by the A.S.T.M.(3)

Acid Number. The acid number will be determined by the method approved by the A.S.T.M.(3)

Appearance Magnified. The film will be examined under a microscope to determine the quality and appearance.

Tall Oil Constituents. The main components of tall oil are the fatty acids, rosin acids, and unsaponifiable materials. The unsaturated fatty acids are the most important fraction as far as esterification is concerned. The chief acids present in this fraction are oleic acid, linoleic acid, and linolenic acid. Each has eighteen carbons, and one, two, and three unsaturated ethenoid linkages respectively.

Driers. Driers are compounds added to drying oils to reduce the time required for drying. They are introduced in the form of oxides, acetates, borates, metallic salts of the oils, or as resinates.(25) The metals most widely used in driers are manganese, cobalt, and lead. These driers form intermediate products which apparently have a catalytic effect and increase the rate of drying. Since they do not appear in the final product they may be classified as catalysts.(24)

III EXPERIMENTAL

A. Purpose of Investigation

1. To determine the practicability of obtaining drying oil characteristics in tall oil by esterifying it with a polyhydroxic alcohol, pentaerythritol.
2. To determine the value of esterified tall oil as a drying oil.

B. Plan of Investigation

The plan for carrying out this investigation is outlined as follows:

1. Review of the Literature
    a. Investigation of the drying theory
    b. Investigation of the source, yields, and composition of tall oil.
2. Construction of the Equipment to be used in the investigation
    a. Construction of the constant temperature oil bath
    b. Construction of the air-driven agitator
3. Experimental
    a. A series of runs using refined tall oil and technical pentaerythritol will be run under the following conditions with an inert atmosphere of carbon dioxide:

	Oil grams	Pentaerythritol grams	Act. Al_2O_3 grams	Temp. $^\circ C$	Time hrs.
1.	225	25	None	250	6
2.	225	25	12.5	250	6
3.	225	25	None	300	6
4.	225	25	12.5	300	6
5.	225	25	None	320	4
6.	225	25	12.5	320	4
7.	225	25	None	320	6
8.	225	25	12.5	320	6

b. A series of runs will be made under the following conditions using refined tall oil and dipentaerythritol with an inert atmosphere of carbon dioxide:

	Oil grams	Dipentaerythritol grams	Act. Al_2O_3 grams	Temp. °C	Time hrs.
1.	225	25	None	250	6
2.	225	25	12.5	250	6
3.	225	25	None	300	6
4.	225	25	12.5	300	6
5.	225	25	None	320	4
6.	225	25	12.5	320	4
7.	225	25	None	320	6
8.	225	25	12.5	320	6

c. A run will be made using crude tall oil under the following conditions:

Oil	225 grams
Pentaerythritol	25 grams
Catalyst	None
Carbon dioxide	8-10 cu.ft./hr.
Temperature	250° Centigrade
Length of run	6 hours

d. A run will be made using crude tall oil under the following conditions:

Oil	225 grams
Dipentaerythritol	25 grams
Catalyst	None
Carbon dioxide	8-10 cu.ft./hr.
Temperature	250° Centigrade
Length of run	6 hours

e. The following tests will be made to determine the value of the esterified tall oil as a drying oil:

1. Iodine number (Hanus Method)
2. Acid Number (ASTM)(3)
3. Drying time
    a. The time required for drying using varsol as a thinner will be determined
    b. The time required for drying using turpentine as a thinner will be determined
    c. The time required for drying using ethyl alcohol as thinner will be determined

C. Materials

Refined Tall Oil. The tall oil was furnished by the Albemarle Pulp and Paper Company, Richmond, Virginia, and is the commercial grade marketed by that company.

Crude Tall Oil. The crude tall oil was furnished by the West Virginia Pulp and Paper Company, Covington, Virginia, and is sold under the trade name of Ligro.

Potassium Iodide. C. P. Lot 31246. Obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Iodine. Resublimed. Lot 5246. Obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Bromine. C. P. Lot 10843. Obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Carbon Tetrachloride. Purchased from Phipps and Bird, Incorporated, Richmond, Virginia.

Sodium Thiosulphate. Crystals-$Na_2S_2O_3.5H_2O$. Lot 112039. Obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Methyl Alcohol. Absolute. Obtained from Phipps and Bird, Incorporated, Richmond, Virginia.

Ethyl Alcohol. Absolute. Obtained from the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Potassium Hydroxide. C. P. (Pellets). Obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

Technical Pentaerythritol. Obtained from the Trojan Powder Company, Allentown, Pennsylvania.

Dipentaerythritol. Obtained from the Trojan Powder Company, Allentown, Pennsylvania.

Carbon Dioxide. Dry. Fifty pound cylinder. Obtained from the Southern Oxygen Company, Roanoke, Virginia.

Glacial Acetic Acid. 99.5%. Technical grade. Can be substituted for C. P. Obtained from the Arthur S. LaPine Company, Chicago, Illinois, through the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Thymol Blue. Obtained from the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Activated Alumina Catalyst. F-10, 4-8 mesh. Obtained from the Aluminum Company of America, St. Louis, Missouri.

D. Apparatus

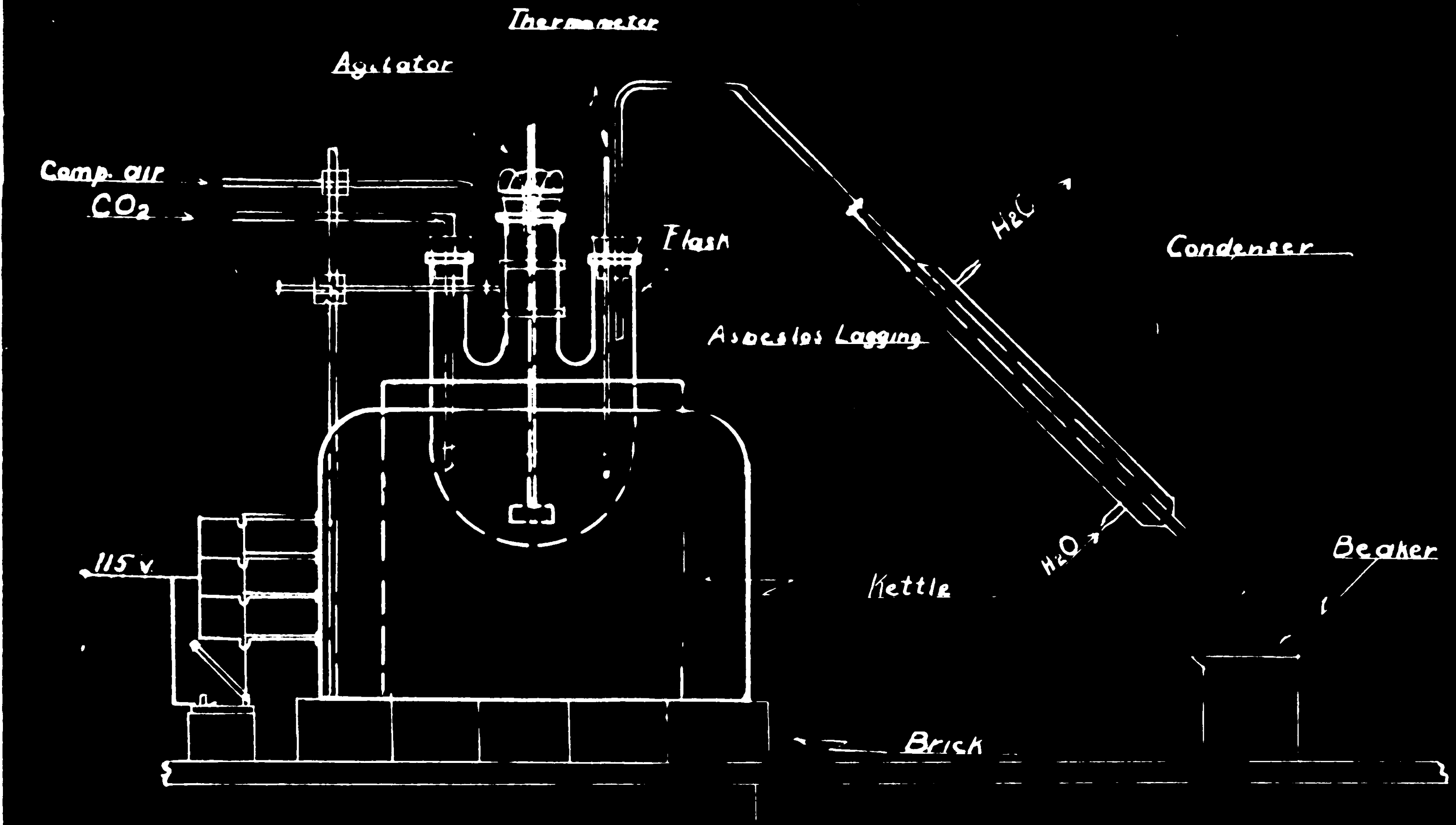
The apparatus used in this investigation consisted of a constant temperature oil bath, a two liter Wolfe three-neck flask, a carbon dioxide pipeline, two thermometers with a range of from 0°C to 360°C, a Sargent Wet Test Meter, an air-driven agitator, and assorted pieces of laboratory glassware.

Constant Temperature Oil Bath. The oil bath container was a nickel kettle, lagged with asbestos, and heated by means of four insulated Nichrome wire coils which were wrapped around the kettle and held in place by the lagging. The heating elements were made of fifteen foot lengths of number 24 Nichrome wire wound into coils. The coils were passed through procelain insulators one-half inch in diameter, and four inches long, and then wrapped around the kettle, the bottom coil being placed one inch above the bottom of the kettle, and the remaining coils being placed above the bottom coil at intervals of two inches. The kettle and coils were then encased in a layer of asbestos two inches thick, and the coils were connected to the source of power through jack-knife switches. Each coil was capable of delivering five hundred watts.

The heating medium used in the bath was S.A.E. 250 gear oil with a minimum guaranteed flash point of 625°F. The bath was tested and found capable of heating the oil to a temperature of 350°C. For a detailed drawing of the bath see Figure I.

Wolfe Flask. The flask was a two liter, glass, three-neck laboratory flask, and was obtained from the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

Air-driven Agitator. The agitator consisted of a sheet metal disc three inches in diameter, a welding rod twelve inches long, a number seven cork, and a stirrer. Eight fins were made in the disc by cutting in a distance of one inch from the outside edge toward the center and bending the cut



DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE, BLACKSBURG, VA.

OIL BATH AND REACTION VESSEL

SCALE: 1" = 5"
DATE: MARCH 7, 1947
DRAWN BY: C.E.A.
CHECKED BY:

portion upward. A hole one-quarter inch in diameter was drilled in the center of the disc, and the disc welded to the welding rod a distance of one inch from the end. A hole was then bored through the cork with the number five cork punch, and a short piece of glass tubing was forced into the hole. The welding rod was then placed through the glass tube in the cork and a stirrer one-half inch wide and one and one-half inch long was welded to the bottom of the rod. Several washers were inserted between the disc and the cork to prevent the disc from revolving directly on the cork. The agitator was driven by a stream of compressed air directed against the fins. For a detailed drawing of the agitator see Figure I.

<u>Carbon Dioxide Pipeline</u>. The pipeline was made of one-quarter inch black iron pipe, and was used to conduct the carbon dioxide from the storage cylinders to the reaction vessel.

<u>Sargent Wet Test Meter</u>. Number 50259. This meter was used to determine the rate of flow of carbon dioxide into the reaction vessel. The meter was made by the Precision Scientific Company, Chicago, Illinois, and was obtained from the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia.

<u>E. Method of Procedure</u>

A sample of 225 grams of refined tall oil was weighed out and placed in a Wolfe flask. The flask was lowered into the constant temperature oil bath until the level of the heating medium was approximately one inch above the level of the tall oil. This was done to insure uniform heating. A thermometer and distillate line were inserted in one neck of the flask, the agitator was inserted in the middle neck, and a carbon dioxide inlet line was inserted in the third neck. The carbon dioxide was bubbled into the tall oil and the rate of flow adjusted by means of the Sargent Wet Test Meter until about ten cubic feet of carbon dioxide were being passed through the oil per hour. The gas provided an inert atmosphere above the oil and prevented oxidation during the esterification process. The heating elements of the oil bath were turned on and the temperature allowed to rise to 200°C. At this point 25 grams of the technical pentaerythritol were added to the tall oil. The air jet was adjusted until the air agitator was turning fast enough to insure thorough agitation of the tall oil. The oil bath was then heated to a temperature of 250°C. When this temperature was reached the run actually began. The temperature was held at this level for a period of six hours, during which time the distillate was collected and the volume recorded. The reaction was observed closely to see what took place. It was important that sufficient agitation was maintained to insure completeness of reaction, and that enough CO_2 was entering to completely blanket the surface of the tall oil and prevent oxidation. After the temperature had been kept at 250°C for six hours the bath and product were allowed to cool to about 150°C, the product removed from the flask, placed in a sample bottle, and saved for future examination. The same procedure was followed for a run of six hours at 300°C, a run of four hours at 320°C, and a run of six hours at 320°C.

Another series of runs was made using 12.5 grams of activated alumina, F-10, 4-8 mesh as a catalyst in an attempt to increase the rate and degree of esterification. Technical pentaerythritol and refined tall oil were used and the procedure for making the runs was the same as outlined above. The catalyst was added with the pentaerythritol when a temperature of 200°C was reached. Six hour runs were made at temperatures of 250°C, 300°C, and 320°C. A four hour run was made at 320°C.

Dipentaerythritol and refined tall oil were reacted together in an attempt to obtain a comparison between this reaction in which pentaerythritol were used. The procedure followed in these runs and the temperatures used were the same as those used in the technical pentaerythritol tall oil reaction. Additional runs were made under the same conditions using 12.5 grams of activated alumina, F-10, 4-8 mesh, in order to determine the effect of the catalyst on the reaction of the dipentaerythritol and tall oil.

Crude tall oil was placed in the reaction vessel, CO_2 supplied at the rate of 8-10 cubic feet per hour, and agitation was begun while the temperature was being brought up to 200°C. At this point 25 grams of technical pentaerythritol were added and the temperature was brought up to 250°C. The 225 grams of crude tall oil and the pentaerythritol were allowed to react together for six hours. Upon completion of the run the product was allowed to cool and was transferred to a sample bottle for future examination. Another run was made under the same conditions using dipentaerythritol in place of pentaerythritol. Agitation was provided in these runs by means of the air-driven agitator.

In all of the previously described runs the flow of carbon dioxide was measured by means of the Sargent Wet Test Meter.

The iodine number of each of the samples of esterified tall oil was determined by the Hanus method as prescribed by the American Society For Testing Materials.(3) An accurately weighed sample of the oil was dissolved in a solvent, mixed with 25 cc. of iodine monobromide solution, and allowed to stand for thirty minutes in a dark place. Ten cc. of 15% potassium iodide solution were added and the sample was titrated with a solution of sodium thiosulfate of known normality. Duplicate runs were made to obtain an average iodine number for each sample.

The acid number of each sample was determined by the method prescribed as standard by the American Society For Testing Materials(3). A known weight of the sample was dissolved in methanol and titrated with a sodium hydroxide solution of known normality using thymol blue as an indicator. Duplicate runs were made to obtain an average acid number.

The drying rates of each of the samples was determined in several ways. The first method was to dissolve 20 cc. of product in enough varsol to give it the consistency of varnish and then quickly dip a strip of galvanized tin into the mixture. The strip of metal was then hung up to dry. The time required for the oil to dry to a point where it could be touched without removing any of the oil was recorded. This was known as tack hardness.

The second method used to determine drying times of the various products was to dissolve 20 cc. of the product in 20 cc. of turpentine, after which the mixture was heated gently for a period of five minutes to drive off some of the excess turpentine. A strip of galvanized tin was then dipped quickly into the mixture and hung up to dry. The time required for the oil to dry to a point where it could be touched without removing any of the oil was recorded as the time to reach tack hardness.

The procedure described in the preceding paragraph was repeated on each of the samples using ethyl alcohol instead of turpentine. The time required for the samples to dry to tack hardness was recorded.

Data and Results

Iodine Number, Acid Number, and Color of The Products of The Esterification of Refined Tall Oil With Pentaerythritol. The acid numbers, iodine numbers, and color of the products of the esterification of 225 grams of refined tall oil with 25 grams of pentaerythritol in an inert atmosphere of carbon dioxide at temperatures of 250, 300 and 320°C, with and without a catalyst, are compiled in Table VII.

Iodine Number, Acid Number, and Color of The Products of Refined Tall Oil Esterified With Dipentaerythritol. The acid numbers, iodine numbers, and color of the products of the esterification of 225 grams of refined tall oil with 25 grams of dipentaerythritol in an inert atmosphere of carbon dioxide at temperatures of 250, 300, and 320°C, with and without a catalyst, are compiled in Table VIII.

Iodine Number, Acid Number, and Color of the Products of Crude Tall Oil Esterified With Pentaerythritol and Dipentaerythritol. The iodine numbers, acid numbers, and color of the products of the esterification of 225 grams of crude tall oil with 25 grams of pentaerythritol and with 25 grams of dipentaerythritol, both in an inert atmosphere of carbon dioxide, at 250°C, are compiled in Table IX.

Drying Rates of The Products of The Esterification of Refined Tall Oil With Pentaerythritol. The rates of drying of the products of the esterification of 225 grams of refined tall oil with 25 grams of pentaerythritol in an inert atmosphere of carbon dioxide at temperatures of 250, 300, and 320°C, with and without a catalyst, are compiled in Table X.

Drying Rates of The Products of Refined Tall Oil Esterified With Dipentaerythritol. The drying rates of the products of 225 grams of refined tall oil esterified with 25 grams of dipentaerythritol in an inert atmosphere of carbon dioxide at temperatures of 250, 300, and 320°C, with and without a catalyst, are compiled in Table XI.

Drying Rates of The Products of the Esterification of Crude Tall Oil With Pentaerythritol and Dipentaerythritol. The drying rates of the products formed by the esterification of 225 grams of crude tall oil with 25 grams of dipentaerythritol, and with 25 grams of pentaerythritol, in an inert atmosphere of carbon dioxide at 250°C are compiled in Table XII.

Table VII

Evaluation of Refined Tall Oil Esterified

With Pentaerythritol

Run No.	Oil. gms.	Penta-erythritol gms.	Time hrs.	Temp. °C	Activ. Al_2O_3 gms.	Iodine Number	Acid No.	Color
1.	225	25	6	250	None	103	30	Light
2.	225	25	6	250	12.5	99	25	Light
3.	225	25	6	300	None	89	3.5	Light
4.	225	25	6	300	12.5	80	3.6	Dark
5.	225	25	4	320	None	85	5.7	Black
6.	225	25	4	320	12.5	73	4.8	Black
7.	225	25	6	320	None	82	5.6	Black
8.	225	25	6	320	12.5	85	5.0	Black

Table VII

Evaluation of Refined Tall Oil Esterified

With Dipentaerythritol

Run No.	Oil gms.	Dipenta-erythritol gms.	Time hrs.	Temp. °C	Activ. Al_2O_3 gms.	Iodine Number	Acid No.	Color
9.	225	25	6	250	None	90	26	Black
10.	225	25	6	250	12.5	89	26	Black
11.	225	25	6	300	None	86	4.8	Black
12.	225	25	6	300	12.5	84	4.6	Black
13.	225	25	4	320	None	75	5.7	Black
14.	225	25	4	320	12.5	77	5.1	Black
15.	225	25	6	320	None	83	5.2	Black
16.	225	25	6	320	12.5	84	4.8	Black

Table IX

Evaluation of Crude Tall Oil Esterified

With Pentaerythritol and Dipentaerythritol at 250°C

Run No.	Oil gms.	Penta-erythritol gms.	Dipenta-erythritol gms.	Time hrs.	Iodine Number	Acid No.	Color
17.	225	25	---	6	123	7.5	Black
18.	225	---	25	6	112	7.0	Black

Table X

Drying Rates of The Products of The Esterification of Refined Tall Oil With Pentaerythritol Using Various Solvents as Thinners

Run No.	Varsol Tack-hard hrs.	Varsol Dry hrs.	Turpentine Tack-hard hrs.	Turpentine Dry hrs.	Ethyl Alcohol Tack-hard hrs.	Ethyl Alcohol Dry hrs.
1.	XX	XX	XX	XX	XX	XX
2.	72	XX	XX	XX	XX	XX
3.	72	XX	96	XX	48	XX
4.	72	XX	72	XX	48	120
5.	40	96	72	XX	48	96
6.	40	96	72	XX	48	96
7.	40	72	72	XX	48	96
8.	40	72	48	72	36	60

XX Indicates sample discarded if not dry after seven days.

Table XI

Drying Rates of the Products of The Esterification of Refined Tall Oil With Dipentaerythritol Using Various Solvents As Thinners

Run No.	Varsol Tack-hard hrs.	Varsol Dry hrs.	Turpentine Tack-hard hrs.	Turpentine Dry hrs.	Ethyl Alcohol Tack-hard hrs.	Ethyl Alcohol Dry hrs.
9.	XX	XX	96	XX	XX	XX
10.	72	XX	XX	XX	72	XX
11.	96	XX	72	XX	48	120
12.	96	XX	72	XX	48	96
13.	40	96	96	XX	48	72
14.	40	96	72	120	48	96
15.	40	72	48	XX	36	72
16.	36	72	48	96	36	72

XX Indicates sample discarded if not dry after seven days

Table XII

Drying Rates of Products of The Esterification of Crude Tall Oil With Pentaerythritol and Dipentaerythritol Using Various Solvents as Thinners

Run No.	Penta-erythritol	Dipenta-erythritol	Varsol		Turpentine		Ethyl Alcohol	
			Tack-hard hrs.	Dry hrs.	Tack-hard hrs.	Dry hrs.	Tack-hard hrs.	Dry hrs.
17.	Yes	No	24	72	10	72	10	36
18.	No	Yes	24	72	10	72	10	36

IV DISCUSSION

__Theory of Drying__. Although the theory of drying has been the subject of many investigations, the question of how does a drying oil dry remains unanswered. Numerous theories have been advanced on the subject, but each one has certain limitations and does not completely answer the question. The most widely accepted theory is that oxygen is absorbed from the atmosphere at the unsaturated linkages in the oil, and that polymerization of the resulting compounds follows. This theory is known as the oxidation and polymerization theory. A great amount of research has been done, and many facts have been uncovered in an attempt to justify the theory. However, the supporters of this theory admit that there are many phases that are not satisfactorily answered by it, and that there are many facts that can be used to disprove it.

The exact part that oxygen plays in drying is not clearly known. Experiments made using linseed oil have proven that oxygen is absorbed by the oil in amounts as high as eighteen percent by weight. When the oil began to lose weight later in the drying cycle no carbon dioxide was detected. It is doubtful if the oxygen combined chemically with any of the components of the oil.

After absorbing the oxygen at the unsaturated linkages the resulting compounds in the oil are supposed to polymerize according to the accepted theory. Polymerization has been defined as the chemical union of a number of similar molecules to form a single, complex molecule of high molecular weight.(7) In order for this to take place there must be present some type of reactivity, either natural or induced. Consequently, saturated compounds do not polymerize. If this definition of polymerization is to be accepted, the supposition that oxygen is absorbed at the unsaturated linkages must be discounted, for if the oxygen is absorbed at these points there no longer exists a state of unsaturation, and polymerization can not take place. If oxygen is not absorbed at these linkages, it follows that drying is merely polymerization without oxidation. The results obtained from investigations made to determine the amount of oxygen absorbed during drying show that as drying continues some of the oxygen absorbed is gradually evolved. It is possible that some of the absorbed oxygen does combine at the unsaturated linkages. Drying requires a long period of time to reach completion, and it is possible that this is because of the small portion of absorbed oxygen. As this oxygen is released by the linkages, the polymerization of those molecules which release the oxygen proceeds. Linseed oil used as heavy bodied linseed oil in the manufacture of printer's ink is treated by blowing large amounts of air through the oil for a period of several hours. The oil becomes thicker than raw linseed oil, and in spite of the fact that it has been exposed to large amounts of atmospheric oxygen, it requires a much longer period of time to dry than ordinary linseed oil. This could be due to the fact that oxygen is absorbed at the unsaturated linkages, thus preventing rapid polymerization.

If oxygen is not absorbed at the unsaturated linkages present in a drying oil, what does prevent an oil that meets the structural requirements of a drying oil from drying? It is possible that there are certain drying "prohibitors" present in the oil. These could be present in the form of sterols and other unsaponifiable compounds. When a drying oil is mixed with a very volatile thinner and spread on a surface in a thin coating drying proceeds much more rapidly than in the case of pure oil spread in a like manner. There is a possibility that the sterols are carried off during the vaporization stage of the volatile thinner. The removal of these compounds would then allow polymerization to take place. Boiled linseed oil dries more rapidly after being boiled than raw linseed oil. The drying "prohibitors" could be removed drying the boiling of the oil. The M. K. Kellogg Company(34) has found that a large portion of drying oils and drying oil fortifiers can be produced by the selective extraction of fish oils and soya bean oil. After this separation the drying oil portions have been found to be very suitable as linseed oil substitutes. It is a distinct possibility that oils now classed as non-drying oils could be converted into drying oils by the removal of the portion of unsaponifiable materials, thus allowing polymerization of the unsaturated linkages.

The fact that previous drying theories leave so many questions unanswered indicates that some factor in the mechanism of drying has been overlooked. The idea that drying is fundamentaly pure polymerization as described in the preceding paragraphs is offered as another attempt to clarify the process involved in drying.

Effect of Temperature on The Esterification of Tall Oil. The time required for the drying of the products of the runs made at 250°C was considerably longer than that required by the products obtained at higher temperatures. The products obtained at 300°C dried in less time than those formed at 250°C, while those formed at 320°C required even less time to dry. (See Tables X and XI). This seemed to indicate that esterification was more complete at higher temperatures. The acid numbers of the high temperature products were lower than those of the low temperature products as is shown in Tables VII and VIII. This low acid number showed that the percentage of free acids in the oil was reduced considerably during the high temperature runs. The iodine numbers (see Tables VII and VIII) of the high temperature products were lower than those of the low temperature runs. This may have been caused by the unsaturated compounds breaking down into smaller compounds with a lower degree of unsaturation, or by the hydroxyl radicals of the alcohols used combining with the unsaturated linkages and thus reducing the amount of unsaturation. Either of these effects may have been caused or accelerated by the high temperatures.

Runs 5, 6, 7, 8, 13, 14, 15, and 16 were made at a temperature of 320°C which is slightly above the decomposition of tall oil(35). It was hoped that esterification would be more complete when the reaction took place just above the point at which a change occurs in the structure of the tall oil. The products obtained from these runs exhibited better drying characteristics than those of the other runs. (See Tables X and XI). This may have been due to the fact that esterification was more easily accomplished when a change occurred in the tall oil.

Effect of Activated Alumina on The Esterification of Tall Oil When Used as A Catalyst. The catalyst used was activated aluminum oxide, F-10, 4-8 mesh. This catalyst was selected because in previous investigations conducted in aluminum containers, esterification seemed to proceed more rapidly.

The catalyst did not have any apparent effect on the reaction in this investigation. The products obtained in the runs using the catalyst showed no improvement over those obtained from the other runs as is indicated in Tables VII, VIII, X, and XI. The catalyst showed no visible signs of change when removed after the runs and cleaned with methyl alcohol.

A Comparison of the Results Obtained By Esterifying Tall Oil With Pentaerythritol and With Dipentaerythritol. The products obtained by esterifying tall oil with pentaerythritol and dipentaerythritol were very similar. The times required for drying of the various samples showed no wide variance, and the acid numbers and iodine numbers were nearly equal. For a comparison of these values see Tables VII, VIII, IX, X, XI, and XII. These facts indicate that nothing is gained by using dipentaerythritol because of its greater number of hydroxyl radicals. It is possible that some of the excess hydroxyl radicals reacted with the unsaturated compounds present at the unsaturated linkages. This might have been the cause of the drop in iodine numbers shown in Tables VII and VIII.

The Effect of Time on The Esterification of Tall Oil. All of the runs made at 250°C and 300°C were six hours in length. Four of the runs made at 320°C were four hours long and the other four runs were six hours long. This was done in an attempt to determine the effect of time on the reaction. The difference in the length of the runs did not seem to materially affect the products. The iodine numbers, acid numbers, and drying times of the products of the four hour runs were practically the same as those of the six hour run products. (See Tables VII, VIII, X, and XI). It was noted that the distillate collected during the six hour runs was double the amount of distillate collected during the four hour runs. The color and type of distillate collected during the various runs were the same.

Recommendations

As a result of this investigation the following recommendations are made:

1. It is recommended that additional work be carried out in the esterification of tall oil at temperatures ranging between 320 and 330°C. Since these temperatures are just above the decomposition point of tall oil, and just below the point of complete destruction of tall oil a better degree of esterification may be obtained.

2. It is recommended that work be done on the extraction of the various components of tall oil to determine more fully the composition of the oil. The work done by the M. K. Kellogg Company(34) using Solexol as a solvent could be used as a guide for this work.

3. It is recommended that a series of drying tests having better control over temperature and humidity of the surrounding atmosphere be devised for use in future investigations.

4. It is recommended that an investigation be made to determine more fully the possibility that drying is pure polymerization without oxidation.

5. It is recommended that an investigation be made to determine the exact part that oxygen plays in drying.

6. It is recommended that an investigation be made to determine what part the sterols and other unsaponifiable materials present in tall oil play in retarding drying, and a quick, economical method for removing them.

V CONCLUSIONS

A. When a sample of 225 grams of refined tall oil is esterified with 25 grams of pentaerythritol in an inert atmosphere of carbon dioxide it is concluded that:

1. The product obtained after six hours at 250°C does not exhibit good drying oil characteristics.

2. The product obtained after six hours at 250°C using 12.5 grams of activated alumina as a catalyst does not exhibit good drying oil characteristics.

3. The product obtained after six hours at 300°C exhibits fair drying oil characteristics.

4. The product obtained after six hours at 300°C using 12.5 grams of activated alumina as a catalyst exhibits fair drying oil characteristics.

5. The product obtained after four hours at 320°C exhibits fair drying oil characteristics.

6. The product obtained after six hours at 320°C exhibits fair drying oil characteristics.

7. The product obtained after four hours at 320°C using 12.5 grams of activated alumina as a catalyst exhibits fair drying oil characteristics.

8. The product obtained after six hours at 320°C using 12.5 grams of activated alumina as a catalyst exhibits fair drying oil characteristics.

B. When a sample of 225 grams of refined tall oil is esterified with 25 grams of dipentaerythritol in an inert atmosphere it is concluded that:

1. The product obtained after six hours at 250°C does not exhibit good drying oil characteristics.

2. The product obtained after six hours at 300°C exhibits fair drying oil characteristics.

3. The product obtained after four hours at 320°C exhibits fair drying oil characteristics.

4. The product obtained after six hours at 320°C exhibits fair drying oil characteristics.

5. The product obtained after six hours at 250°C using 12.5 grams of activated alumina as a catalyst does not exhibit good drying oil characteristics.

6. The products obtained after six hours at 300 and 320°C, and after four hours at 320°C, using 12.5 grams of activated alumina as a catalyst, exhibit fair drying oil characteristics.

C. When samples of 225 grams of crude tall oil are esterified with 25 grams of pentaerythritol and with 25 grams of dipentaerythritol for six hours at 250°C in an inert atmosphere of carbon dioxide, it is concluded that the products obtained do not exhibit good drying oil characteristics.

VI SUMMARY

An investigation of the literature was made to determine the scope of previous investigations into the possibilities of obtaining drying oil characteristics in tall oil. Refined tall oil was esterified in an inert atmosphere with pentaerythritol at temperatures of 250, 300, and 320°C. Carbon dioxide was used to maintain an inert atmosphere. The esterification was carried out in a glass, Wolfe, three-necked flask heated in a constant temperature oil bath using S.A.E. 250 gear oil as a heating medium. Agitation was supplied by means of an air driven agitator. The runs were six hours in length with the exception of one four hour run made at 320°C. The procedure was repeated using activated alumina as a catalyst. The same procedure was repeated using dipentaerythritol in place of pentaerythritol. Crude tall oil was esterified with both pentaerythritol and dipentaerythritol at 250°C for six hours in an inert atmosphere of carbon dioxide.

The products of the runs were tested for iodine numbers by the Hanus method and for acid numbers by the A.S.T.M.(3) method. Tests were made to determine the drying rates of each of the products. A sample of each of the products was mixed in varsol, turpentine, and ethyl alcohol. The samples were then placed on strips of galvanized metal and hung up to dry. The times required for the samples to reach tack-hardness and to completely dry were noted.

It was found that there was a marked decrease in acid number in the products from that of the original tall oils. The products of high temperature runs had lower numbers than did those of low temperature runs. The iodine numbers of the products decreased as the temperature of the runs increased. The values obtained for the products were considerably less than those of the original tall oils.

The time required for drying of the products of high temperature runs was less than that required by the products of low temperature runs.

It was determined that refined tall oil esterified with either pentaerythritol or dipentaerythritol at temperatures of 300°C and 320°C gave a product that exhibited fair drying oil characteristics. The products obtained at 250°C did not exhibit even fair drying oil characteristics.

Crude tall oil esterified at 250°C with both pentaerythritol and dipentaerythritol gave products with fair drying oil characteristics.

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