SYMPOSIUM: TALL OIL. PART II

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J. P. KRUMBEIN, PRESIDING

H. P. DUPUY, PROGRAM CHAIRMAN

Modern Techniques for the Production of Crude Tall Oil

R. E. THRUSH, The DeLaval Separator Company, Poughkeepsie, New York

Abstract

A short background of the methods for the production of crude tall oil is given.

A simplified flow sheet of the continuous acidulation process is shown and a new type centrifuge is introduced for the continuous separation of the various components of the acidulated sulfate reaction mixture.

The separation section of the process is described with particular emphasis given to the operation of the centrifuge.

Performance of the process is discussed with respect to yield and quality of the crude tall oil.

Introduction

CHEMICAL PULPING or "delignification" is a process for the separation of the cellulose contained in wood from the lignin and other compounds, such as, hemicelluloses, resins, mineral constituents, etc.

The alkaline, chemical pulping process known as the Kraft process produces soaps of the fatty substances and resins which are of primary interest so far as the production of crude tall oil is concerned. The soap from this sulfate process is contained in the cooking liquor, or spent lye, which is known as black liquor.

This black liquor, with its content of dissolved fatty and resin soaps, is concentrated in multiple-effect evaporators to a point where it can be burned in special boilers for recovery of the inorganic salts and the production of steam which is so important in maintaining an economic balance for the Kraft process.

TABLE I

Average Analysis of Crude Oil[a]

Property	Value	
	Minimum	Maximum
Density (at various temps)	0.95	1.024
Acid number	100	175
Saponification number	120	180
Iodine number	140	150
Ash, %	0.04	4.6
Moisture, %	0.8	7.2
Material insoluble in petroleum ether, %	0.1	8.5
Fatty acids, %	20	60
Resin acids, %	20	65
Nonacid bodies, %	5	35

[a] Modified from article on tall oil in Kirk-Othmer: *Encyclopedia of Chemical Technology.*

In the evaporation stage, when the black liquor has been concentrated to 25–30% solids, it is transferred to a holding tank, which is so sized and arranged as to allow the sulfate soap curd to rise to the surface where it can be skimmed off. These skimmings contain 60% soap, which is the starting material for the production of crude tall oil.

Table I (1) indicates an average analysis of crude tall oil.

Shortly after the turn of the century, a method for the production of crude tall oil was developed in Sweden and Finland. This method was a batch process treatment of black liquor skimmings with sulfuric acid. The reaction was carried out in large wooden tanks at temps of between 200F and 210F. The acidulated mixture was settled by gravity and the crude tall oil was decanted off the top, leaving a residue of lignin, spent sulfuric acid and inorganic salts. The quantity of the crude tall oil obtained by this process was dependent upon wood species, pulping method, method of acidulation and mill practices, and usually amounted to approximately 65 lb/ton of pulp as recovered in an average mill. This represents about 88–90% of the available tall oil.

This batch method, with minor improvements, was the only system available for many years.

Modern Processes

Semicontinuous Process

In the early 1950's, a process was developed for the recovery of crude tall oil which should properly be called a semicontinuous process since acidification was batchwise and the separation of the crude tall oil and the spent acids and lignins was carried out con-

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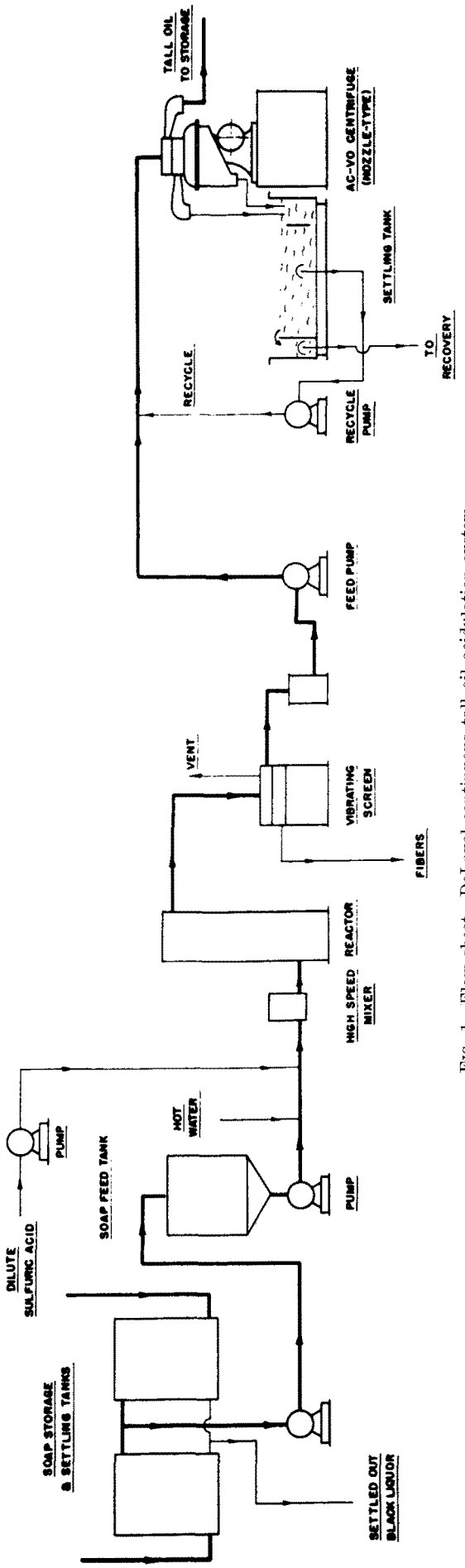

FIG. 1. Flow sheet—DeLaval continuous tall oil acidulation system.

tinuously in a nozzle-type centrifuge. This semicontinuous process offered the advantages of elimination of the gravity settler, with a correspondingly higher yield (96–97% of available tall oil vs. 88–90% with batch acidulation and gravity settling) and improved quality of crude tall oil.

Continuous Process

In the mid-1950's, a continuous process was developed by Sullivan (2), which consisted of adding a proportioned amount of diluted sulfuric acid continuously to the settled black liquor skimmings. This acidulated mixture was screened to remove fiber and release the gases, such as hydrogen sulfide, mercaptans, sulfur dioxide, etc., produced by the reaction. After this screening, the material was separated continuously in the nozzle-type centrifuge. A schematic flow sheet of this continuous process is shown in Figure 1 (3).

A number of improvements were made to this original continuous system for the recovery of crude tall oil, such as elimination of the vibrating screen and redesign and modification of the nozzle-type centrifuge so that the fibers would pass through the nozzles with less chance of plugging, etc. Numerous plants have been installed throughout the world utilizing these improvements and operations have been quite satisfactory.

Other improvements in the basic process have been made from time to time in the last few years. These include more accurately controlled proportioning of the reagents and controlled mixing and degasification, followed by the separation of the tall oil in a special new type of centrifuge.

Description of Centrifuge

This new type of centrifuge, commonly called a self-cleaning, or self-opening separator, is designed in much the same manner as the standard disc type separator for the efficient separation or clarification of liquids at relatively high thru-put rates. However, in the case of the self-cleaning type separator, the solids may be efficiently removed and discharged from the unit through large slots in the bowl wall while the bowl is still rotating at full speed. A self-cleaning, or self-opening, type separator is primarily used in applications where the amount and character of the solids are such that they would quickly fill up the bowl of a standard solid wall type separator, or clog the nozzles in the periphery of the nozzle type bowl, as with soaps containing calcium sulfate which precipitates on acidulation.

The liquid to be separated flows through the disc stack, as in a standard disc separator bowl, and all solids are retained in the sludge space of the bowl, while the clarified liquid, or liquids, are pumped out of the bowl by the paring device located in the top of the bowl.

The paring device is located at the top of the bowl and is really nothing more than a centripetal pump. The impeller is stationary with the liquid revolving around the impeller at the same speed as the bowl. The stationary impeller pares the liquid from the inner surface of the rising, rapidly rotating column of centrifuged material and conducts it smoothly into the outlet pipe. In this manner, the kinetic energy of the liquid is converted into a hydraulic head which is used for pumping the liquid away from the centrifuge. The amt of liquid pared off varies automatically with the thru-put and the size of the impeller. Dis-

charge pressures up to 50 psig can be obtained in this manner. The impeller pares off the liquid gently without creating foam, which is a definite advantage in many applications.

Because of centrifugal action within the centrifuge bowl, the pressure builds up in the liquid in the rotating bowl and increases as the distance increases from the axis of rotation. This pressure exerts a downward force on a free sliding bowl bottom, while operating water acting on a larger diameter develops a greater total pressure upward. This retains the sliding bowl bottom up against the sealing ring. The bowl is closed when this balance of forces is in effect. This confines the liquid to be clarified within the bowl. The hydraulic forces exerted by this operating water cause an upward force on the bowl bottom of almost 100 tons.

The operating water which closes the sliding bowl bottom is supplied from an outside source through an operating water inlet pipe. The water supply pressure to the pipe is controlled with a standard pressure regulating valve. On some occasions, the operating water may be adjusted to a greater or lesser pressure and flow in order to accomplish either slower or more rapid opening of the bowl. There are several modifications of the self-opening type bowl which follow the same basic pattern of operation, except that with these modifications the amt of sludge being discharged can be controlled thereby, eliminating the necessity of interrupting the feed to the machine during bowl shooting.

It is possible to obtain a drier sludge and consequently, less loss of the liquid by controlling the amount of sludge or material in the bowl which is discharged during the shoot. This entire operation of opening, cleaning, closing and coming back on stream takes only a matter of a few seconds. During this time, the centrifuge is still rotating at normal speed.

Acidulation and Separation

The acidulation, or soap splitting, section of the process follows the original Sullivan patent in principle, except for the elimination of the vibrating screen and improvement of several operating procedures.

Figure 2 is a schematic flow diagram of the continuous acidulation process using the self-opening type separator.

Sulfate soap skimmings from the evaporators are pumped to large storage tanks. These tanks act as surge tanks and also as settling tanks for the removal of excess black liquor from the soap skimmings. This, of course, reduces the amount of sulfuric acid required for the acidulation of the soap. The settled black liquor is periodically drawn off and pumped back to the evaporators. The soap is pumped to a service tank, or day tank, which is usually equipped with a high capacity pump for recirculation through the tank to obtain a homogeneous mixture of the soap.

The soap mixture is pumped through a twin strainer to the acidulation, mixing and reaction section. Hot water is usually added ahead of the strainers and pump to reduce the viscosity of the soap. Further quantities may be added after the strainers, if required. A steam injector brings this soap up to a final temperature of 190–200F. The soap is then mixed with dilute sulfuric acid, or the waste acid from a sulfuric acid-chlorine dioxide pulp bleaching plant, in a high-speed mixer. The mixture then flows

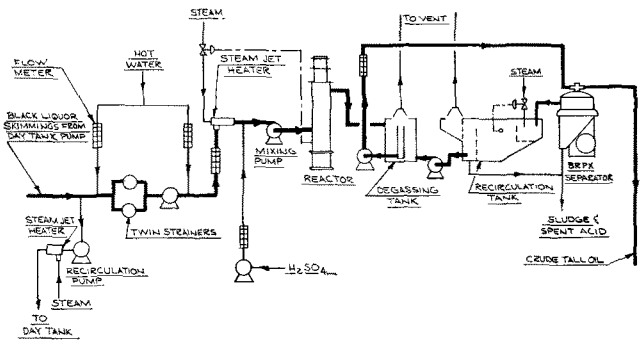

FIG. 2. Schematic flow digaram of De Laval tall oil recovery plant.

through the reaction vessel, to the degassing tank, and then to the self-opening type separator.

This reaction mixture will actually contain four different components of different specific gravities: crude tall oil, which is the lightest fraction; a solids phase (principally precipitated lignin); the spent acid phase (mainly a solution of sodium sulfate) and, lastly, the most dense material which consists mostly of gypsum and fiber.

There are also some entrained gases present which were formed during acidulation and these gases are released through the degassing tank before the mixture is introduced into the centrifuge. This is a most important phase of the process patent since these gases must be released before the mixture is fed to the centrifuge. All of our experimental and plant tests show that if these gases are not released before centrifuging, the separating efficiency of the centrifuge is appreciably reduced.

This final reaction mixture of acidulated skimmings being fed to the centrifuge is separated almost instantly into the four phases. These four phases are discharged from the separator through different outlets in accordance with their relative densities.

The crude tall oil is discharged from the light phase outlet and is sent to storage tanks. The heaviest material is automatically discharged from the bowl while it is rotating at full speed by the action of a timing device operating automatically at predetermined intervals.

The spent acid, with its lignin content, is discharged through the intermediate phase outlet into a recirculation tank. This tank is so constructed that the lignin rises to the surface, passes over a weir and is discharged from the tank with some of the spent acid. The heavy phase discharge from the centrifuge is added to the lignin-spent acid mixture, neutralized with white liquor and returned to the evaporation section of the mill for recovery of the chemicals.

The almost lignin-free spent acid in the bottom of

TABLE II

Typical Analysis of Crude Tall Oil From Continuous Acidulation System

Fatty Acids Mainly Containing 18C	Per Cent of Total	Per Cent of Fraction
Unsaturated acids	30-35	
Oleic		46-48
Linoleic		43-45
Linolenic		1-2
Saturated acids	5-7	
Rosin (resin) acids	35-60	
Abietic		20-25
Neobietic		22-27
Palustric		8-10
Dihydroxyabietic		4-5
Isodextropimaric		3-4
Unidentified		29-43
Unsaponifiables	5-10	
Phytosterols		25-35
Higher alcohols		5-15
Hydrocarbons		35-60

the recirculation tank is drawn off from a point below the surface and recycled through the degassing tank.

The self-opening type of centrifuge, with its complete bowl opening feature, is not influenced by the fibrous material in the feed and can be operated for long periods of time without stopping for cleaning.

Conclusions

This modern continuous acidulation process discharges only two streams, crude oil and the spent acid mixture, which is returned to the mill. For this reason, it is quite simple to calculate the yields of the plant.

The spent acid mixture produced from the average plant amounts to about 1.8 times the tall oil output, by volume. The average spent acid specific gravity is 1.10 to 1.18.

The oil content of the spent acid stream is below 2%, usually between 1 and 2%. This oil is not lost since it is returned to the chemical recovery system and recycled in the process until it again returns to the splitting process.

The yield of crude tall oil is from 98 to 99% of the oil available in the feed.

The quality of the crude tall oil produced by this continuous acidulation system is excellent.

There are, of course, some variations in the tall oil, depending upon the type of wood used, the section of the country from which it comes, climatic conditions, etc.

An average plant utilizing this method of recovery can be expected to produce a crude tall oil with a typical analysis as indicated in Table II and having the following amounts of major impurities: ash content, 0.02 to 0.03%; residual lignin content, 0.2 to 0.06%; free mineral acid, 0.009%.

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Plasticizing Properties of Esters of Monohydric Alcohols and Tall Oil Fatty Acids

S. T. BAUER and RANDALL HASTINGS, Research Laboratories, Crosby Chemicals, Inc., Picayune, Mississippi

Abstract

Tall oil fatty acid esters prepared as intermediates in an epoxy ester plasticizer program were similarly evaluated as low-temp plasticizers in polyvinyl chloride resins. Performance characteristics as primary and secondary plasticizers in polyvinyl sheeting and extruded tapes were determined on esters from methyl to heptadecyl tallate.

Results indicate that these materials impart low-temp properties which would make them of value as low-cost plasticizers in extruded and molded products where light and heat stability are not primary factors.

Introduction

SIMPLE ALKYL ESTERS of saturated fatty acids exhibit a relatively low degree of compatibility and solvency with most polymeric materials. This is said to be due to the low ratio of oxygen to hydrocarbon units of the aliphatic chain. In polyvinyl chloride where these esters are partially compatible, they find specialty uses as secondary plasticizers. Mixed octyl esters of fatty acids have also proved useful in providing low-temp flexibility as primary plasticizers for chloroprene and other synthetic rubbers. The above is also true of the unsaturated fatty alkyl esters where their low volatility, light color, mild odor and low toxicity permits their usage as low-temp plasticizers in many polymeric materials (1).

TABLE I

Evaluation of Tall Oil Esters as Low-Temp Plasticizers in Polyvinyl Chloride Tapes

	Ester					
% DOP Replaced	DOP Control	2-Ethyl hexyl	Iso octyl	Tetra hydro furfuryl		
Property	0	25	25	5	20	40
Ultimate tensile strength psi	3140	3000	3060	3090	3000	3250
Ultimate elongation	350	330	370	370	350	355
100% Secant mod.	1560	1550	1570	1320	1315	1440
Volatility (24 hr at 90C) loss %	3.7	1.9	2.0	2.3	3.0	2.2
Extraction soap soln. loss %	0.2	0.2	0.2	0.4	0.4	0.5
Gasoline 10 hr @25C loss %	5.5	8.3	6.6	5.1	7.6	7.0
Low-temp properties Clash-Berg T_F 135,000 —°C.	—21	—32	—31	—22	—26	—32

While as stated above that long chain aliphatic compounds generally exhert a flexibilizing effect upon materials with which they are compatible, introduction of a polar functional group was found to be necessary to insure this compatibility.

The monumental work of Swern and co-workers (2–5) at the Eastern Regional Research Laboratory has been greatly responsible for the tremendous usage of fatty epoxy derivatives as plasticizer-stabilizer components of polyvinyl chloride film.

Initial investigations into the introduction of oxirane groups at the unsaturated bonds of the fatty acid chains of soybean oil resulted in materials which imparted excellent low-temp plasticizing properties to polyvinyl resins. The interest and research of commerical producers of hydrogen peroxide resulted in commercially feasible processes for the manufacture of economically priced epoxy derivatives (6–8).

After the initial impact of these investigations, attention was directed to the possible functional performance of fatty acid epoxy esters of monohydric alcohols. One of the most prevelent sources of high purity fatty acids of the semi-drying type is by fractional distillation of tall oil. Tall oil fatty acid esters of essentially all the commercially available monohydric alcohols have been prepared and in most instances converted to the epoxy derivative for testing in these programs.

During our investigation of the plasticizer-stabilizer properties of a variety of tall oil monoalcohol epoxy esters, it was decided to subject a number of the ester