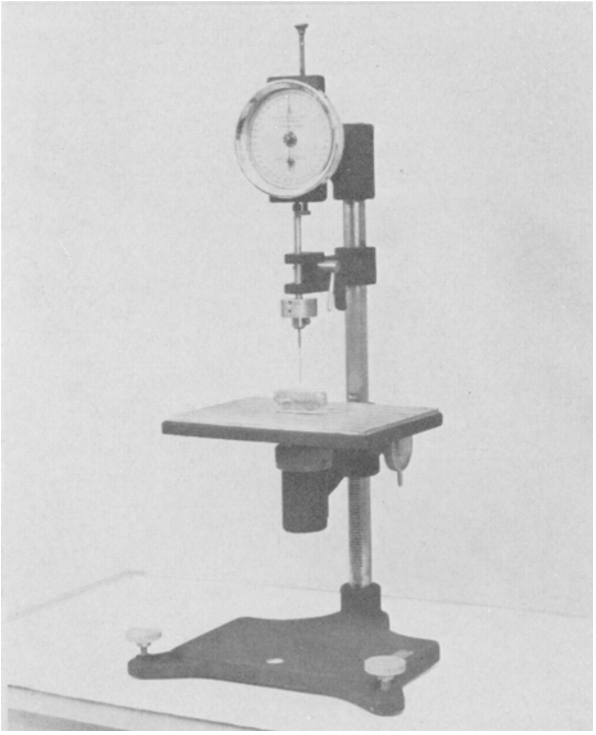

FIG. 4.

Abietic and dehydroabietic acid is determined on tall oil rosin which has been subjected to some treatment such as disproportionation or dehydrogenation to produce rosin specialties. In general, a modification of the method developed during World War II by the Rubber Reserve (10) is used. A sample is dissolved in either ethanol or methanol, and its absorption is measured at wavelengths 241, 273, 276, 279, and 300 mμ, using a Beckman Model DU quartz spectrophotometer.

Color is determined according to A.S.T.M. D 509-55, using U. S. government rosin standards.

The hardness of tall oil rosin is a good criterion for low fatty-acid content. It is not satisfactory for quantitative determinations but can be used with advantage as a quick test for control of still operations. We adopted for this purpose a Precision Universal A.S.T.M. Penetrometer. The rosin is poured into a mold consisting of a ring ¼ in. high and ¾ in. in diameter. The rosin held by the ring is cooled to 25°C. in a water bath, and the penetration is determined by using a penetrometer needle, a 150-g. weight, and a 10-second release time. (The rosin cubes used for color determinations, suitably cooled, may also be used.) We have recommended this method to our friends, and it is now used by several producers of tall oil rosin. The needle must be replaced frequently to assure uniformity of results. While it is a good qualitative method, all efforts to make it a quantitative measure for fatty acid have failed because of the many factors that influence hardness in rosin.

Optical rotation is very useful for the control of processing rosin by heat treating, disproportionation, and dehydrogenation. We dissolve the rosin in chloroform and determine its rotation in a 1-decimeter tube, using a Rudolf Model 60 Polarimeter with a sodium lamp. The results are expressed as specific rotation. The rotation can also be measured on the solid rosin, which is poured into a special metal and glass cuvette and allowed to cool. The results are not as accurate because strains set up in the rosin during cooling influence the rotation.

The softening point of rosin is determined by the ring and ball method A.S.T.M. E 28-51T.

Summary

The principal standard methods used by the American industry for the analysis and quality control of tall oil products have been discussed, and some of the work of the A.S.T.M. in developing these methods has been reviewed.

Further growth of the tall oil industry will undoubtedly result in new products of greater refinement and wider utilization. New and improved methods of analysis will be required. These can be worked out by the industry in continued collaborative work under the auspices of the A.S.T.M. and A.O.C.S. Undoubtedly instrumental test methods such as infrared and ultraviolet spectroscopy and gas chromatography will play a role of increasing importance in the analysis of tall oil products.

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Continuous Acidulation Process for Tall Oil Production

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THE ORIGINAL METHOD for producing tall oil was a batch system, developed in Sweden and Finland (1) about 1905, which consisted simply of reacting the black liquor skimmings with sulfuric acid in a large wooden tank at temperatures near 200°F.(93°C.). The acidified mixture was gravity-settled; and the upper layer, the crude tall oil, was skimmed off leaving a residue of lignin, spent sulfuric acid, and salt cake. Until recently this batch method, with minor improvements, has been the only system available; and, for that matter, some companies are still using it (2).

As a result of a cooperative program between Newport Industries and De Laval, a nozzle type of centrifuge was installed and placed in commercial operation in 1953 at Newport's plant in Alabama. This

[1] Presented at the Spring Meeting, American Oil Chemists' Society, Memphis, Tenn., April 21–23, 1958.

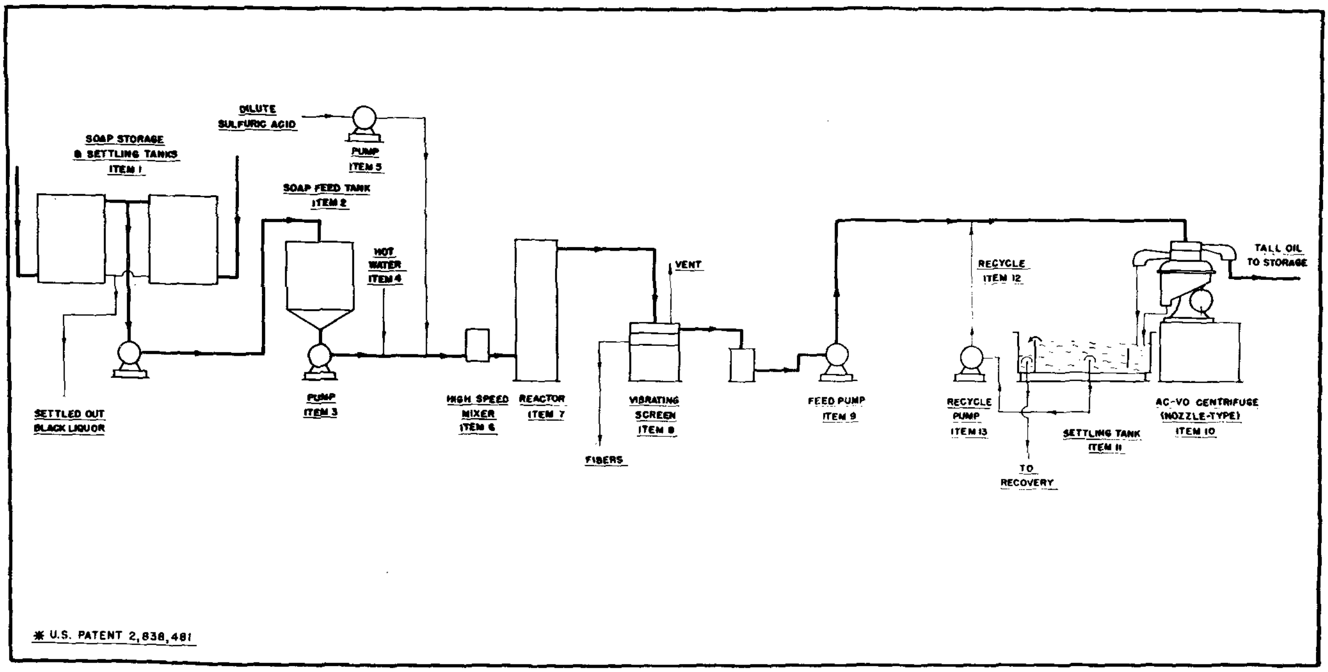

FIG. 1. Flow sheet for De Laval Continuous Tall Oil Acidulation System.

process should properly be called a semicontinuous one since acidification is batchwise and centrifugal separation is continuous. Batches of black liquor skimmings are alternately acidulated in the monel metal tanks. When one batch reaction is complete, the mixture is quickly pumped from the acidulation reactor into the centrifuge feed tank. This feed tank holds the entire charge from one batch acidulator. From the feed tank the reaction mixture is then pumped to the De Laval AC-VO nozzle centrifuge for the separation of tall oil. The feed mixture to the centrifuge consists primarily of tall oil, spent sulfuric acid with salts, plus suspended lignin and some wood pulp fibers. Tank volumes have been fitted to reaction time and centrifuge capacity so that continuous centrifugal separation is maintained.

The reaction mixture is pumped from the feed tank to a vibrating screen, where most of the fiber is removed prior to centrifuging. Since the mixture is batch-acidulated in large vented tanks, most of the reaction gases, such as mercaptans, hydrogen sulfide, and sulfur dioxide, are released during acidulation. This system has been operating satisfactorily since 1953 and has been producing high-quality tall oil.

The yield of tall oil from the black liquor skimmings has consistently been greater than 98%. By this we mean that more than 98% of the available tall oil in the skimmings has been recovered as crude tall oil.

In a later continuous process a proportioned amount of diluted sulfuric acid is continuously reacted with settled black liquor skimmings. The mixture is screened, and the gases are released. It is then continuously separated into tall oil and waste products in the AC-VO nozzle type of centrifuge.

This new process was first installed during the spring of 1956 for a major pulp mill in Jesup, Ga. The flow sheet of this continuous system is shown in Figure 1. It is schematic and represents the general principles of the Continuous Process (3).

The flow may be traced as follows. Skimmings from the black liquor skimmers are gravity-settled in several large soap storage tanks (Item 1). The settled soap, with as much black liquor removed as is practical by settling, is pumped to a soap feed tank (Item 2). The soap is continuously pumped to processing by a variable speed, positive displacement pump (Item 3). Prior to acid addition, hot water (Item 4) is added to reduce soap viscosity. To this soap-water stream, dilute sulfuric acid is added by a variable speed proportioning pump (Item 5). This acidified mixture immediately enters a high-speed mixer (Item 6), where the soap is intimately contacted with the acid and then passed to a paddle type reactor (Item 7), where the reaction is completed.

The reacted mixture flows from the reactor to a continuously discharging vibrating screen (Item 8). The purpose of this screen is to remove wood pulp fibers and also to release entrained gases from the reaction mixture. These gases, if not released at this point, reduce centrifugal separating efficiency.

The screened, de-gassed mixture is then pumped (Item 9) to an AC-VO nozzle type of centrifuge (Item 10), where the tall oil is continuously separated from the other products of reaction. The AC-VO's nozzle discharge, along with the water discharge over its gravity ring, flows to a settling tank (Item 11), which acts as a skimming basin to remove the lignin, also as a source of recycle. Lignin floats to the surface and is discharged over a weir at one end with the spent acid phase. A portion of the clear settled liquor, dilute sulfuric acid and salts in solution (Item 12), is recycled to the main feed to the centrifuge by the recycle pump (Item 13). This recycle acts as a flushing medium to aid in removing lignin from the centrifuge and levels out the centrifuge feed volume.

The lignin along with the spent acid and its dissolved salts is returned to the pulp mill recovery system along with the black liquor settled out from the soap tanks. The tall oil is pumped to storage for use as is, or it may be further processed for separation into rosin and fatty acids.

This flow sheet (Figure 1) describes the basic system and the principles involved in the Continuous Tall Oil Process. Numerous improvements and variations to this basic system have been added.

The most valuable innovation is the use of waste sulfuric acid, which is available at those mills, by employing the sulfuric acid-chlorine dioxide pulp-bleaching process. We find that this waste sulfuric acid is an ideal material for acidulating the black liquor skimmings. However this waste material, usually 8 to 10 N as H_2SO_4, contains enough chlorates and soluble salts to create problems in controlling corrosion and salt precipitation during processing. A typical analysis of this waste acid from such a chlorine dioxide bleaching plant is given in Table I.

TABLE I (4)
Analysis of Waste Acid from Chlorine Dioxide Bleaching Process

Sodium chlorate	10 to 35 g./liter
Total acidity (as H_2SO_4)	420 to 450 g./liter
Chlorine and chlorine dioxide	2 to 3 g./liter
Total sodium [a]	1.2 to 1.25 g./liter
pH	0.1
Specific gravity at 60°/60°F.	1.40 to 1.45
Methanol	Trace

[a] *Sodium is mostly present as the bisulfate.*

Corrosion of the vibrating screen (Figure 1) was very serious since the screen, usually 60 mesh with a wire size of 0.0075 in., corroded into shreds in a matter of hours even though made from Type 316 stainless steel. First attempts to solve this problem involved different materials of construction for the screen. Inconel, monel, and various types of the 300 series stainless steels were tried but produced no satisfactory solution. Based on the system as originally designed, fibers caused the nozzles of the centrifuge to plug, and eventually the entire bowl filled with a compact mass of interwoven fibers, lignin, and salt cake whenever the screen wire corroded through. This problem was first solved by carefully screening the soap skimmings at the tall oil plant prior to acidulation.

AT ANOTHER pulp mill, in St. Marys, Ga., a radical approach was used, that is, to eliminate all screening and modify the centrifuge so that fibers would be passed through the centrifuge nozzles without plugging. The system as now installed, while retaining all the basic principles, has been considerably modified and also simplified. Gas release, after the reactor, is accomplished in a large-volume, large-surface tank located between the reactor and the centrifuge. The vibrating screen and all line strainers have been removed, and the centrifuge has been modified to allow the use of very large nozzles which pass all the fibers. Successful removal of the fibers by the centrifuge has eliminated the screen.

The corrosiveness of this waste bleaching acid does require some design and specification differences from those for a plant designed for commercial sulfuric acid. The additional cost for these features is well under 3% of the total plant cost. Corrosion resistance in such a plant is now so satisfactory that neither operating nor maintenance costs are increased by this waste acid usage. Differences in operating procedures in the two types of plants are definitely minor.

This use of waste sulfuric acid from the bleach plant, even though somewhat corrosive, has many advantages; the principal one, of course, is profit. The average consumption of sulfuric acid in producing tall oil is 20–24% as concentrated acid, based on tall oil produced. In a plant producing 5,000 lbs. per hour of tall oil which, on a weekly basis of five, 24-hr. days, would amount to some 300 tons of tall oil per week, about 60 tons per week of 66° Bé sulfuric acid would be required. At $23 per ton for this acid, the cost to such a plant would be $1,400 per week. The use of waste acid, which is normally burned only for its sulfate content, would add a profit of some $1,400 per week.

If carried one step further, it may be said that a tall oil plant producing 5,000 lbs. per hour, operating on a 24-hr. day and a 250-day year would, by using this spent bleaching acid, save about $70,000 per year. Such an operating saving greatly reduces a plant's pay-out period. Incidentally all the sulfate in the waste acid is still recovered in the by-product reaction mixture from the tall oil plant.

As a minor additional advantage, the traces of chlorine compounds in this waste sulfuric acid produce a lighter colored tall oil since some color bodies are removed by its bleaching action. Our tests prove that this mild bleaching action does not increase the oxidation product content of the tall oil.

A NEW TALL OIL PLANT is now under construction at Mobile, Ala., where the Continuous System will have all the advantages of the simplified process and, in addition, the plant will operate at high capacity on an eight-hour-day basis. Labor costs per ton of tall oil will be reduced by producing a large amount of tall oil per day with only one eight-hour operator. The system is also designed for the use of waste sulfuric acid from the pulp bleach plant. The savings from the use of waste sulfuric acid along with the labor savings will make this a very economical plant.

Some typical operating data have been collected from the various De Laval installations. These have been averaged in order to present general information on the usage of steam, electricity, and a reagent consumption (Table II).

It should be observed that the major cost is sulfuric acid, which is eliminated by the use of waste bleaching acid, and that sulfuric acid is the only reagent used in this process.

In Table III are shown some typical analyses of tall oil produced by the mills using this Continuous Process.

The water washing of crude tall oil is yet another phase of processing in this tall oil field. It had been found that much of the crude tall oil produced by the batch-settling plants throughout the industry suffered from variations in product quality. This is understandable since each batch must essentially be

TABLE II
Direct Cost Data for 6,000 lbs.-per-Hour Continuous Tall Oil Plant

Item	Price	Amount per ton tall oil	Cost per ton tall oil
66° Sulf. acid	$23/ton	470 lbs.	$5.19
Steam	30¢/M lbs.	400 lbs.	0.12
Power	1¢/kwh.	12 kwh.	0.12
Labor	$2/hr.	$0.67	0.67
Total cost/ton of tall oil			$6.10

TABLE III

	Plants			
	Bay Minette[a]	Jesup	St. Marys	Pensacola
% Rosin acid	42.5	45.0	52.4	46.6
% Fatty acid	48.4	43.0	35.7	42.1
% Ash	....	0.025	0.02 to 0.05	0.025
% Mineral acid	0.011	0.002 to 0.004	0.002 to 0.020	0.002 to 0.009
% Neutrals	2.13	2.0 to 2.7	1.5 to 1.7	1.38
% Unsaponifiable	4.6	7.8	8.4	6.6
% Lignin	0.23	0.09 to 0.16	0.11 to 0.26	0.06 to 0.25
% Moisture[b]	2.1	1.1 to 1.5	1.5 to 1.9	1.5 to 1.7
Acid value	....	169	166	170
Lovibond color[c]	....	35/4.0	35/2.4 to 3.0	35/1.5 to 2.4

[a] Semicontinuous plant.
[b] From centrifuge; 0.6% or less from storage tank.
[c] 5% in benzol, 1 in.

hand-treated. Consequently the reaction time, the treat, and the skimming-off of tall oil are subject to human error. Two washing plants have been installed for a major naval stores producer at two tall oil distillation plants. Briefly the system consists of an AC-VO nozzle-type centrifuge, as used in the continuous tall oil installations, preceded by water washing. Wash water is mixed with the crude tall oil fed to the centrifuge in order to remove the soap, excess mineral acids, and lignin present in most of the batch-produced tall oil. This company has found it imperative that lignin be reduced to a minimum before distilling. From the standpoint of corrosion in their expensive fractionating towers, excess mineral acids must also be reduced to a negligible amount.

This washing system is not required on tall oils produced in the continuous acidulation process, even if they are distilled. For that matter it is not essential for tall oil from batch systems, which are very well controlled.

Summary

The conventional batch process for tall oil production was changed to a semicontinuous one by properly sizing tanks to reaction times and adding a screen and a continuous centrifugation step.

As a further improvement an entirely new, continuous acidulation process has been developed which includes proportioning of reagents, controlled mixing, and degasification, followed by tall oil separation in a special form of nozzle type of centrifuge. Both these processes produce higher quality tall oil at lower cost than the original batch process.

The economy of the process has been improved by modifying the centrifuge to remove fibers, which eliminates a costly and troublesome screening step. Lowest costs are produced by a plant specifically designed to use waste acid from a chlorine dioxide bleaching process.

Acknowledgments

Particular acknowledgment is tendered to J. P. Krumbein for his assistance and cooperation during the mutual development of the semicontinuous process. Others who were of material aid in applying the new fully continuous process are S. G. Palmgren, Lowell McGinnis, E. K. Murphy, S. M. Rollinson, William S. Gray Jr., C. Rothrock, Thomas Lalor, and Don Carey.

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Corrosion Testing and Corrosion Problems in Processing of Tall Oil

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IT IS OUR INTENT to present information on the corrosion problems encountered in tall oil processing. Some of the information is new, some has been published previously. We shall briefly summarize some of the information published to date, present new plant corrosion test data, and point up areas where empirical corrosion data are lacking or conflicting.

Corrosion test work may be performed in several stages. Laboratory tests using actual or synthesized solutions yield a great deal of information and, in the absence of other means of testing, must be the basis for construction of process equipment.

The next step in corrosion testing frequently will be the pilot-plant stage. Corrosion can be studied by visual observation of corrosion effects on equipment. Samples exposed to the solution can additionally be analyzed by weight loss computed to traditional units for expressing corrosion penetration as inches per year or mils per year.

The ultimate stage for testing would be in the operating plant. Samples exposed to operating conditions of the full-scale plant will yield the most accurate corrosion information. Differences of significance may exist between plant conditions and laboratory or pilot operations, producing inaccurate and sometimes erroneous results. Plant corrosion information comes from examination of equipment after service periods or from special test rods carrying samples of interest as potential construction material. Examination of equipment will yield only qualitative results. Test rods also furnish information of a qualitative nature, and, of greater importance, quantitative