Nov. 5, 1963 F. W. KEITH, JR 3,109,839

PRODUCTION OF ORGANIC ACIDS

Original Filed Nov. 4, 1957 3 Sheets-Sheet 1

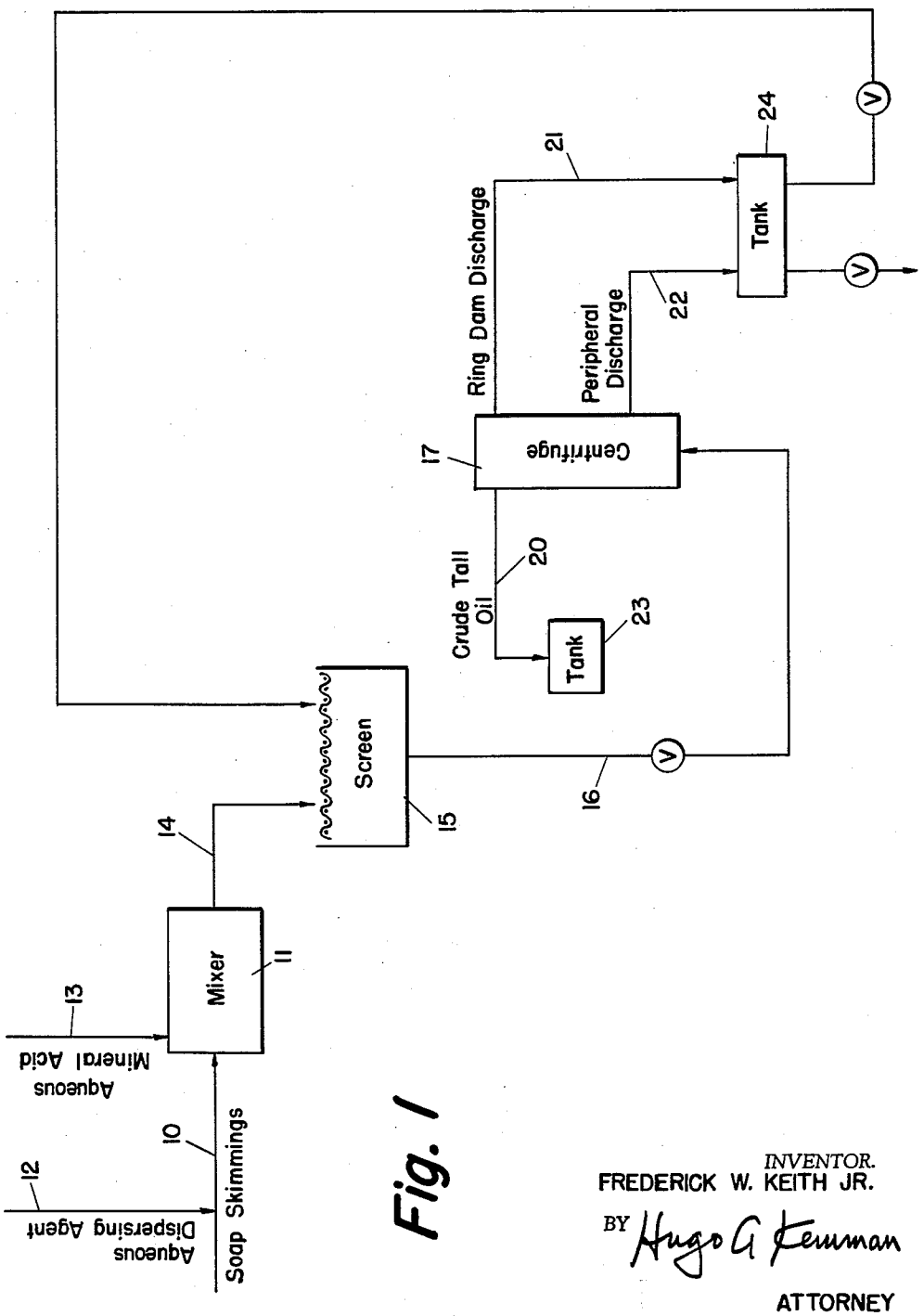


Fig. 1

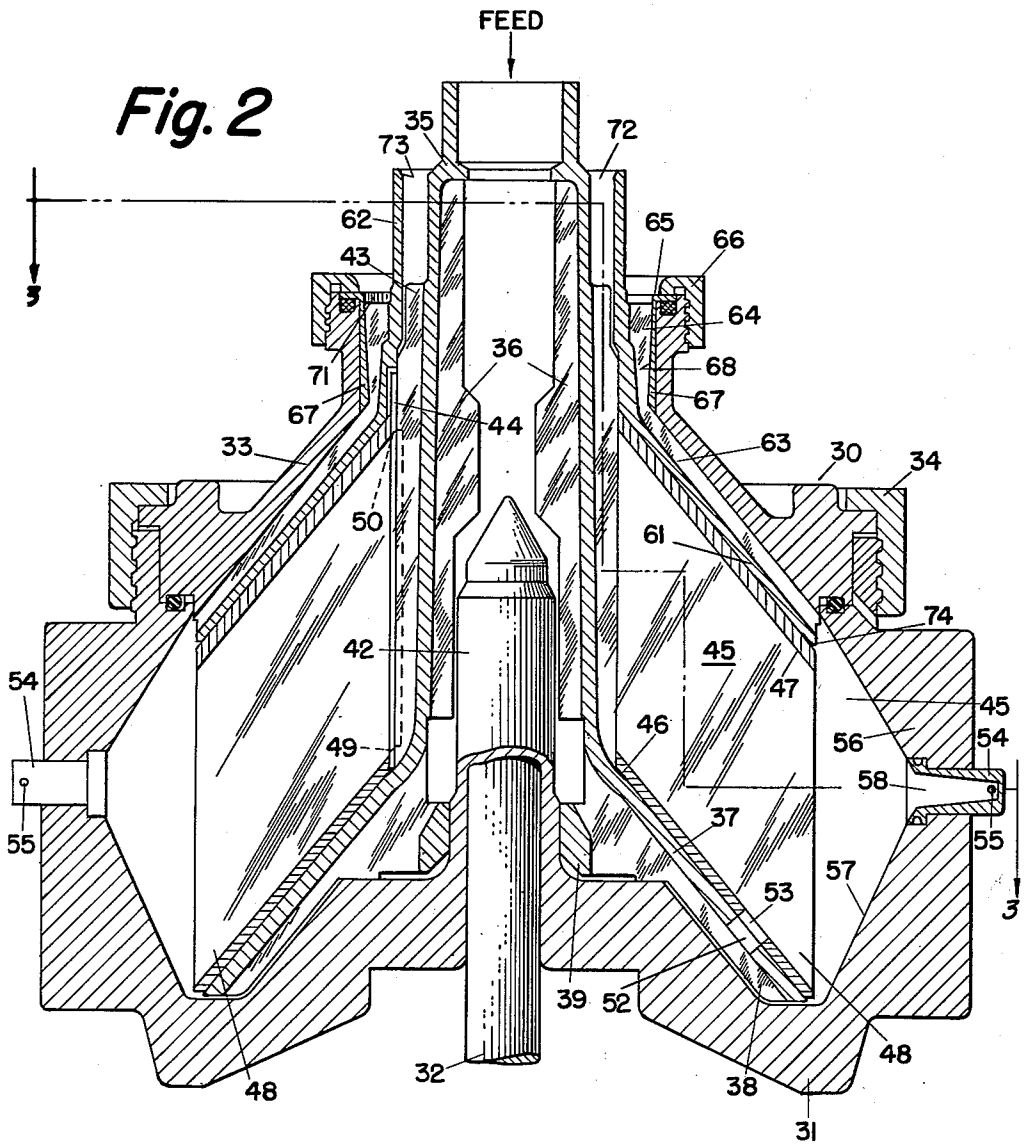
INVENTOR.
FREDERICK W. KEITH JR.
BY Hugo G. Kenman
ATTORNEY

Nov. 5, 1963 F. W. KEITH, JR 3,109,839

PRODUCTION OF ORGANIC ACIDS

Original Filed Nov. 4, 1957 3 Sheets-Sheet 2

Fig. 2



INVENTOR.
FREDERICK W. KEITH JR.

BY Hugo G Kemman

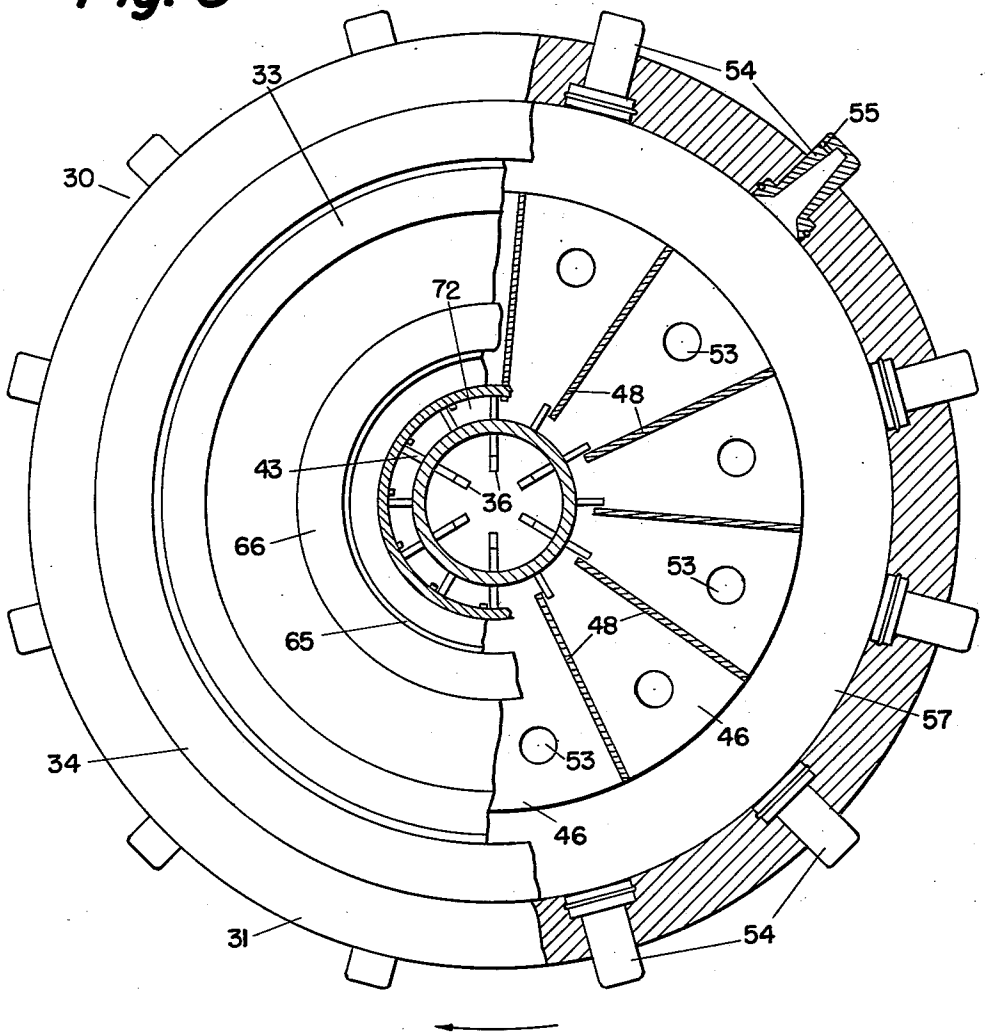
ATTORNEY

Nov. 5, 1963 F. W. KEITH, JR 3,109,839

PRODUCTION OF ORGANIC ACIDS

Original Filed Nov. 4, 1957 3 Sheets-Sheet 3

Fig. 3



INVENTOR.
FREDERICK W. KEITH JR.
BY Hugo A. Kemman
ATTORNEY

United States Patent Office

3,109,839

Patented Nov. 5, 1963

3,109,839

PRODUCTION OF ORGANIC ACIDS

Frederick W. Keith, Jr., Gladwyne, Pa., assignor to The Sharples Corporation, a corporation of Delaware

Continuation of application Ser. No. 694,367, Nov. 4, 1957. This application Feb. 26, 1962, Ser. No. 175,724

6 Claims. (Cl. 260—97.7)

This invention pertains generally to the production of organic acids, and particularly to the production of organic acids from soap skimmings obtained in the alkaline paper pulp industry, in connection with which it will be more particularly described.

Typical of soap skimmings is the scum obtained upon concentration of the black liquor of the sulphate (kraft) process of wood pulp manufacture. Such concentration is usually accomplished in vacuum evaporators. As a result of the concentration of the black liquor, its electrolyte concentration is increased to the point where soap begins to separate from solution, and such concentration is usually carried to the point where substantially all of the soap separates. The soap floats to the top of the black liquor in the evaporator, carrying with it not only saponified saponifiables, but also a rather wide variety of unsaponifiable substances detrimental to the production in high yield and good quality, upon acidulation of the soap scum, of the corresponding mixture of acids referred to in the art as tall oil. Since the soap scum is frequently removed from the black liquor by skimming, the separated soap scum is known in the art as soap skimmings, and also on occasion as tall oil soap skimmings, irrespective of the method employed for the separation of the soap scum from the black liquor. For example, a method other than skimming for the separation of soap scum from the liquor obtained in the paper pulp industry is described in Patent 1,778,523. For convenience in description, the separated soap scum will be referred to herein as soap skimmings, irrespective of the method employed for the separation of soap scum from the liquor, and irrespective of the source of the liquor from which the soap scum is obtained. It is well known that all such soap scums are contaminated with difficultly separable unsaponifiable substances, hereinafter for convenience called impurities, some of which are fibrous in character while others are of a crystalline and/or amorphous nature.

These impurities interfere to a very large extent with the acidulation of the soap skimmings, and particularly with the separation of the resulting tall oil from the acidulation mass in good yield and in high quality.

Depending upon the particular wood employed in the sulphate process of wood pulp manufacture, upon the technique employed in the concentration of the black liquor or otherwise in the production of soap skimmings, and the technique employed in separating the soap skimmings from the black liquor, typical present day soap skimmings usually will contain between approximately 45 to 55% of available rosin acids and fatty acids in the form of their sodium salts. Since these acids are very weak as compared to the strong mineral acids, such as hydrochloric acid or sulphuric acid, or their acid salts, the treatment of soap skimmings with such reagents theoretically should yield a product comprised of the mixed organic acids in high quality and in high percentage of their availability. It also would seem that, since the chemical reaction involved in the acidulation is extremely simple, and the separation of phases of different density, either by settling or by centrifuging, old and well known, the process of recovering the mixed organic acids from the soap skimmings should lend itself to the simplest of

operations. Experience, however, has shown this to be far from the case.

Tall oil is a very valuable product that finds a wide variety of uses in the trade, such as in the production of core oils, linoleum, oil cloth, hard floor coverings, soaps, and detergents to name a few. Though outstanding advances have been made in the continuous low cost recovery of tall oil from soap skimmings, such as in the practice of the process described and claimed in U.S. Patent 2,802,845, a considerable area of desired improvement has remained from the standpoint of continuous operation with less frequent shutdowns for cleaning purposes.

By the use of the invention of the above-mentioned patent, the action of the mineral acid on the soap skimmings is greatly accelerated, and the organic acids in the soap skimmings are rapidly released. Whereas prior to the invention described and claimed in said patent, a long time factor running into many hours was involved to effect acidulation of the soapstock, and to cause the formation of phases sufficiently distinct for satisfactory separation in high yield, either by gravity or by centrifuging, by the use of said invention this time factor is markedly reduced, which made possible for the first time industrially acceptable continuous operation through continuous acidulation and centrifugal separation.

It is found, however, that soap skimmings contain various impurities that ordinarily are not removable or are removable only with great difficulty, prior to the centrifuging in said continuous operation, such as by the use of an industrial screen, or other device. These impurities which are of a solid and/or semi-solid nature are carried over into the centrifuge bowl, and heretofore have resulted in clogging of the centrifuge bowl, albeit after extended operation running into many many hours.

Since shutdowns which become necessary for purposes of bowl cleaning are relatively costly, not only from the standpoint of overhead, but also of labor costs, the advantages of greatly extending the interval between necessary shutdowns for bowl cleaning purposes are obvious, and it is to the solution of this problem that the present invention is directed.

Apart from fibrous substances which are taken out by screening, there are present in the acidulated reaction mass reaching the centrifuge three broad classes of impurities. One class is comprised of solids of relatively high density and more or less of a calcareous-like nature which during centrifuging are deposited on the inner periphery of the bowl. The second class is comprised of solids and/or semi-solids more or less of a ligneous nature which when initially separated in the centrifuge bowl are of an apparent density intermediate between that of the organic acids and that of the aqueous phase which contains the spent acid including any residual mineral acid, its reaction product, such as sodium sulphate if the mineral acid is sulphuric acid, and possibly other dissolved substances. The third class is comprised of high molecular weight organic substances, such as sterols, wood sugars, hydrocarbons, etc. which are carried out readily with the aqueous phase, and therefore present no difficulty in the separation.

While it has not been definitely established, it appears that the ligneous substances initially have absorbed therein and/or adsorbed thereon both liquid phases, namely, the organic acid phase and the aqueous phase, and that the dispersing agent employed in the above-mentioned patent causes sufficient organic acid to be released from the ligneous material to cause it to be suspended or to sink in the aqueous phase, and to be carried off from the centrifuge bowl along with aqueous phase.

It has been found, however, that, after many hours of operation, clogging of the centrifuge bowl ensues. Upon

inspection, it has been discovered that this has been due in very large part to the accumulation of ligneous substances, that such substances have adhered to metal parts radially inwardly of the periphery of the bowl, and that they have become more or less desiccated of the lighter phase so as to be of greater apparent density.

Moreover, it has been discovered that when employing centrifuge bowls equipped for the peripheral discharge of finely divided solids compatible thereto, i.e. the calcareous-like materials, such as by continuous flow through nozzles, or intermittent flow through intermittently opening and closing valves, clumps of the so-called more or less desiccated ligneous materials will occasionally become loosened, and become deposited on the inner periphery of the bowl, whereupon such clumps travel to the nozzles or valves to clog the same, thus making a shutdown necessary for this reason.

After long and exacting experimentation, it has been discovered that, contrary to accepted theory, the sticking of the ligneous materials to metal parts, and its resulting desiccation, can be very materially reduced, if not entirely avoided, by drastically reducing the separating efficiency of the centrifuge bowl. It also has been discovered, contra to accepted theory, that upon drastically reducing the separating efficiency of the centrifuge bowl, its throughput capacity for the acidulated mass undergoing separation is very materially increased, without reduction in separating results.

It is well known that centrifugal force is a factor contributing to separating efficiency, but it is also well known that the interior construction of the bowl is a far greater factor. For example, it has been calculated by methods available in the published literature that a conventional disc bowl of a given size, and equipped with a disc stack having sixty discs, has of the order of twenty-eight times the separating efficiency of the same bowl when operating at the same speed, but with the disc stack substituted by, for example, twelve circumferentially spaced longitudinal vanes or wings.

Comparative runs made under the same conditions, with the bowl when containing the disc stack, and with the same bowl when containing the twelve circumferentially spaced longitudinal vanes or wings, showed that the bowl, when containing the disc stack, would plug within a matter of several hours, whereas the same bowl, when containing the twelve circumferentially spaced longitudinal vanes or wings, evidenced no signs of plugging even after five days of continuous operation.

Other interior bowl constructions resulting in markedly reduced separating efficiencies will become apparent to persons skilled in the centrifuge art upon becoming familiar herewith, for example, the substitution of longitudinal vanes or wings of other shapes, such as curved, or otherwise formed.

As is well known, separating efficiency can be expressed in terms of a quantity called "Sigma." Units of Sigma are expressed in square meters, a single unit standing for the separating efficiency of a simple gravity settling tank having a horizontal cross sectional area of one square meter. The rate of settling will, of course, vary with the mixture being settled, but since the quantity Sigma is employed to express the separating efficiency of a centrifuge in terms of the separating efficiency of a simple gravity settling tank operating on the same mixture, the nature of the mixture to be separated cancels out.

Referring again to the particular bowl mentioned above, calculations show that when it contains the disc stack, its Sigma is 14,900 square meters, whereas when it contains the twelve circumferentially spaced longitudinal wings instead of the disc stack, its Sigma is 525 square meters.

Although the formula for calculating the Sigma of a bowl having a disc stack varies from the formula employed for calculating the Sigma of a bowl having circumferentially spaced longitudinal wings, since both are

referred to the area of a simple gravity settling tank, obviously the quantity Sigma for a bowl having a disc stack may be compared to the quantity of Sigma for a bowl having circumferentially spaced longitudinal wings.

While in the practice of this invention, it is preferred to operate with values of Sigma between 400 and 1,000, certain advantages of this invention may be realized when operating with values of Sigma falling within the range of from 300 to 3500. For example, outstanding results have been obtained when operating with values of Sigma of approximately 2500, over those obtained when operating with relatively high values of Sigma, e.g. values of Sigma obtained with bowls having disc stacks comprised of a large number of closely spaced discs.

While any suitable temperature may be employed during the centrifugal separation, it is advantageous to employ temperatures in the mass being separated between 170° F. and 215° F., 190° F. to 200° F. having proved to be particularly suitable in many cases. The same or similar considerations apply to other stages of the process.

Further features of the invention will become apparent to persons skilled in the art as the specification proceeds and upon reference to the drawings in which:

FIGURE 1 is a flow sheet;

FIGURE 2 is an elevation partly in section illustrating a novel centrifuge bowl useful in the practice of the invention; and

FIGURE 3 is a section on line 3—3 of FIGURE 2.

Referring now to FIGURE 1, soap skimmings flow through line 10 to mixer 11. A dispersing agent enters the soap skimmings through line 12. Mineral acid, such as sulphuric acid, or hydrochloric acid, with or without dilution water, enters mixer 11 through line 13.

The dispersing agent, and the mineral acid, are conveniently fed in aqueous solution. This is a convenient way for adjusting the water content in mixer 11 to any desired level. Obviously, however, the feeding of these reagents and of water, as desired, lends itself to wide versatility.

In mixer 11 alkali metal soaps, e.g. sodium soaps, as well as any alkaline earth soaps that might be present, such as calcium soaps, are decomposed, thus releasing the corresponding organic acids therefrom, and forming the corresponding alkali metal and alkaline earth salts of the particular mineral acid employed, which conveniently is sulphuric acid.

The reaction mass flows from mixer 11 through line 14 which, as shown, leads to screen 15. Screen 15 is conveniently employed to screen out fibrous matter not previously removed from the soap skimmings.

Mixer 11, and screen 15, may be of any desired type, many different forms of which are available in the trade.

The reaction mass flows from screen 15, through line 16, to centifuge 17 which preferably is of the three stream discharge type. Centrifuges of this general type are well known in the art, and conventionally discharge two streams over respective weirs, and a third stream, continuously or intermittently, at the periphery of the bowl. The latter discharge may be either through nozzles of small interior diameter, or through intermittently operating valves, or otherwise. Typical centrifuges of this general type are shown in FIGURES 3 and 4 of an article by C. M. Ambler, which appeared in Chemical Engineering Progress, May 1948, pages 405–410.

As illustrated, crude tall oil leaves centrifuge 17 through line 20, aqueous phase through line 21, and a mixture of aqueous phase and solids through line 22. Crude tall oil is illustrated as being collected in tank 23 and, aqueous phase and solids in tank 24.

If desired, solids may be settled out in tank 24, and a part of the aqueous phase recycled through screen 15, as might be found convenient by the operator to meet the liquid requirements of centrifuge 17 according to his preferred type of operation, as will be readily understood by persons skilled in the art.

While any dispersing agent capable of dispersing the soap skimmings and of maintaining the soap skimmings dispersed in the reaction zone may be employed, outstanding reagents for dispersing the soap skimmings are particularly set forth in the above-mentioned U.S. patent. Among these reagents are the naphthalene sulphonates in which two or more naphthalene nucleii are joined by alkaline groups; the tertiary acetylenic glycols, e.g., 2,5-dimethyl-3-hexyne-2,5-diol, and 3,6-dimethyl-4-octyne-3, 6-diol; quebracho extract; sodium hexametaphosphate type dispersing agents; and dispersing agents comprising lignin derivatives, such as lignosulphonic acid compounds and lignosulphonate compounds representative of which are sodium lignosulphonate and calcium lignosulphonate.

A centrifuge bowl highly satisfactory for use in the practice of the invention is shown in FIGURES 2 and 3.

Referring now more particularly to FIGURES 2 and 3, bowl 30 is shown as having a shell 31 mounted on spindle 32, and a bowl top 33 held in position on shell 31 by annular ring 34 which threadedly engages shell 31.

Center tube 35 is provided with internal wings 36 conveniently secured thereto by any suitable means, such as welding, and with a skirt 37 shown integral therewith. Wings 38 are interposed between and secured to skirt 37 and hub 39, center tube 35 together with wings 36, skirt 37, wings 38 and hub 39 conveniently being made into a unitary structure which fits down over center post 42 on shell 31.

Center tube 35 is also shown provided with exterior wings 43 conveniently made integral therewith, one wing 43 being provided with an extension to form key 44.

Positioned about center tube 35 and wings 43 is an accelerating-decelerating device 45 comprised of a lower frusto conical member 46, and an upper frusto conical member 47, between which are interposed and to which are secured a plurality of circumferentially spaced radially-extending longitudinal wings or plates 48, forming open separating spaces therebetween which extend longitudinally and radially. Members 46 and 47 are provided with notches 49 and 50 respectively which fit over key 44 for purposes of orienting device 45 in position within the centrifuge bowl. As shown, wings 48 extend radially inwardly beyond the outer radial edges of wings 43.

Skirt 37 is provided with a plurality of circumferentially spaced feed holes 52 which register with an equal number of circumferentially spaced feed holes 53 in lower member 46 of device 45. As shown, each feed hole 53 occupies a position between adjacent wings or plates 48 to lead directly into an open separating space.

Shell 31 is shown provided with a plurality of circumferentially spaced nozzle holders 54 extending through the peripheral wall of shell 31, each nozzle holder 54 being provided with a nozzle 55. It will be noted that interior walls 56 and 57 of shell 31 slope toward nozzle holders 54, each nozzle holder 54 having an interior channel 58 leading to its nozzle 55.

Positioned above upper member 47 of accelerating-decelerating device 45 is dividing cone 61 having a longitudinal extension 62. Positioned around dividing cone 61, and extending up about extension 62, are a plurality of circumferentially spaced wings 63 having longitudinal extensions 64. Wings 63 are conveniently secured to the dividing cone 61, extensions 64 to its extension 62. Bowl cover 33 contacts the frusto conical portion of wings 63 to form inwardly and upwardly sloping channels which become longiutdinal along dividing cone extension 62.

Ring dam 65 is held in position by annular ring 66 which threadedly engages the top of bowl cover 33. As shown ring dam 65 is provided with a downwardly extending annular extension 67. As illustrated, annular extension 67 on ring dam 65 has an interior surface 68 which slopes radially outwardly and upwardly toward the annular discharge edge 71 on ring dam 65.

In operation the reaction mass flows from screen 15 through line 16 into the top of center tube 35 wherein it is

brought up to speed by wings 36. The reaction mass continues its downward flow, and its tangential velocity is accelerated further as it flows outwardly between wings 38. The reaction mass enters the spaces between wings 48, after flowing through holes 52 and 53, in which spaces separation of organic acids from the aqueous phase and insoluble substances takes place. The organic acid phase being of lower density progresses radially inwardly, and flows upwardly between wings 43 into the annular space 72 between dividing cone extension 62 and center tube 35, from which it is discharged over upper edge 73 of dividing cone extension 62, and collected in any conventional manner, such as with the use of a bowl cover, not shown.

A large part of the aqueous phase together with suspended ligneous substances which due to the drastically reduced separating efficiency do not become desiccated, flows upwardly about the outer edge 74 of dividing cone 61, inwardly and upwardly between wings 63, upwardly between wing extensions 64, outwardly over annular edge 71 of ring dam 65, and outwardly over ring 66, to be collected in any conventional manner such as with the use of a bowl cover not shown.

Insoluble salts that may be present, such as calcium sulphate, and other finely divided insoluble solid substances of higher density, are deposited on walls 56 and 57, and slide toward and into channels 58 of nozzle holders 54, and are discharged peripherally through nozzles 55 along with aqueous phase. It will be seen that nozzles 55 are pointed backwardly, the direction of rotation being clockwise as shown in FIGURE 3.

The following examples of the operation of this invention are given by way of illustration and not of limitation.

Example 1

Soap skimmings were fed to a mixer such as mixer 11 at a rate to produce 3200 pounds of crude tall oil per hour. Into the stream of soap skimmings flowing to the mixer was fed an aqueous solution of a dispersing agent of the well-known naphthalene sulfonate type, and sold in the trade under the trademark Tamol, at the rate of 4.8 pounds per hour, dry weight. Into the mass in the mixer was introduced sulfuric acid of 66° Baumé at the rate of 648 pounds per hour. The acidulated reaction mass flowing from the mixer, after being subjected to screening such as by flowing through screen 15, was fed to a centrifuge such as centrifuge 17. The centrifuge bowl was of a design such that its Sigma at the particular speed of operation was 590 square meters. Aqueous phase discharged peripherally from the centrifuge bowl, such as through nozzles 55 of the bowl shown in FIGURES 2 and 3, and discharged over the ring dam or weir, such as ring dam 65, was collected in tank 24. A part of this discharged aqueous phase was returned to the bowl at the rate of 1460 gallons per hour, after being clarified such as by settling, for purposes of supplying additional heavy phase for adjusting the interface between organic acids and aqueous phase in the bowl, an expedient well known in the art when employing nozzle discharge centrifuges. The temperature of the stream fed to the centrifuge bowl was between 190° F. and 199° F. At the end of five days of continuous operation there was no sign of plugging or other interference with the discharge of the various streams from the bowl, or of plugging or caking within the bowl. The organic acids were recovered in very high concentration and yield, i.e. above 98%, and the percentage of organic acids in the aqueous discharges from the centrifugal bowl was substantially nil.

Example 2

This run was made under conditions similar to those of Example 1, except that the centrifuge bowl was of a design such that at the particular speed of operation it

had a Sigma of 5300 square meters. Plugging began upon the lapse of 60 hours of continuous operation.

Example 3

This run was made under conditions similar to those of Example 1 including the same centrifuge bowl operated at the same speed, except that the feed rate was increased so as to produce 6300 pounds of crude tall oil per hour. There was no sign of clogging over several hours of continuous operation, after which the feed rate had to be dropped back because soap skimmings were produced by the mill at only about half the above feed rate. The crude tall oil was recovered in very high concentration and yield, i.e. above 98%, and the percentage of organic acids in the aqueous discharges from the centrifuge bowl was substantially nil.

Example 4

This run was made with a bowl of a design such that at the particular speed of operation it had a Sigma of 14,900 square meters. Other conditions of operation were maintained about the same as employed in Example 1, except that no dispersing agent was employed. Separation of the components was very unsatisfactory from the very beginning for the separated organic acids contained solids and aqueous phase which increased from upwards of 3% to 6% by volume over a 4 hour period, and the aqueous discharges contained a substantial amount of organic acids.

As is well known, the quantity Sigma may be varied by varying the interior construction of a centrifuge bowl, or by varying its speed of rotation, or both. The outstanding advantages of the present invention are cogently demonstrated by the comparative runs of the foregoing examples, and have been repeatedly confirmed by a multitude of other runs under various conditions of operation.

While the industrial benefits of this invention are better realized in the treatment of a continuously fed stream of soap skimmings in the acidulation zone, and the continuous centrifugal separation of the acidulated mass flowing from the acidulation zone, it is to be understood that certain advantages of this invention may be realized if the acidulation of the soap skimmings in the presence of a dispersing agent is carried out in batch or in semi-batch operations, followed by centrifugal separation employing values of Sigma within the larger range, and particularly within the preferred range, set forth hereinabove.

It is to be understood that the flow sheet of FIGURE 1 has been presented in simplified form for convenience in describing the new process, and that the use of flow controllers, valves, flow meters, gauges, pumps, surge tanks, etc. will occur to persons skilled in the art upon becoming familiar with the invention, and particularly when indicated by good engineering practice. Likewise other centrifugal bowl designs and constructions will occur to persons skilled in the art upon becoming familiar with this invention.

This application constitutes a continuation application of my co-pending application Serial Number 694,367, filed November 4, 1957, and now abandoned.

It is to be understood, therefore, that the particular description of the invention is by way of illustration, and that changes, omissions, additions, substitutions and/or other modifications may be made without departing from the spirit thereof. Accordingly, it is intended that the patent shall cover, by suitable expression in the claims, the various features of patentable novelty which reside in the invention.

I claim:

1. A process for the production of organic acids from soap skimmings obtained in the alkaline paper pulp industry, said soap skimmings containing three broad classes of impurities, one of which consists essentially of solids of relatively high density, another of which consists essentially of substances of a ligneous nature, and a third of which consists essentially of high molecular weight organic substances, comprising subjecting said soap skimmings to the action of a mineral acid in aqueous media to release the corresponding organic acids, thereafter to separate said mass into three effluents subjecting said reaction mass to centrifugal force in a centrifuging zone having a plurality of circumferentially arranged open separating spaces extending longitudinally and radially from the inner boundary of the zone to the outer boundary of the zone, discharging constituents other than tall oil from said centrifuging zone through the periphery thereof and also at a locus positioned radially inwardly of said periphery, and discharging separated tall oil from said centrifuging zone at a locus positioned radially inwardly of said first-mentioned locus, the accumulation of ligneous substances in said centrifuging zone being avoided in large part by effecting said centrifugal separation under conditions of lowered separating efficiency which expressed in terms of Sigma fall between 300 and 3500 square meters.

2. A process as described in claim 1, wherein said mineral acid is sulphuric acid.

3. A process as described in claim 1, wherein a dispersing agent is present as the soap skimmings are subjected to the action of the mineral acid.

4. A process as described in claim 1 including the additional step after reaction with acid of screening the resulting reaction mass to remove fibrous matter therefrom before subjecting the mass to centrifugal force.

5. A process as described in claim 1 wherein the separating efficiency falls between 400 and 1000 square meters.

6. A continuous process for the production of organic acids from soap skimmings obtained upon concentration of black liquor produced in the sulphate process for wood pulp manufacture, said soap skimmings being contaminated with difficultly separable unsaponifiable substances present in said black liquor including substances of a ligneous nature, which comprises mixing a stream of said soap skimmings with a stream of aqueous sulphuric acid to produce organic acids from said soap skimmings, thereafter subjecting a continuous stream of the resulting reaction mass to centrifugal force in a centrifuging zone for the separation of tall oil from said reaction mass, and maintaining conditions of separating efficiency in said centrifuging zone expressed in terms of Sigma between 400 and 1000 square meters, the zone having a plurality of circumferentially arranged open separating spaces extending longitudinally in the zone and radially from the inner boundary of the zone to the outer boundary of the zone, discharging constituents other than tall oil from said centrifuging zone through the periphery thereof and also at a locus positioned radially inwardly of said periphery, and discharging separated tall oil from said centrifuging zone at a locus positioned radially inwardly of said first-mentioned locus.

References Cited in the file of this patent

UNITED STATES PATENTS

2,294,446	Brown et al.	Sept. 1, 1942
2,802,845	Sadler	Aug. 13, 1957
2,838,481	Sullivan	June 10, 1958

OTHER REFERENCES

Ambler: Chem. Eng. Progress, volume 44, pages 405–410 (1948).

Perry: Chemical Engineer's Handbook, 3rd edition, pages 992–1013 (1950).