Nov. 13, 1962 J. D. COCHRANE III, ET AL 3,063,981

MANUFACTURE OF NITROCELLULOSE

Filed May 27, 1960 2 Sheets-Sheet 1

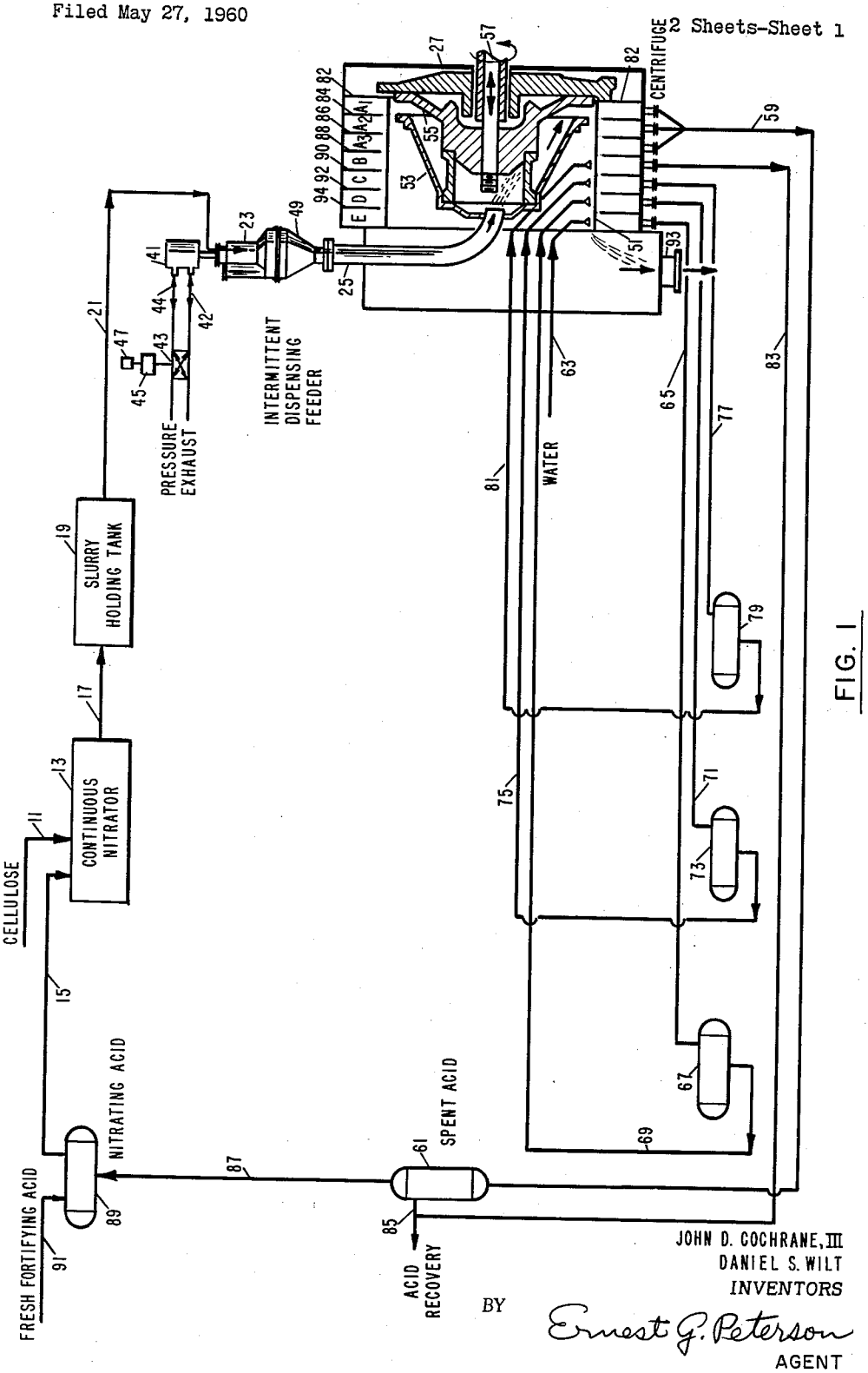



FIG. 1

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Filed May 27, 1960 2 Sheets-Sheet 2

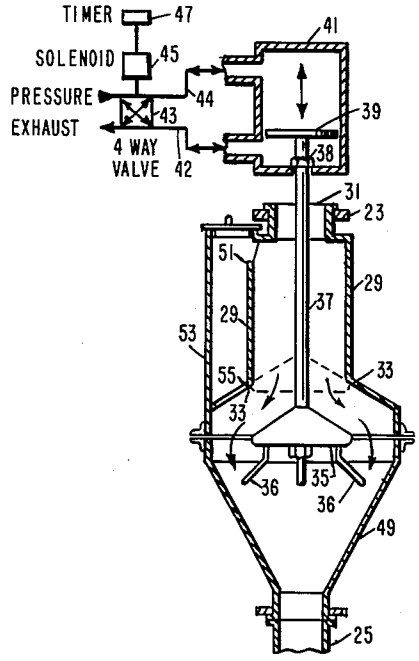



FIG. 2

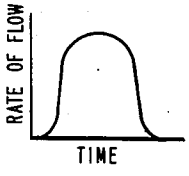



FIG. 3

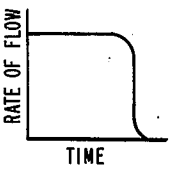



FIG. 5



FIG. 4

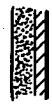


FIG. 6

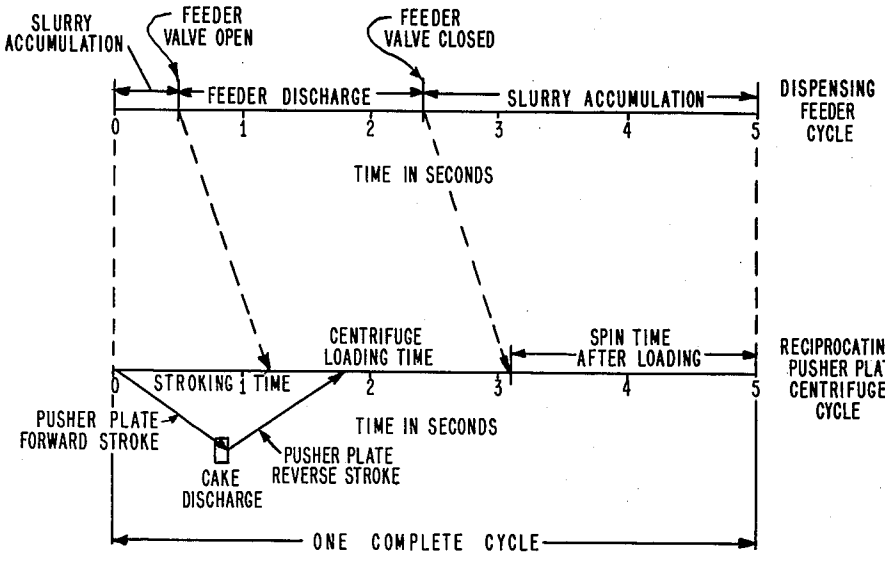



FIG. 7

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3,063,981

# MANUFACTURE OF NITROCELLULOSE

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Filed May 27, 1960, Ser. No. 32,390
8 Claims. (Cl. 260—220)

This invention relates to improvements in the continuous manufacture of nitrocellulose and more particularly to improvements in method and apparatus for charging a slurry of nitrocellulose in spent nitrating acid to a continuous centrifuge for separation and recovery of spent acid therefrom.

The continuous manufacture of nitrocellulose employing a continuous centrifuge having a reciprocating pusher plate for separation and recovery of spent nitrating acid from the nitrocellulose requires that the nitrocellulose slurry be fed to the centrifuge in measured increments at predetermined intervals, the size of each incremental slurry charge being predetermined by the capacity of the centrifuge, with the slurry feed cycle being coordinated with the reciprocating cycle of the centrifuge. U.S. Patent 2,913,149 describes a method and apparatus designed for feeding nitrocellulose slurry in measured increments at predetermined intervals to a continuous centrifuge having a reciprocating pusher plate.

It will be seen by reference to U.S. Patent 2,913,149 that the device described and claimed therein operates on the displacement principle and comprises a reservoir for holding a body of slurry and having an inlet and an overflow communicating with an outlet, a vertically reciprocating displacement member disposed in the reservoir for partial submersion in the slurry, mechanical means for imparting a measured reciprocating stroke to the displacement member, and agitating means disposed in the body of slurry in the reservoir. To operate the mechanism for the purposes of the patent, a continuous feed stream of nitrocellulose slurried in spent nitrating acid is introduced via the inlet into the reservoir and is agitated therein, and the desired cyclic reciprocating stroke is imparted to the reciprocating displacement member. When the level of slurry in the reservoir reaches the overflow level of the reservoir at the bottom of the displacement member downward stroke, the mechanism becomes fully operative to deliver an intermittent measured volume of slurry with each succeeding cycle of operation; on the upward stroke the slurry level in the reservoir drops below the level of the overflow and there is no discharge of slurry, and on the succeeding downstroke the displacement member displaces an accumulated measured volume of slurry which overflows into the outlet. During the downstroke the displacement member progressively raises the level of slurry in the reservoir and in so doing progressively increases the hydraulic head of slurry above the overflow of the reservoir. Conversely, during the upstroke of the displacement member the hydraulic head of slurry above the overflow progressively decreases. Inherently, therefore, the rate of slurry delivery during each cycle starts at zero, gradually builds up to a maximum and then gradually returns to zero.

While the apparatus of U.S. Patent 2,913,149 is an efficient device well suited for its purpose, further development work has been pursued to accomplish the objectives of the device at lower initial investment and with lower operating and maintenance costs.

In the course of this further development work a wholly unobvious and unexpected discovery was made. In accordance with the present invention it was discovered



that feeding the nitrocellulose slurry to the centrifuge in a particular manner as hereinafter described results in improved spent acid recovery, improved throughput capacity of the centrifuge, and greatly reduced loss of fine nitrocellulose particles through the centrifuge screen.

More particularly, it was discovered that in the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating mixture is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate for separation and displacement of spent nitrating mixture from the nitrocellulose, and in which each measure of slurry feed is separately accumulated in said dispensing feeder for discharge therefrom into said centrifuge, the improvement which comprises instantaneously releasing the whole accumulated measure of slurry feed for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, results in the unexpected and important process economies as set forth above. Based on continuous operation over a period of two months, loss of fine nitrocellulose particles through the centrifuge screen was reduced by about 64% in accordance with the present invention; throughput capacity of the centrifuge was increased by about 10%; and recovery of retained spent nitrating acid was increased by about 33% in contrast to the results of gradual or progressive release of the slurry charge, as for example, by the aforementioned displacement feeding.

In a preferred embodiment of the invention, therefore, a measured increment of nitrocellulose slurry is accumulated in the dispensing feeder, and the whole accumulated increment of slurry is instantaneously released for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, the delivery cycle of the dispensing feeder being coordinated with the timed reciprocating cycle of the centrifuge to deliver said increment of slurry to the centrifuge for distribution under substantially constant compacting force on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke. These steps are, of course, repeated with each cycle of the centrifuge.

Apparatus especially suitable for accomplishing the purposes of this invention comprises in combination a dispensing feeder for accumulating and holding a measured volume of slurry, a continuous centrifuge having a reciprocating pusher plate, and a conduit of large cross sectional area throughout communicating at the intake end thereof with said dispensing feeder and at the discharge end thereof with the interior of said centrifuge, said dispensing feeder having an inlet, and a discharge port communicating with the intake end of said conduit, said dispensing feeder also having quick-opening valve means associated with the discharge port thereof for instantaneous release of the whole accumulated measure of slurry for delivery from said dispensing feeder through said discharge port at a substantially constant and unrestricted rate of flow and valve operating means connected with said valve means for opening and closing the same on a timed cycle.

A preferred embodiment of the invention has been chosen for purposes of illustration and description and is shown in the accompanying drawings forming a part of the specification.

FIG. 1 is a diagrammatic flow sheet illustrating continuous cyclic manufacture of nitrocellulose embodying the present invention;

FIG. 2 is a front elevation, shown partly in section, of one embodiment of a dispensing feeder according to the present invention;

FIG. 3 is a diagrammatic sketch of slurry flow pattern obtained by gradual or progressive slurry feeding, as for example, by displacement feeding;

FIG. 4 is a diagrammatic sketch of nitrocellulose mat or cake formation on the side walls of the centrifuge basket resulting from displacement feeding of the slurry as depicted in FIG. 3;

FIG. 5 is a diagrammatic sketch of slurry flow pattern according to the present invention;

FIG. 6 is a diagrammatic sketch of nitrocellulose mat or cake formation on the side wall of the centrifuge basket resulting from slurry feeding in accordance with the present invention as depicted in FIG. 5;

FIG. 7 illustrates coordination of the delivery cycle of the dispensing feeder with the reciprocating cycle of the centrifuge in accordance with the present invention.

With reference to FIG. 1, a suitable form of cellulose, such as shredded, pelletized, diced, or other particulate form of wood pulp or cotton linters, in predetermined amount is continuously introduced via line **11** into nitrating vessel **13**. Nitrating acid in predetermined amount is simultaneously continuously introduced via line **15** into nitrating vessel **13**. Following nitration, the slurry of nitrocellulose suspended in spent nitrating acid is discharged in a continuous stream from nitrating vessel **13** and is conveyed via line **17** to an agitated slurry holding tank **19**. The slurry of nitrocellulose in spent nitrating mixture is then discharged from slurry holding tank **19** in a continuous stream and is conveyed via line **21** into dispensing feeder **23** where the continuous feed stream of slurry is converted into an intermittent feed stream for delivery in accordance with the present invention in measured increments at predetermined intervals via conduit **25** to continuous centrifuge **27** having a reciprocating pusher plate. Slurry holding tank **19**, while useful and desirable for promoting and/or maintaining uniform dispersion of nitrocellulose in the slurry, can be dispensed with in a continuous system if desired, and the slurry discharged from nitrating vessel **13** can be conveyed directly to dispensing feeder **23**. If desired, part of the spent acid may be removed from the slurry by providing suitable deliquifying means, such as a screened port or valve, at any convenient point between the nitrating vessel and the centrifuge, in order to increase the solids content of the slurry delivered to the centrifuge. Such deliquefying means can conveniently be associated with any one or several of the structural elements between the nitrating vessel and the centrifuge, including the agitated slurry tank, the dispensing feeder, and feed lines between the nitrating vessel and the dispensing feeder.

An embodiment of a suitable dispensing feeder for the purposes of this invention is illustrated in FIG. 2. It will be seen that the dispensing feeder **23** of FIG. 2 comprises a vertically disposed cylindrical body **29** having an inlet **31** and a circular valve seat **33** at its lower extremity defining a discharge port of substantially the same cross sectional area as that of cylindrical body **29**. Quick-opening conical plug or flush valve **35**, with its apex end upward and its lower diameter slightly larger than the diameter of valve seat **33**, shown in its lowered position, seats in valve seat **33** to close the discharge port when in its upper (dotted) position, and thus seal cylinder **29** for accumulation of a measured volume of slurry. Rod **37** axially disposed interiorly in cylinder **29** connects plug valve **35** to piston **39** in a reciprocating pressure cylinder mechanism **41** which is actuated from a conventional hydraulic or pneumatic pressure source (not shown) through the 4-way valve **43** operated by means of solenoid **45**. A timer **47** in the solenoid circuit controls the reciprocating cycle of the pressure cylinder mechanism for opening and closing plug valve **35**. Adjustable coupling **38** on rod **37** insures proper seating of plug valve **35** in valve seat **33**, and provides for further adjustment when necessary. An adaptor or transition casing **49** connects cylindrical body **29** to conduit **25**. It will be seen that adapter casing **49** has a bulge near its upper end of substantially larger diameter than cylinder **29** to provide ample unrestricted flow space around plug valve **35** for slurry released from cylinder **29** by lowering plug valve **35** to its open position, and then tapers down in diameter to the diameter of conduit **25**. For convenience, transition casing **49** may be made of two or more sections joined together by flanges or equivalent means, if desired. As a safety measure cylinder **29** is provided with an overflow port **51** adjacent its top end, said port communicating with an enclosed chute **53** which opens into adaptor casing **49** by means of discharge port **55**. Overflow port **51**, chute **53** and discharge port **55** are optional, however. As an additional optional safety measure, plug valve **35** is provided on its lower face with a plurality of short rods **36** projecting downwardly and outwardly beyond its lower periphery to prevent plug valve **35** from plugging conduit **25**, if for any reason plug valve **35** became detached from rod **37**.



Dispensing feeder **23**, in performing its intended functions in accordance with this invention, operates as follows:

Timer **47**, set on a predetermined time cycle to coordinate with the reciprocating cycle of centrifuge **27**, energizes solenoid **45** to deliver pressurizing fluid through the 4-way valve **43** via line **42** to hydraulic cylinder mechanism **41**, and to exhaust via line **44**. This raises piston **39** and thereby raises plug valve **35** into its seating position in valve seat **33**, thus closing cylinder **29** for accumulation of a predetermined volume of slurry introduced thereinto via inlet **31**. After a predetermined set time interval, timer **47** energizes solenoid **45** to deliver pressurizing fluid through the 4-way valve **43** via line **44** to hydraulic cylinder mechanism **41** and to exhaust via line **42**. This lowers piston **39** and thereby drops plug valve **35** to its open, lowered position. This instantaneously releases the whole accumulated volume of slurry which flows by gravity from cylinder **29** and is delivered at a substantially constant and unrestricted rate of flow via conduit **25** into centrifuge **27**, whereupon the plug valve is closed again for accumulation of another measure of slurry. Each repetition of the aforestated operations, therefore, delivers a measured volume of slurry to the centrifuge at predetermined timed intervals in accordance with the present invention.

In the centrifuge the bulk of spent nitrating acid is centrifuged off and is recovered, and the moist mat of nitrocellulose containing retained spent nitrating acid is then washed substantially free of acid in the centrifuge by a series of rapid, stage-wise, zonal displacement washes, the acid thus displaced also being recovered, as more fully described hereinafter.

Operations in the centrifuge **27** are initiated by imparting the desired rotary motion to the centrifuge basket **51**, slurry distributor mechanism **53**, and pusher plate **55**, and by imparting the desired reciprocating stroke to pusher plate **55** by means of centrifuge shaft **57** operatively connected to these parts and actuated by conventional rotary driving means (not shown), and by conventional timer-operated reciprocating mechanism (not shown). Then with the centrifuge in operation, a measured volume of a slurry of nitrocellulose in spent nitrating acid is delivered from dispensing feeder **23** via conduit **25** to the spinning centrifuge and is guided by distributor mechanism **53** so that the slurry charge is dis-

tributed on the wall of centrifuge basket 51 in zone $A_1$ adjacent to the pusher plate 55, while the pusher plate is returning to rest during its reverse stroke and after the pusher plate has come to rest following completion of its reverse stroke. In this initial position in the centrifuge a major portion of the spent nitrating acid is centrifugally separated from the nitrocellulose, forming a mat of nitrocellulose moist with retained spent nitrating acid on the wall of the centrifuge in zone $A_1$. After a suitable but short wringing period during which the pusher plate of the centrifuge remains at rest, the timer-operated reciprocating mechanism of the centrifuge actuates the pusher plate, and the pusher plate then moves rapidly forward and then immediately rapidly backward through the predetermined measured stroke of its reciprocating cycle and again comes to rest at the end of the reverse stroke of the cycle. During the forward stroke of the reciprocating cycle the pusher plate compresses the initially formed mat of nitrocellulose and pushes the compressed cake to a new location on the wall of the centrifuge basket in zone $A_2$ where additional spent acid is centrifugally separated from the nitrocellulose. The reverse stroke of the reciprocating cycle returns the pusher plate to its rest position and leaves the portion of the wall of the centrifuge basket adjacent to the pusher plate in zone $A_1$ bare for receiving another measured volume of the slurry of nitrocellulose in spent nitrating acid, which is fed to the centrifuge from the dispensing feeder in accordance with this invention as soon as practicable after the pusher plate commences its reverse stroke.

It is essential, therefore, in practicing this invention to coordinate the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to deliver each measured increment of slurry feed to the centrifuge for distribution on the side wall of the cenrifuge basket adjacent the reciprocating pusher plate of the centrifuge as soon as practicable after said pusher plate commences its reverse stroke. FIG. 7 illustrates coordination of the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge based on the following data typical of a practical operating cycle.

*Data Illustrating Coordination of the Delivery Cycle of the Dispensing Feeder with the Timed Reciprocating Cycle of the Centrifuge*

| | Seconds |
|---|---|
| *Centrifuge Cycle:* | |
| Forward stroke of pusher plate | 0.9 |
| Reverse stroke of pusher plate | 0.9 |
| Total forward and return strokes of pusher plate | 1.8 |
| Pusher plate at rest after reverse stroke | 3.2 |
| Loading of centrifuge | 1.9 |
| Spin time after loading with pusher plate at rest | 1.9 |
| Total cycle | 5.0 |
| *Dispensing Feeder Cycle:* | |
| Dispensing feeder closed for slurry accumulation prior to delivery period | 0.5 |
| Delivery period between opening and closing of quick-opening valve means | 1.9 |
| Dispensing feeder closed for slurry accumulation after delivery period | 2.6 |
| Total period during which dispensing feeder is closed for slurry accumulation | 3.1 |
| Total cycle | 5.0 |

After initiation of operations, and with repeated cycles a continuous mat of nitrocellulose is thus built up on the wall of the centrifuge basket, and the centrifuge may be considered as divided into zones $A_1$, $A_2$, $A_3$, B, C, D and E, for example, with the nitrocellulose advancing intermittently from zone to zone. In zones $A_1$, $A_2$ and $A_3$, collectively identified as the spent acid zone, the major portion of the spent acid is centrifugally separated from the nitrocellulose and is recovered and conveyed via line 59 from the centrifuge to spent acid storage vessel 61; in each succeeding zone the acid remaining in the nitrocellulose is displaced by an acid weaker in acidity than the acid present in the nitrocellulose moving into that zone, and finally in the last zone, zone E, for example, by water. Operation in all zones is, of course, proceeding simultaneously, and the zonal displacement washing in each of zones B, C, D aand E is continuous.

Desirably the amount of water used in the final displacement wash is just sufficient so that the wash discharge therefrom has an acid concentration suitable for use as the washing medium in the immediately preceding displacement wash. In like manner the amount of washing medium used in each of the preceding displacement washing steps is preferably just sufficient so that the wash discharge therefrom has an acid concentration suitable for use as the washing medium in the immediately preceding displacement wash. Accordingly, therefore, since the wash discharge from each displacement washing step is more concentrated with respect to acid strength than the washing liquid employed to produce that particular wash discharge, by recycling the wash discharge from each succeeding wash as the washing liquid for the immediately preceding step, the concentration of acid in the wash discharges is built up to a point where it becomes economically attractive to recover the acid therefrom. In this way the recovered acid ultimately leaving the system as the wash discharge from the first zonal displacement wash, zone B, approaches the strength of the spent acid from nitration, and is therefore sufficiently high in acid concentration to make recovery of acid therefrom economically attractive.

Typical operations in the stage-wise zonal displacement washing of nitrocellulose in the centrifuge are illustrated in FIG. 1 as follows:

Water via line 63 is employed as the washing liquid for the nitrocellulose in zone E, and the wash discharge from zone E is conveyed via line 65, storage tank 67, and line 69 and is employed as washing liquid for the nitrocellulose in zone D. The wash discharge from zone D is conveyed via line 71, storage tank 73, and line 75 and is employed as washing liquid for the nitrocellulose in zone C. The wash discharge from zone C is conveyed via line 77, storage tank 79, and line 81 and is employed as washing liquid for the nitrocellulose in zone B. The wash discharge from zone B is withdrawn from the centrifuge via line 83 and is sent to acid recovery via line 85. Curbs 82, 84, 86, 88, 90, 92 and 94 disposed in the centrifuge casing around the centrifuge basket serve to segregate the several wash discharges and the centrifuged spent nitrating acid from each other for suitable recovery.

The washed nitrocellulose discharged from centrifuge 27 is withdrawn from the system through line 93 and is passed into conventional equipment (not shown) for any desired additional treatment such as final purification, stabilization, adjustment of viscosity, dehydration, and the like.

Part of the spent nitrating acid from spent acid storage tank 61 is conveyed via line 87 to nitrating acid mix tank 89 where it is fortified with fresh fortifying acid introduced via line 91, and the fortified acid is recycled via line 15 as nitrating acid for the nitration reaction in nitrating vessel 13. The remainder of the spent nitrating acid which accumulates in spent acid storage tank 61 is sent to acid recovery via line 85.

The principal and necessary function of the present invention is to intermittently deliver measured volumes of slurry feed at predetermined intervals to the centrifuge at a substantially constant and unrestricted rate of flow

within about 2 seconds for distribution on the wall of the centrifuge basket under a substantially uniform compacting force. Just why this method of delivery is advantageous is unknown but by hindsight it is postulated that slurry fed to the centrifuge in accordance with this invention forms a nitrocellulose cake or mat which is of uniform texture and porosity throughout which results from a uniform randomness of fiber distribution throughout the cake structure, rather than an orderly orientation of fibers during the initial and final phases of formation of the cake. It is also postulated that the uniform porous texture of the nitrocellulose cake produced in accordance with this invention is directly responsible for the important and unexpected process economies made possible by this invention, namely, improved spent acid recovery, improved throughput capacity, and greatly reduced loss of fine nitrocellulose particles through the centrifuge screen. Because of the uniform porous texture of the nitrocellulose cake formed, separation of spent nitrating acid and the zonal displacement washing of the cake are more efficient, thus leading to improved spent acid recovery. Because of improved efficiency of displacement washing, it has been possible to increase the amount of slurry charged in each cycle of operation, and thereby increase throughput capacity. It is also postulated that the mechanics of cake formation when the accumulated measure of slurry is delivered to the centrifuge at a substantially constant and unrestricted rate of flow in accordance with this invention favors retention of fine nitrocellulose particles within the cake, instead of a high loss of such particles through the centrifuge screen during the initial phases of cake formation.

A graphic illustration of the Rate of Flow-Time relationship of slurry delivery to the centrifuge in accordance with this invention is depicted by FIG. 5, and the uniformly porous texture of the nitrocellulose cake formed thereby is depicted by FIG. 6. The Rate of Flow-Time relationship for slurry delivery by the displacement principle, on the other hand, is depicted by FIG. 3. It will be seen by reference to FIG. 3 and FIG. 5 that the rate of flow curve for displacement delivery of slurry follows a distinctly different pattern than the rate of flow curve obtained in accordance with the present invention. Whereas the rate of flow according to this invention is substantially constant during delivery of the accumulated increment of slurry, it will be seen from FIG. 3 that the rate of flow by the displacement principle starts at zero, builds up gradually over a short time interval to a maximum, and then returns gradually to zero again, following substantially the reverse of the build-up curve. It is postulated that a flow delivery pattern as depicted by FIG. 3 produces a somewhat nonuniformly textured cake of nitrocellulose as depicted by FIG. 4, and that the mechanics of cake formation by such a flow delivery pattern favors a high loss of fine nitrocellulose particles through the centrifuge screen during the initial phase of cake formation while rate of slurry flow is building up, and also favors orientation of nitrocellulose fibers during the initial and final phases of cake formation during both build up and recession of slurry flow rate at the beginning and end of each displacement delivery cycle. It is postulated that such fiber orientation tends to produce zones of greater compaction in the nitrocellulose cake adjacent to the centrifuge wall and on the exposed surface of the cake which tend to interfere with the most efficient spent acid separation and subsequent zonal displacement washing.

It is evident from the foregoing, therefore, that there is an intimate relationship between the manner in which the accumulated increment of slurry is delivered to the centrifuge and the mechanics of cake formation and the physical characteristics of the nitrocellulose cake formed thereby; which affect the degree of loss of fine nitrocellulose particles through the centrifuge screen and the efficiency of separation and displacement washing of spent acid from the nitrocellulose cake.

However, irrespective of whether the above postulated explanation is correct or not, the fact remains that the instantaneous release of the whole accumulated measure of slurry for delivery at a substantially constant and unrestricted rate of flow to the centrifuge within about 2 seconds effects unexpected and unobvious improvement in spent acid recovery, improvement in throughput capacity of the centrifuge, and greatly reduced loss of fine nitrocellulose particles through the centrifuge screen in contradistinction to the gradual, progressive and variable release of the slurry charge, as for example, by displacement feeding.

It is important, therefore, in practicing the present invention, that the whole accumulated measure of slurry be instantaneously released, for only in this manner is it possible to obtain delivery of the accumulated slurry charge at a substantially constant rate of flow. By instantaneous release of the whole accumulated measure of slurry is meant that such release is accomplished without delay as by the quick opening of a flush valve or equivalent valve means to permit free and unrestricted flow of slurry from the dispensing feeder. Such flow is characterized by being free of impedence, and free of obstruction.

It is also important and essential in practicing this invention that the accumulated slurry charge be delivered to the centrifuge within about 2 seconds or less. The reason for this time limitation for slurry delivery will be more clearly understood by reference to FIG. 7, from which it is apparent that each cycle of centrifuge operation must provide not only a time interval for loading the centrifuge but also a period of at least about 2 seconds or more in duration for proper initial nitrocellulose mat formation and consolidation before pushing the mat to a new location on the centrifuge wall. A spin time after loading of the centrifuge appreciably less than about 2 seconds is insufficient to accomplish satisfactory initial mat formation and consolidation. The centrifuge cycle must also provide a time interval for the forward stroke of the pusher plate (more or less a fixed interval determined by the mechanical or hydraulic control characteristics of the centrifuge), as well as 0.2–0.3 second of the reverse stroke of the pusher plate. Moreover, it must be clearly understood that the centrifuge cycle is made as short as possible consistent with efficient separation of spent acid and displacement washing in order to reduce as much as possible any hydrolytic damage to the nitrocellulose. A 5 second centrifuge cycle has been found to represent about the optimum cycle consistent with accomplishing the purposes of this invention. With a 5 second cycle, as illustrated by FIG. 7, therefore, by adding the time interval required for the forward stroke of the pusher plate, 0.9 second, plus 0.3 second of the reverse stroke of the pusher plate, and the time interval required for satisfactory initial mat formation and consolidation, 1.9 seconds, it is seen, therefore, that the slurry charge must be delivered to the centrifuge within about 1.9 seconds or less, and accordingly, the dispensing feeder must be capable of delivering the desired increment of slurry to the centrifuge within this time limitation imposed by the centrifuge cycle.

For the purposes of this invention the dispensing feeder can conveniently be apparatus as shown as shown in the

drawings. However, the invention is not limited in this respect, for any dispensing feeder which can be operated on a timed cycle to accumulate and hold a measured volume or increment of slurry, and to instantaneously release the whole accumulated volume of slurry for delivery at a substantially constant and unrestricted rate of flow to the centrifuge within about 2 seconds is equivalent for the purposes of this invention. Those skilled in the art, having been instructed herein concerning the essential requirements of a dispensing feeder for achieving the objectives of this invention, will readily visualize numerous mechanical equivalents of the specific dispensing feeder illustrated in the drawings, within the scope of the present invention.

The body of the dispensing feeder must be of sufficient capacity or size to hold the volume of slurry necessary for charging the centrifuge during each cycle of operation. Except for this minimum requirement as to capacity, the body of the dispensing feeder can be of larger capacity if desired, and can be varied as desired with respect to physical configuration and disposition. The inlet to the dispensing feeder will, of course, be sufficiently large to accommodate the feed stream of slurry without holdup or plugging. The discharge port must be large enough to permit free and unrestricted flow of the slurry charge from the dispensing feeder within about 2 seconds or less.

The valve means associated with the discharge port of the dispensing feeder must be quick-opening to instantaneously release the whole accumulated measure of slurry and permit free and unobstructed flow of the accumulated slurry charge from the dispensing feeder at a substantially constant rate of flow, and there are numerous valves known to the art which are equivalent to the specific flush valve shown in the drawings for accomplishing the objectives of the present invention, and which, therefore, come within the scope of the present invention. Valves which inherently open gradually or progressively obviously are incapable of accomplishing the objectives of this invention and are therefore to be distinguished from the quick-opening valve means of the present invention.

For the purposes of this invention the valve operating mechanism for opening and closing the quick-opening valve can conveniently be a reciprocating pressure cylinder mechanism operatively connected to the valve with a shaft or the like, and actuated by a conventional hydraulic and/or pneumatic pressure source through a suitable valve operated by means of a timer-controlled solenoid, as illustrated in the drawings. However, it will be appreciated that other mechanical devices such as levers, cams, and the like, or electrical-mechanical devices such as solenoids can be employed to open and close the quick-opening valve, instead of a reciprocating pressure cylinder, and that various timer circuits, solenoids, and the like are available for actuating such valve-operating means on any desired cycle.

The conduit 25, connecting the dispensing feeder with the interior of the centrifuge, must be of large cross sectional area throughout in order to permit free and unrestricted flow of slurry from the dispensing feeder to the centrifuge, and preferably should be at least equal in cross sectional area to the cross sectional area of the discharge port of the dispensing feeder.

There are various conventional centrifuges having reciprocating pusher plates known to the art which can be employed in practicing the present invention. Accordingly, it is not deemed necessary to burden the present description with detail of such centrifuges.

Materials of construction for the various parts of the nitration system, such as pipe lines and conduits, pumps, storage vessels, nitrating vessel, slurry holding tank, dispensing feeder, and parts of the centrifuge exposed to spent nitrating acid, acidic wash liquids and fumes obviously must be chosen to be resistant to corrosion and deterioration. Certain parts not subject to mechanical stress or wear, such as pipe lines, etc., can be made of chemically inert plastic substances such as Teflon and the like, if desired. Parts subject to mechanical stress or wear, on the other hand, should be of corrosion resistant metals. Ordinary carbon steels will suffice for conventional nitrating mixtures of nitric acid, sulfuric acid and water. However, mixtures of nitric acid, magnesium nitrate and water dictate employment of stainless steel equipment to avoid excessive corrosion.

Cellulose nitration in accordance with this invention can be carried out either batch-wise or continuously as desired. When conventional batch-wise nitration is employed, an agitated slurry holding tank between the nitrating vessel and the dispensing feeder should be employed with suitable pumping means for conveying the slurry therefrom to the dispensing feeder. It is preferred, however, to nitrate the cellulose continuously, as for example, by the method and apparatus disclosed in U.S. Patent 2,927,845.

Any of the usual commercial forms of cellulose, such as cotton, purified cotton linters, purified wood pulp, regenerated cellulose, and the like can be employed in practicing this invention. The cellulose will be in bulk form such as picked linters, shredded, pelletized, diced, or other particulate form of wood pulp or cotton linters, fluffed bulk fibers, granules, finely cut or ground fibers, film shreds, and the like.

This invention contemplates the formation of all commercial types of nitrocellulose embracing the entire range of useful nitrogen content. For this purpose, any of the known mixed acid compositions which have been employed to prepare nitrocellulose may be employed. For example, the nitrating mixture can be the usual mixed acids made up of various mixtures of nitric acid, sulfuric acid and water. Typical commercial nitrating acids and the nitrogen content of nitrocelluloses produced therefrom are set forth in Table 7 on page 722, Cellulose and Cellulose Derivatives, 2nd Edition, Part II, edited by Emil Ott and Harold M. Spurlin, Interscience Publishers, Inc., New York, New York, copyright 1954. Other typical nitrating mixtures involving mixtures of nitric acid, sulfuric acid and water appear in Table 5, page 719, and in Table 6, page 720, of the above-cited text on Cellulose and Cellulose Derivatives.

However, nitration of cellulose with mixtures of nitric acid, sulfuric acid and water is by no means limited to mixtures as illustrated in Tables 5, 6 and 7 of the aforementioned text on Cellulose and Cellulose Derivatives. It has been found that mixtures of nitric acid, sulfuric acid and water which contain up to about 75% by weight of nitric acid are eminently satisfactory nitrating mixtures for the purposes of this invention. For convenience, such mixtures may be termed high nitric acid-low sulfuric acid nitrating mixtures since the weight of nitric acid always exceeds the weight of sulfuric acid in such mixtures. Above about 75% nitric acid by weight in such mixtures, however, the ratio of sulfuric acid is so low that it loses its effectiveness as a dehydrating agent, with resultant nonuniform nitration. It is presently preferred to employ high nitric acid-low sulfuric acid nitrating mixtures containng between about 40% and about 75% nitric acid, the sulfuric acid and water content of such mixtures being proportioned to obtain the desired level of nitrogen substitution in the cellulose in accordance with the usual established practice in the art.

Table I following illustrates some typical examples of

cellulose nitration employing high nitric acid-low sulfuric acid nitrating mixtures.

lowing lists some typical nitrating mixtures containing essentially nitric acid, magnesium nitrate and water, to-

*Table I*

| Ex. | Nitrating mixture composition, percent by weight | | | | Type of cellulose | Nitration temp., °C. | Nitration time, minutes | Ratio nitrating mixture to cellulose by weight | Percent nitrogen in nitrocellulose |
|---|---|---|---|---|---|---|---|---|---|
| | Nitric acid | Sulfuric acid | Oxide content expressed as $HNOSO_4$ | Water | | | | | |
| 1 | 71.04 | 13.13 | 2.07 | 13.76 | Shredded sulfite wood pulp | 40 | 20 | 51:1 | 11.37 |
| 2 | 51.50 | 28.47 | 3.51 | 16.52 | do | 44 | 16 | 54:1 | 11.47 |
| 3 | 60.03 | 22.02 | 2.98 | 14.97 | do | 44 | 16 | 54:1 | 11.60 |
| 4 | 71.27 | 13.54 | 1.66 | 13.53 | do | 50 | 15 | 51:1 | 11.60 |
| 5 | 69.62 | 17.84 | 2.62 | 9.92 | Sulfite wood pulp tablets [1] | 51 | 20 | 10:1 | 11.86 |
| 6 | 75.63 | 11.46 | 1.24 | 11.67 | Picked linters | 44 | 15 | 40:1 | 11.89 |
| 7 | 70.91 | 14.37 | 2.43 | 12.29 | Shredded sulfite wood pulp | 50 | 4 | 51:1 | 11.97 |
| 8 | 70.01 | 15.35 | 2.26 | 12.38 | do | 48 | 5 | 40:1 | 11.99 |
| 9 | 70.25 | 14.86 | 2.90 | 11.99 | Shredded prehydrolyzed sulfate wood pulp hard sheet | 44 | 10 | 31:1 | 11.99 |
| 10 | 70.25 | 14.86 | 2.90 | 11.99 | Shredded sulfite wood pulp | 50 | 2 | 31:1 | 12.07 |
| 11 | 69.73 | 16.24 | 2.14 | 11.89 | do | 50 | 2 | 51:1 | 12.18 |
| 12 | 69.10 | 15.84 | 2.93 | 12.13 | Picked linters | 49 | 10 | 41:1 | 12.33 |
| 13 | 69.73 | 16.24 | 2.14 | 11.89 | do | 50 | 10 | 51:1 | 12.46 |
| 14 | 70.74 | 22.68 | 1.24 | 5.35 | Shredded sulfite wood pulp | 50 | 15 | 51:1 | 13.46 |
| 15 | 74.32 | 21.24 | 0.70 | 3.74 | Picked linters | 34 | 20 | 100:1 | 13.60 |
| 16 | 70.60 | 26.11 | 0.90 | 2.39 | Shredded sulfite wood pulp | 50 | 5 | 51:1 | 13.62 |
| 17 | 62.75 | 33.75 | 0.93 | 2.57 | Picked linters | 34 | 20 | 100:1 | 13.65 |

[1] The sulfite wood pulp used in Example 5 above was a medium formation sheet cut into tablets 1/16 inch x 1/8 inch x 1/20 inch.

NOTE.—The sulfite wood pulp used in Examples 1, 2, 3, 4, 7, 8, 10, 11, 14 and 16 was a medium formation sheet shredded in conformance with conventional practice as set forth in U.S. Patent 2,028,080.

Thus, it will be seen that within Tables 5, 6 and 7 of the Ott and Spurlin text on Cellulose and Cellulose Derivatives cited hereinabove, and within Table I above relating to high nitric acid-low sulfuric acid nitrating mixtures, there are listed various nitrating mixtures for preparing any particular nitrocellulose desired. Likewise, within these tables there are listed nitrating mixtures suitable for preparing substantially all commercial types of nitrocellulose. The particular nitrating mixture employed will, therefore, be largely a matter of choice governed by economic and end use considerations. For certain purposes, when desirable, the sulfuric acid in such mixed acids can be replaced with phosphoric acid, phosphorous pentoxide or acetic anhydride as the dehydrating agent.

Alternatively, the nitrating mixtures of this invention may be various mixtures of nitric acid, magnesium nitrate and water containing essentially between about 45% and about 94% nitric acid, between about 3.3% and about 34% magnesium nitrate, and between about 2.7% and about 21% water by weight, the ratio of magnesium nitrate to water being at least about 1.2:1 and not more than about 2.2:1. It will be understood, of course, that the sum of the three essential components will constitute substantially 100% of the nitrating mixture, any $N_2O_3$ being only an incidental ingredient in the nitrating mixture, since it is well recognized that concentrated nitric acid often contains small percentages of $N_2O_3$, usually on the order of 0.1% or less. Within the aforestated limits are various nitrating mixtures for preparing any particular nitrocellulose desired, as well as nitrating mixtures suitable for preparing substantially all commercial types of nitrocellulose. The particular nitrating mixture employed will, therefore, be largely a matter of choice governed by economic and end use considerations, it being apparent that the higher nitrogen type nitrocellulose require nitrating mixtures high in nitric acid content and low in water content within the limits set forth. Table II fol-

gether with the nitrogen content of nitrocellulose produced therefrom.

*Table II*

NITRATING MIXTURE COMPOSITION, PERCENT BY WEIGHT

| Example | Nitric acid | Magnesium nitrate | Water | $N_2O_3$ | Percent nitrogen in nitrocellulose produced |
|---|---|---|---|---|---|
| 1 | 60.00 | 23.30 | 16.70 | | 11.05 |
| 2 | 56.00 | 27.30 | 16.70 | | 11.76 |
| 3 | 50.00 | 31.72 | 18.28 | | 11.91 |
| 4 | 60.00 | 24.40 | 15.70 | | 11.95 |
| 5 | 54.00 | 29.00 | 17.00 | | 12.16 |
| 6 | 50.00 | 32.70 | 17.30 | | 12.26 |
| 7 | 67.30 | 19.27 | 13.41 | 0.02 | 12.37 |
| 8 | 69.73 | 18.12 | 12.13 | 0.02 | 12.57 |
| 9 | 58.91 | 27.45 | 13.63 | 0.01 | 12.87 |
| 10 | 69.74 | 20.00 | 10.24 | 0.02 | 13.23 |
| 11 | 75.20 | 15.80 | 9.00 | | 13.39 |
| 12 | 89.33 | 5.78 | 4.75 | 0.14 | 13.36 |
| 13 | 84.80 | 9.13 | 6.00 | 0.07 | 13.57 |
| 14 | 79.76 | 11.84 | 8.37 | 0.03 | 12.59 |
| 15 | 93.62 | 3.63 | 2.65 | 0.10 | 12.76 |
| 16 | 90.47 | 5.56 | 3.92 | 0.05 | 13.46 |

The quantity of nitrating mixture employed per part of cellulose in accordance with this invention is sufficient to form a fluid, stirrable slurry therewith, which slurry will flow freely and which can be agitated to form and maintain a uniform dispersion of cellulosic phase in nitrating mixture. This is the minimum operable quantity, and will vary depending upon the physical form of cellulose employed. For example, dense fibrous granules of cellulose can be readily slurried with as little as 6 parts nitrating mixture to 1 part cellulose by weight. Wood pulp shredded by the method set forth in U.S. 2,028,080 normally requires about 28 parts nitrating mixture to 1 part of cellulose by weight. On the other hand, wood pulp dry fluffed in an Osterizer, and known in the art as Bauer

Dry Fluffed wood pulp, normally requires about 50 parts nitrating mixture to 1 part of cellulose by weight, while wood pulp wet shredded in an Osterizer, and known in the art as Brown Wet Shredded wood pulp, normally requires about 45 parts nitrating mixture to 1 part cellulose by weight. Picked cotton linters normally require about 39 parts nitrating mixture to 1 part of cellulose by weight to form a suitable slurry, and which will nitrate to form a uniformly substituted nitrocellulose having desirable solubility characteristics. It will be apparent, of course, that larger quantities of nitrating mixtures can be employed, such as 50, 75 or even 100 parts per part of cellulose, when desired. It is, of course, most economical and practical to nitrate with the lowest ratio that will produce a fluid, stirrable slurry without sacrificing production of a uniform, high quality nitrocelullose. It should be pointed out that even 6 parts nitrating mixture to 1 part cellulose represents an excess of nitrating capacity over theoretical stoichiometric requirements to form nitrocellulose.

The rate of introduction of cellulose and of nitrating mixture to the nitrating vessel is substantially governed by the throughput capacity of the centrifuge. In other words, the amount of nitrocellulose produced in the nitrating vessel within a given period of time should coincide with the amount of nitrocellulose which can be processed through the centrifuge within substantially the same period of time.

Sufficient residence time of the reaction slurry in the nitrating vessel is provided to permit the nitration reaction to proceed to completion, the extent of nitration at equilibrium being governed primarily by the composition of the nitrating mixture. With conventional nitrating mixtures consisting of mixtures of nitric acid, sulfuric acid and water, nitration is substantially complete within about 18 minutes. With high nitric acid-low sulfuric acid nitrating mixtures as illustrated in Table I, many nitrations are substantially complete within about 10 minutes. Nitration with mixtures of nitric acid, magnesium nitrate and water has been found to be substantially complete within about 10 minutes. Residence time of the nitration reaction slurry in the nitrating vessel will, therefore, be of at least sufficient duration to permit the nitration reaction to proceed to completion, and may be of greater duration, if desired. Analysis of the discharged nitrocellulose for nitrogen content and observation of the solubility characteristics of the nitrocellulose provide an ample check on whether sufficient residence time has been provided. If the nitrogen content of the discharged nitrocellulose closely approaches the calculated nitrogen content expected from the nitrating mixture employed, and the discharged nitrocellulose dissolves substantially completely in test solvents to form clear, smooth solutions substantially free of undissolved fibers or particles, it can be concluded that residence time of the reaction slurry in the nitrating vessel has been sufficient to permit the nitration reaction to go to completion.

A wide range of temperatures can be employed for the nitration of cellulose in accordance with this invention. For practical reasons, however, it is not desirable to employ temperatures below about 15° C. or higher than about 70° C. Below about 15° C. the reaction becomes too slow to be economically attractive, and above about 70° C. the nitrocellulose tends to decompose. Desirable operating temperatures are readily attained by heating the nitrating acid prior to introduction into the nitrating vessel, and heat exchange facilities, such as vessel jacketing, usually are not necessary to maintain desired reaction temperatures. A preferred range of nitrating acid temperatures lies between about 20° C. and about 50° C. Normally, a small temperature rise due to heat of reaction results in the nitration reaction mixture, and this small temperature rise is taken into consideration in determining the temperature to which the nitrating acid is preheated. However, it is within the scope of this invention to employ heating or cooling means, such as vessel jacketing or equivalent means, when necessary or desirable, to maintain reaction temperatures at any predetermined level, or within any predetermined temperature range.

Nitration of cellulose with nitrating acid in the nitrating vessel produces a slurry of nitrocellulose suspended in spent nitrating acid. The slurry of nitrocellulose in spent nitrating acid is then conveyed by suitable means, such as by pumping, gravity flow, or other equivalent conveying means from the nitration vessel, via an agitated slurry holding tank, when deemed necessary or desirable, to the dispensing feeder for delivery in measured increments at predetermined intervals in accordance with this invention to the centrifuge for separation and displacement of spent acid from the nitrocellulose.

It has already been pointed out hereinbefore how separation of the bulk of spent nitrating acid and displacement of retained spent acid by a series of rapid stage-wise zonal displacement washes are accomplished in the centrifuge in accordance with this invention. It is important that these operations in the centrifuge be carried out rapidly in order to avoid degradation of the nitrocellulose by unnecessary exposure of the nitrocellulose to moist air. There should be no appreciable time lapse between separation of the bulk of spent acid and the first displacement wash. Similarly, the second, third, fourth, etc. washes should each follow the preceding wash immediately without time lapse, and each wash is carried out rapidly in the shortest possible time commensurate with accomplishing effective displacement washing. To this end the reciprocating cycle of the centrifuge is set as short as possible consistent with efficient displacement washing and will vary somewhat, from about 4 seconds to about 10 seconds, for example, depending largely upon the physical characteristics of the nitrocellulose mat or cake formed on the centrifuge wall.

Stage-wise displacement washing in accordance with this invention obviously must be adapted to the nitration system being employed. For example, in the case of nitration with nitric acid-sulfuric acid mixtures, the washing liquids will be mixtures of nitric acid and sulfuric acid, with each succeeding washing liquid being of decreased acid concentration approaching zero as the limit, the final washing liquid being either very dilute acid, or preferably water.

As a further example, in the case of nitration with mixtures of nitric acid, magnesium nitrate and water, it is very important to displace retained spent nitrating mixture which is relatively high in magnesium nitrate content with a nitric acid liquid which is much lower in magnesium nitrate content at an early stage in the washing program. Accordingly, therefore, the nitrocellulose, following removal of the bulk of spent nitrating mixture, is subjected to a displacement wash with fresh nitric acid of about 60% to about 75% concentration substantially free of magnesium nitrate. In a majority of cases where the retained spent nitrating mixture remaining in the nitrocellulose, following removal of the bulk of spent nitrating mixture, contains up to about 75% to 80% nitric acid, the fresh nitric acid of about 60% to about 75% concentration substantially free of magnesium nitrate will be employed as the first displacement wash after removal of the bulk of spent nitrating mixture, and the discharge from the fresh nitric acid wash will be recovered. However, in some instances, particularly when the retained spent nitrating mixture remaining in the nitrocellulose contains on the order of about 80% or more nitric acid, the fresh nitric acid of about 60% to about 75% concentration substantially free of magnesium nitrate will be employed as the second displacement wash, recycling the discharge from the fresh nitric

acid wash as the first displacement wash following removal of the bulk of spent nitrating mixture, and recovering the discharge from the first displacement wash. Following the displacement wash with fresh nitric acid of about 60% to about 75% concentration substantially free of magnesium nitrate, the nitrocellulose is then subjected to a series of stage-wise zonal displacement washes in which each succeeding washing liquid is of decreased nitric acid content, approaching zero as the limit, the final washing liquid being either very dilute acid, or preferably water.

A fresh nitric acid displacement wash, similar in principle to that described above for systems utilizing nitrating mixtures containing nitric acid, magnesium nitrate and water, can also be employed in the washing procedure for nitrocellulose prepared with nitric acid-sulfuric acid mixtures, whenever it is advantageous to displace retained acid liquid which is relatively high in sulfuric acid content with an acid liquid which is much lower in sulfuric acid content.

This invention also contemplates other variations in the stage-wise displacement washing of nitrocellulose, such as incorporation of other specific wash acid streams into the wash system, which variations would readily occur to those skilled in the art with a knowledge of the objectives and purposes of the present invention.

Obviously, in any nitration system the number of stage-wise displacement washes could be very large with very small decreases in acid strength with each succeeding washing liquid. Ordinarily, however, the number of such washes will be held to as few as possible consistent with economic recovery of a substantial proportion of the spent nitrating acid remaining in the nitrocellulose. Four or five washes are usually adequate for this purpose. Cooling of the washing liquids has been found to be advantageous.

The quantity of washing liquid employed in each washing step is governed primarily by the quantity employed for the final washing step. The amount of washing liquid employed for the final washing step is, in turn, governed largely by the practical and economic consideration of abstracting an equivalent amount of water from the spent acid sent to acid recovery. Hence, although larger amounts can be employed, it is desirable to hold the quantity of final washing liquid, and therefore the other washing liquids likewise, to a practical minimum consistent with accomplishing a satisfactory degree of washing without undue dilution of the recovered wash discharge. It has been found that this can be satisfactorily accomplished with approximately 0.06 to 0.2 gallon of final washing liquid per pound of nitrocellulose.

Although the washing procedure in accordance with this invention necessarily involves initiating the washing operations with previously prepared washing liquids of predetermined composition, it will be apparent that equilibrium conditions will be rapidly established, owing to the recirculation features of this invention, wherein the composition of each wash discharge is governed largely by the composition of the spent acid adhering to the nitrocellulose entering the washing schedule and the number and composition of washes making up the washing schedule. In a specific embodiment as illustrated by the drawings, for example, in which four washing steps are employed, the initial composition of the washing liquids employed to initiate the washing schedule can conveniently be water for the washing liquid in Zone E, 20% mixed nitric-sulfuric acid for Zone D, 40% mixed nitric-sulfuric acid for Zone C, and 60% mixed nitric-sulfuric acid for Zone B. After equilibrium has been attained, it has been found that the wash discharge from Zone E ordinarily contains between about 15% and about 25% mixed nitric-sulfuric acid; the wash discharge from Zone D contains between about 25% and about 40% mixed nitric-sulfuric acid; the wash discharge from Zone C contains between about 40% and about 50% mixed nitric-sulfuric acid; and the wash discharge from Zone B contains between about 50% and about 60% mixed nitric-sulfuric acid, and is recovered for reclaiming acid values therein. It will be understood, however, that the composition and number of washing liquids set forth above are merely by way of example, and other compositions and numbers of washing liquids come within the scope of this invention.

As much as necessary of the spent acid separated from the nitrocellulose in the spent acid zone of the centrifuge is fortified with fresh concentrated nitric acid and fresh concentrated sulfuric acid to reconstitute nitrating acid for reuse in the process. Sometimes displaced spent acid recovered as the discharge from displacement washing is also used for this purpose. Ordinarily, however, there is a residuum of spent acid over and above the amount which can be fortified for reuse, and this residuum of accumulated spent acid must be sent to acid recovery to reclaim acid values therein.

The following example sets forth a specific embodiment of the invention. It is to be understood, however, that the invention is in no way limited to this example, since this invention may be practiced by the use of various modifications and changes within the scope of the invention as hereinabove described.

## EXAMPLE

In this example a continuous system for the manufacture of nitrocellulose as illustrated by FIG. 1 was employed. The nitrating vessel **13** and the method of nitration in this system was the method and apparatus disclosed in U.S. Patent 2,927,845. A dispensing feeder as illustrated by FIG. 2 was employed, and the dispensing feeder delivery cycle was coordinated with the reciprocating cycle of the centrifuge, a 5 second cycle being selected as illustrated by FIG. 7.

The nitrating acid employed in this example had the following composition:

| | Percent by weight |
|---|---|
| $HN_3$ | 50 |
| $H_2SO_4$ | 33.9 |
| $H_2O$ | 14.1 |
| Oxide content expressed as $HNOSO_4$ | 2.0 |

and prior to introduction to the nitrating vessel was heated to a temperature of about 40° C.

The cellulose employed was wood pulp shredded by the method described in U.S. Patent 2,028,080, and the nitrating acid and cellulose were each continuously introduced into the nitrating vessel, the ratio of nitrating acid to cellulose being 28.1 to 1 by weight, the rate of introduction of the nitrating acid being approximately 25 gallons per minute.

Residence time for the reaction slurry of cellulose in nitrating acid in the nitrating vessel was adjusted to 30 minutes to produce nitrocellulose in equilibrium with a spent nitrating acid having the following composition:

| | Percent by weight |
|---|---|
| $HNO_3$ | 46.0 |
| $H_2SO_4$ | 35.7 |
| $H_2O$ | 16.0 |
| Oxide content expressed as $HNOSO_4$ | 2.3 |

The slurry of nitrocellulose in spent nitrating acid of the above composition was discharged continuously from the nitrating vessel **13** at the rate of approximately 25 gallons per minute and was conveyed via line **17** into an agitated slurry holding tank **19**, from which holding tank the slurry was continuously delivered via line **21** to dispensing feeder **23**, FIG. 2, at the rate of approximately 25 gallons per minute where the continuous feed stream of slurry was converted into an intermittent feed stream for delivery in measured increments at predetermined intervals to the centrifuge **27** via conduit **25** in accordance with the present invention.

Approximately 2.1 gallons of slurry during each delivery cycle of the dispensing feeder were delivered to the centrifuge for distribution on the centrifuge wall in Zone $A_1$. With repeated cycles a continuous mat of nitrocellulose was built up on the wall of the centrifuge, with the nitrocellulose advancing intermittently from zone to zone. In zones $A_1$, $A_2$, and $A_3$, collectively identified as the spent acid zone, the major portion of the spent acid was centrifugally separated from the nitrocellulose and was conveyed via line 59 to spent acid storage vessel 61. In each succeeding zone the acid remaining in the nitrocellulose was displaced by an acid weaker in acidity than the acid present in the nitrocellulose moving into that zone, and finally in the last zone, Zone E, with water. Operation in all zones proceeded simultaneously, and the zonal displacement washing in each of Zones B, C, D and E was continuous. Approximately one pound of water per pound of nitrocellulose produced, via line 63, was employed as the final washing liquid for the nitrocellulose in Zone E, and the wash discharge from Zone B, amounting to approximately 1.035 pounds per pound of nitrocellulose produced and having the following composition, was recovered via line 83 and was sent to acid recovery via line 85;

| | Percent by weight |
|---|---|
| $HNO_3$ | 48.1 |
| $H_2SO_4$ | 24.9 |
| $H_2O$ | 26.9 |
| Oxide content expressed as $HNOSO_4$ | 0.1 |

The washed nitrocellulose was withdrawn from the system via line 87 for final conventional purification, stabilization, viscosity adjustment and dehydration. The nitrocellulose thus produced had a nitrogen content of 12.1%. A 12.2% by weight test solution of this nitrocellulose dissolved in a solvent composed of 55% toluene, 20% ethyl acetate and 25% ethyl alcohol, by weight, was exceptionally smooth and sparkling clear, and free of any undissolved particles or fibers, thus demonstrating that the nitrocellulose produced in accordance with this invention was unusually uniform and of the highest quality. This nitrocellulose was suitable for use in all applications wherein a standard RS ½ second type nitrocellulose is required.

Approximately 16.171 pounds of spent nitrating acid per pound of nitrocellulose produced were conveyed from spent acid storage vessel 61 via line 87 to nitrating acid storage tank 89 where it was refortified with 2.417 pounds of fresh fortifying acid composed of

| | Pounds |
|---|---|
| $HNO_3$ | 1.851 |
| $H_2SO_4$ | 0.537 |
| $H_2O$ | 0.029 |

The refortified acid thus produced was then recirculated via line 15 to the nitrating vessel as nitrating acid for the nitration of additional cellulose.

The residuum of accumulated spent nitrating acid over and above the amount which was fortified for reuse in the system was sent to acid recovery via line 85.

This invention provides important and substantial operating economies in the manufacture of nitrocellulose. Among the advantages realized by practice of this invention is improved spent acid recovery, improved throughput capacity of the centrifuge, greatly reduced loss of fine nitrocellulose particles through the centrifuge screen, reduced initial capital investment, and reduced operating and maintenance expenses.

What we claim and desire to protect by Letters Patent is:

1. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating mixture is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating mixture from the nitrocellulose, and in which each measure of slurry feed is separately accumulated in said dispensing feeder for discharge therefrom into said centrifuge, the improvement in feeding said measure of slurry to said centrifuge which comprises instantaneously releasing the whole accumulated measure of slurry feed for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds.

2. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating mixture is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating mixture from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder, instantaneously releasing the whole accumulated increment of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, and repeatedly performing the aforestated steps.

3. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating mixture is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating mixture from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder closed for accumulation of the slurry charge, opening the dispensing feeder upon accumulation of the incremental slurry charge to instantaneously release the whole accumulated charge to flow by gravity at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, closing the dispensing feeder after delivery of the accumulated slurry charge for accumulation of the next measured increment of slurry, and repeatedly performing the aforestated steps.

4. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating acid is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating acid from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder, instantaneously releasing the whole accumulated increment of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher

plate has come to rest following completion of its reverse stroke, repeatedly performing the aforestated steps to form a continuous mat of nitrocellulose on the side wall of the centrifuge basket by intermittently advancing the nitrocellulose from zone to zone along the side wall of said centrifuge basket with repeated reciprocating cycles of the centrifuge, centrifugally separating the bulk of spent nitrating acid from the nitrocellulose in the spent acid zone and recovering the spent acid thus separated, thereafter subjecting the nitrocellulose to a series of rapid, stage-wise, zonal displacement washes in the centrifuge in which each succeeding washing liquid is of decreased acid concentration approaching zero acid concentration as the limit, and in which the discharge from the first of said zonal displacement washes is recovered and the discharge from each succeeding zonal wash is recycled to the preceding zonal wash.

5. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating acid is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating acid from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder, instantaneously releasing the whole accumulated increment of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, repeatedly performing the aforestated steps to form a continuous mat of nitrocellulose on the side wall of the centrifuge basket by intermittently advancing the nitrocellulose from zone to zone along the side wall of said centrifuge basket with repeated reciprocating cycles of the centrifuge, centrifugally separating the bulk of spent nitrating acid from the nitrocellulose in the spent acid zone and recovering the spent acid thus separated, thereafter subjecting the nitrocellulose to a series of rapid, stage-wise, zonal displacement washes in the centrifuge in which each succeeding washing liquid is of decreased acid concentration, the final washing liquid being water, and in which the discharge from the first of said zonal displacement washes is recovered and the discharge from each succeeding zonal wash is recycled to the preceding zonal wash.

6. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating acid is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating acid from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder, instantaneously releasing the whole accumulated increment of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, repeatedly performing the aforestated steps to form a continuous mat of nitrocellulose on the side wall of the centrifuge basket by intermittently advancing the nitrocellulose from zone to zone along the side wall of said centrifuge basket with repeated reciprocating cycles of the centrifuge, centrifugally separating the bulk of spent nitrating acid from the nitrocellulose in the spent acid zone and recovering the spent acid thus separated, and thereafter subjecting the nitrocellulose to a series of rapid, stage-wise, zonal displacement washes in the centrifuge.

7. In the manufacture of nitrocellulose, in which a slurry of nitrocellulose in spent nitrating mixture is fed in measured increments at predetermined intervals from a dispensing feeder into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle for separation and displacement of spent nitrating mixture from the nitrocellulose, the improvement comprising accumulating a measured increment of said slurry in the dispensing feeder, instantaneously releasing the whole accumulated increment of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said increment of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, repeatedly performing the aforestated steps to form a continuous mat of nitrocellulose on the side wall of the centrifuge basket by intermittently advancing the nitrocellulose from zone to zone along the side wall of said centrifuge basket with repeated reciprocating cycles of the centrifuge, centrifugally separating the bulk of spent nitrating mixture from the nitrocellulose in the spent acid zone and recovering the spent nitrating mixture thus separated, thereafter subjecting the nitrocellulose to a rapid fresh acid displacement wash, recovering the discharge from the displacement wash, subjecting the nitrocellulose to a series of rapid, stage-wise displacement washes after said fresh acid displacement wash in which the discharge from the first of said stage-wise displacement washes is recovered, and the discharge from each succeeding stage-wise displacement wash is recycled to the preceding wash.

8. A continuous system for the manufacture of nitrocellulose which comprises subjecting cellulose to a nitration reaction in which cellulose is reacted with an excess of nitrating acid to form a slurry of nitrocellulose in spent nitrating acid, feeding said slurry in measured volumes at predetermined intervals into a continuous centrifuge having a reciprocating pusher plate operating on a timed reciprocating cycle by accumulating a measured volume of said slurry in a dispensing feeder, instantaneously releasing the whole accumulated volume of slurry for delivery at a substantially constant and unrestricted rate of flow from the dispensing feeder into the centrifuge within about 2 seconds, coordinating the delivery cycle of the dispensing feeder with the timed reciprocating cycle of the centrifuge to distribute said volume of slurry on the side wall of the centrifuge basket adjacent the reciprocating pusher plate of said centrifuge while said pusher plate is returning to rest during its reverse stroke and after said pusher plate has come to rest following completion of its reverse stroke, repeatedly feeding measured volumes of said slurry to the centrifuge as set forth above to form a continuous mat of nitrocellulose on the side wall of the centrifuge basket by intermittently advancing the nitrocellulose from zone to zone along the side wall of said centrifuge basket with repeated reciprocating cycles of the centrifuge, centrifugally separating the bulk of spent nitrating acid from the nitrocellulose in the spent acid zone and recovering the spent acid thus separated, thereafter subjecting the nitrocellulose to a series of rapid, stage-wise, zonal displacement washes in the centrifuge in which each succeeding washing liquid

is of decreased acid concentration, the final washing liquid being water, and in which the discharge from the first wash is recovered and the discharge from each succeeding wash is recycled to the preceding wash, withdrawing the washed nitrocellulose from the system, fortifying part of the recovered spent nitrating acid with concentrated nitric acid and concentrated sulfuric acid and recycling the resulting fortified acid as the nitrating acid for the nitration reaction, and recovering the acid values from



the remainder of the recovered spent acid and from the recovered discharge from the first zonal displacement wash.

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