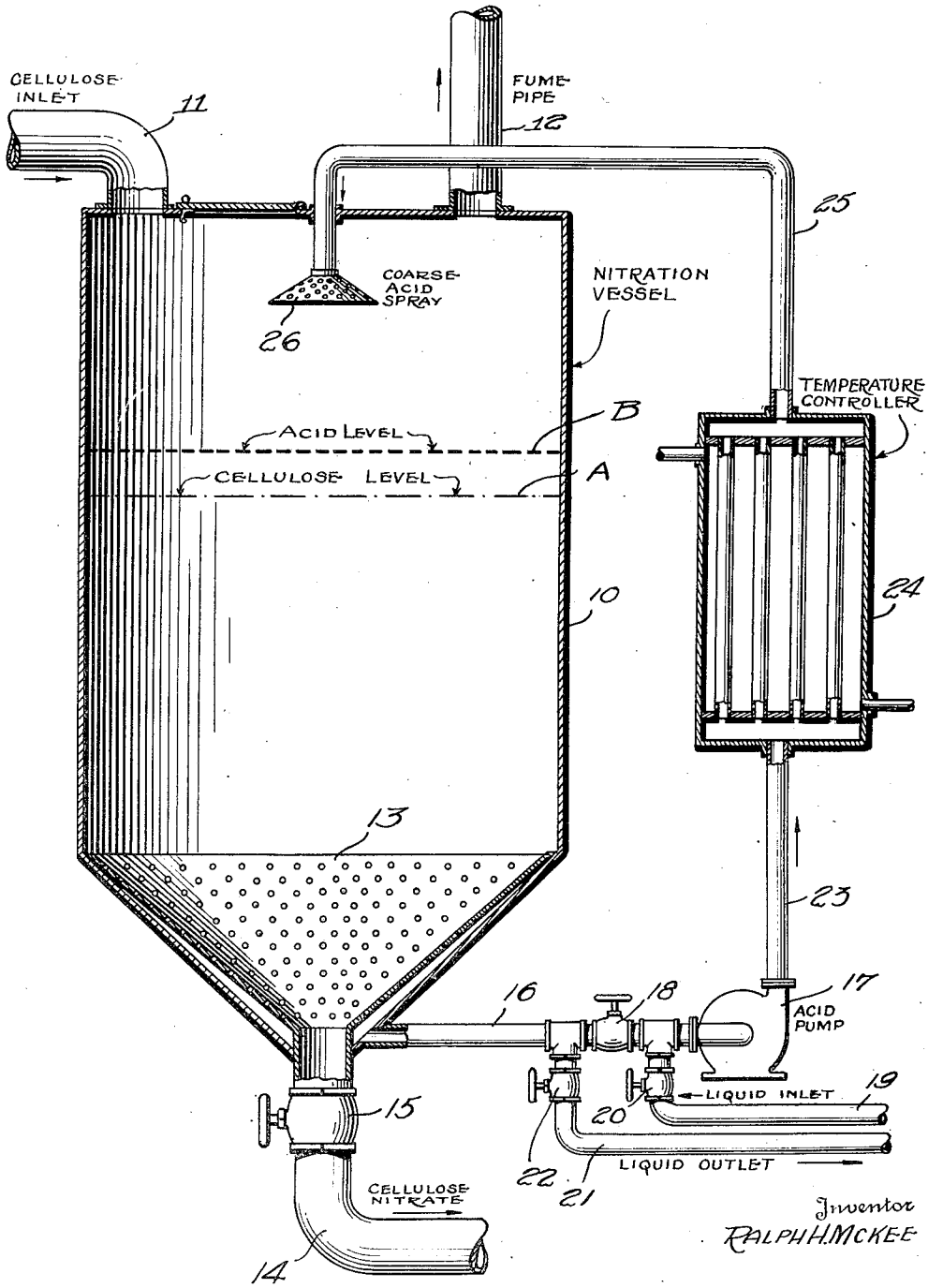
June 5, 1945. R. H. McKEE 2,377,435

MANUFACTURE OF CELLULOSE NITRATE

Filed Dec. 20, 1941



Inventor
RALPH H. McKEE

By

Attorney

Patented June 5, 1945

2,377,435

UNITED STATES PATENT OFFICE

2,377,435

MANUFACTURE OF CELLULOSE NITRATE

Ralph H. McKee, New York, N. Y.

Application December 20, 1941, Serial No. 423,857

3 Claims. (Cl. 260—220)

This invention relates to the manufacture of cellulose nitrate, particularly for use in the munitions industry.

The principal object of the present invention is to provide an improved process of nitrating cellulose.

An important object of the present invention is to provide a process of making cellulose nitrate on the basis of large scale production at low labor costs.

Another object of the invention is to provide a process of nitrating cellulose wherein the disadvantages and dangers of local heating, fuming, fire and explosion are avoided.

A further object of the invention is to provide a process of making nitrocellulose which avoids the loss of strong nitrating acid and in which the spent acid is recovered in easily reworkable form.

Further objects and advantages of the invention will become apparent during the course of the following description.

As will more fully hereinafter appear, the present process possesses numerous advantages over any of the processes commercially used for the manufacture of cellulose nitrate, the three most common of which are the so-called "pot process," the "Du Pont process," and the "Thompson (or displacement) process."

In the "pot process," a mixture of sulfuric and nitric acids of proper strength is introduced into an earthenware pot. A small charge (about 2 or 3 pounds) of finely divided, dried, purified cellulose is introduced into the pot and pushed under the surface of the acid by means of an aluminum fork. The charge of cellulose is allowed to stay in the acid for a predetermined time, then removed to a draining board, and pressed by means of the fork so that much of the excess acid will drain back into the pot. The thus treated material is then "drowned" by submerging it in water. The amount of strong acid lost by this dilution generally considerably exceeds the weight of cellulose nitrate produced.

In the second method referred to above, the pot is much larger and of steel and has a mechanically driven propeller or propellers to push the dried cellulose under the surface of the acid. In this method the charge of cellulose is increased to about 25 pounds and the mixed nitrating acid to about 1500 pounds. At the completion of the nitration, a valve is opened at the bottom of the pot and the whole charge of acid and cellulose nitrate is dumped into a centrifuge. The centrifuging of the nitrocellulose removes most of the acid, following which the nitrocellulose is "drowned" by dumping it into an excess of water, resulting in a substantial loss of nitrating acid.

In the "Thompson process," which is more widely used in England than in this country, a charge of about 700 pounds of mixed acids and about 25 pounds of dried cotton linters are placed in a large flat earthenware funnel and a perforated earthenware plate or plates placed on top of the charge in order to force the cellulose below the acid level. About one-half inch of ice water (at approximately 4° C.) is run in on top of the earthenware plate. After the nitration is completed, the valve below is partially opened and additional chilled water is run in on top of the perforated plate. The acid is gradually displaced by the water and the water gradually passes down through the 5 or 6 inch layer of cellulose nitrate, washing out the bulk of the acid. A part of the strong acid is recovered and a part is found to be mixed with water and too much diluted for reuse. The cellulose nitrate obtained is "drowned" in water.

Other processes which are used commercially are generally modifications of the processes referred to above. For example, the German method of nitration involves treatment in a two-speed centrifugal and the removal of excess acid by rapid whirling of the centrifugal, after which the nitrated cotton is manually removed, washed and purified.

As will be noted, in all of the above mentioned processes there is a high labor cost due to the small charges of cellulose used, the manual handling of the cellulose charges, and the manual handling of the cellulose nitrate after treatment and before purification thereof. Moreover, in each case the first nitration is done with the strongest acid and, consequently, the final nitration is accomplished with weaker acid, with the resulting disadvantages hereinafter referred to. In addition, much strong nitration acid is lost in the "drowning" operation in these processes.

As a result of extensive research and experiment directed to overcoming the above described disadvantages of the prior art processes, I have developed a process of nitrating cellulose which not only is free from these disadvantages but is more efficient, less expensive in operation, and capable of producing excellent yields of cellulose nitrate of improved quality.

In my new process, the cellulose to be nitrated is subjected to a succession of nitrating acids of increasing strength. The cellulose is first treated with nitrating acid of a strength capable of only partially nitrating the cellulose, following which

the partially nitrated product is treated with a stronger nitrating acid to complete the nitration thereof. In commercial practice, a nitrating vessel is partially filled with relatively weak nitrating acid. A stream of finely divided cellulose is then introduced into the upper portion of the nitrating vessel and, simultaneously therewith, a relatively weak nitrating acid is sprayed into the upper portion of the nitration vessel. During the addition of the streams of cellulose and nitrating acid spray, used nitrating acid is withdrawn from the lower portion of the nitration vessel. The rate of withdrawal of used acid is so proportioned with respect to the introduction of the stream of finely divided cellulose and the acid spray that the cellulose in the nitration vessel is maintained submerged in acid at all times. After the vessel has been charged with the total amount of cellulose to be nitrated, the addition of the finely divided cellulose is discontinued. Thereafter, a portion of the acid in the vessel is continuously withdrawn, cooled, and returned to the vessel. After this treatment has been continued for a predetermined period, the used weak acid is withdrawn from the nitration vessel and replaced with stronger nitrating acid which is continuously circulated through the partially nitrated cellulose, out of the nitration vessel, through an acid cooler, and back to the nitration vessel. After the completion of this treatment, the used strong acid is then displaced by chilled dilute wash acid to partially wash the nitrocellulose. This wash acid is then withdrawn and replaced with water to complete the washing of the cellulose.

In the accompanying drawing, I have shown diagrammatically one form of apparatus suitable for use in practicing the present invention.

In this drawing, the numeral 10 designates an acid-resistant nitration vessel which may suitably be made of stainless steel. The nitration vessel is provided at the upper portion thereof with a cellulose inlet pipe 11 and an outlet pipe or stack 12 for discharging any fumes or mist from the vessel. The nitration vessel is provided at the lower portion thereof with a perforated, funnel-shaped false bottom 13, the lower portion of which is spaced slightly from the bottom wall of the nitration vessel 10. The false bottom 13 is connected with a nitrocellulose discharge pipe 14, which is provided with the discharge control valve 15.

The lower portion of the nitration vessel 10 is also provided with a liquid outlet pipe 16 which opens directly into the space or liquid chamber between the lower portion of the false bottom 13 and the lower portion of the wall of the nitration vessel. The pipe 16 connects the nitration vessel with the pump 17 and is provided with a control valve 18. A liquid inlet pipe 19, having a control valve 20, connects with the pipe 16 at a point between the pump 17 and the control valve 18. A liquid outlet pipe 21, having a control valve 22, connects with the pipe 16 at a point between the nitration vessel 10 and the control valve 18.

The pump 17 is connected by means of a pipe 23 with a temperature controller or heat interchanger 24 which is of conventional construction. Liquid which is pumped through the temperature controller 24 is discharged therefrom into the pipe 25 which is adapted to deliver liquid to the upper portion of the nitration vessel 10 through a coarse spray nozzle 26.

The general method for practicing the process in the form of apparatus shown in the drawing is as follows:

Weak nitrating acid capable of but partially nitrating cellulose, say a 60—18—22 acid (60% sulfuric acid, 18% nitric acid and 22% water and less than 1% of nitrous oxides), is delivered from a suitable acid storage tank (not shown) to the liquid inlet pipe 19. With the valve 20 open, (and the valves 15—18—22 closed) the fresh weak nitrating acid is pumped through the pipe 23, the temperature controller 24 and the pipe 25 into the nitration vessel 10. After the nitration vessel has been partially filled, say one-fourth filled, with weak nitrating acid, the valve 18 is opened to provide for circulation of acid from the bottom of the vessel 10 through the pipe 16 to the acid pump 17, and thence back to the nitration vessel through the pipe 23, the heat interchanger 24, the pipe 25 and the spray nozzle 26. At the same time, the cellulose to be nitrated is introduced, preferably by a current of air, through the pipe 11 into the nitration vessel 10. The rate of introduction of the cellulose into the vessel 10 from the pipe 11 is so proportioned with respect to the rate of withdrawal of acid through the pipe 16 and the introduction of fresh nitrating acid through the pipe 19 is such that the cellulose introduced into the nitration vessel 10 will at all times be submerged in acid. Thus, when the level of cellulose in the nitration vessel has reached the point A, the acid in the vessel should be approximately at the level B, and when such levels have been reached, further introduction of cellulose from the pipe 11 is discontinued and the valve 20 in the liquid inlet pipe 19 is closed to stop the addition of further amounts of fresh acid into the system.

The cellulose introduced into the nitration vessel 10 is preferably in finely divided form, such as shredded cotton linters or wood pulp. Such cellulose should be in purified condition as in other processes of making cellulose nitrate. However, the cellulose need not be in substantially dry condition. In other processes of making cellulose nitrate it has been necessary to get the moisture content down to less than 1%. However, in the present process cellulose having a moisture content of from 6 to 10% works just as satisfactorily as dry cellulose, although there is some dilution of the first nitrating acid by the moisture present in the cellulose.

After the introduction of the charge of cellulose and the fresh nitrating acid has been discontinued, the acid present in the nitration vessel 10 is withdrawn through the pipe 16 and circulated by means of the pump 17 through the pipe 23, the temperature controller 24, and the pipe 25 back to the nitration vessel where the acid is delivered in spray form by means of the nozzle 26. This circulation of acid is continued until the nitration of the cellulose is as complete as the strength of acid employed will give. This normally requires circulation for from 15 to 30 minutes after the charge of cellulose has been fed into the nitration vessel. In the process of nitration some heat is given off, resulting in the warming of the acid. In order to compensate for this temperature rise, the acid is cooled in the heat interchanger 24 during its circulation from the bottom of the nitration vessel back to the spray nozzle 26. This may be accomplished by passing water at ordinary temperature, or chilled water, through the inner compartment of the temperature controller 24. This cooling of the nitrating acid prevents local heating in the nitration vessel and thus obviates danger of fuming, fire, or explosion.

After partial nitration of the cellulose has been effected in the above described manner, the spent nitrating acid is then replaced by an acid stronger in nitric acid, say a 60—22—18 acid, and the nitration is completed with this acid. Of course, progressively stronger nitrating acids may be used in a 3-step or 4-step process if desired. However, I have found that 2-step process in which treatment with a weaker nitrating acid is followed by a treatment with a stronger nitrating acid, is commercially satisfactory.

In replacing the spent weaker nitrating acid with a stronger nitrating acid, the valve 18 is closed, the valve 22 is partially opened to permit withdrawal of spent acid through the liquid outlet pipe 21, and a stronger acid from a storage tank (not shown) is delivered through the pipe 19 to the pump 17, the valve 20 being open, of course. The addition of stronger acid through the pipe 19 and the withdrawal of weaker acid through the pipe 21 are effected relatively slowly in order to avoid intermingling of the two nitrating acids. For example, I have found that it ordinarily requires in the neighborhood of one-half hour satisfactorily to displace the weaker acid with the stronger acid. Although the stronger acid has a slightly higher density than the weaker nitrating acid, there will be but little mixing of the two acids if the strong acid is added slowly and the weak acid is withdrawn slowly, as suggested above.

After the weak acid has been completely displaced with strong acid, the valves 20 and 22 are closed and the valve 18 is opened. This provides for circulation of the stronger acid from the vessel 10, through the pipe 16 to the pump 17, through the pipe 23, through the temperature controller 24 where the acid is cooled in the above described manner, through the pipe 25 and back into the top of the nitration vessel 10 from the spray nozzle 26. This circulation is continued as in the first nitrating treatment until nitration has been completed, which ordinarily requires in the neighborhood of 20 minutes.

After the completion of the nitration with the strong nitrating acid, the inlet pipe 19 is connected to a source of weak wash acid (not shown), the valve 18 is closed, and the valves 20 and 22 are opened. This results in the displacing of the strong nitrating acid with a weak wash acid, which may be a 45—5—50 acid. A spent nitrating acid diluted to about 50% with water will serve as a suitable wash acid.

As will be apparent, the dilute wash acid will be cooled as it passes through the temperature controller 24 so that local heating is avoided when the diluted acid comes in contact with the stronger acid in the nitration vessel prior to the complete discharge of the liquid through the liquid outlet pipe 21.

After the strong nitrating acid has been completely displaced by wash acid, in the manner described above, the liquid inlet pipe 19 is then connected to a source of water (not shown) and the weak wash acid is completely displaced with water, which is cooled by the temperature controller 24 before being introduced into the nitration vessel 10. After the weak wash acid has been completely removed and the nitration vessel filled with water, the nitrocellulose in the vessel may be permitted to stand for about 30 minutes in contact with water to permit diffusion of absorbed acid in the fibers into the wash water. The water is then withdrawn and replaced with fresh water for the purpose of again washing the nitrocellulose. The washing is preferably continued until less than ½% of acid, and preferably less than $\frac{1}{10}$% acid (calculated as H_2SO_4) is present in the outflowing wash water.

After the cellulose nitrate has been completely washed, the valve 15 is opened and the cellulose nitrate is discharged through the pipe 14 and carried, as by a stream of water, to the customary purification vessels.

In the practice of the present process, the first nitration step requires that the acid be added from the top but the second nitration step may be effected either by pumping the acid in at the top or by pumping it in at the bottom and overflowing it at the top. However, there appears to be no gain from this reversal of direction.

As pointed out above, the finely divided cellulose to be nitrated is introduced from the pipe 11 simultaneously with the addition of weak nitrating acid delivered through the nozzle 26. The reason why the cellulose is not introduced into the nitration vessel first and then the nitrating acid added either from above or from below is that such a procedure will not work. What happens is that the first cellulose coming into contact with the nitrating acid uses up the HNO_3 but leaves the H_2SO_4 which then comes into contact with fresh cellulose and by partial hydrolysis, causes it to jell with the result that the whole vessel would be plugged by this layer of jell and no more circulation could take place. Cellulose nitrate is stable toward H_2SO_4 but cellulose is quickly hydrolyzed to a jell by any strength of sulfuric acid above about 30%. By the simultaneous addition of the finely divided cellulose and the nitrating acid, this partial hydrolysis and jelling is avoided in the present process.

The following specific examples of the practice of the present process are illustrative of the invention:

Example 1.—A nitrating acid having a 60—18—22 composition was run in to a nitration vessel to a depth of six inches. Then, with a continuous drawing off of acid at the bottom, a charge of shredded, purified, undried cotton linters having a moisture content of 8%, and a spray of the above mentioned nitrating acid were simultaneously and continuously run in at such a rate that the linters were covered by nitrating acid, until a layer of cellulose two feet in depth was obtained. This required twenty minutes. Circulation of the nitrating acid by drawing it off from the bottom and cooling enroute, was continued for twenty minutes. A sample of the nitrated cellulose (removed, washed and analyzed) showed a nitrogen content of 8.0% N. In this particular case, the rate of flow of the acid during circulation was approximately two and one-half inches per minute in the nitration vessel.

As indicated above, the first nitration was effected in approximately twenty minutes after the charge of cellulose had been fed into the nitration vessel. Had the thickness of the cellulose layer to be nitrated been increased, say to six feet, then the time required for the nitration would have had to be increased, to approximately three times that given for this particular example. Had the temperature of the nitrating acid been increased, it would have had no effect on the period required for completion of the nitration. In other words, the time required for

the nitration depends primarily upon the depth of the cellulose layer.

After the initial nitration had been effected the weak nitrating acid was then displaced by a stronger nitrating acid of a 61—22—17 composition, by adding the same at the top of the nitration vessel and continuing the drawing off of the weaker acid at the bottom until all the weaker acid had been displaced. This required thirty minutes. Faster removal would have intermingled the two nitrating acids. After the weaker acid had been displaced by the stronger acid, circulation of the acid, in the manner described above, was continued for another twenty minutes to complete the nitration. A sample of the cellulose nitrate (removed, washed and analyzed) showed a nitrogen content of 13.1%.

In the above mentioned nitration steps, the temperature within the nitration vessel was maintained at approximately 20° C., the temperature being controlled by the regulation of temperature in the temperature controller 24 through which the nitrating acids were passed during the circulation of the acids, as described.

After the completion of the second nitration, the strong nitrating acid was then displaced by a weak wash acid having a 45—5—50 composition. This wash acid was then displaced by water. After the weak wash acid had been removed and some water passed through, the nitrocellulose in the nitration vessel was allowed to stand thirty minutes in contact with the water to permit the diffusion into the wash water of the acid absorbed in the fibers of the material under treatment. The nitrocellulose was again washed with a small amount of water and then dumped from the nitrating vessel and carried by a trough of water to the usual purification vessels.

Example 2.—Using a bleached wood pulp made by the hydrotropic process of applicant's copending application Serial Number 207,823, filed May 13, 1938, now Patent No. 2,308,564, issued January 19, 1943, and a first nitrating acid having a 63—19—18 composition, and a second acid having a 61—21—18 composition, a nitration was made at 20° C. in a manner similar to that described in Example 1. The differences from the first example were: The percentage of alpha cellulose in the wood pulp was 90%; the time required for wetting down the cellulose was two minutes; and the percentage of nitrogen after the first nitrating acid treatment 8%, and after the second nitrating acid treatment 12.4%.

Example 3.—Using the same strength acids in the same method as Example 2, but using a dry dense, bleached sulfite pulp of bond grade (85% alpha cellulose) which was shredded but poorly, penetration of the particles by the acid was apparently not complete and still a nitrogen content of 8.6% was obtained. This nitrated pulp did not completely dissolve in acetone.

Example 4.—In this case the cellulose material consisted of a hemlock pulp made by removal of the lignin by use of hot strong acetic acid, such pulp having an alpha cellulose content of 91%. Using the acids and conditions specified in Example 2, the first nitration treatment gave a cellulose nitrate showing an analysis of 8.2% N, and after the second nitration 11.9% N.

Example 5.—Using as the first nitrating acid a mixed acid low in sulfuric acid and high in nitric acid, the mixed acid having a 56—25—19 composition, with the type of cellulose and other conditions the same as in Example 1, the first nitration step gave a cellulose nitrate having over 11% nitrogen. The second nitration treatment brought this up to 13.0% nitrogen.

Example 6.—This example was a duplicate of Example 5, except the first nitrating acid was of a reverse type, i. e., a mixed acid high in sulfuric and low in nitric acid. The first nitrating acid had a 74—13—13 composition and, at the end of the first stage of nitration, gave a nitrocellulose of 8.1% nitrogen content and after the second stage 12.9% nitrogen.

Examples could be multiplied but it is sufficient to point out that other conditions of nitration may be varied as understood in the art and with corresponding effects produced. For example, an increase of nitration temperatures from 20° C. to 30° C. and on up to 40° C. increased the speed of nitration, increased the percentage of nitrogen in the product, and decreased the viscosity of the cellulose nitrate of a given percentage of nitrogen when dissolved in the customary solvents.

As will be apparent, by the choice of proper grades of cellulose, proper acid concentrations, proper times, and proper temperatures, the extent of the nitration and the properties of the cellulose nitrate produced can be variously changed with the result that it is possible to obtain nitrocellulose satisfactory for low viscosity lacquers, high viscosity lacquers, plastics, or explosives, as may be desired.

In the commercial operation of the present process, it will be apparent that it is important to avoid waste of the nitrating acids. In a plant, the wash waters would be sent to the waste drains, the strong acid returned to its supply tank for "butting up" to the original strength and the weak nitration acid excess volume (about 10%) due to the water in the cellulose, water formed in the reaction, and some mixing of this acid with strong nitrating acid at one point and with weak wash acid at another point, would be sent to denitration columns for purification and recovery of acids. The balance of the weak nitration acid would be returned to the proper storage tank. It may be found that "butting up" of this weak acid may be required before being reused.

As compared with processes heretofore used, the advantages of the present process are many and important. For example, in the present process the temperature of nitration is controlled externally by controlling the temperature of the acid during circulation thereof in the system. Due to the 2-step washing, first with a chilled dilute acid (about 50% water) and then with pure water, there is little local heat evolved, and so no danger of fuming, as in the prior art where the cellulose nitrate, wet with strong nitrating acid, is brought into contact with water. Furthermore, the control of the temperature of the nitrating acids and washing liquids gives perfect control of the nitration process and also the washing. Hence, fuming, fires and other similar troublesome incidents are avoided. An important advantage of the present process is that large charges are useable. For example, a ton of nitrocellulose can be made at a time without danger of fuming, fire or explosion. The present process also saves more of the strong nitrating acid than any other process. A further advantage is that the cellulose nitrate is washed in the nitrating vessel and with but little dilution of the nitrating acid. This involves use of much less water than other processes.

In addition to the above advantages, there are

other important advantages, particularly with respect to the cost of equipment and also labor costs. For example, the equipment required per pound of cellulose produced is inexpensive. There is no stirring equipment necessary in the nitration vessel, nor movement of the cellulose during nitration. No centrifuge is used or needed. Labor costs are minor, whereas in the usual processes labor costs are a major cost. An important feature is that the yields are excellent, i. e., nearly theoretical, and a very high quality nitrocellulose is produced. A further saving in the cost of manufacture results from the fact that the used or spent acid is clear and clean and, consequently, is easily reworked. Moreover, the cellulose nitrate produced is clean, contains less mineral matter than that produced by other methods, and is readily stabilized.

While I have described in detail the preferred practice of my process, it is to be understood that the details of procedure may be variously modified without departing from the spirit of the invention or the scope of the subjoined claims.

I claim:

1. The process of manufacturing cellulose nitrate which comprises partially filling a nitration vessel with relatively weak nitrating acid, simultaneously introducing into the upper portion of said vessel a stream of finely divided cellulose and a spray of relatively weak nitrating acid, the finely divided cellulose being wet with the spray of said relatively weak nitrating acid before it reaches the level of the body of the acid in said nitration vessel, withdrawing used nitrating acid from the lower portion of said vessel during the introduction of said cellulose and said acid spray, the acid spray being introduced and the used acid being withdrawn at such rates with respect to the introduction of the stream of finely divided cellulose that the cellulose is maintained submerged in acid in said vessel, discontinuing the addition of the cellulose after the vessel has been charged with the total amount of cellulose to be nitrated, continuously withdrawing from said vessel a portion of the acid remaining therein, cooling the withdrawn acid, returning the cooled acid to the vessel, thereafter displacing the used relatively weak acid in the vessel with relatively strong nitrating acid, continuously recirculating said relatively strong acid from the vessel, through a cooler and back to the vessel, displacing the used relatively strong acid with chilled dilute wash acid to partially wash the nitrocellulose, and displacing the dilute wash acid with water to wash the thus treated nitrocellulose.

2. In the manufacture of cellulose nitrate, the improvement which comprises the steps of passing through a body of cellulose a current of nitrating acid of a strength capable of partially nitrating the cellulose, cooling the nitrating acid, passing a current of cooled acid through the body of material to be treated, thereafter passing through the body of partially nitrated cellulose a current of stronger nitrating acid to effect further nitration thereof, cooling the stronger nitration acid, and passing a current of the cooled stronger nitrating acid through the body of partially nitrated cellulose, the cellulose material under treatment being maintained submerged in nitrating acid throughout the practice of said steps.

3. In the manufacture of cellulose nitrate wherein cellulose to be nitrated is subjected to the action of nitrating acid in a nitration vessel, the improvement which comprises adding the nitrating acid and cellulose simultaneously to the nitration vessel in streams, the stream of cellulose being wet by the stream of nitrating acid during such addition.

RALPH H. McKEE.