Feb. 9, 1943. F. NESSLER 2,310,862

METHOD OF WASHING NITROCELLULOSE TO RECOVER NITRATING ACIDS

Filed June 13, 1939 2 Sheets-Sheet 1

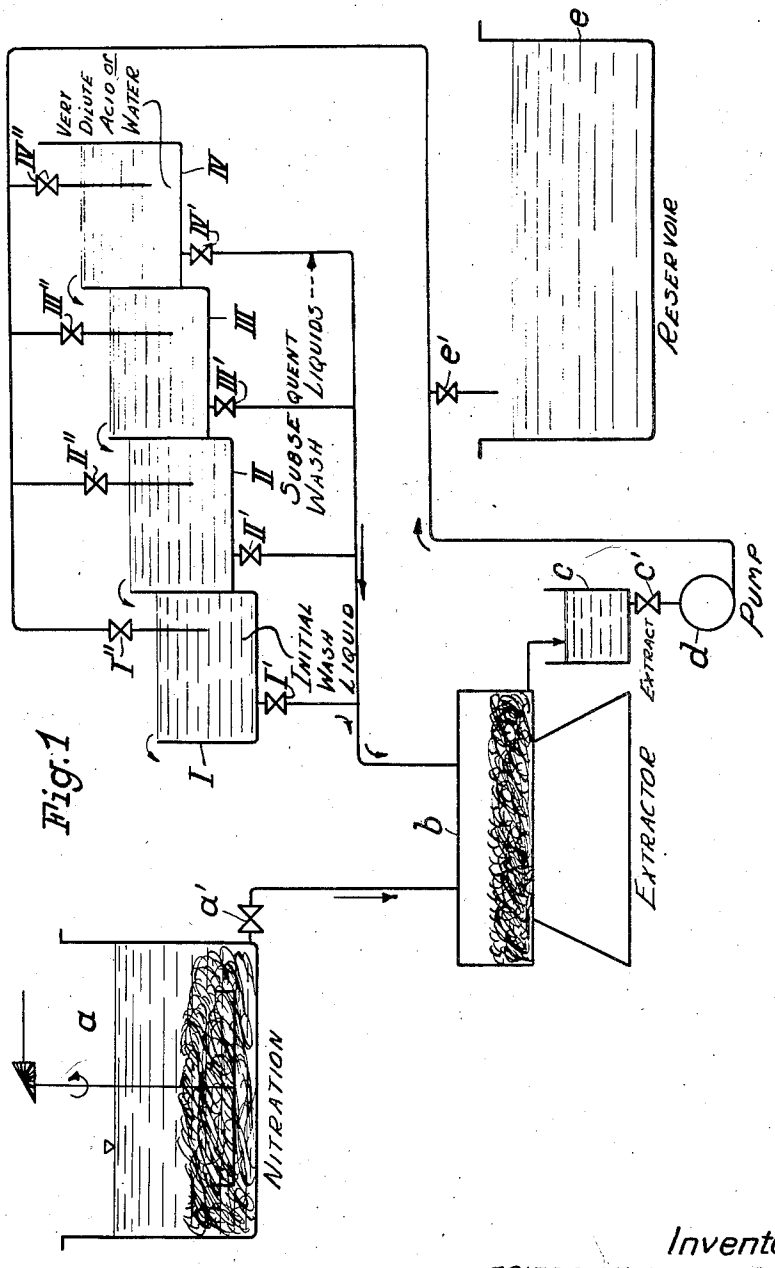

Fig. 1

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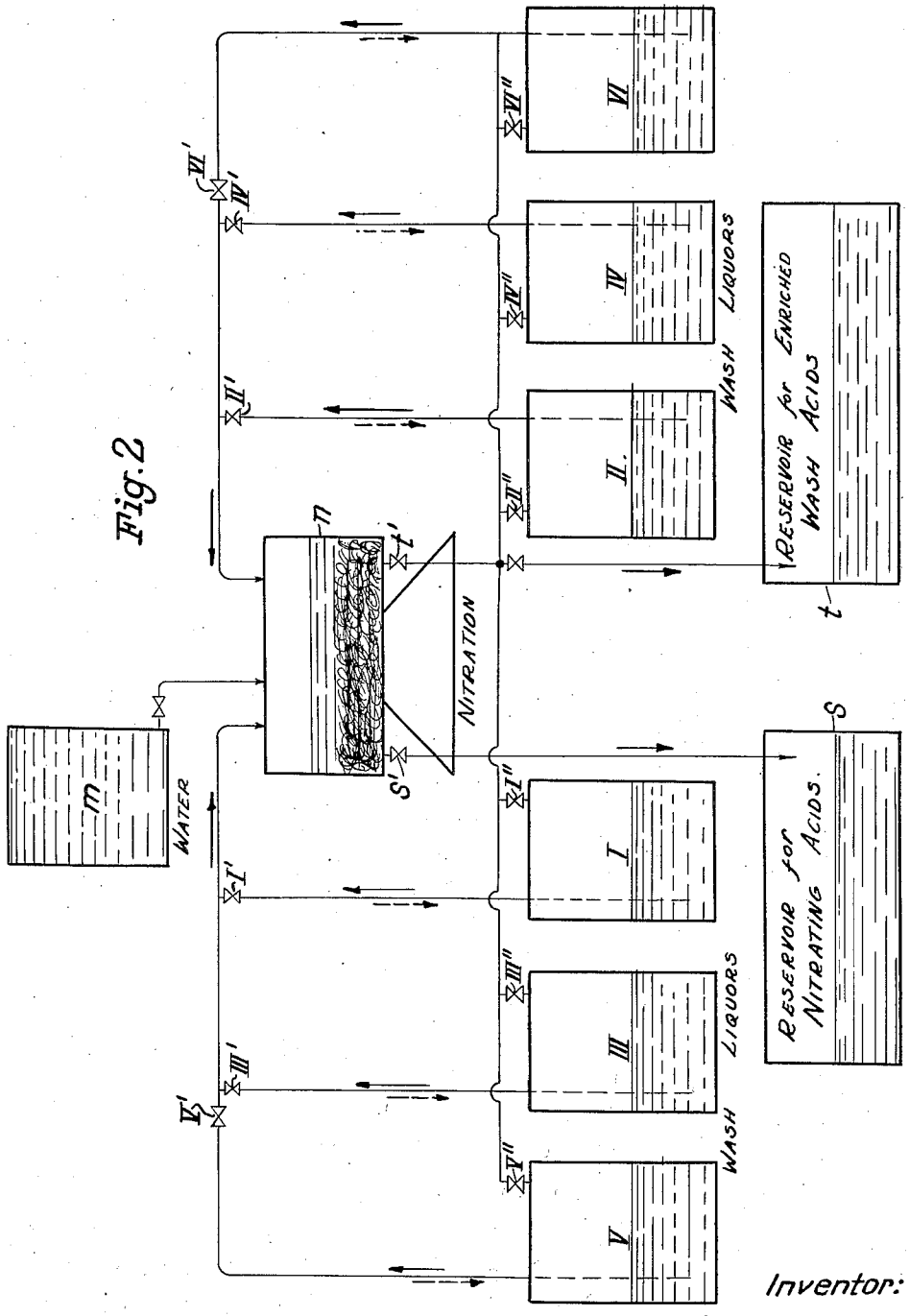
Fig. 2



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METHOD OF WASHING NITROCELLULOSE TO RECOVER NITRATING ACIDS

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1 Claim. (Cl. 260—224)

The invention relates to the recovery of the acid still adhering to the nitrocellulose during its production after the centrifuging and the squeezing out and the other steps of manufacture i. e. the so-called adhesion-acid.

Many attempts have already been made to resolve this problem. A part of these propositions is based on the displacing process of Thompson acording to which a layer of water is applied to the nitrating acid still adhering to the nitrocellulose so as to displace the adhesion-acid out of the nitrocellulose during the discharging of the acid. This method has not been able to gain a solid footing in the industry because it shows considerable drawbacks: It requires an extensive installation for the reason that long periods of nitration are necessary. Furthermore, the yield of the recovery is small and, moreover, the waste acids are diluted to a higher degree, owing to the unavoidable diffusion and the difficulty of the exact separation of the two layers, than in the case where a displacement by water is not effected, so that the costs of the stronger regeneration becoming thereby necessary mostly compensate or even overstep the economies realised by the discovery.

A further series of propositions aims to cover firstly the nitrocellulose eliminated by centrifugal action from the nitrating acid with sulphuric acid or nitric acid of equal concentration which may be cooled. After the displacement of the waste acid, it is then necessary to wash out by means of water the strong sulphuric or nitric acid substituted for the recovered acid. Also these methods have not gained entrance in the practice because, instead of the adhesion-acid, a corresponding amount of the acid used for covering the nitrocellulose is lost. Moreover, the qualities of the nitrocellulose so prepared are varied in an undesired manner, for instance, by the sulphuric acid and by the nitric acid exercising the former a swelling action and the latter an oxydising action upon the nitrocellulose. In the main, also these methods intend to avoid a burning out of the nitrocellulose freed from the leaving acid.

According to the invention, the adhesion-acid can be recovered to a high degree during the production of nitrocellulose, without provoking the described inconveniences, by treating the nitrocellulose, after the elimination of the nitrating acid used in excess, step by step with mixed acid of increasing water content and by eliminating after each treatment the washing acid by centrifuging or squeezing or by means of a similar operation. The washing liquid, i. e. the diluted mixed acid of each step is enriched by the adhering-acid of higher concentration being introduced together with the nitrocellulose in this step. According to the proportion of the nitrocellulose to the quantity of washing acid, the enrichment takes place more or less rapidly i. e. already after one or several employments of the washing acid in the same step. Therefore, the washing acids of lower steps advance after corresponding enrichment and the most concentrated washing acid is continuously or periodically drawn off and worked down or concentrated in any suitable way.

It is generally known—it is true—to realise washing processes by washing out according to the counter-current principle, but the application of this washing principle to the manufacture of nitrocellulose meets the known fact that in the case of the esterification of the cellulose, for instance, into the trinitrate, it is the question of a reaction of equilibrium according to the equation:

$$C_6H_{10}O_5+3HNO_3=C_6H_7O_5(NO_2)_3+3H_2O$$

in which the ester equilibrium is displaced towards the side of the trinitrate only when the produced water of reaction is fixed to a high degree. Therefore, it is common practice to prepare nitrocellulose having a determined content of nitrogen by using mixed acids with an exactly determined small amount of water. Furthermore, it is well known to convert a nitrocellulose having a higher content of nitrogen into a nitrocellulose having a lower percentage of nitrogen i. e. to denitrate the former nitrocellulose by treating this nitrocellulose by means of a mixed acid having a higher content of water. The more surprising is the result obtained according to the invention and consisting in that a denitration of the nitrocellulose does not take place or is effected only to an insignificant degree owing to the treatment of the nitrocellulose step by step with mixed acid of increasing water content. Even in the most disadvantageous cases it has been found a decrease of nitrogen of only 0.1 per cent which can be easily compensated by aiming from the first at the manufacture of a product nitrated to a degree higher by this amount which is possible without difficulties. However, according to the invention, the first washing step of the process is realised by maintaining working conditions avoiding a decomposition of nitrocellulose and, to this end, in this step, there is used a concentration not essentially higher than the concentration corresponding to a total content of acid of about 65 per cent, because a decomposition or a saponi-

fication of the nitrocellulose takes place when higher concentrations are employed.

A further surprising result of the process according to the invention consists in that the burning out of the nitrocellulose is practically avoided. Owing to the fact that the displacement of the acid adhering to the nitrocellulose is effected step by step, also the dilution heat of the adhesion-acid becomes operative only to a limited extent corresponding to the concentration fall actually chosen and is distributed among the several steps. The heat communicated to the different steps can be easily eliminated by cooling because each step is separately drawn off. Therefore, it is advantageous, for instance, in the case of gun-cottons requiring the use of a mixed acid of a higher strength, to work in more steps than in the case, for instance, of technical cottons which are prepared by means of a mixed acid of a lower concentration. As regards the usual washing out in counter-current, the method according to the invention shows also the difference of working in several steps in such a way that the mixed acid employed as second washing water during the first step is used as first washing acid for the second step, whilst the third washing water is employed as second mixed acid and so on.

The method according to the invention can be realised in detail so as to cause each washing acid already after one employment to advance always one step, or each washing acid is used more than once in the same step and, after having been correspondingly enriched, is caused to advance one step. In the last step, there is added water, for instance, by washing out finally the nitrocellulose by means of water. In order to maintain a counter-current, the process can be carried out also in such a way that a portion of the washing liquid of a lower step flows to the next higher step, a corresponding part of the enriched washing acid being taken from the first step, whilst the last step is completed by adding water or diluted acid. In this case it is advantageous to admit water in the last step only in a quantity corresponding to the amount of adhesion acid introduced by the nitrocellulose into the washing process.

The accompanying drawings illustrate schematically in Figures 1 and 2 by way of example two installations permitting the execution of the process according to the invention and showing also the practical details of the method.

According to Figure 1, the nitrating vessel *a* is connected with the acid-hydro-extractor *b* by means of a pipe containing the valve *a'*. The mass of nitrocellulose coming from the vessel *a* through the valve *a'* is freed in the centrifugal apparatus *b* from the excess of nitrating acid and the excess acid flows from the centrifugal apparatus *b* towards the container *c*. This container *c* is connected by means of a pipe containing a valve *c'* with the suction orifice of a pump *d*, the pressure orifice of which is in communication through the valves I'' to IV'' with four receptacles I, II, III, IV arranged in the form of steps whilst the centrifugal apparatus *b* communicates through the valves I' to IV' with the receptacles I to IV.

First, the receptacles I to IV are separated from the pump *d* by closing the appertaining valves I'' to IV'' and the pump *d* presses the separated acid from the container *c* through the valve *e'* into the collecting reservoir *e*. Then, the valve *e'* is closed and the valves I' and I'' are opened and washing liquid having a total content of acid of, for instance, 50 per cent is conducted from the receptacle I through the valve I' to the nitrocellulose in the centrifugal apparatus *b* and still containing the adhesion acid and, after having traversed the centrifugal apparatus *b* and the container *c*, this liquid is forced by the pump *d* through the valve I'' again into the receptacle I. A corresponding portion of enriched washing acid representing recovered adhesion-acid enriched, for instance, to 50 to 60 per cent flows out of the receptacle I over an overflow border.

In an analogous manner, after having closed the valves I', I'' and opened the valves II', II'', the washing acid of the receptacle II and, then, after having closed the valves II', II'' and opened the valves III', III'', the washing acid of the receptacle III and, finally, after having closed the valves III', III'' and opened the valves IV', IV'', the washing acid of the receptacle IV is conducted and employed. In each of these four steps I to IV, there is a portion of washing acid of lower concentration which flows into the next higher step. In the last step, water or very diluted acid is employed. Instead of four steps, also a smaller or higher number of steps can be provided in the case of need. The washing acids may be continuously cooled.

According to Figure 2, there is provided a nitrating centrifugal apparatus *n* from which, after the termination of the nitration, the excess acid is drawn off through the valve *s'* into the collecting reservoir *s*. The first step is realized by using the most concentrated washing acid which has been enriched in the former processes but does not contain essentially more than 65 per cent total acid. The receptacle I constitutes a pressure vessel containing this washing acid. The acid is forced by means of compressed air from the receptacle I through the valve I' into the centrifugal apparatus *n* whereby the nitrocellulose contained in the apparatus *n* is washed. The washing fluid of this step which has been still more enriched is drawn off from the centrifugal apparatus *n* through the valve *t'* into the collecting reservoir *t* in order to be worked off in any suitable way. Hereupon, the nitrocellulose contained in the centrifugal apparatus *n* is washed by means of the less concentrated washing acid of the pressure receptacle II which is admitted through the valve II' to the centrifugal apparatus *n*, and the excess washing acid is conducted through the valve I'' into the pressure receptacle II where it is then employed for the next nitration in the first step.

In an analogous manner, the more and more diluted washing acids of the pressure receptacles III to VI are used by manipulating correspondingly the appertaining valves III'' to VI'' and III' to VI'. The washing acids may be cooled at the same time if necessary. Finally, a washing is effected by means of water taken from the measuring container *m* and which is admitted to the pressure receptacle VI after having traversed the centrifugal apparatus *n*. It is advantageous to use not more water than adhesion-acid is introduced into the washing process with respect to the concentration desired in the first step. The latest residues of acid eventually still adhering to the nitro-cellulose can be eliminated by washing out the nitro-cellulose by means of an excess of water taken from the container *m*. In the most cases, however, this washing out is no more necessary and the nitrocellulose can be rendered stable and dried in the usual manner.

The process according to the invention permits the recovery of 50 to 90 per cent of the adhesion-acid according to the manner of working. Furthermore, it is important that the whole recovered adhesion acid is gained in a high concentration, for instance, of 50 to 65 per cent of the total content of acid. Owing to the fact that no strange acid but only water is introduced into the washing process and that the ratio between, for instance, sulphuric acid and nitric acid varies only unessentially during the washing process, the working up and the concentration of the recovered adhesion-acid to mixed acid is especially economical and remunerative although another working up and employment of the adhesion-acid is also possible.

Having now described and ascertained the nature of my invention I declare what I claim is:

In a process for removing and substantially recovering concentrated nitrating acid still adhering to a nitrocellulose material after nitration while substantially avoiding decomposition of the nitrocellulose in which the nitrocellulose is washed step by step with separate volumes of acid washing liquids of decreasing concentration, the steps comprising initially washing said material with a relatively large volume of an aqueous washing liquid taken from a first container and comprising a mixture of sulfuric acid and nitric acid of not more than 65% total acid contents but which is substantially not less than 50% concentration to avoid decomposing the nitrocellulose, recovering said washing liquid having an acid concentration greater than that before use, thereafter washing said material with a second volume of aqueous washing liquid taken from a second container and comprising a mixture of sulfuric acid and nitric acid of acid concentration less than that of washing liquid first used, returning the increased volume of washing liquid obtained as a result of said second washing operation to said second container, thereby displacing from said second container an equivalent volume of such increased washing liquid and removing such displaced liquid to said first container, thus recovering individual volumes of washing liquids of increased acid concentration, and repeating such washing operations with liquid of decreasing concentration to produce a nitrocellulose material substantially free of adhering acid, which nitrocellulose is substantially undecomposed.

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