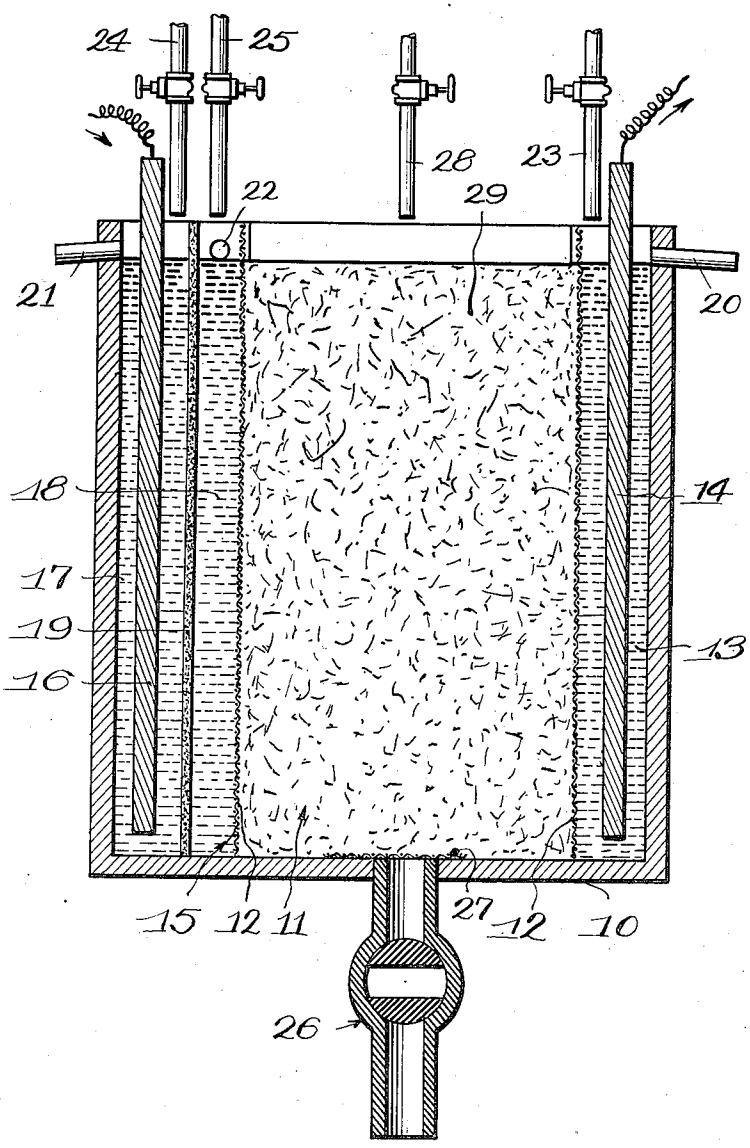
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METHOD OF TREATING NITRATED CELLULOSE FIBERS

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METHOD OF TREATING NITRATED CELLULOSE FIBERS

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1 Claim. (Cl. 204—1)

The present invention relates to the manufacture of derivatives of cellulose and like solids which are subjected to chemicals for reaction therewith to form derivatives having a solid form. It has particular reference to fibers of cellulose in the manufacture of esters of cellulose, such as the nitrate and the acetate.

The nitration of cotton or wood fibers for the manufacture of nitro-derivatives, such as gun cotton, soluble cotton, and the lower nitrated forms exemplified by the collodion type of materials, is chosen for the purpose of illustrating the invention, its objects, its nature, and its advantages. It is chosen for the reason that large quantities of nitrocellulose are produced annually, and because its procedure is generally standardized and is perhaps oldest and best known of the esterifying processes.

It has long been a practice to treat cotton fibers, such as linters, and more recently treating chemical wood fibers, with a nitrating acid known as "mixed acid". This comprises a regulated mixture of sulphuric-acid and of nitric acid and a regulated proportion of water. The nitric acid is the essential reactive ingredient, but the sulphuric acid is present as a dehydrating agent to induce the reaction and to take up the water liberated in the reaction. Whether or not the sulphuric acid takes part in the reaction is immaterial.

However, it is known that during the process there are formed some products of the fiber constituents and sulphuric acid, which are not stable compounds. It is believed that other unstable compounds or products are also formed, perhaps of dehydration, which eventually become stable in the process regularly employed to treat the fibers after the nitration reaction. This step or process is called "stabilization", and it is to this phase of the nitration process that the preferred application of this invention relates. Other phases of the invention will also be discussed.

The mixed acid is a very strong and concentrated acid mixture, the unused portion of which is customarily recovered. The cellulose, whether it be cotton fibers, wood pulp fibers, or other forms of cellulose, hereinafter referred to as "pulp", is ordinarily separated from the acid by centrifugal force, the nitration mass of pulp and acid being dumped into a whirling "wringer." This effects a partial separation and large amounts of spent acid are readily recovered.

The pulp from the wringer contains residual acid which adheres to it against the forces of the wringing, and other acid which is united to the pulp by bonds of a chemical nature. The pulp is customarily removed from the wringer and submerged in water, a process designated as "drowning". A large amount of residual acid that is held mechanically is removed by this process of dilution. However, the drowning is not effective to remove all the acid and other impurities that must be removed or destroyed to produce stabilized nitrocellulose. Further treatment is carried out over a prolonged period of time which appears necessary to obtain the stabilized product of commerce. A number of variations in subsequent treatment are known, and some are rigidly specified by ordinance divisions of the principal nations of the world for the production of munitions.

The U. S. Navy specifications are referred to in "Technology of Cellulose Esters" by Worden, Edition of 1921, Vol. 1, part III, pages 2260 to 2262. It is a very complex procedure and includes boiling for 40 hours with not less than four changes of water. It is then pulped in fresh water in the presence of sodium carbonate. It is then poached by boiling 6 hours in fresh water, using carbonate of soda in specified proportion. Then it is boiled for 6 hours again in clean water, with five changes of water, and finally is given ten cold water washings of one half hour each. Further treatment is specified, all requiring manipulation and agitation. The specifications include less than 0.4% ash as a requirement.

The British specifications for stabilization, also found in the above reference, require a minimum time of 42 hours with active manipulation. They require less than 2% mineral content in the dry nitrocellulose.

All the procedures require heat, agitation, filtration, chemical treatment, large amounts of water, a long period of time, and a source of sufficiently pure water. In the present invention the use of chemicals is dispensed with. A very small amount of water is required. Even water containing considerable amounts of mineral matter may be used, and the water itself becomes purified along with the nitrocellulose. Little or no agitation is required, and manipulation may be minimized. Boiling is not necessary and no steam is required.

In all the common treatments for stabilization more or less mineral matter is present through the natural hardness of water or the materials used to treat the water, or because of the use of chemicals in the stabilizing process. The pulp, in the form of fibers especially, has a very large surface area in proportion to its mass, and the electrical

forces of absorption cause considerable amounts of mineral and other impurities to be held to the surface of the pulp in such a way that ordinary processes of leaching or dissolution, as by water, do not completely remove these impurities, even though they may by nature be soluble. In consequence, the washed product now in general use contains adsorbed impurities.

One of the objects of the present invention is to stabilize nitrated cellulose pulp by subjecting it to the action of an electric current.

Another object of the invention is to treat pulp of the nature of nitrated cellulose to electrodialysis to remove both electropositive and electronegative impurities therefrom.

Another object of the invention is to break down by the use of an electric current the unstable compounds, especially those containing acid in their composition and which decompose or hydrolyze to liberate free acid in the usual stabilization processes.

A further object of the invention is to produce a solid acid derivative of a carbohydrate type of solid, such as an ester of cellulose, like nitrocellulose which contains less adsorbed impurities than similar products treated by processes heretofore employed; which products may be made substantially free from acids and/or inorganic impurities, and colloidal impurities.

Various other and ancillary objects and advantages of the invention will become obvious or will hereinafter be referred to throughout the following description and explanation of the invention.

I have made tests upon commercial stabilized forms of soluble cotton containing, as purchased on the market, 30% ethyl alcohol, in order to determine whether the union between the nitric acid and the cellulose molecule is sufficiently stable to prevent destruction of the nitrocellulose when the latter is submerged in ordinary water and the mass subjected to the action of a direct current carried by the suspension. A sample of the commercial nitrocellulose was washed free of its alcohol content and submerged in water to form a thick slurry. It was placed in a compartment cell and a current of electricity passed through it at a density of about 2 amperes per sq. ft. of cross sectional area of suspension for 24 hours, the temperature being at no time over 70° C. No destruction was found by the usual tests for nitrocellulose. The solubility, the viscosity characteristics, the appearance, the stability, and the nitrogen content showed that no appreciable effect was produced upon the nitrocellulose base by the prolonged flow of current. A considerable reduction in ash content was found.

In order further to test the effect of the electric current on the nitrocellulose when acid is present in the suspension, freshly nitrated wood pulp was drowned to remove excess acid and the drowned product submerged in water and subjected to the passage of a direct current of electricity. A considerable amount of free and loosely combined acid is present in drowned pulp, and it was found that the presence of these acids did not cause the ultimately desired nitrocellulose base to break down under the action of the current. It was found, however, that the unstable esters or other compounds were more quickly and more easily broken up or converted into suitable stable forms than in the ordinary stabilizing processes. I have found that in at least 7 to 10 hours a quiescent mass of submerged pulp carrying current may be sufficiently stabilized for the formation of soluble cotton for use in lacquer.

As a specific example of the invention the following detailed description and discussion is given, referring to the accompanying drawing as an example of the type of cell which may be employed.

An insulating box **10**, such as a wooden box, is divided into electrode and pulp compartments by suitable diaphragm material. A pulp chamber **11** is formed having two opposing walls of diaphragm sheets, such as thick canvas or duck **12**, capable of confining the pulp in a limited region of the liquid which lies in the cell on both sides of the two diaphragms.

A cathode chamber **13** lies on one side of one diaphragm **12** and contains a suitable electrode **14** to function as cathode. It may be in the form of rods, slabs, or screen of nickel, Monel or other metal.

An anode compartment **15** lies behind the other diaphragm **12** and contains an anode **16**, preferably of carbon or graphite to minimize corrosion. I prefer to have the anode compartment subdivided into an electrode compartment **17** and a flushing compartment **18** by an acid resisting diaphragm of low diffusing power, such as a porous silica plate **19**.

The compartments **13**, **17** and **18** have overflow outlets **20**, **21** and **22** respectively, and valved water-feeding means **23**, **24** and **25** respectively. Pulp compartment has valved outlet **26** at the the bottom with an insulating screen, such as cloth netting **27**. A water-feeding means **28** is also indicated for adding water to the pulp compartment.

Into the pulp chamber I place water in which may be suspended the solid product to be treated, such as the nitrated fibers of chemical wood pulp derived from the drowning process which follows nitration. The pulp suspension which is formed is indicated at **29**, and may vary in concentration. It should not be too thin, as the process will not operate efficiently. It should not be so thick that the fibers are tightly packed so as to substantially close water channels through the mass. A thick slurry of about 5% nitrocellulose is satisfactory.

Water is placed in the remaining compartments, but acid could be placed in the anode compartment containing the electrode in order further to strengthen the acid. The level of the liquids in the various compartments is made such that there is a minimum hydrostatic pressure to induce undesirable diffusion of liquid through the diaphragms. An electric potential is applied to the electrodes preferably such that a direct current flows from anode to cathode, passing through the suspension. The voltage applied and the resistance of the cell will determine the strength of current which flows. A current of about 2 amperes per square foot of cross sectional area of suspension is sufficient, but the exact value of the current is immaterial and affects primarily the time of the process. The greater the distance between the diaphragms, the longer will be the time to bring the mass to a definite stage of completion for a given current. Increased current gives more heating effect, and the heat may be regulated by control of the current or the application of cooling means if desired. Temperature does not materially affect the process.

I prefer to let the current flow for a sufficient length of time determined by the size of the cell, the strength of current, and the desired degree of completion. It may be continued until tests show

the pulp to be sufficiently pure or sufficiently stabilized, using any one of well known tests.

For producing soluble cotton I prefer to use as raw material the pulp obtained by using the nitration process of W. C. Wilson, disclosed in his copending application Ser. No. 119,995, filed July 1, 1926, now U. S. Patent No. 1,883,215, issued October 18, 1932, by means of which a prepared cellulose may be nitrated to produce a product with low viscosity characteristics, commonly required for lacquers. The product of this nitration process may be stabilized and used for lacquer manufacture without the special treatments ordinarily employed for the lowering of viscosity characteristics. Accordingly the present invention used in combination with the said nitration process of said application has the advantage that the purified low-ash product obtained by electrodialysis need not be associated with water or other chemicals to effect the lowering of viscosity, and there is therefore no opportunity in such a process for introducing additional impurities, such as inorganic matter and electrolytes.

Where requirements other than stability are made the current may be continued until all or a predetermined quantity of an impurity has been removed from the pulp, whether it be acid which moves to the anode compartment, or positive or negative colloidal particles which move toward the cathode or anode respectively, or metallic substances such as the ions of sodium, calcium, magnesium, etc., that move to the cathode.

I prefer to flush the electrode compartments with fresh water, either continuously or intermittently to carry the migrated impurities out of the cell. In flushing the anode compartment I may consider the conservation or concentration of acid in the electrode compartment 17, and may flush the compartment 18 when acid concentration therein is too high and likely to diffuse back into the pulp chamber. By the arrangement shown the special acid compartment 17 may be used as a collecting chamber for concentrating acid. This advantage is to be compared with the disadvantage of the ordinary stabilizing processes where acid is removed by processes of extended dilution. In the beginning of the electrical treatment with direct current the migration of acid will be heaviest and a considerable quantity will be concentrated about the anode in the absence of flushing. Later, near the end of the purification treatment it is desirable to have a low acid concentration on the anode side of the pulp chamber.

It is to be considered that the present invention contemplates treatment of nitrated fibers to stabilize them, of stabilized nitrocellulose and other solids to purify them, and of such other products as have been or may be hereinafter referred to.

The invention is particularly applicable to releasing adsorbed impurities not readily removed by dissolution processes, even though the impurities be ordinarily soluble. Adsorption is believed to be an electrical phenomena accompanied by a neutralization of opposite charges and the release of energy. The application of an electric potential appears to weaken the adsorbing forces, to supply the energy which permits desorption. By the flow of current the impurities are at least released to some extent from the forces of adsorption. While this condition exists the liquid and pulp may be mutually separated during the flow of electric current through the mixture. This may be accomplished in the cell described by opening the drain 26. The water then carries away the impurities which would, but for the current, normally be adsorbed by the pulp. The separation may also, and would preferably be effected by separating the pulp from the liquid in such a way that when separated, the pulp is out of the path of the current. For nitrocellulose this will decrease the possibility of accident.

An alternative procedure is to flush out the pulp chamber with fresh water as current flows through the mass, especially during the first part of the treatment at which time the acid concentration is highest. Flushing may be intermittent or continuous.

The unstable compounds which are broken down in ordinary stabilization processes are believed to include loose compounds between acid and cellulose, such as sulphate esters. They are formed in concentrated acid, probably by the laws of mass action, and hence decompose in diluter acids by the same laws. The decomposition, or hydrolysis, is slow and at best requires from 6 to 12 hours boiling, in acid, followed by manipulation to remove acid from the fiber. The present process of electrodialysis appears to speed up the normal tendency of these compounds to decompose, and completes the hydrolysis simultaneously with the removal of the acid. The effect of the current appears to be to remove the hydrolyzed acid product from the source of hydrolyzing unstable compound, and also to weaken the forces of union by reason of the electric potential. In accordance with these views the process of washing fibers during the flow of current therethrough would be expected to stabilize the mass at an increased rate, as well as to purify the fibers of adsorbed materials.

In the ordinary stabilizing processes where large amounts of water are used and wasted, the pulp readily adsorbs minerals and other impurities and these may be carried away by the pulp into the remainder of the steps employed upon the material. These impurities account for the ash content of commercial nitrocellulose. They are present in finishing lacquers, and in gun cotton, and perhaps are one cause of the measurable deterioration of these materials, especially in light and heat. From other experiences with the effect of adsorbed mineral and other ingredients in fibrous material, I am of the impression that the impurities may catalyze destructive reactions.

The colloidal impurities that can be removed by the process may be colored ones, and the reduction of them in quantity, or their absence, renders the product less colored, and permits the manufacture of a better grade of product. Such a product may be employed in lacquer formation to produce a lacquer, or a nitrocellulose solution with a greater degree of clarity.

I do not limit the invention to removing the impurities during stabilization. The invention in its broadest aspect contemplates treating cellulose esters, or nitrocellulose which has been stabilized, to the action of an electric current in water suspension. Nitrocellulose or other esters treated or purified by means of this invention may have a reduced ash content, or may be substantially ash-free. Nitrated cellulose may readily be obtained which has less than 0.1% ash.

Purified esters may be employed with suitably pure organic solvents to preserve the favorable conditions secured by purifying the ester according to this invention. Solvents and other materials to be associated with the purified product may be chosen with a view to minimizing the introduction of impurities into a composition in-

volving the purified ester. Sufficiently pure organic solvents may be obtained by distillation. Other organic substances may be employed in their best known pure forms, and purer forms may readily be produced in some instances by well known methods. Gums and resins, plasticizers, and the like may be chosen which are free from mineral ingredients where it is desired to make low ash, or an ash-free product involving the purified ester. Gun cotton for high explosives, pyroxylin plastics, filaments and films, lacquers, and the like may be made which are highly pure and better than is permitted by use of products known heretofore.

As an example of a composition involving a purified ester, the following formula for a nitrocellulose lacquer is given, it being understood that all the ingredients named are to be low in one or more specific impurities, for example being ash-free:

	Per cent
A solvent	75
A base	25

Solvent	Percent	Base	Percent
Purified amyl acetate	20	Purified nitrocellulose	50
Purified ethyl acetate	20	Purified dibutyl phthalate	25
Purified butanol	15	Purified glycerol phthalic acid-ester resin	25
Purified toluol	45		

Such a lacquer is useful in electrical insulation work, wherein the absence of acidity, electrolytes, minerals, etc., gives it more desirable electrical properties. It is of course not essential in making an improved lacquer or other composition that all the ingredients of the composition be highly purified, such as being ash-free. The use of ash-free or low-ash nitrocellulose of this invention contributes to a lower total ash for a given composition over that which would obtain using the present available forms of nitrocellulose. In the case of lacquer the absence or the reduction in quantity of mineral and other impurities in the solid nitrocellulose gives to solutions of the nitrocellulose a greater degree of clarity and freedom from color.

It is to be understood that much of the foregoing discussion refers to both cellulose acetate and cellulose nitrate. The invention contemplates processes and products of either variety of ester of cellulose, and of other materials in which like conditions exist, it being well known that other esters are known. I also contemplate application of the invention to other materials such as derivatives of cellulose which may be esterified without the base losing its solid form. Other forms of carbohydrates may be esterified in processes chemically analogous to those dealing with cellulose and its derivatives. For example, starch in granular form may be nitrated and acetylated without loss of its granular form. Such esterified granules may be treated by electrodialysis without departure from the spirit and scope of the present invention.

However, I prefer to consider that the invention in its most practical embodiment is best applicable to fibrous materials, such as cellulose. Fibers are relatively large as compared to granules; they mat well; they permit filtrations without difficulty; they permit use of rather coarse and open diaphragms in the electric cell through which colloidal materials may easily migrate in the process of purification. In certain respects fibers offer special advantages in the conduction of electricity.

I consider the nitration of cellulose as the preferred field for practice of the invention. The process uses very little water and permits manufacturing operations where large amounts of water are not economically available. The water employed need not be pure and may be purified in the practice of the invention as an incident thereto. The acid removed may be concentrated and not lost as heretofore. The process is more rapid, and requires less equipment, labor and manipulation. Steam and heat are not essential.

The product is distinctly purer in itself than products obtained heretofore, and it may be employed with associated substances to make higher grade commercial products than have heretofore been available.

I aim to set forth the invention in all the aspects herein described and referred to, and in the foregoing I do not limit the invention short of its scope as presented in the accompanying claim.

I claim:

A method of treating nitrated cellulose fibers derived from a nitration reaction which consists of suspending the fibers in water, passing a current of electricity through the suspension, and changing the water during the flow of electric current.

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