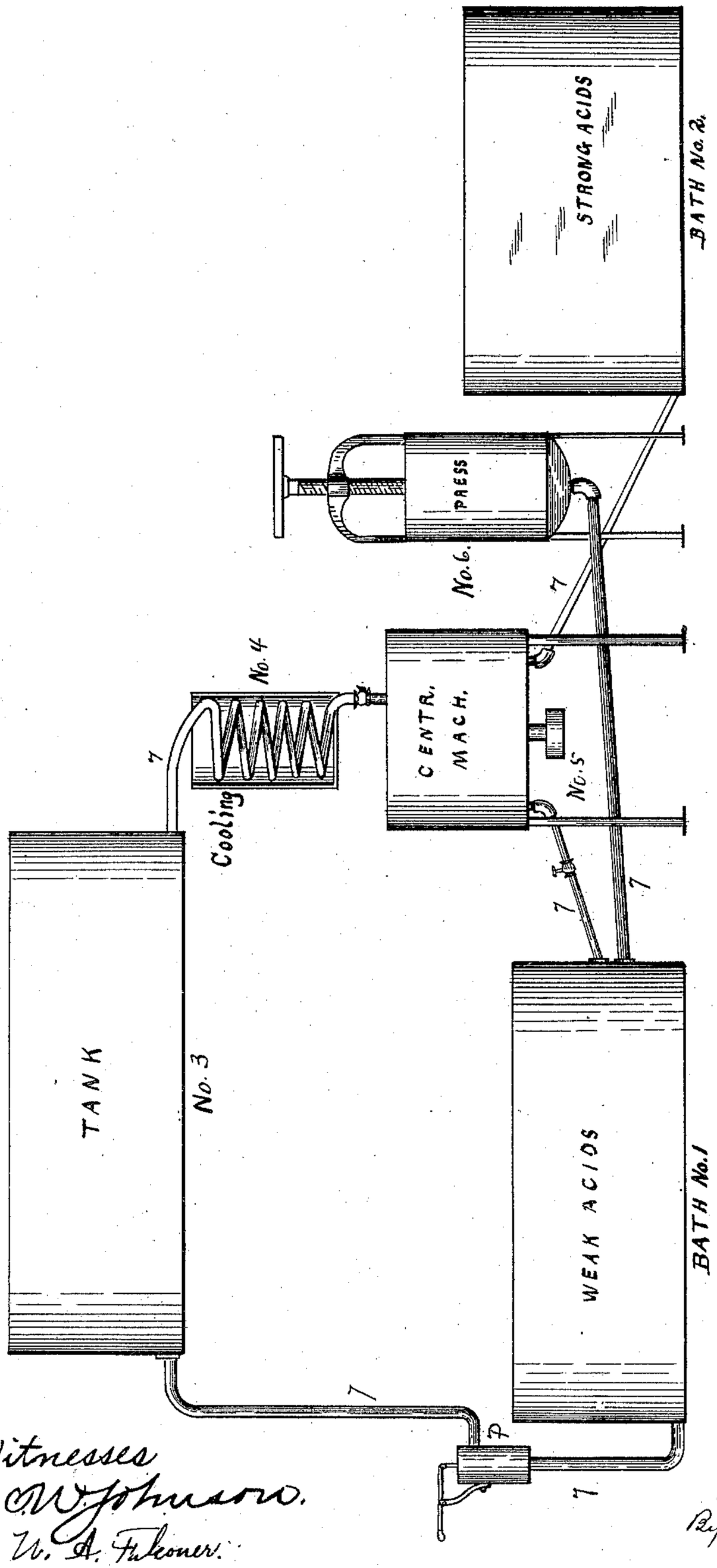
(No Model.)

H. MAXIM.

PROCESS OF MAKING NITROCELLULOSE.

No. 474,778. Patented May 10, 1892.



Witnesses
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UNITED STATES PATENT OFFICE.

HUDSON MAXIM, OF NEW YORK, N. Y., ASSIGNOR TO THE COLUMBIA POWDER MANUFACTURING COMPANY, OF SAME PLACE.

PROCESS OF MAKING NITRO-CELLULOSE.

SPECIFICATION forming part of Letters Patent No. 474,778, dated May 10, 1892.

Application filed May 14, 1891. Serial No. 392,701. (No specimens.)

To all whom it may concern:

Be it known that I, HUDSON MAXIM, at present residing at the city of New York, in the county of New York and State of New York, have invented certain new and useful Improvements in Methods of Producing Pyroxyline, of which the following is a specification, reference being had therein to the accompanying drawing.

My invention relates to the manufacture of nitro substitution compounds of cellulose—such as pyroxyline or gun-cotton—and is chiefly designed to provide in a more simple and efficient manner than heretofore for the production of trinitro-cellulose or nitro-cellulose of the highest degree of nitration.

The object of my invention is to produce pyroxyline of various degrees of nitration, such as dinitro-cellulose and trinitro-cellulose, but more especially the highest nitro compound—that is to say, trinitro-cellulose or gun-cotton proper—with the consumption or expenditure of a less quantity of acids and with less labor than has been heretofore required, and consequently at a correspondingly lower cost per pound for the gun-cotton produced.

In carrying my said invention into practice I prefer to employ two immersion-baths of the mixed acids, each bath being of different strengths and the proportion of nitric and sulphuric acids being slightly different in each bath. The acids of the second bath are more highly concentrated than the acids of the first bath, and the proportion of the nitric to the sulphuric acid is greater in the second bath, and the waste acids of the second bath are utilized for replenishing or restoring the strength of the acids of the first bath. Each bath should contain a quantity of the mixed acids from fifty to one hundred and fifty times the weight of that of the cellulose to be immersed therein. The cellulose is placed in the first bath and is allowed to remain therein until about from one-half to two-thirds of the conversion of the cellulose into gun-cotton or trinitro-cellulose has taken place and until thoroughly converted into a lower nitro compound, such as dinitro-cellulose, or thereabout, but of course into as high a nitro compound as may be possible with the acids employed. The time necessary for a thorough conversion into dinitro-cellulose in the first bath depends upon the strength and proportion of the mixed acids in this bath and the temperature at which the bath is kept and the character and preliminary treatment of the cellulose before immersion therein. The temperature at which I usually keep the first bath is from 20° to 30° centigrade, and the time of immersion varies from half an hour to twenty-four hours. The cellulose is then removed from the first bath, and as much as is practicable of the acids is removed or squeezed out of it, and the acids thus removed are allowed to run back into the first bath. The lower nitro compound of cellulose thus removed from the first bath is then placed in the second bath, which I term the "digest" or "finishing" bath, where it is allowed to remain from twelve to forty-eight hours to become thoroughly converted into the trinitro-cellulose, the time of immersion depending upon circumstances, such as temperature and the character of the cellulose material employed; or I can, if desirable or preferable, wash the nitro-cellulose taken from the first bath with water to thoroughly remove the acids and then dry it and immerse it in the second bath. This would require a little more labor, but would prevent dilution of the stronger acids of the second bath with the weaker acids of the first. The cellulose material is allowed to remain in the second or digest bath until thoroughly converted into the highest nitro compound, which is called "trinitro-cellulose" or "gun-cotton" proper and which is insoluble in a mixture of ether and alcohol. Although a good trinitrate may often be obtained in less time, I usually allow the cellulose material to remain in this bath for from sixteen to twenty-four hours and at a temperature ranging from 15° to 25° centigrade. I then remove the gun-cotton from the second bath and squeeze out or remove with a centrifugal machine or by other suitable means the excess of the concentrated acids adhering to the gun-cotton, and then wash out the remainder of the strong acids in or with the weaker acids of the first bath

for the purpose of strengthening or restoring the latter, as hereinafter mentioned. The gun-cotton is then freed from as much acid as practicable by a centrifugal machine or by other means, and the remainder of the acids adhering to the gun-cotton are removed in the usual way by copious washings and boiling with water.

The figure represents an apparatus which may be used.

No. 1 indicates a tank or bath.

No. 2 indicates another tank or bath.

No. 3 indicates an elevated tank.

No. 4 indicates a cooling-chamber.

No. 5 indicates a centrifugal or other drying machine.

No. 6 indicates a press.

Nos. 7 7 7, &c., indicate connecting-pipes.

P denotes a pump.

The acids employed for the second bath are the most concentrated obtainable in commerce—viz., nitric acid, 1.52 specific gravity; and sulphuric, 1.84 specific gravity. After the immersion of the cellulose and the completion of its conversion into the highest nitrate in the second bath the acids become slightly diluted with water evolved by the action of the acids on the cellulose. The proportion of the acids in this bath, which at first should be about one part nitric acid to three parts sulphuric acid, also necessarily becomes slightly altered, part of the nitric acid being taken up in the conversion of the dinitro-cellulose into trinitro-cellulose. I therefore add to this bath after the removal of the cellulose therefrom a quantity—say from six to nine pounds for each pound of cellulose—of the strongest mixed acids in the above proportion, or thereabout—viz., one part nitric acid to three parts sulphuric acid—to restore or partially restore the somewhat weakened acids. On removing the gun-cotton from the second bath I allow to adhere to it or remain absorbed by it from six to ten pounds of the acids of this bath, or a quantity equal to that supplied to it for the purpose of restoration, as above explained, or equal to that quantity plus the acids which come from the first bath to the second bath in and absorbed by the cellulose material from the first bath if and when the cellulose material is not washed and dried before immersion in the second bath. The said acids which adhere to the gun-cotton on its removal from the second bath being of greater strength and more highly concentrated than the acids of the first bath, I wash out these stronger acids from the gun-cotton with a quantity of the weaker acids for use again in the first bath. This may be done by placing the gun-cotton only for a few minutes into the first bath and allowing the more concentrated acids contained in the gun-cotton to mingle with the weaker acids in the first bath, or the gun-cotton may be washed in small portions in correspondingly small quantities of the first-bath acids in any practicable way, the weaker acids after restoration being returned to the first bath; but I prefer to proceed in the following manner, viz: After a batch of cellulose material has been treated in and removed from the first bath, I pump into a reservoir sufficiently elevated for the purpose such a quantity of the weakened acids from the first bath as will, when combined with the concentrated acids removed from the second bath in the gun-cotton (allowing for the acids lost in the subsequent washing of the gun-cotton with water) be sufficient to refill the first bath to the desired height. The remainder of the weakened acids of the first bath not thus pumped out are drawn off to give room for the above acids. I then remove the gun-cotton from the second bath in suitable quantities at a time and place the same in a centrifugal machine. The excess of acids above what is required for restoring the first bath and for keeping the second bath constant, as hereinbefore explained, are allowed to flow back into the second bath. This is done by giving the centrifugal machine a rotation sufficiently rapid to remove such a quantity and no more. I then give the centrifugal machine a much more rapid rotation, thus removing a further portion of the acids, which are allowed to flow in another direction and into the first bath, at the same time causing a stream of the before-mentioned weaker acids to flow into the centrifugal machine near its axis, where by centrifugal force the acids are thrown outward and made to pass rapidly through the gun-cotton, removing or washing out the stronger acids and displacing them with weaker acids. I usually allow from fifty to one hundred and fifty pounds of the weaker acids to pass through the centrifugal machine and through the gun-cotton in this manner for every pound of gun-cotton placed in the machine, such quantity of weaker acid depending of course upon the quantity of acids employed for the first bath per pound of cellulose immersed in it. The cellulose is partially converted in bath No. 1 of the weaker acid. It is then passed to the centrifugal machine and the acids mixture removed as far as possible and may then go to a press and thence to strong bath No. 2, or it may go from the cetrifugal machine to bath No. 2. The acids removed by the centrifugal machine and press flow back into bath No. 1. After the treatment of the cellulose in bath No. 2 it may be put back into the centrifugal machine and the weaker acids from bath No. 1 drawn through the material (by means of pumping into an elevated tank or otherwise) and the strong acids washed from the material and carried to bath No. 1, thus strengthening the acids in bath No. 1. Now if trinitro-cellulose or the highest nitro compound be immersed for the necessary time and at the proper temperature in an acid mixture suitable for the production of dinitro-cellulose the trinatrate will be converted into a lower substitution compound; but if the temperature be kept very low—say below 10°

centigrade—and the time of immersion made short this result is either nearly or entirely obviated. I therefore cool the said weaker acids of the first bath to a proper temperature before admitting them to the centrifugal machine to wash the gun-cotton. This may be done by allowing the acids to flow from the said elevated tank to the centrifugal machine through a coil of pipe surrounded with cold water or with ice and water, or with a freezing mixture of ice and salt or in any other convenient manner.

A great advantage of my said invention is that in the last or digest bath very highly concentrated acids are employed, and in such quantity that the cellulose material is fully immersed and flooded with the acids to a sufficient extent to preclude any possibility of fuming off from the heat evolved from the reaction which at this stage of the process is yet necessary to complete the conversion.

From one-half to two-thirds of the conversion of the cellulose into gun-cotton or the highest nitro compound being effected by a previous immersion in a preliminary bath, supplied by the waste acids from a second bath, a great saving in the acids is effected, and by the completion of the conversion into gun-cotton in a second bath of hightly-concentrated acids a more highly and uniformly nitrated product is obtained. Moreover, by washing the gun-cotton, on its removal from the last and concentrated acid bath, with the weaker acids of the first bath the stronger acids are recovered and replaced by the weaker acids, which latter are removed by subsequent washings with water.

I have herein described my process as employing two baths only, one a first immersion bath of weaker acids, the other a second digest or finishing bath of stronger acids; but two or three or more first immersion baths might be employed, together with one large digest bath to receive the cellulose material after it has been immersed in the first bath or baths, and all to attain the result hereinbefore described. Moreover, two or more digest or finishing baths might be employed to attain the same end, so long as the last bath or baths employed contains an acids mixture sufficiently stronger than the acids employed for the first bath to finish the conversion of the lower nitro compound made in the first bath to the highest nitro compound or to a nitro compound of the degree of nitration required in the second or last bath, and so long as the acids in the last bath as well as in the first bath shall be in sufficiently large excess to thoroughly immerse and cover the cellulose material to be placed therein or to sufficiently cover it or saturate it to attain the desired end, and provided the acids of the first bath or baths are restored or strengthened by the use of the more concentrated acids removed from the second bath or baths, as herein described, the same ends may be attained.

What I claim is—

1. The improvement in the manufacture of pyroxyline, which consists in converting cellulose into a lower nitro compound in a bath of comparatively weak acids mixture, then expressing or removing the excess of the acids from the material and converting the material into a higher nitro compound in a bath of a stronger acids mixture, then withdrawing the materials from the second bath and washing the adherent strong acids therefrom into the first bath by passing the weaker acids mixture through it and back into the bath, substantially as described.

2. In the manufacture of pyroxyline, the process of first converting the cellulose into a lower nitro compound, such as dinitro-cellulose, in a preliminary bath of suitable acids, then removing the excess of acids from the cellulose material by suitable mechanical means, then washing out the balance of acids with water, then drying the cellulose material, and immersing it in a stronger bath of acids of a strength and character suitable to convert it into trinitro-cellulose or pyroxyline, substantially as described.

In testimony whereof I affix my signature in presence of two witnesses.

HUDSON MAXIM.

Witnesses:
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H. B. SWINNEY.