UNITED STATES PATENT OFFICE.

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MANUFACTURE OF PYROXYLINE.

SPECIFICATION forming part of Letters Patent No. 350,497, dated October 12, 1886.

Application filed January 27, 1886. Serial No. 189,968. (No specimens.)

To all whom it may concern:

Be it known that I, GEORGE M. MOWBRAY, a citizen of the United States, residing at North Adams, in the county of Berkshire and State of Massachusetts, have invented new and useful Improvements in Manufacture of Pyroxyline, of which the following is a specification.

The generic term "pyroxyline" has been applied to three several combinations of cellulose with nitric acid, viz: First, trinitro-cellulose or gun-cotton; second, dinitro-cellulose or soluble pyroxyline, used by photographers; and, third, mononitro cellulose or xyloidine. Variations of temperature and of the strength of the nitric acid or mixtures of nitric and sulphuric acid used for the acid bath in which the cellulose is immersed cause variations of the product; hence manufacturers who aim to produce dinitro-cellulose of uniform quality are very conservative in venturing on change of process lest certain properties which render it useful to form zylonite or celluloid, &c., "plastic compounds capable of being molded by heat and pressure" should be affected to their detriment. Further, the hygroscopic properties of fibrous cellulose in the form of tissue-paper and bleached cotton, offering so large a surface to moist air, and the absorption of aqueous vapor from the atmosphere by the acids used weakens the acid bath, and thus vary the quality of the product, these variations of quality being accompanied by a diminution of the quantity yielded under these variable conditions.

Apart from the specified strength of the acids stated hereinafter, which are given as being especially suited for making soluble pyroxyline, the process and apparatus herein described are likewise adapted for the manufacture of gun-cotton and xyloidine.

In manufacturing soluble pyroxyline the method practiced heretofore has been to prepare a standard mixture of nitric and sulphuric acids to serve as an acid bath in which is immersed some form of cellulose—such as fine tissue-paper, bleached cotton, ramie fiber, &c.—after immersion for half an hour, more or less, the cellulose having been converted into nitro-cellulose, it was lifted out of the acid bath, and the adhering "spent acid" amounting to nearly one-fourth of the original bath, was in part removed by means of a centrifugal machine, and the nitro-cellulose plunged beneath water and washed until all traces of acid were removed. The acid bath was then replenished from the standard mixture of nitric and sulphuric acids and immersion of cellulose repeated, as before. The acid removed by the centrifugal machine, termed "spent acid," was treated as a by-product, being usually returned to the chemical works, and there credited at about one-fourth of its original cost, exclusive of labor, handling, repacking, shipping, transportation, breakage of carboys, &c. It would seem that the acid separated from the nitro-cellulose by the centrifugal machine was supposed to differ from that left in the converting-vessel, and the fact that they are identical, if not overlooked, was disregarded. Meanwhile this spent acid accumulated at a rate of from fifteen to twenty kilos for each kilo of nitro-cellulose produced; but the most serious defect of this mode of nitration lies in the step-by-step weakening of the converting-bath at each and every immersion with the inevitable consequence that the product of the first immersion differed in quality from each subsequent immersion, the percentage increase of weight diminishing in proportion and giving rise to the observation that "no two batches of pyroxyline were alike." Owing to this unsatisfactory state of the process from time to time the acid in the converting-pots was emptied out and returned to the chemical works as spent acid. Some manufacturers erected settling-tanks, devised processes of filtration or precipitation, and having accummlated a large quantity subjected it to analysis and corrected its defects.

My improvements secure uniform quality of product, greater yield, using spent acid over and over again until consumed, the labor, cost, and time in clarification, filtration, settling, &c., is avoided. One-fourth the stock of acids on hand suffices to supply a factory, as compared with former methods. I will describe these improvements, referring to my application (Case C) filed of even date herewith for

the details of the apparatus, and simply enumerate them in this application: first, a turn-table mounted with eight converting-vessels, each having a capacity of thirty gallons, more or less; second, a centrifugal machine; third, a spent-acid tank; fourth, a concentrated mixed-acids tank; fifth, a building-up acid-tank with appliances; sixth, a temperature-controlling coil; seventh, a dumping-trough with water-supply, drainage, &c.; eighth, a washing-tank with pure-water supply, drainage, &c.

Gages to acid-cylinders, air-supply at a pressure of about twenty pounds to the square inch, and all necessary appliances will be found figured and described in said application C. Into each of the eight converting-vessels I enter one hundred and fifty kilos of "normal standard mixed" acid for making soluble pyroxyline consisting of—

H_2SO_4, 65.00 per cent., or thereabout.
HNO_3, 17.78 per cent., or thereabout.
H_2O, 17.22 per cent., or thereabout.

100.00

A convenient charge of cellulose (fine tissue-paper, bleached cotton-yarn or bleached ramie, &c.) is one kilo and three hundred and twenty-five grams to the one hundred and fifty kilos of acid, and time of immersion suitable twenty-four and one-half minutes, more or less; temperature of acid 85° Fahrenheit, which is attained by passing acid through tempering-coil. Warming and cooling the contents of the converting-vessels directly by the old method of immersing a copper worm connected to a steam-hose or by running a stream of ice-water through said coil interferes with nitration, besides risk of steam or water escaping into the mixed acid.

The composition of the concentrated mixed acids used by me in manufacturing soluble pyroxline is as follows:

H_2SO_4, from 58.20 to 65.00 per cent.
HNO_3, from 38.80 to 32.00 per cent.
H_2O, from 3.00 to 3.00 per cent.

100.00 100.00

These acids are weighed in the iron drums and forced direct from the drums by compressed air into the concentrated mixed acids tank.

The building-up acid, serving to refill the converting-vessels after each immersion, is composed as follows: Concentrated mixed acids, one part, by volume, equals two hundred and fifty-six pounds, by weight. Spent acid from centrifugal, five parts, by volume, equals twelve hundred and sixty pounds, by weight. The building-up acid tank should be of large capacity, so as to contain two days' supply, if necessary, or, better, there should be two of these tanks, so that a day's supply may always be ready a day beforehand. This renders night labor or overtime work unnecessary, always a source of dissatisfaction to employer and employed. A convenient proportion of cellulose in the form of strips of tissue-paper I have found to be thirteen hundred and twenty-five grams, to be immersed in one hundred and fifty kilos of normal standard mixed acid and warmed to 85° Fahrenheit.

Each converting-vessel is charged in manner as follows: The cellulose being entered into each vessel of acid at intervals of three and one-half minutes, so that by the time the first-charged vessel arrives at the centrifugal machine the eighth vessel will have received its charge, and twenty-four and one-half minutes will have been occupied, a period that has proved sufficient for conversion with thin tissue-paper. The nitro-cellulose is now rapidly transferred from the converting-vessel to the centrifugal machine, which in two or three minutes separates about thirty-two kilos of spent acid, flowing by gravity to the spent-acid tank. The rinsed nitro-cellulose, which persistently retains from six to seven kilos—averaging 6.4 kilos—is next plunged beneath water in the dumping-tank, whence it passes into the washing-tank. On an average each converting-vessel will be found to lose 38.4 kilos, while the total contents of the vessel have deteriorated in strength. By the old method this deficiency, amounting to about thirty-eight kilos, was replenished with normal-standard mixed acid, leaving one hundred and twelve kilos of spent acid in each converting-vessel unfortified, and, as this omission was repeated twenty-five times in each vessel every working-day, we can now understand how it was that it was current remark "no two batches of pyroxyline were alike." In fact, each day's product was made up of various qualities.

My improvement, in lieu of using the normal-standard mixed acid to replenish the converting-vessels and rejecting more or less of the spent acid from the centrifugal machine, substitutes what I term a "building-up acid," which includes all the spent acid of the previous day's working fortified with concentrated mixed acid, and, as proven by months of consecutive work, observes the following conditions and limitations: First, reserves all the spent acid separated by the centrifugal machine to-day for the next day's work; second, the volume of concentrated nitric and sulphuric acids added does not exceed the volume of spent acid subtracted and lost in the washing-water; third, the concentrated nitric and sulphuric acids contain not merely the same equivalents as a like volume of normal-standard mixed acid, but, in addition, enough nitric acid to replace that which has been consumed in nitrating thirteen hundred and twenty-five grams of cellulose, also what is lost in fumes by evaporation during conversion and in the centrifugal process; fourth, the degree of concentration of the new acids used with the spent acid is such as to take up the water formed both by the chemical reaction and by absorption from

the atmosphere during the twenty-four minutes necessary for conversion; fifth, the building-up acid is not so concentrated nor so different from the normal-standard mixed acid that if accidentally an over supply or an under supply should reach a converting-vessel the product would be seriously affected. These five conditions and limitations of my invention during consecutive work on a large scale have been observed with the result of producing soluble pyroxyline of uniform quality, and without perceptible deterioration of the acid bath.

The arrangement of eight converting-vessels, one centrifugal machine, and one dumping-trough of water, since I charge a converter every three and a half minutes, has the effect that eight three-and-half-minute intervals occur between immersion and removal, or a period of about twenty-four and one-half minutes is allowed for converting the cellulose into nitro-cellulose. Meanwhile there takes place at every intermission of three and a half minutes—viz., an immersion of thirteen hundred and twenty-five grams of cellulose—a removal of nitro-cellulose to centrifugal basket, and thence to water; flow of about thirty-two kilos of spent acid to spent-acid tank, and replenishing the converter with 38.4 kilos of building-up acid, ready for next series of immersions, &c.

I am aware of Patents No. 251,938, January 3, 1882, and No. 274,335, March 20, 1883, wherein the process of clarifying the residual acid, then ascertaining by analysis the constituents thereof, precedes restoration, it being alleged in said patents "these acids cannot be used again with satisfactory results unless the matter in suspension, assumed to be 'flock' detached from the fiber during treatment, be first separated." This "flock," so called, being ferric sulphate, $Fe_2(SO_4)_3$, as it disappears in the washing-water, and in no wise interferes with nitration, I disregard, thus saving from thirty-six to seventy hours' time and precipitant. I also dispense with analysis, the process itself being elastic enough to control the resultant product should that product, itself the best of tests, indicate variation of quality. I disclaim, therefore, settling, clarification, separation of flock, and analysis of residual acids preceding restoration.

My invention, without stopping to analyze, or clarify, or estimate, or weigh, provides for uniform nitration. As a necessary consequence, the deterioration of the residual acids is uniform, and it follows their restoration can be defined with precision. It only remains to trace the converting-acid through the process of nitration to its final destination, viz: the greater portion, "nearly three-fourths," remains in the nitrating-vessel. About five-sixths of the remaining fourth is separated by the centrifugal machine from the acid-dripping nitro-cellulose, whence it passes into the spent-acid tank, while the remaining one-sixth of said one-fourth, persistently adhering to the nitro-cellulose during centrifugal action, is lost in the washing-water when the nitro-cellulose is plunged into the washing-trough. To restore, we force up the contents of the spent-acid tank into the building-up-acid tank, and note how many inches of level it has reached, as shown by the glass gage. We will suppose forty inches. We now direct from the concentrated-acid mixture enough of said concentrated mixed acid to further raise the level of the acid in the building-up-acid tank from seven to eight inches higher—say until the glass gage marks forty seven or eight inches. As soon as a charge of "acid-dripping nitro-cellulose" has been transferred from a nitrating-vessel to the centrifugal machine, the turn-table is moved so as to bring the converting-vessel, from which the nitro-cellulose has been removed, beneath the stop-cock connected with the building-up-acids tank, the stop-cock is opened, and a volume of this building-up acid equal to that removed with the rinsed nitro-cellulose is permitted to flow into the converting-vessel until the normal level that indicates a content of one hundred and fifty kilos is reached. Thereupon the supply is shut off. In fact, about one twenty-fourth of concentrated mixed acid, by volume, or kilos 6.4, by weight, together with a volume of spent acid equal to that removed by the centrifugal machine from one batch of nitro-cellulose equal to thirty-two kilos, has practically restored the spent acid (kilos 111.6) left in the converting-vessel to its original strength and volume of one hundred and fifty kilos. It is now in condition to nitrate another batch of thirteen hundred and twenty-five grams of cellulose.

I do not limit myself to the precise weights or volumes mentioned in the above specification, as they may be varied slightly; nor do I limit myself to the exact proportions of tissue-paper or other form of cellulose to the normal mixed acid, it being desirable to increase slightly the quantity of nitric acid when the atmosphere is saturated with moisture in the summer months, and diminish slightly the proportion of nitric acid in the winter. The product itself is an unerring guide to an operator skilled in the art, requiring more building-up acid when the converted cellulose appears ragged, soft, or burned through, technically termed as "being cut," and less building-up acid when it is found on washing and drying to be imperfectly dissolved in a solution consisting of one part of camphor to ten parts of alcohol.

Having thus described my invention, what I claim is—

As an improvement in the art of manu-

facturing nitro-cellulose, the within-described process of restoring the spent acid of the nitrating bath in strength and bulk without precipitation and analysis by fortifying and adding to the drained spent acid of a previous nitration a mixture of concentrated sulphuric and nitric acids, in the manner and about in the proportions herein set forth.

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

GEORGE M. MOWBRAY.

Witnesses:
HARRY S. MOWBRAY,
MERRITT T. WHITE.