Caustic soda can be used with nearly as good results. The main advantage in the substitution is the lower price of caustic soda.

LABORATORY OF CORNELL AND ANDREWS.

PYROXYLIN, ITS MANUFACTURE AND APPLICATIONS.

BY WALTER D. FIELD.

(*Continued from Vol. 15, p. 140.*)

Received September 12, 1893.

PART II.

NITRATION OF THE FIBER.

MIXED cotton and flax fiber in the form of paper, from two to three one-thousandths of an inch thick and cut into one inch squares, is nitrated by the Celluloid Manufacturing Company, and the same paper, left in long strips, one inch wide, is used for nitration by the Zylonite Manufacturing Company, of North Adams, Mass. The Celluloid Manufacturing Company introduce the cut paper into the mixed acid by means of the arrangement shown in Fig. 1, H, which is a rapidly revolving,

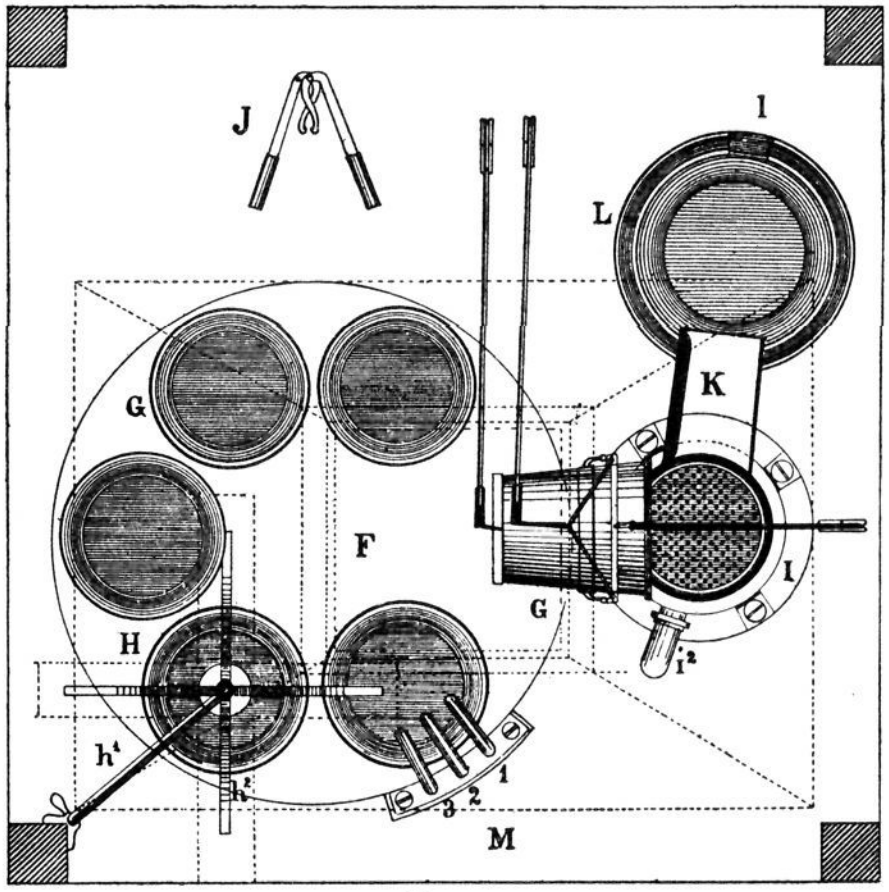


FIG. 1.

hollow tube, flared at the lower end, and immersed in the mixed acid. The centrifugal force of the revolving tube throws the paper towards the sides of the vessel G, leaving the center of the vessel ready for fresh paper. The Zylonite Manufacturing Company simply cut the paper into long strips and introduced it into the mixed acids by means of forks. The arrangement used by this company for holding the mixed acids was a cylindrical vessel divided into a number of sections, the whole revolving like a turntable, thus allowing the workman to nitrate successively each lot of paper at a given point. This company did not remove the acid from the paper after its immersion, but plunged it immediately into the water, thus losing a large proportion of acid. The Celluloid Company, on the other hand, by using the paper in smaller pieces, using more paper to a pound of acid, and wringing the mixed acid from the paper before immersion, had by much, the best process of nitration. Their method of separating the acid and paper will be seen in Figs. 1 and 2, G and I.

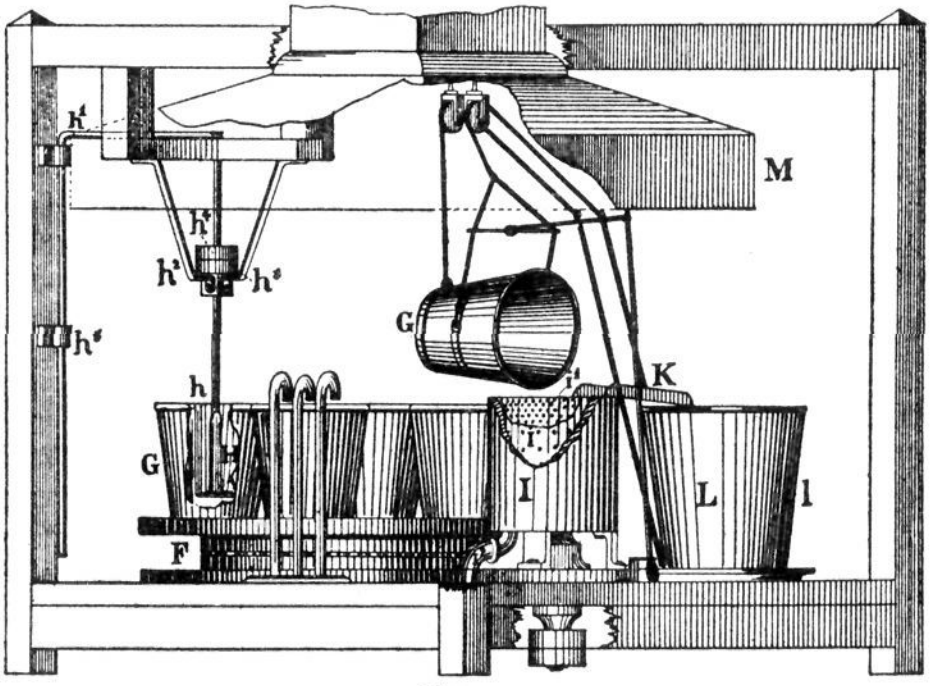


FIG. 2.

The other manufacturers of pyroxylin use earthenware vessels and glass or steel rods, hooked at one end, having small pieces of rubber hose pulled over the other end to prevent the hand from slipping. The form of vessel in general use is that given

in Fig. 3. It is sufficient in size to nitrate one pound of cotton. The hook on one end of the rod enables the workmen to pull the pyroxylin apart and thus insures saturation of the fiber.

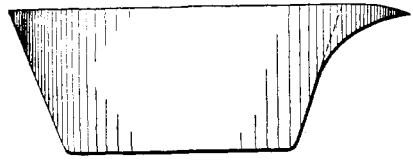
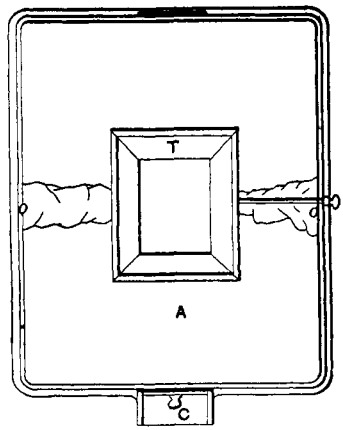


FIG. 3.

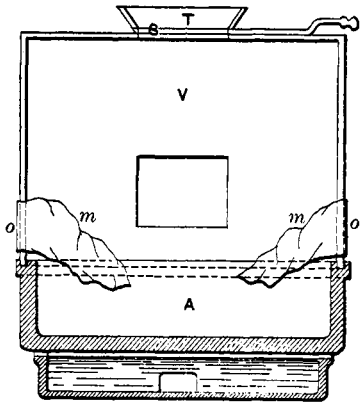
The nitrating apparatus of Tribouillet and de Besaucele (Eng. Pat., No. 5,057, 1878; Ger. Pat., No. 6,828, 1879) is given by both Bockman (Das Celluloid, 1888) and Heinzerling (Die Fabrikation Kautschuk and Guttapercha Waaren, 1883), and it is the only apparatus they mention, although Hyatt's apparatus was then in use. The plans for this nitrating box have been reproduced in Figs. 4 and 5. It is of a very unhandy construction and any workman using it would soon discard the hood V as unnecessary. The rubber sleeves would only be in his way and the acid would rot them out in a very short time.

FIG. 4.



PLAN.

FIG. 5.



SECTION.

In working by hand, at the present time, it is customary to protect the workmen from the fumes of the acid by means of a hood which is being constantly exhausted by a powerful fan or blower. They are furnished with gauntlet gloves made of white rubber, and also aprons of the same material. In the winter season the room in which the nitrating is done must be kept at a tem-

perature of about 70° F., in order to secure equality in the batches.

The nitrating apparatus of White and Schupphous (U. S. P., No. 418,237, 1889) is both novel and excellent in its general plan. The cage B (Fig. 6), with its central perforated cylinder B′ (Fig. 7), is intended to insure the rapid and perfect saturation of the tissue paper used for nitrating. The patentees say that no stirring is required with their apparatus. This might be true when paper is used, or even cotton, when the temperature of nitration is from 30° to 35° C., but would not be true if the temperature were raised to 50° or 55° C. In carrying out their process they proceed as follows: The paper is nitrated in the cage B, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder B′. After nitration the cage is carried to the wringer E, Fig. 8, of which it forms the

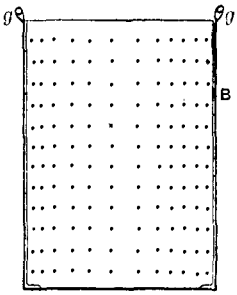


FIG. 6.

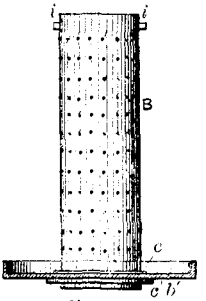


FIG. 7.

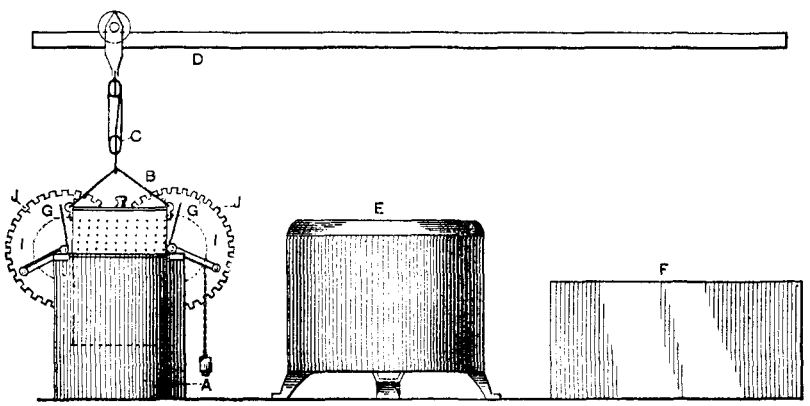


FIG. 8.

basket, and the acids removed. Finally the cage is taken to the plunge tank F where the paper is removed from the cage by simply pulling out the central perforated cylinder B′. Fig. 9, shows the nitrating pot with its automatic cover. The plunge tank F is shown in section and plan in Fig. 10. This appara-

tus is given in detail because it is the only patented method that seems to be suitable for the nitration of cotton fiber in bulk at high or low temperatures.

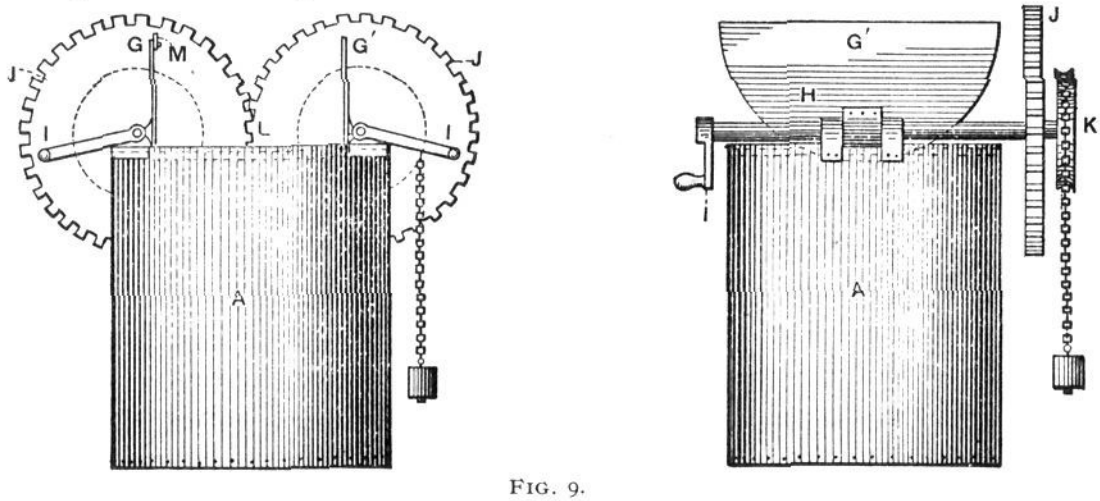


FIG. 9.

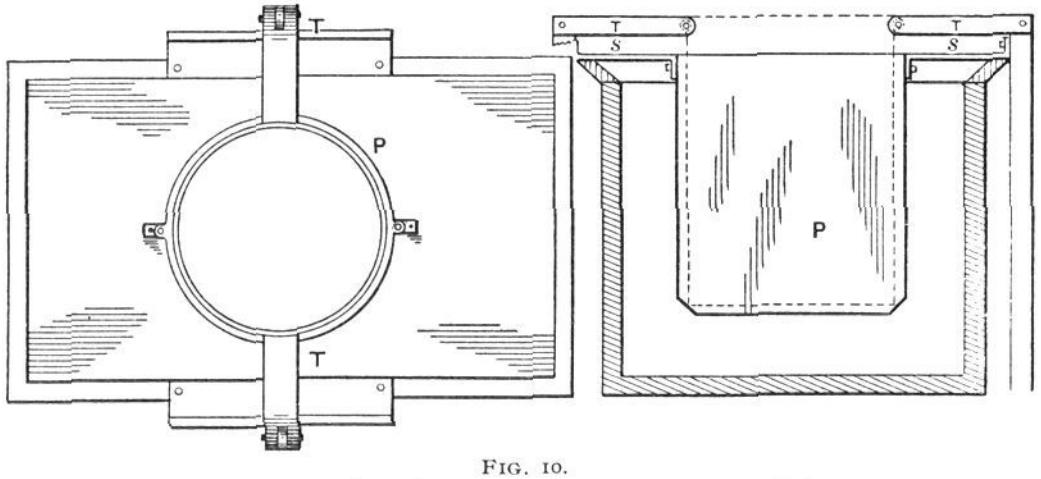


FIG. 10.

We now come to what is probably the most elaborate method of nitrating yet suggested—that is, the method patented by Mowbray, August 12, 1890 (U. S. P., No. 434,287), by which he proposes to nitrate paper in continuous lengths. The method is as yet untried. The paper loops shown in the sectional drawing (Fig. 11) are merely theoretical, for the paper web would not maintain any such position, but would settle down in the bottom of the acid tank. He allows the paper web to remain in the nitrating, or acid tank (15), from twelve to twenty minutes, then as the first part of the paper web is drawn forward, a fresh portion takes its place. One of the great problems in such an operation is how to maintain the strength of acid required in the nitrating

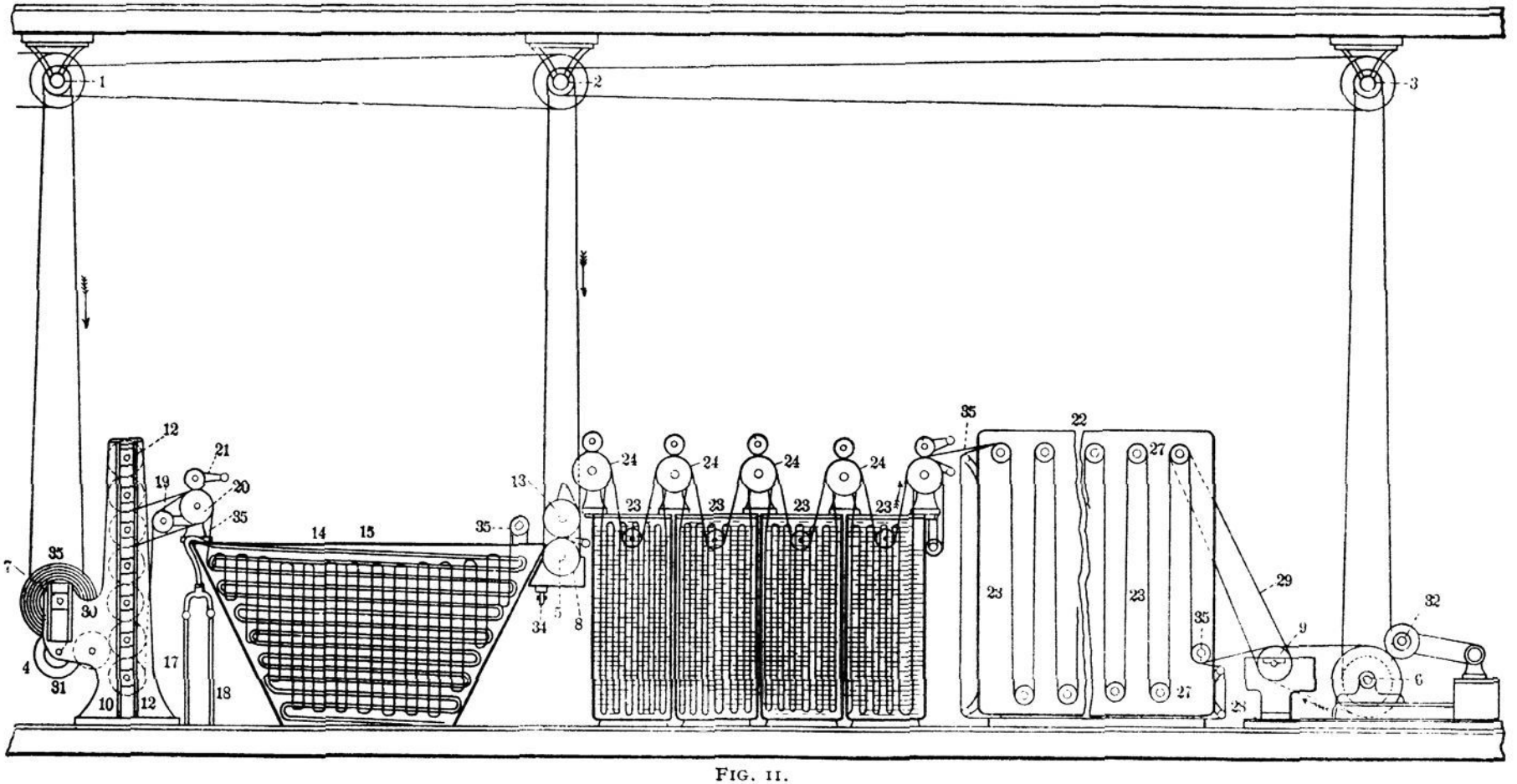

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FIG. 11.

tank. Mowbray claims to be able to do this by using the methods described by him in U. S. P., Nos. 350,497, and 350,498. Such a method as Mowbray describes is certainly no better than that of Hyatt (210,611).

The best material from which to construct the various tanks required for storing the acids for nitrating vessels and for other things is, undoubtedly, steel. Mowbray, in his patent No. 350,489, 1886, claims "the use of homogeneous metal, otherwise called 'Bessemer steel' plates, for tanks, to serve as containing vessels for the mixed acids used in the process of converting cellulose into nitrocellulose." He also claims "the use of steeled cast-iron pots for holding the mixed acids, in which the cellulose is immersed during the process of conversion." Mowbray says, in the same patent: "I have discovered that cast-iron vessels treated so as to diminish the carbon therein (by exposure to continued heating, surrounded by infusoria, or iron peroxide), can be successfully used for this purpose, and that the action of acids upon metals forms a ferric sulphate which, being insoluble in the mixed nitric and sulphuric acid used, does not injuriously affect the product."

One way of constructing the vessel for holding the waste acids from the nitrating pots can be seen in Fig. 12. The inside vessel, A, is of earthenware, and may have a capacity of from 100 to 500 gallons, according to necessity. The outside vessel is of boiler steel with a flanged top, E, F. The pipe D is connected with the compressed air, and the pipe C conducts the acid as it is forced out to the desired place. It is a construction that prevents any accidents when moving the acids from place to place.

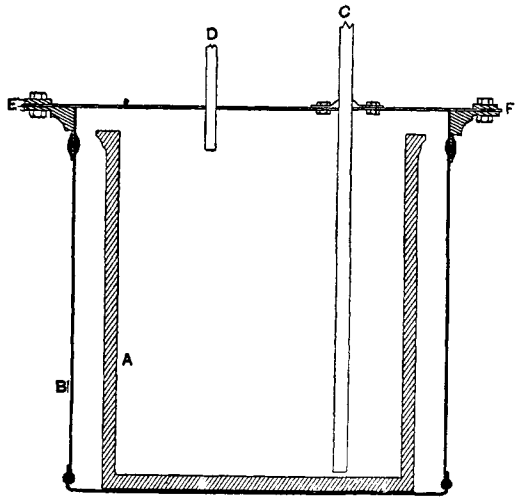

FIG. 12.

Hyatt, in U. S. P., No. 299,388, a patent for a combination of tanks so arranged as to allow of the convenient handling of the mixed acids, simply says in regard to the construction of the tanks: "We prefer to construct our tanks of wrought iron, and protect them from the corrosive action of the acids by acid-proof coatings." Steel drums will hold the mixed acids so long as they are closed from the air, but if air is allowed to enter, the sulphuric acid in the mixed acids takes up the moisture in the air, are reduced in strength at the surface, and soon begin to eat the iron or steel away. There is some choice, perhaps, in the steel to be used for such a purpose, but wrought iron is as good as steel if the air is carefully excluded from the tank. All the plants and arrangements of tanks, etc., both for nitrating and storing and using the waste acids, have been designed for an acid mixture having about the following strength:

Sulphuric acid	66 parts (absolute).
Nitric acid	17 "
Water	17 "

the acids being used at a temperature of 30° C.

The arrangement of the plant, as described by Mowbray in U. S. P., No. 350,496, or the arrangement described in U. S. P., No. 299,388, by Hyatt, Pool, Everding, Stevens, and Wood, could not be used were the acid mixture in use of the following composition:

Sulphuric acid	62 parts (absolute).
Nitric acid	24 "
Water	14 "

and using a temperature of 60° C. for immersion.

The nitrating apparatus of Schupphous, Mowbray, and Hyatt, were all designed for use with tissue paper as the cellulose material. The design of Schupphous might be used for cotton at low temperatures, but would be inconvenient on account of the length of time (five or six hours) required for nitrating at low temperatures.

Thus it is apparent that both the cellulose material and the method of nitrating control the construction of the nitrating plant. No plant has yet been designed for nitrating cotton fiber in its natural form at high temperatures, and using more than one pound of cotton at an immersion.

The Acid Mixture.—Many formulas have been published for producing soluble nitrocellulose. Few of them give detail enough to make them available for practical working. In many instances, although the observations were correct for the single experiment, a dozen experiments would have produced a dozen different products. Some formulas give no temperature for the immersion, others neglect even to give any specific gravities for the acids, and rather than attempt to utilize any published formula, it would be much better to spend months working out a new one to one's own satisfaction and instruction.

In the last five years, the manufacture of a pyroxylin that is almost the equivalent of the collodion cotton, has enormously increased, by reason of its use in the manufacture of pyroxylin varnishes and transparent films for photographic plates.

At the present time not more than three different formulas are in use by the manufacturers of soluble nitrocellulose in this country. The one used by the celluloid manufacturers, another in which the cotton is nitrated at high temperatures, and a third in which the temperature of the immersion is low and the time of the nitration about six hours. Of the three, the best method is the last one, or the one in which the cotton is immersed at a low temperature and then the reaction allowed to proceed in pots holding from five to ten pounds of cotton.

The following formula is essentially the one in use by the celluloid manufacturers for the production of the low form of nitrated product which they use:

Sulphuric acid	66	parts by weight.
Nitric acid	17	" " "
Water	17	" " "

Temperature of the acids at the immersion, 30° C., and the time of the immersion from twenty to thirty minutes. Cellulose in the form of tissue paper about two one-thousandths of an inch thick, one pound to 100 of acid mixture.

The nitrocellulose produced by this formula is very insoluble in the compound ethers and other solvents of pyroxylin, and is seemingly only converted or gelatinized by the action of the solvent.

The next formula produces a mixture of tetra- and penta-nitrocelluloses, hardly soluble in methyl alcohol (free from

acetone), but very soluble in anhydrous compound ethers, ketones, and aldehydes.

Nitric acid, sp. gr., 1.435	8 pounds.
Sulphuric acid, sp. gr., 1.83.....	15¾ "

Cotton, fourteen ounces, temperature of immersion, 60° C. Time of the immersion, about forty-five minutes. The 60° of temperature is developed by mixing the acids together. The cotton is allowed to remain in the acid until it feels "short" to the rod.

We have here the temperature record for a single batch, (made in the form of bowl given in Fig. 1) during the time of the nitration. From four to five minutes were required to immerse the fourteen ounces of cotton and then the acids had risen in temperature from 60° to 65° C. In ten minutes the temperature in the upper part of the bowl was 63½° C., and in the bottom 66° C. The batch was then turned over in the bowl and in another ten minutes the temperature of the top of the cotton was 59° C.; and in the bottom 62° C.

At the end of thirty minutes the temperature of the top was still 59° C., and the bottom 60° C. During the remaining hour and ten minutes the temperature of the top of the acid ranged from 53° to 56° C., and from 64° to 67° C. in the bottom. The time of the immersion was one hour and forty minutes. The pyroxylin produced in this immersion was not a very soluble one, quite a large proportion being insoluble in compound ethers. It will be noticed that there were two periods in which the temperature in the batch rose, and two distinct reactions took place. If the temperature during the first thirty minutes has gone up to 70° C., or 4° higher than it did go, the cotton would have been finished inside of forty-five minutes, and the pyroxylin produced would have been perfectly soluble in compound anhydrous ethers. These observations have been verified a large number of times.

The table given below is a careful record which plainly shows the great variation in the time of the immersion and the temperature by seemingly very slight causes. The table extends over fourteen working days, during which time it rained four days. The formula used is that last given, except that the

specific gravity of the nitric acid is somewhat lower. The pyroxylin produced differs only from that produced by using a nitric acid of sp. gr. 1.43, in being soluble in methyl alcohol. From thirty to thirty-five pounds of pyroxylin were produced in each of the fourteen days.

Weather.	Specific gravity.		Time.				Temperature, degrees C.		Percentage.	
	Sulphuric.	Nitric.	Hours.	Minutes.	Hours.	Minutes.	From.	To.	Increase	Loss.
1. Clear	1.8380	1.4249	..	20	4	..	57°	62°	31	..
2. "	1.837	1.4249	..	20	2	..	60°	62°	18	..
3. Cloudy	1.837	1.4226	..	45	2	..	60°	62°	7	..
4. Rain	1.837	1.4200	..	20	1	20	60°	63°	0	0
5. Clear	1.8377	1.42	1	15	2	..	58°	62°	15	..
6 Rainy	1.8391	1.422	..	35	1	40	58°	62°	..	2
7. Cloudy	1.835	1.4226	..	20	..	35	62°	64°	..	10
8. Clear	1.835	1.4222	..	35	1	10	60°	62°	5	..
9. Partly clear	1.824	1.4271	..	20	1	..	50°	60°	..	3
10. " "	1.83	1.4271	..	10	..	25	58°	60°	..	10
11. Cloudy	1.832	1.425	..	10	..	50	58°	60°	8	..
12. Rainy	1.822	1.425	..	10	..	20	58°	60°	..	10
13. Partly clear	1.8378	1.4257	..	50	1	40	50°	58°	20	..
14. Cloudy	1.837	1.4257	1	56	4	40	50°	60°	16	..

A careful examination of this table will prove very instructive. The increase in yield varies from thirty-one per cent. to nothing, and the loss runs as high as ten per cent., yet it would be unjust to say that care was not taken to make the product uniform in quality.

On the days it rained there was a loss, with the exception of the fourth day when there was neither a loss nor a gain. On the days it was partly clear, as just before or after a rain, the table shows a loss in product. We can explain this fact by reason of the moisture-absorbing qualities of the cotton. On the rainy days it would absorb the moisture from the air until, when immersed in the acids, they were weakened, and the fiber dissolved more or less in the weakened acid, producing what is known as "burning" in the batch. It will also be noticed that on the days which show a loss, the time of the immersion was correspondingly short, as on the tenth, twelfth, and seventh days.

The lesson this table teaches is, that it is almost impossible to nitrate cellulose in small quantity and get uniform results when the nitration is carried on at high temperatures.

In the next table we have the condensed results from a month's work with the above formula.

Cotton (scoured, upland)	416 pounds,	12 ounces
Nitric acid, sp. gr. 1.42–1.425 water white	4,957 "	
Sulphuric acid, sp. gr. 1.83–1.837	9,803 "	
Product	513 "	6 ounces

The high temperature nitrating formula taken as the example in this article will be found to lead to a correct judgment of the working of all such formulas. The consideration of the cold nitration method I shall make the subject of a separate paper at some later date.

IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

BY PETER S. GILCHRIST.

Received May 14, 1894.

IN the JOURNAL for November, 1893, I gave a brief outline of the Hacker and Gilchrist pipe columns for saving chamber space, quoting results which had then been obtained in actual working. I wish to follow this with results of much greater interest.

As stated previously, the pipe columns were added to a plant having large chambers, the first three being each 160 feet long, and consequently not so effective as in combination with short chambers, the best work being seventeen cubic feet of chamber space per one pound of sulphur per twenty-four hours, and this with Glover and Gay-Lussac towers. The ratio of chambers have an important bearing on the amount of work done in a given space.

It has long been thought that short chambers were essential to good work, repeated experiments in Europe having demonstrated this, but there has been much tardiness in adopting them.

An observer of the chamber process notices that as the gases pass from one chamber to another a greater reaction sets in, consequently followed by an increased production of sulphuric acid. The reasons for this are obvious; the vapors strike against the surfaces of the chamber ends and the sides of the connection, causing the particles forming to interact more quickly. Again,