UNITED STATES PATENT OFFICE.

HILAIRE DE CHARDONNET, OF BESANÇON, FRANCE.

PROCESS OF MANUFACTURING ARTIFICIAL SILK.

SPECIFICATION forming part of Letters Patent No. 531,158, dated December 18, 1894.

Application filed January 24, 1894. Serial No. 497,913. (No specimens.) Patented in France June 30, 1893, No. 231,230.

To all whom it may concern:

Be it known that I, HILAIRE DE CHARDONNET, a citizen of the Republic of France, and a resident of Besançon, (Doubs,) France, have invented certain new and useful Improvements in the Processes of Manufacturing Artificial Silk, (which invention is the subject of Letters Patent in France, dated June 30, 1893, No. 231,230,) of which the following is a specification.

This invention relates to improvements in the manufacture of artificial silk, for which I have secured patents in the United States, No. 394,559, dated December 18, 1888, No. 410,404, dated September 3, 1889, and No. 455,245, dated June 30, 1891.

My improved process comprises the following described operations:

I. *Preparation of pyroxylin.*—Any material containing cellulose may be employed. If wood pulp is used, it must be treated for purifying it and separating foreign substances; but if cotton is used, it may be taken directly from the gin or card without further preparation. One kilogram of cellulose is soaked in a mixture of nine liters of nitric acid of density 1.3, and fifteen liters of sulphuric acid of density 1.835, being kept at a temperature of 28° to 30° centigrade. The reaction is allowed to go on for from twelve to twenty-four hours. The resulting mass (pyroxylin and acid) is then subjected to the action of a filter press in order to squeeze out as much as possible of the acid. To reconstitute the acid bath for subsequent nitrations, eighty-five parts by volume of the bath already used has added to it fifteen parts of fresh acid consisting of three volumes of nitric acid of density 1.48, and four volumes of monohydrated sulphuric acid. This reconstituted bath acts the same as the first bath. The pressed and drained pyroxylin is then washed with an abundance of water for from eight to twelve hours in the same manner that paper pulp is washed. During the washing the pyroxylin is bleached with a little chloride of lime, to which is added an excess of nitric or hydrochloric acid. When the pyroxylin is freed from the acids it is air dried until it contains not more than twenty five or thirty per cent. of water. According to my invention, however, I avoid any further drying in order to retain the pyroxylin in this condition, wherein it constitutes a hydrate which is much more soluble than dried pyroxylin. This hydrate cannot be produced by soaking dried pyroxylin in water.

To avoid any further drying of the pyroxylin with the danger attending it, I prefer to treat it centrifugally while still moist with either alcohol or hydrated ether, and then press it. If ether is used, the same ether may serve indefinitely.

II. *Preparation of the collodion.*—The pyroxylin while quite moist is placed in large pugs or turning barrels. With twenty-eight or thirty kilos of moist pyroxylin, I mix forty liters of alcohol and sixty liters of ether. The pyroxylin rapidly dissolves, producing liquid collodion. This collodion is then filtered under pressure either of air or a hydraulic piston by passing it through two or three filters containing layers of carded cotton, whereupon it is ready for the spinning operations. In order to increase the fluidity of the collodion or the solubility of the pyroxylin, a few hundredth parts of the following substances may be added:—Ethers, ethyl and methyl hydrochlorate, metallic chlorides (magnesium, aluminium, manganese, tin, &c.) acetic acid, aldehyde, acetone, carbon bisulphide, hydrochloric, nitric or sulphuric acids.

III. *Spinning of the collodion.*—This may be done by the apparatus described in my said patent of 1888. All thick collodions containing more than fifteen to twenty per cent. by weight of pyroxylin may be spun either by discharging the threads into water as described in my said patent, or by simply discharging them into the air. In the latter case part of the guides may be left out, or the threads may be made to rub along a sponge or other moist body to coagulate them more rapidly. Thus the same spinning machine such as shown in my said patent may serve without change to spin collodions prepared as herein described either with or without water. The spinning without water is possible because collodion containing the water of combination of the hydrated pyroxylin hereinbefore described rapidly becomes firm in the air, the threads do not become glued together, and

the filaments remain more open and supple than when any other process is employed.

IV. *Denitration.*—After spinning and winding, the skeins of pyroxylin thread are subjected to denitration in the following manner:—To make the denitration bath, I mix together eight kilos of monosulphide of calcium, four kilos of commercial sulphate of ammonia, and one hectoliter of water. The mixture is agitated and left to react for an hour or two. The solid precipitate is then separated by filtration or otherwise, and the clear bath is used for denitrating the skeins. This bath is heated in a wooden tank to 28° or 30° centigrade by a steam coil, and the skeins are plunged into it and moved about in it for about an hour, two kilos of silk being thus treated for each hectoliter of bath. For utilizing the spent bath it is first rendered slightly acid by adding a little sulphuric acid. A quantity of calcium sulphide is then added proportioned to the sulphate and nitrate of ammonia existing in the bath. The precipitate is separated as before, and the bath is then ready for subsequent use.

I claim as my invention the following defined novel features or improvements, substantially as hereinbefore specified, namely:

1. The new substance hydrated pyroxylin which differs from ordinary pyroxylin by containing at least twenty-five per cent. of water, and which has the property of greater solubility.

2. The improved process consisting in treating cellulose with nitric and sulphuric acids to convert it into pyroxylin, washing the latter, and then treating it while still moist with hydrated ether to preserve it as hydrated pyroxylin.

3. The process consisting of treating cellulose with nitric and sulphuric acids to form pyroxylin, washing it, and then while still moist dissolving it to form collodion, whereby the collodion thus formed is more fluid and more easily coagulable by air than ordinary collodion.

4. In the manufacture of artificial silk, the improved process consisting in dissolving hydrated pyroxylin to form collodion, and spinning the collodion into threads by discharging it through nozzles, whereby it instantly solidifies in the air.

5. In the manufacture of artificial silk, the improved process consisting in dissolving hydrated pyroxylin to form collodion, mixing therewith a substance, such as described, adapted to increase the fluidity of the collodion, and then spinning the fluid collodion into threads by discharging it through nozzles.

6. In the manufacture of artificial silk, the process of denitrating the spun collodion, consisting in immersing it in a denitrating bath consisting of a mixture of calcium monosulphide and an ammoniacal salt capable of decomposing said monosulphide.

7. In the manufacture of artificial silk, the process of denitrating the spun collodion consisting in preparing a bath by mixing monosulphide of calcium, sulphate of ammonia and water, separating the precipitate, and immersing the skeins in the clear bath.

8. In the manufacture of artificial silk, the process consisting of preparing a denitrating bath by mixing monosulphide of calcium, sulphate of ammonia and water and separating the precipitate, immersing the skeins to be denitrated in this bath, and subsequently regenerating the spent bath by adding sulphuric acid, and then adding calcium monosulphide and separating the precipitate.

In witness whereof I have hereunto signed my name in the presence of two subscribing witnesses.

HILAIRE DE CHARDONNET.

Witnesses:
THOS. N. BROWNE,
VACHORE.