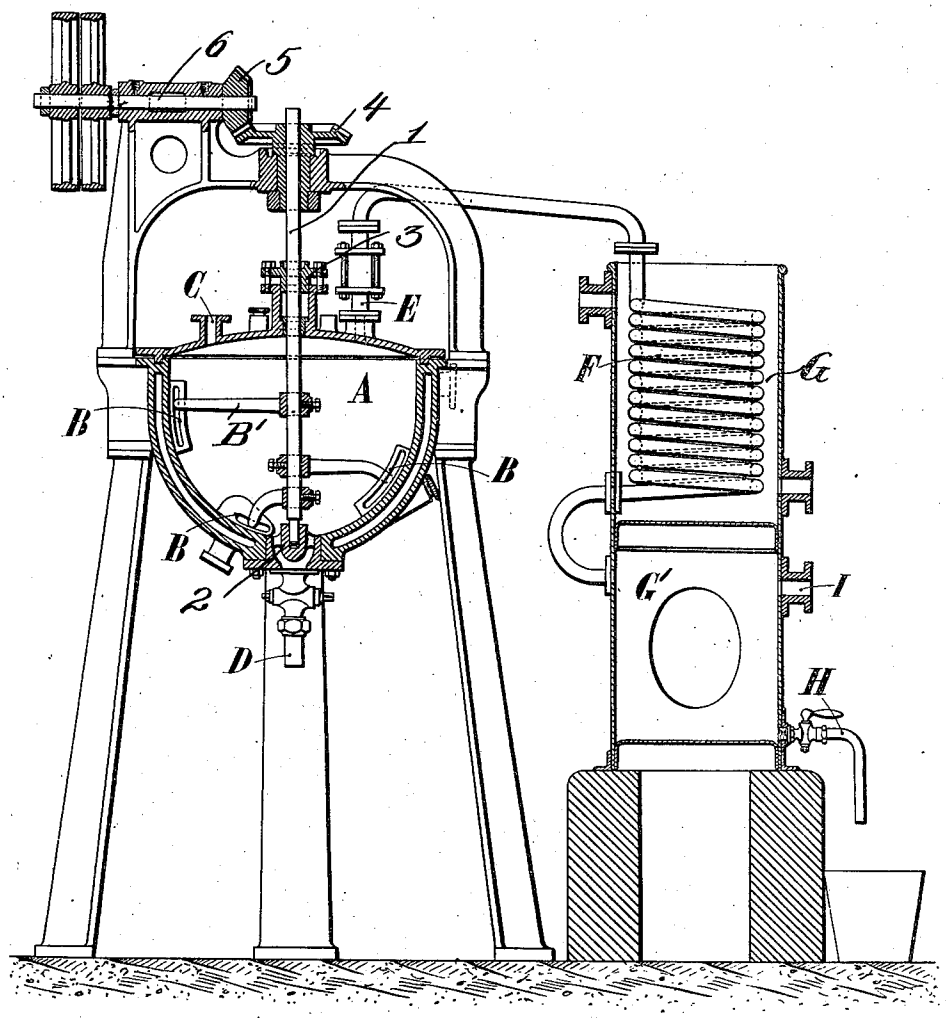
L. NAUDIN.

PROCESS OF CONCENTRATING AND MATURING VISCOSE.

APPLICATION FILED APR. 5, 1907.

986,306. Patented Mar. 7, 1911.

SPECIMENS.



Witnesses:

C. E. Keslor

Inventor

Laurent Naudin

By James L. Norris.

Atty.

UNITED STATES PATENT OFFICE.

LAURENT NAUDIN, OF PARIS, FRANCE, ASSIGNOR TO SOCIÉTÉ FRANÇAISE DE LA VISCOSE, OF PARIS, FRANCE, A CORPORATION OF FRANCE.

PROCESS OF CONCENTRATING AND MATURING VISCOSE.

986,306. Specification of Letters Patent. Patented Mar. 7, 1911.

Application filed April 5, 1907. Serial No. 366,634. (Specimens.)

To all whom it may concern:

Be it known that I, LAURENT NAUDIN, citizen of the French Republic, residing at Paris, Department of the Seine, France, have invented certain new and useful Improvements in Processes of Concentrating and Maturing Viscose, of which the following is a specification.

This invention relates to a process of making viscose, and it has for its object to provide an improved process that insures a product that is comparatively rich in cellulose and possesses elastic and plastic properties so that the viscose may be used to better advantage in the manufacture of films, such as those used in photography and for other purposes, also as dressings or coatings for various materials, and is also capable of being used to better advantage than ordinary viscose in paper manufacture, the product when derived in the form of a thread or film being also useful for various purposes.

In the spinning industry, and also in film manufacture, it has been found that in order to obtain the best results in the working of the viscose, the latter should have reached a certain state of maturity, that is to say, the xanthate of cellulose must reach, either by spontaneous reaction, or otherwise, a certain degree of density. Several processes of treating viscose to obtain such a result, have been proposed, one of these processes involving a heating of viscose to a temperature varying between 70° and 90° C., together with the application of an alkali, such a process being described in French Patent No. 323,473, dated August 4, 1902. Another treatment proposed is described in French Patent 330,753, dated March 31, 1903, and according to the latter treatment, the viscose undergoes a slow and prolonged treatment in a tank at a relatively low temperature, say of 15° to 18° C. In treating the viscose in accordance with either of the processes above described, a considerable loss occurs by reason of the large percentage of by-products resulting therefrom, such as carbonate, sulfo-carbonate, etc. Another process that has been proposed consists in heating the viscose until the xanthate is coagulated in the presence of carbonated and sulfureted by-products, the material being next washed to eliminate the by-products, and is then treated with an alkaline solution to condense or reconstitute the viscose. But the objection to such process, even when operated under the most favorable conditions, is that only a small percentage of cellulose, the essential factor or constituent in the practical application of viscose, is retained, and for the reason above stated, the practical uses of viscose have been necessarily limited.

According to my present invention, a viscose relatively rich in cellulose and possessing elastic and plastic properties is obtained by evaporating the water which is the solvent, by the application of heat to the mass at a relatively low temperature and while the material is *in vacuo*, a boiling of the material being thereby obtained at a temperature of say 32° to 35° C., the mass being kept in a constant state of agitation, and the quantities of water evaporated being controlled properly at each operation, and in this manner a viscose is obtainable that is much richer in cellulose; and, moreover, the chemical factors are more nearly in equilibrium regarding the amount of cellulose, the proportion of non-combined soda, with reference to the saline by-products, and the molecular state of the xanthate which does not exceed the molecular size C_{18}, the complete formula being represented by $C_{18}H_{29}O_{14}OCS.SNa$.

Experience has shown that xanthate of cellulose in aqueous solution, under the influence of a sufficiently high temperature, passes through different states of molecular condensation in which states the carbon successively has the values C_6, C_{12}, C_{18}, C_{24}, C_{36}. Above the value C_{36} the mass is coagulated and it cannot be used for practical purposes. Practice demonstrates that the viscose is most stable when the carbon is of approximately the value C_{18}. Below this value, that is to say, when the carbon is expressed by the term C_6 or C_{12}, the molecule does not possess solidity, and the resulting products in those cases would be devoid of resistance. Hence, viscose may be worked to the best advantage in spinning and other industries when the carbon has a value of between C_{18} and C_{24}.

The composition of the viscose as matured by the process of my invention is variable to a considerable extent, it depending upon the proportions of the reacting elements such as alkali, cellulose, carbon disulfid and water. The proportion should be determined according to the intended use of the cellulose for, in some cases, it would not be a disad-

vantage to use a large excess of free soda, while in other cases, the presence of an excess of soda must be prevented.

An example of an average composition of my matured viscose may be given as follows:

Pure cellulose	14.00
Caustic soda	8.00
Carbonated soda	1.30
Sulfid, polysulfid, and hyposulfite of soda	1.00
Water	75.70
	100.00

Fifteen per cent. of pure cellulose may be considered as the maximum. Above this percentage, the mass even without coagulation, is so thick that concentration becomes impossible at the low temperature involved in the present process. A viscose possessing greater stability may be obtained without altering the proportion of cellulose by augmenting the amount of free caustic soda. For example, the composition may be in the following proportions:

Pure cellulose	14.00
Caustic soda	10.00
Carbonated soda	1.30
Sulfid, polysulfid, and hyposulfite of soda	1.00
Water	73.70
	100.00

The accompanying drawing illustrates an apparatus that is capable of being used in performing the process in accordance with the present invention, the mixing tank and the condensing apparatus being shown in section.

This apparatus comprises a tank A of suitable form, to receive the mass for treatment, the tank being surrounded by a jacket adapted to receive a fluid that serves to heat or refrigerate the contents of the tank. The mass within the tank is agitated by one or more scrapers B carried by the respective arms B′ secured to an operating shaft 1, the scrapers being preferably arranged so as to operate on all portions of the tank. The shaft 1 is journaled at its lower end in a bearing 2 arranged within the tank, and its upper end extends through a stuffing box 3 and is provided with a gear wheel 4 which coöperates with a corresponding gear wheel 5 mounted on a suitable driving shaft 6. The top of the tank is provided with an inlet C through which the mass to be treated may be introduced into the tank, and the mass is withdrawn from the tank after treatment through a discharge D, the inlet and outlet being provided with means for closing them in order that a vacuum or pressure may be maintained within the tank. The vapor freed from the mass is withdrawn through a discharge pipe E which leads to a condensing coil F, the latter being mounted in a condensing tank G adapted to contain water or the like for cooling the coil F, the cooling coil discharging into a separate chamber G′ in the lower portion of the tank and the latter may be maintained at a vacuum pressure by means of a vacuum pump of any suitable kind, that is to be connected to the nipple I. The condensed vapor may be withdrawn from the chamber G′ by means of the drip pipe H.

According to the present invention, the viscose is preferably filtered and is then introduced into the tank through the opening C, and a vacuum is maintained within the tank by exhausting air from the chamber G′ and from the cooling coil F and the discharge pipe E, the mass being at the same time heated to a temperature preferably ranging between 32° and 35° C. The motion of the scrapers B serves to agitate the mass during the distillation and to prevent local overheating of any portion of the mass. By reason of the vacuum pressure within the tank, the viscose will boil at a relatively low temperature, or at the temperature above mentioned, and the air and gaseous sulfureted by-products are liberated from the mass together with the water from the same which is freed in the form of steam or vapor, these products being withdrawn through the pipe E and the moisture contained in them is condensed in the cooling coil F, the gases being finally withdrawn through the opening I, and the liquid or condensation collects in the chamber G′. By heating the mass to the temperature above described while *in vacuo* and during agitation, the material is simultaneously concentrated and matured, the treatment being maintained for a period determined according to the desired state of concentration, a period of one or two hours being usually sufficient.

If the mass is maintained *in vacuo* during the entire treatment, a very large percentage of water contained in the viscose, escapes in the form of vapor, and in this case the product will be highly concentrated, and the viscose will be very rich in cellulose. On the other hand, should the communication between the tank and the vacuum pump be cut off after the air and sulfureted by-products have been extracted from the mass, the viscose will mature without concentration, because of the interruption of evaporation. The viscose, after the treatment has been completed, is withdrawn from the tank through the discharge pipe G, and the treatment may be repeated with a fresh mass of material.

In the manufacture of cellulose, it is first transformed into alkali cellulose and there-

after sulfureted. The xanthate thus produced is dissolved in a suitable quantity of sodium hydroxid. The percentage of cellulose in the viscose so formed does not exceed ten per cent. Moreover, the prolonged agitation of the mass in the presence of air converts the mass into a thick emulsion. While in that condition, the substance is not suitable for the preparation of films. According to the present invention, however, viscose at ten per cent. or less is boiled at a low temperature and *in vacuo* as hereinbefore described, as a result of which the following results are obtained: First, the percentage of cellulose is increased practically up to fifteen per cent., secondly, the elimination of gases, such as air and carbon sulfid, is effected thereby enabling the films to be produced without bubbles. Lastly, a quick maturing of the mass is obtained, several hours being sufficient, whereas heretofore, three days has been required. At this stage in the manufacture, the viscose should be used, and in manufacturing films, the viscose is spread or laid upon webs or papers and converted in the usual manner into the films.

The sulfuration of cellulose is effected with an excess of carbon disulfid, and during the polymerization, carbon disulfid is freed. Water and carbon disulfid are found in the condenser. The presence of carbon disulfid in the distilled vapors occurs if the refrigeration is very effective, otherwise carbon disulfid, the boiling point of which is relatively low, escapes to the atmosphere through the vacuum pump which works continuously during the concentration.

Viscose obtained in accordance with the process above described, contains a relatively high percentage of cellulose that enables it to be used to greater advantage in various industries, and the equilibrium between its component constituents insures a product in the form of a thread or film which possesses a high degree of elasticity and plasticity.

I claim as my invention—

1. A process of treating viscose consisting in simultaneously heating and agitating a viscose solution while *in vacuo* of a degree sufficient to cause boiling of the mass at a relatively low temperature, and maintaining the mass under treatment *in vacuo* and at the said temperature to remove the water evaporated from the mass to effect concentration and maturing thereof.

2. A process of treating viscose consisting in heating and agitating a viscose solution *in vacuo* of a degree sufficient to cause distillation of the water in the mass at a relatively low temperature, maintaining the mass *in vacuo*, thereby withdrawing the water evaporated from the mass until the desired concentration is effected, and allowing the temperature to descend to normal temperature.

3. A process of treating viscose which consists in subjecting a viscose solution to agitation *in vacuo* and while heated to a temperature ranging between 32 and 35° C. to effect distillation of the water contained in the mass, and maintaining the mass *in vacuo* and substantially at such temperature for a period sufficient to effect concentration and maturing thereof.

In testimony whereof I have hereunto set my hand in presence of two subscribing witnesses.

LAURENT NAUDIN.

Witnesses:
EMILE KLOTZ,
GEORGES LEDAY.