UNITED STATES PATENT OFFICE.

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ART OF PREPARING ARTIFICIAL SILK.

SPECIFICATION forming part of Letters Patent No. 562,626, dated June 23, 1896.

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To all whom it may concern:

Be it known that I, FRIEDRICH LEHNER, a citizen of Germany, residing at Zurich, Switzerland, have invented certain new and useful Improvements in the Art of Preparing Artificial Silk; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to the art of producing, artificially, a fiber or thread having the glossy appearance and all the desirable characteristics and quality of natural silk and other threads produced by organic beings.

More particularly the invention relates to the art of producing such threads or fibers, which involves as an important step the nitration of cellulose.

The object of the said invention is to produce a thread possessing greater strength and stability of structure than those obtained under the processes heretofore practiced, and, with this object in view, my said invention involves the production or separation and fixing of nitrocelluloses differing, essentially, from those usually obtained in this and other arts.

Briefly stated, the essential features of my invention, which consists in the process described and the product resulting therefrom, are as follows: The new process embodying my invention starts out with the production and isolation of trinitrocellulose and tetranitrocellulose instead of the mixture of di, penta, and hexa nitrocellulose, which formerly was always obtained as the basis of the process. The tri and tetra nitrocellulose are always obtained together and have not been separated from each other. The new process, moreover, involves the fixing for the desired time of these two nitrocelluloses, which heretofore, even when produced, were rapidly converted into the other nitrocelluloses. This fixing is performed by the agency of free sulfuric acid. In order to produce a perfectly homogeneous mixture of nitrocelluloses, I have found that it is necessary to gradually add the cellulose to the nitrating-bath and to gradually raise the temperature of the nitrating-bath as the nitration proceeds. After the completion of the nitrating process the product, consisting mostly or entirely of tri and tetra nitrocellulose, in a homogeneous mixture, is freed, as far as possible, from the nitrating-acids by centrifugal action, and not by washing in water and drying, the method heretofore adopted, and which always resulted in a slow transformation of a portion of the nitrocellulose. It is then immersed into sulfuric acid and again subjected to centrifugal action, and the acid-wet resultant mass is then mixed with a vulcanized drying-oil for the purpose of maintaining the otherwise unstable nitro compounds unchanged, and later, after the nitro groups have been deoxidized, to fill the pores of the fiber with cement-like filling. The mixture thus produced is then dissolved in a suitable solvent and drawn into a thread. The thread so produced is then submitted to a deoxidation of the nitro groups to render the same less easily combustible and susceptible of being dyed by the usual method. By this means an intermediate compound is produced which, though not a nitrocellulose or amido compound, is not cellulose, but a peculiar new compound, consisting of cellulose combined with nitrogen and insoluble in the solvents of nitrocellulose.

Having thus outlined the process forming part of my invention, I will now more particularly describe the same.

Cellulose in any form occurring in nature, such as wood, cotton, jute, ramie, and the like, and, when necessary, reduced to filaments and freed from mechanical and chemical impurity, is dried and nitrated in the following manner: The well-dried cellulose is, in small quantities, gradually introduced into a mixture of three volumes sulfuric acid of 66° Baumé and two volumes of nitric acid from 1.31° to 1.32° specific gravity, at an initial temperature of 30° Celsius. At each fresh addition of cellulose care is taken that the nitrating-acids are at a somewhat higher temperature. The temperature is then increased progressively up to, but not exceeding, 40° Celsius. Finally, the whole mixture is maintained at this temperature for several hours. Under this process, principally tri and tetra nitrocellulose are obtained, other nitrocelluloses being present only in small quantities. They are freed as much as pos-

sible from the adhering nitrating-acids by centrifugal action in a manner sufficiently well understood by those skilled in the art, and hence needing no further explanation. The weight of the nitrocellulose produced is reduced to about forty per cent. by this treatment. The nitrating-acids are recovered and may be used for fresh nitration by strengthening them by the addition of strong nitric acid. The nitrocellulose, damp with acid, is then placed into sulfuric acid of about 1.35 specific gravity. It is well distributed therein and again submitted to centrifugal action, after which a mass remains, containing said nitrocellulose with about forty per cent. of sulfuric acid of 1.4 specific gravity and some nitric acid. The product, damp with sulfuric acid, is now mixed with a vulcanized drying-oil, which may be obtained by treating any oil which dries in the atmosphere, such as, *e. g.*, cotton-seed oil, poppy-oil, linseed-oil, nut-oil, &c., in the following manner: The oil to be treated is diluted with half its weight of sulfuric ether in order to prevent too quick a reaction. To this from ten to twenty per cent. of sulfur chlorid (according to the nature of the oil and the consistency of the liquid required) is slowly added while continually shaking the mixture. After a short time it is found that a reaction has taken place and a yellow product or precipitate has separated out. The latter quickly settles and the thick clear liquid is separated therefrom by decanting. About ten per cent. by weight of the vulcanized oil or chemically-transformed liquid so obtained is then added to the acid-wet nitrocellulose last obtained, and the whole mixture then dissolved in about five times its weight of methyl-alcohol acetone or ethyl-alcohol alcohol-ether. After filtration it forms the raw material or solution from which the artificial thread or fiber is produced. This artificial thread is formed by simply allowing the solution to flow out from an orifice, preferably from one-fourth to one-half millimeter in diameter, into a suitable liquid or congealing bath, or directly into the atmosphere. The threads are by this means instantly solidified and are more or less fine according to the greater or lesser speed at which they are drawn out. They are immediately twisted or spun on the same machine. The twisted threads, wound on suitable spools or otherwise, are warmed for a long time in water as soon as possible, whereby the greater part of the free acid in the thread is removed therefrom. The solvent methyl-alcohol, acetone, ethyl-alcohol, ether, or the like is also driven out and may be partially recovered. By this treatment with warm water the combination of the nitrocellulose with the vulcanized oil, mechanically and chemically, is strongly aided, and much greater firmness and tenacity thereby imparted to the threads. The product obtained, however, is still too easily combustible, and it is difficult or even impossible to dye it by the usual methods in this condition. It is, therefore, submitted to deoxidation. This deoxidation might, as is known, be effected by partially eliminating the nitro groups in the nitrocellulose by heating the same with sulfur compounds, which give off sulfureted hydrogen. This method, however, is objectionable, for the reason that it seriously impairs the firmness of the threads. The product always suffers and may, in fact, be rendered quite worthless thereby. Moreover, I have found that an alkaline deoxidizing agent reacts quickly, but greatly prejudices the firmness of the thread. I have also found that the firmness of the thread after deoxidation greatly depends upon uniformity of the product worked upon with regard to its degree of nitration. By the process so far described, I obtain a product having such a high uniformity of nitration.

I prepare a deoxidizing liquid which will not injure the thread and which avoids injurious alkalinity, in the following manner: Concentrated ammonium hydrosulfid, prepared in any of the usual ways, is diluted with water to about ten per cent., and in it a suitable neutral magnesium salt is dissolved in about equivalent proportions. The threads are dipped into this liquid at about 40° Celsius, and kept there until the rainbow colors of cellulose are visible under the microscope in polarized light. The thread is thereupon washed in much water, dried, and finished.

In lieu of the ammonium hydrosulfid, potassium or sodium hydrosulfid may be used together with a magnesium salt. In order to prevent the precipitation of magnesia, any suitable ammonium salt is added, whereby a soluble ammonium-magnesium salt is formed.

Although I speak in the above of a deoxidation of the nitrocellulose and a retrogression of the same into, or, rather, toward, pure cellulose, by reduction with sulfureted hydrogen, which is the generally-accepted explanation of the reaction, I have always found that the resultant compound, though a derivative of cellulose, always contains nitrogen. Inasmuch as the same contains nitrogen, it is not cellulose. On the other hand, it is insoluble in the solvents of nitrocellulose, and has other properties which distinguish it from the same. It, therefore, is not nitrocellulose, or an amido compound, but rather a peculiar substance of its own kind, which is an intermediate compound between the same and cellulose.

The advantages and novel results flowing from my invention may, perhaps, be best shown by comparing the same with the art as heretofore practiced.

Nitration has hitherto been effected by immersing the cellulose for a long time into a mixture of sulfuric and nitric acids, or saltpeter, then squeezing out the nitrating-acids, thoroughly washing the nitrocellulose or pyroxyline several times in water, until there is

no longer any acid reaction, and then drying at a low temperature and dissolving in a suitable solvent. By this process several different nitrated products of cellulose are obtained, ranging from dinitrocellulose to hexanitrocellulose, and this mixture is what is commonly known under the name of "pyroxylin." Naturally, the portion of the cellulose first brought into contact with the nitrating-acids becomes most highly nitrated, the acids being then more concentrated. As the nitration proceeds, the acids become gradually weaker and hence lower nitrates are produced. Moreover, my experiments have shown that the after treatment of the nitrocellulose and the washing with water after removal of the nitrating-acids gives rise to a slow transformation, particularly of the tri and tetra nitrocellulose, and this transformation is hastened by the drying process.

The nitrocelluloses formed are the following: dinitrocellulose, $C_{12}H_{18}(NO_3)2O_8$; trinitrocellulose, $C_{12}H_{17}(NO_3)3O_7$; tetranitrocellulose, $C_{12}H_{16}(NO_3)4O_6$; pentanitrocellulose, $C_{12}H_{15}(NO_3)5O_5$; hexanitrocellulose, $C_{12}H_{14}(NO_3)6O_4$. Of these, the dinitrocellulose, pentanitrocellulose, and hexanitrocellulose are the constant products, and, when obtained in the usual way, are always mixed. They are, however, not very suitable on account of their low degree of solubility in the usual solvents. Moreover, the very great difference in the degree of nitration of these components causes a great inequality in the subsequent retrogression toward cellulose in the process of deoxidation. This inequality is very disadvantageous with regard to the strength of the thread produced.

Most thorough investigations and experiments conducted by me, moreover, have shown that the trinitrocellulose and the tetranitrocellulose are the most suitable compounds for producing a thread of the requisite strength, on account of their high degree of solubility in the ordinary known solvents of pyroxylin. Their solution, in a high degree of concentration, in such solvents is not of a glue-like consistency, as is the case with the other nitrocelluloses, and it may be readily worked, and subsequently it can be well deoxidized. The tetranitrocellulose and trinitrocellulose when obtained free from or mixed only with a small amount of the other nitrocelluloses have the advantage of differing only a little in their degree of nitration, and, hence, their subsequent retrogression toward cellulose is very uniform. They, therefore, yield a thread of much greater strength and tenacity than when the other nitrocelluloses are employed.

The tri and tetra nitrocellulose are ordinarily obtained together with other nitrocelluloses, but heretofore, as before stated, they are, by the further treatment of pyroxylin, converted into the lower dinitrocellulose and the higher penta and hexa nitrocellulose.

The presence of free sulfuric acid, upon which one feature of my invention is based, and the omission of the washing and drying step, however, effectually prevent or greatly retard this conversion. This I have demonstrated in the following way: Optically, in polarized light, dinitrocellulose appears uniformly clear, either directly after nitration or when precipitated from a collodion solution. It is only distinguished from cellulose in that the colors of the spectrum do not appear. This is the case, even if the material be washed for a long time with water and then dried. Pentanitrocellulose appears brown, with dark-blue stripes. It can be made by dissolving nitrocellulose in nitric acid and precipitating with sulfuric acid. Hexanitrocellulose appears in pure blue lines. Trinitrocellulose combined with tetranitrocellulose (they cannot be obtained separately or isolated) after nitration, and when the acids have been pressed out, appear, without any further treatment, glossy and of a feeble yellow color, without colored stripes or lines. If, however, they are freed from the acid by washing and gently warmed, the dark-brown stripes of the pentanitrocellulose appear directly in polarized light, indicating that the conversion into the higher nitrocellulose has taken place.

My treatment of the product with sulfuric acid after nitration, and the omission of the washing and drying steps in the process, hence favors the persistence of the uniform nitration and the yield of only the tri and tetra nitrocellulose. No appreciable heating of the fiber takes place, and decomposition does not set in, as is always the case on immersion into water. Above all, no higher product of nitration is formed. The nitrating-acid is also removed partly by the sulfuric acid and partly mechanically, so that the washing with water and subsequent drying, which I have shown to be incompatible with the production of the tri and tetra nitrocelluloses, for the purpose of removing the nitrating-acids, is avoided.

The advantage of that feature of my invention which consists in gradually adding the cellulose to the nitrating-bath and progressively raising the temperature of the bath after each fresh addition of cellulose is that a uniform product of nitration is obtained and not, as heretofore, a product varying greatly in the degree of nitration of its constituents, which, as above stated, seriously affects the strength of the thread produced, in view of the unequal retrogression of these products toward cellulose.

Under the old methods, where the cellulose was all introduced into the nitrating-bath at one time and the bath was maintained at the same temperature throughout the entire process, the portion of the cellulose first acted upon by the nitrating-acids yielded the higher products of nitration, and, as the bath became weaker, lower products of nitration were pro-

duced. A very unequal pyroxyline or nitro product was hence formed. This very undesirable result is obviated by the new treatment invented by me, and which, as stated, involves the gradual introduction of the cellulose into the nitrating-bath and the progressive heating of the same as the addition of fresh cellulose proceeds.

The advantage of the addition of the chemically-altered drying-oil is that thereby the otherwise unstable nitro compounds (the tri and tetra nitrocellulose) are maintained unaltered and uniformly nitrated. Another advantage is that thereby an unalterable compound is introduced and later on after deoxidation remains present between the molecules of the thread or fiber, thereby filling the same as with a cement and obviating too great looseness in its texture. This closing up or cementing of the fiber is hastened by the small quantity of nitric acid from the nitrating-acids in the dissolved mixture still present in the thread.

Having thus fully described my invention and the preferred manner of carrying out the same, what I claim, and desire to secure by Letters Patent, is—

1. The process which consists in gradually introducing cellulose into a nitrating-bath, and progressively raising the temperature of the nitrating-bath as the introduction of the cellulose proceeds, whereby a homogeneous mixture of tri and tetra nitrocellulose is obtained.

2. The process which consists in gradually introducing cellulose into a mixture of sulfuric and nitric acids, in the proportions and densities, substantially as specified, and raising the temperature of the mixture at each fresh addition of cellulose.

3. The process which consists in gradually introducing cellulose into a mixture of sulfuric and nitric acids, in the proportions and densities substantially as specified, and raising the temperature of the mixture at each fresh addition of cellulose, and finally maintaining the whole mixture at the final temperature for several hours.

4. The process which consists in gradually introducing cellulose into a nitrating-bath, and progressively raising the temperature of the nitrating-bath as the introduction of the cellulose proceeds, and treating the nitrocelluloses thus produced with sulfuric acid, to remove the nitrating-acids and to prevent the conversion of the nitrocelluloses obtained.

5. The process which consists in gradually introducing cellulose into a nitrating-bath, and progressively raising the temperature of the nitrating-bath as the introduction of the cellulose proceeds, and treating the nitrocelluloses thus produced with sulfuric acid, to remove the nitrating-acids and to prevent the conversion of the nitrocelluloses obtained, and mixing the acid-wet nitrocellulose with vulcanized oil.

6. The process which consists in gradually introducing cellulose into a nitrating-bath, and progressively raising the temperature of the nitrating-bath as the introduction of the cellulose proceeds, treating the nitrocelluloses thus produced with sulfuric acid, to remove the nitrating-acids and to prevent the conversion of the nitrocelluloses obtained, mixing the acid-wet nitrocellulose with vulcanized oil, and dissolving the mixture in acetone, an alcohol or alcohol ether.

7. The process which comprises the following steps: gradually introducing cellulose into a nitrating-bath and progressively raising the temperature of the bath as the cellulose is added, then maintaining the whole mixture at the final temperature for several hours, then separating the nitrating liquid by centrifugal action, then immersing the acid-moist resultant mass in sulfuric acid, then adding thereto a vulcanized drying-oil, and finally dissolving the mixture in a suitable solvent, such as acetone, an alcohol or alcohol ether, all substantially in the manner and in the proportions set forth.

8. The process which consists in drawing a thread from a mixture of trinitrocellulose and tetranitrocellulose with a vulcanized drying-oil dissolved in a suitable solvent, then immersing the same for a long time in warm water, and finally dipping the threads in a solution of the hydrosulfid of an alkali metal or radical and a neutral magnesium salt, to reduce the combustibility of the thread.

9. The process which comprises the following steps: gradually introducing cellulose into a nitrating-bath and progressively raising the temperature of the bath as the cellulose is added, then maintaining the whole mixture at the final temperature for several hours, then separating the nitrating liquid by centrifugal action, then immersing the acid-moist resultant mass in sulfuric acid, then adding thereto a vulcanized drying-oil, then dissolving the mixture in a suitable solvent, and finally immersing the same in a solution of the hydrosulfid of an alkali metal or radical, to reduce the combustibility of the thread.

10. The process which consists in dipping a thread consisting substantially of dinitrocellulose and tetranitrocellulose into a solution containing about ten per cent. of ammonium or other alkali hydrosulfid and a neutral magnesium salt at about 40°, Celsius, and keeping the same therein until the rainbow colors of cellulose are visible under the microscope in polarized light.

11. The process which comprises the following steps: gradually introducing cellulose into a nitrating-bath and progressively raising the temperature of the bath as the cellulose is added, then maintaining the whole mixture at the final temperature for several hours, then separating the nitrating liquid by centrifugal action, then immersing the acid-moist resultant mass in sulfuric acid, then adding thereto a vulcanized drying-oil, and finally dissolving the mixture in a suit-

able solvent, such as acetone, an alcohol or alcohol ether, then drawing the thread and immersing the same in warm water, and finally dipping the same in a solution to reduce the combustibility of the same.

12. The process which comprises the following steps: gradually introducing cellulose into a nitrating-bath and progressively raising the temperature of the bath as the cellulose is added, then maintaining the whole mixture at the final temperature for several hours, then separating the nitrating liquid by centrifugal action, then immersing the acid-moist resultant mass in sulfuric acid, then adding thereto a vulcanized drying-oil, and finally dissolving the mixture in a suitable solvent, such as acetone, an alcohol or alcohol ether, then drawing the thread and immersing the same in warm water, and finally dipping it into a solution of ammonium or other alkali hydrosulfid and a neutral magnesium salt at about 40°, Celsius.

13. The process which comprises the following steps: gradually introducing cellulose into a nitrating-bath and progressively raising the temperature of the bath as the cellulose is added, then maintaining the whole mixture at the final temperature for several hours, then separating the nitrating liquid by centrifugal action, then immersing the acid-moist resultant mass in sulfuric acid, then adding thereto a vulcanized drying-oil, and finally dissolving the mixture in a suitable solvent, such as acetone, an alcohol or alcohol ether, then drawing the thread and immersing the same in warm water, then dipping it into a solution of ammonium or other alkali hydrosulfid, and finally washing, drying and finishing the same.

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

FRIEDRICH LEHNER.

Witnesses:
H. HALBERG,
EMILIE MAJORES.