

1

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METHODS FOR MAKING NITROCELLULOSE

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6 Claims

ABSTRACT OF THE DISCLOSURE

A process of nitration of cellulose. The process includes first impregnating cellulose with a chlorinated aliphatic solvent and then subjecting it to nitration using a nitrating bath comprising concentrated nitric acid and chlorinated aliphatic solvent. The quantity of nitric acid in the nitrating bath being less than or equal to 50% and the nitration temperature being 0° to 45° C. The invention further provides a process for the preparation of pure, stable microcrystalline nitrocellulose.

Present methods for making nitrocellulose generally consist in nitrating cellulose in a sulphonitric mixture. Such methods have several disadvantages, including: the necessity to stabilize the nitrocellulose obtained; a certain degradation of the nitrocellulose in relation to the cellulose used; the practical impossibility of obtaining nitrocellulose with nitrogen contents of more than 13.8.

Various attempts have been made to overcome these disadvantages; for example, elimination of sulphuric acid from the nitration bath can, in certain conditions, allow the stabilization operation to be dispensed with. To this end, it is advisable to use nitric acid alone or mixtures of nitric acid and phosphoric acid or of nitric acid and acetic acid. In the last two cases, a perceptible degradation of the nitrocellulose obtained in relation to the cellulose used is always observed; furthermore, the nitration ratios

$$R = \frac{\text{quantity of nitrating mixture}}{\text{quantity of cellulose}}$$

are always very high. When using nitric acid alone, operation is very delicate for the cellulose gelatinizes very quickly in concentrated nitric acid, forming a protective layer which greatly impedes nitration in depth.

In order to avoid this and other disadvantages, it has been proposed to nitrate cellulose by means of a nitric acid/methylene chloride mixture in excess. But likewise in this case, the nitration ratios R are very high (in the order of 100 to 300) and more often lead to a partial gelatinization of the nitrocellulose.

Furthermore, in all these processes, the cellulose to be nitrated must be in a subdivided form, giving rise to the necessity for preliminary operations, such as "opening" of the cotton used.

An object of the present invention is to provide an improved method for the nitration of cellulose which minimizes or removes the aforesaid disadvantages.

According to this method, the cellulose to be nitrated is first impregnated with a chlorinated aliphatic solvent and then subjected to nitration by means of a nitrating bath composed of concentrated nitric acid, a chlorinated aliphatic solvent and, optionally, a strong dehydrating agent, using a nitration ratio of 10 to 50, a nitric acid content in the nitrating bath less than or equal to 50%

2

b.w., and a nitration temperature of 0° to 45° C.; after nitration, the nitrocellulose obtained is recovered, after having been stabilized, if required.

Methylene chloride, chloroform, carbon tetrachloride or the like, or a mixture of these solvents are particularly suitable as the chlorinated aliphatic solvent. The preferred solvent is methylene chloride.

Phosphorus pentoxide, sulphur trioxide, oleum, acetic anhydride and the like can be mentioned as suitable strong dehydrating agents. The preferred dehydrating agent is phosphorus pentoxide. The presence of a strong dehydrating agent in the nitrating bath is necessary in the case where it is desired to obtain a nitrocellulose which has a nitrogen content which is higher than 13.8.

In the preliminary stage of impregnating the cellulose, a weight ratio of impregnation solvent: cellulose of approximately 1:1 to 6:1 is used.

The present invention has the following advantages:

the possibility of using a relatively low nitration ratio of 10 to 50;

the possibility of obtaining a non-degraded nongelatinized nitrocellulose which has substantially the structure of the initial cellulose and its degree of polymerization;

obtaining a product which is generally stable directly after washing, without requiring any special stabilization treatment;

the possibility of nitrating celluloses of very varied constitution and origin, such as cotton linters, wood pastes, hydrolyzed celluloses, hydrocelluloses;

the possibility of nitrating celluloses which are in forms other than the sub-divided form, such as floss, threads, linen, paper, cotton, shavings, while keeping the original form;

facility of regulation of the desired nitrogen content up to complete substitution of the hydroxyl groups of the cellulose by nitro groups, by a choice of the nitration ratio in the range of 10 to 50 and a nitric content in the nitrating bath in the range of 0 to 50%;

the possibility of obtaining a very weak divergence of the nitrogen content around the desired average.

Furthermore, there are other advantages, such as the speed of the reaction and reliability in manufacture when the present invention is used.

The process according to the invention can be used in a general manner as follows:

PRELIMINARY IMPREGNATION

This is fulfilled by bringing a cellulose in any form and of any kind into contact with a chlorinated aliphatic solvent. It can be fulfilled, for example, continuously by sprinkling or intermittently by soaking.

Impregnation can be easily carried out in a liquid bath at ordinary temperatures. Its duration varies according to the type of cellulose used and its form (from 30 seconds to several minutes). It can equally be effected in the vapour phase.

The amount of the chlorinated aliphatic solvent should be between 1 and 6 times the amount of the cellulose to be nitrated. An amount of more than 6 would give a composition of the nitration bath which would risk division into 2 phases during nitration. An amount lower than 1 could lead to heterogeneity of the impregnation and to a risk of gelatinization of certain badly-impregnated parts of the cellulose.

The use, as the chlorinated aliphatic solvent, of methylene chloride, chloroform and carbon tetrachloride, for example, leads to appreciably similar results. Nevertheless, the ternary miscibility diagram (water-nitric acid—CHCl₃ or CCl₄) has a very restricted zone of homogeneous mixture and limits the range of nitration baths which

can be used with these solvents. This disadvantage is much less appreciable with methylene chloride.

NITRATION

This is fulfilled by bringing the cellulose, which has previously been impregnated with the aliphatic chlorinated solvent, into contact with the nitrating bath. The latter is composed of concentrated nitric acid with additions of a chlorinated aliphatic solvent and possibly a strong dehydrating agent. The reaction, which can be carried out continuously or intermittently, is effected in known manner.

The water content of the concentrated nitric acid used should preferably be lower than 6% b.w. when using methylene chloride as the chlorinated aliphatic solvent, taking into account the ternary miscibility diagram (water-nitric acid- CH_2Cl_2). However, since homogeneity of the liquid phase is favourable to obtaining a nitrocellulose of a more homogeneous quality, it is preferable, in order to take into account the water produced at the time of the reaction and the speed of diffusion of water throughout the fibre in relation to the speed of the reaction, to use concentrated nitric acids which have a water content of less than 1.5%.

It is advisable to limit the amount of nitric acid in the total nitration bath (impregnated chlorinated aliphatic solvent included) to a value less than or equal to 50%, so as to eliminate any risks of gelatinization.

The nitration ratio must be more than 10 and, particularly, from 10 to 50.

The temperature of nitration can vary between 0° and 45° C. Thus the reaction can easily be conducted at the reflux boiling point of the reaction mixture.

FINISHING OPERATION

Generally, once the nitration reaction has ended, the nitrocellulose is dried, rinsed in a chlorinated aliphatic solvent to recover the nitric acid which is impregnated therein and then immersed in water; the chlorinated aliphatic solvent is then recovered by distillation.

When nitrating hydrolyzed cellulose and when it is desired to obtain a very pure nitrocellulose, the finishing operations must include alcohol stabilization followed by rinsing in twice-changed water and then by rinsing in alcohol in the cold state. The latter is eliminated by boiling under agitation, for example.

The nitrocelluloses thus obtained are immediately stable and have practically the same degree of polymerization as the original cellulose. They likewise keep the same fine structure.

An important industrial application of the process of the invention is the manufacture of hydrolyzed cellulose or hydrocellulose trinitrates, which cannot be prepared by the known process of nitration of cellulose by a sulphonic bath, which gives gellatinized products which are particularly unstable.

Other uses consist in for example, the manufacture of cellulose trinitrates, cellulose nitrates of high viscosity, and nitrated papers, cardboards, linen or threads having good mechanical properties.

Regulation of the nitrogen content between 0 and 13.8 is easily done by varying the nitration ratio of 10 to 50 and the nitric acid content in the mixture of nitric acid-water-chlorinated aliphatic solvent at between 0 and 50%.

When it is desired to obtain nitrocelluloses with a nitrogen content of more than 13.8 (between 13.8 and 14.14), it is necessary to introduce a strong dehydrating agent into the nitration bath. Obviously the dehydrating agent will also be capable of use for the manufacture of nitrocellulose with a nitrogen content of less than 13.8.

Another use of the invention concerns the preparation of a pure, stable, microcrystalline nitrocellulose which is especially used as a source of atomic vapour for analysis by spectrophotometry of atomic absorption.

The invention is illustrated by the following non-

limitative examples of the use of the process according to the invention:

EXAMPLE 1

304 g. of phosphorus pentoxide, 1000 cc. of methylene chloride and then 460 g. of 99% nitric acid were introduced into a nitration reactor. A mixture of 500 cc. of methylene chloride and 162 g. of hydrolyzed cellulose with a polymerisation degree of 135 was then stirred in.

The reagents and the reactor had previously been cooled to -5° C. After admixing the reagents, the temperature rose to about +25° C. The mixture was left to react for 30 minutes, whilst being stirred.

The nitrocellulose obtained was dried and then rinsed in methylene chloride. A dried specimen had a nitrogen content of 14.0 and a polymerization degree of 130.

EXAMPLE 2

Wood paste in the form of 7 mm. squares cut up into sheets 1.2 mm. thick weighing 800 g./m.² was impregnated with methylene chloride and immersed in a mixture of 99% nitric acid-methylene chloride under agitation in such a way that the amount of nitric acid in the resulting bath was 22% and the nitration ratio 25.5. The mixture was brought to the boil under reflux for 15 minutes. Its nitrogen content was 11.2 and it was soluble in ethyl alcohol.

EXAMPLE 3

A eucalyptus paste in the form of 5 mm. squares cut into sheets 0.9 mm. thick weighing 700 g./m.², was stirred in a reactor with 6 times its weight of methylene chloride. 99% nitric acid diluted by methylene chloride was poured in whilst maintaining strong agitation, until the nitric acid content was 24.5% in the bath of nitric acid-methylene chloride and the nitration yield 35.5. The mixture was left to react for 30 minutes at 20° C. under agitation. Nitrocellulose with a nitrogen content of 12.0 was obtained.

EXAMPLE 4

Cotton linters which had been impregnated with methylene chloride were immersed in a mixture of 99% nitric acid-methylene chloride. For a nitration ratio of 30, an amount of 45% nitric acid in the resulting bath, the nitrogen content of the nitrocellulose obtained after 20 minutes of reaction at 30° C. under agitation was 13.4.

EXAMPLE 5

A cloth woven with fine cotton threads of long fibres in a width of 15 mm. was impregnated with twice its own weight of methylene chloride and then nitrated for 30 minutes at 25° C. in a bath of 99% nitric acid-methylene chloride. The amount of nitric acid in the nitration bath was 30%, and the nitration ratio was 45. A nitrated cloth 0.30 mm. thick with a nitrogen content of 13.0 was obtained.

The tensile strength for a test piece 1 cm. in size was 11 kg. for the non-nitrated cloth and 10.5 kg. for the nitrated cloth.

In the following example, the effect of the process of the invention is described with a view to the preparation of a pure, stable, microcrystalline nitrocellulose, particularly used as a source of atomic vapour for analysis by atomic absorption spectrophotometry.

Such a method of analysis is based on the fact that an atomic vapour absorbs radiation in a wavelength which is specific to the cation contained in the vapour.

For example, in order to effect the analysis of a cation by atomic absorption spectrophotometry, the liquid containing the cation to be measured is usually atomized in the flame of a Bunsen-burner.

According to another method, molecular dissociation and then the change to the atomic state, is caused by the gas evolving from the combustion of a nitrocellulose base powder, and the samples to be measured are either impregnated or simply mixed with the powder. Such a

method can be used on much smaller specimens and the specimens to be measured do not have to be made into a solution.

To make up a suitable source, the nitrocellulose powder must simultaneously have several properties:

(a) As the proportion of the number of atoms excited to the number of atoms in the fundamental state must always be constant (according to the principle of measurement by atomic absorption spectrometry), it is important that the flame temperature of the powder is constant; furthermore, this temperature depends essentially on the nitrogen content of the nitrocellulose used, which must deviate very little within the test sample and very constant from one sample to the other;

(b) Similarly, the rate of combustion of the test sample must be as constant as possible (by radiation and convection, the length of combustion has an effect on the temperature of the gases); furthermore, this rate is a function of the nitrogen content of the powder;

(c) The powder must be free of the cations which are to be determined so that they cannot falsify the result;

(d) Impregnation of the powder by the measuring liquid must be as even as possible in order to avoid at the heart of the mass preferential concentrations of the cations to be measured, which can cause "dispersion" effects, the consequence of which would be to completely falsify the result by default;

(e) The powder must be stable with time and not decompose spontaneously.

Known nitrocelluloses do not allow a nitrogen content to be attained which is sufficiently constant to be conveniently utilizable. Moreover, their method of manufacture introduces a certain number of cations which would consequently be undesirable.

Furthermore, it has been discovered according to the invention that when starting from a hydrolyzed cellulose which has been freed from all its amorphous parts, viz. a microcrystalline cellulose, the present method of nitration enables nitrocellulose to be obtained which has kept its microcrystalline character, the nitrogen content of which is very little dispersed around the desired average, and the degree of polymerisation of which is strictly constant.

Such a nitrocellulose becomes very useful as a source of atomic vapour in atomic absorption spectrophotometry after one or more stabilization treatments, according to the invention, in ethyl alcohol at boiling point, the object of which is to remove all the fibres of weakly-nitrated cellulose.

The ratio of alcohol:nitrocellulose in the course of this treatment is more than 1, preferably being about 2:1 to 3:1.

Such treatment is followed, after drying and cooling teh mass of stabilized nitrocellulose, by a certain number of rinses in twice-exchanged water and then in ethyl alcohol in the cold state, with drying taking place after each washing.

There are preferably 5 washes in twice-changed water under mechanical agitation at atmospheric pressure at a temperature of about 10° to 40° C., with a nitrocellulose:water ratio of about 1:5 to 1:50, lasting about 15 minutes per washing, with drying under vacuum taking place after each washing.

These rinses in twice-changed water are followed by drying in vacuum of the mass of nitrocellulose used and then by cold washing with alcohol, using the same alcohol:nitrocellulose ratio of about 1:1 to 5:1.

This preparation will be illustrated by the following example.

EXAMPLE 6

Nitration

304 g. of phosphorus pentoxide, 1000 cc. of methylene chloride and then 460 g. of 99% nitric acid were intro-

duced into a nitration reactor in order to form the nitrating bath.

162 g. of hydrolyzed cellulose with a polymerization degree of 135 which had been previously impregnated with 500 cc. of methylene chloride was stirred into the bath.

The reagents and the reactor had previously been cooled to -5° C. After mixing the reagents, the temperature rose to about +25° C. The mixture was left to react for 30 minutes under agitation.

The nitrocellulose obtained was dried and rinsed in methylene chloride in order to obtain nitrocellulose (280 g.) which had a nitrogen content of 14.0 and a degree of polymerisation of 130.

Stabilization

100 g. of the nitrocellulose already obtained was treated for an hour with 200 cc. of 95% ethyl alcohol at the boiling point in atmospheric pressure. This treatment was followed by drying in vacuum, after which a new stabilization was effected with 200 cc. of 95% ethyl alcohol at the boiling point for an hour at atmospheric pressure; the nitrocellulose thus stabilized was again dried under vacuum and cooled to ambient temperature.

Washing with twice-exchanged water

There were 5 successive washings with twice-exchanged water in a water-bath at 30° C. under mechanical agitation and atmospheric pressure. Each washing was carried out with 1 litre of twice-exchanged water and lasted 15 minutes. Each washing was followed by drying under vacuum.

Washing in ethanol in the cold state

The nitrocellulose, stabilized and washed in twice-exchanged water, was then subjected for 5 hours to washing in ethanol (200 cc.) in the cold state (4° C.), at atmospheric pressure under mechanical agitation, and was then dried under vacuum.

Pure, stabilized nitrocellulose was finally obtained (85 g.).

The purity of the product of this example was shown by measuring metallic elements in comparison with the initial microcrystalline cellulose which had not undergone the treatments according to the invention.

Metallic element measured:	Microcrystalline nitrocellulose	
	Before treatment, p.p.m.	After treatment, p.p.m.
Ca.....	50	5
Fe.....	10	1
Ca.....	5	(1)
Na.....	50	(1)
Co.....	50	(1)
Al.....	50	(1)
Li.....	50	(1)
Pb.....	50	(1)
Mg.....	50	(1)

¹ None.

The homogeneity of the product according to the invention is determined as a function of the error made in measuring the absorption by the flame of a microcrystalline nitrocellulose, in perfectly defined experimental conditions, of the radiation given out by a given metallic element, in this case copper (wavelength 3247 A.).

Relative error	Microcrystalline nitrocellulose	
	Before treatment, percent	After treatment, percent
For a series of 30 measurements with a coefficient of probability of 95%.....	2.2-2.6	1.2-1.5

The stability of the product according to the invention is illustrated by the Taliani test carried out on samples

7

of microcrystalline nitrocellulose with a nitrogen content of 13.5% having been stabilized with ethyl alcohol at the boiling point for different periods of time:

Sample tested:	Taliani test, min.
Nitrocellulose stabilized for 30 min. -----	83.75
Nitrocellulose stabilized for 1 hour -----	84.25
Nitrocellulose stabilized for 2 hours -----	87.25
Microcrystalline nitrocellulose, not stabilized -----	81.00

We claim:

1. A process of nitration of cellulose which comprises impregnating cellulose with a chlorinated aliphatic solvent in a weight ratio of solvent:cellulose of about 1:1 to 6:1, and then subjecting said impregnated cellulose to nitration using a nitrating bath comprising concentrated nitric acid and chlorinated aliphatic solvent, the quantity of nitric acid in the nitrating bath being no greater than 50% and the nitration temperature 0° to 45° C.

2. A process according to claim 1, wherein the chlorinated aliphatic solvent is methylene chloride.

3. A process according to claim 1 wherein a strong dehydrating agent is present in the nitrating bath.

4. A process according to claim 3, wherein the dehydrating agent is phosphorus pentoxide.

5. A process according to claim 1 for the preparation

8

of pure, stable microcrystalline nitrocellulose, wherein the resultant nitrated cellulose is subjected to a stabilization treatment in ethyl alcohol at the boiling point using an alcohol:nitrocellulose ratio of more than 1 and the stabilized nitrocellulose is cooled, dried and washed in twice-exchanged water, under mechanical agitation, at a temperature of about 10° to 40° C., using a nitrocellulose:water ratio of about 1:5 to 1:50 and is finally dried and washed in cold ethyl alcohol using an alcohol:nitrocellulose ratio of about 2:1 to 5:1.

6. A process according to claim 5, wherein the alcohol:nitrocellulose ratio in the first stage is in the range of 2:1 to 3:1.

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