PUBLISHED

APRIL 27, 1943.

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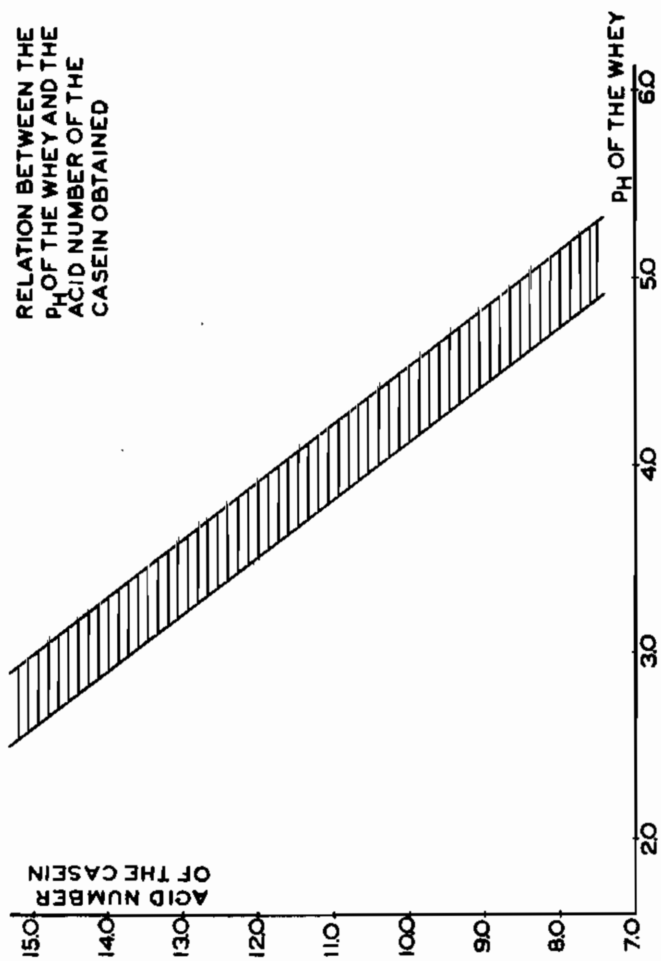
Filed Jan. 20, 1940

Serial No. 314,880



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Published Apr. 27, 1943

Serial No. 314,880

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE MANUFACTURE OF FIBRES, FILAMENTS, THREADS, FILMS AND THE LIKE FROM SOLUTIONS OF PROTEINS, PARTICULARLY CASEIN

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Application filed January 20, 1940

For the manufacture of fibres, filaments, threads, films and the like from solutions of proteins, particularly casein, the protein is dissolved in diluted alkali at temperatures below 30° C, whereupon the solution is aged some time, during which aging time a remarkable increase of the viscosity occurs and after that the solution is spun in an acid spinning bath in a manner known per se.

This increase of the viscosity by the aging is considered to be of great importance, since a suitable viscosity is desirable for an exact proceeding of the spinning process. This is the reason why several more or less efficient measures for regulating or keeping constant the viscosity are mentioned. In this connection the literature also mentions variations of the alkalinity. According to the invention it has appeared that the alkalinity of the spinning solution, also for other reasons, is very important, viz. particularly an alkalinity range, in which, to some extent, the alkalinity runs counter to the easy dissolving of the protein.

In order to elucidate this further, it is first necessary to give an exact definition of which has to be understood by the alkalinity of a protein solution, because the composition of e. g. a casein solution is not sufficiently defined by indicating the amounts of casein and alkali used, since it is necessary to mention thereby the acidity or preferably the acid number (i .e. the number of cm^3 N/10 NaOH necessary for neutralising 1 g casein with phenolphthalein as an indicator) of the casein used. For this acid number depends on the manner in which the protein, particularly the casein, is precipitated, viz. in such a manner that the acid number of the protein increases as the pH prevailing during the precipitation decreases.

The annexed drawing shows a diagram indicating by way of example this relation between acid number and pH for casein. The hatched area contains a very large number of points being determined experimentally. This relation is not represented by a single line, since mostly small deviations of a straight line are found in consequence of incidental and periodical variations of the buffer value of milk.

Therefore, speaking about an amount alkali to be used for dissolving, this amount has to be split up into a part being necessary for neutralising the protein and an excess, hereinafter called "free alkali", which in reality represents the alkali content of the solution. Starting e. g. from the so-called "textile casein", having an acid number of approximately 10,5 and using for 100 kg dry casein 9,56 kg NaOH to obtain a solution of 17%, there will be approximately 0,91% free NaOH; using 7,73 kg NaOH, there will be approximately 0,60% free NaOH (or 0,88 mol/kg casein).

In case with a view to more easy dissolution of the protein, such as casein, a method is used, in which at first a part of the water is retained in order to add this later on for obtaining the desired concentration, even a very much higher percentage free alkali will temporarily be present.

It is known that an extreme excess NaOH strongly decomposes protein material, such as casein, so that it is impossible to spin such solutions. Nor does applicant aim at solutions having a content of free NaOH of 0,6–0,9% and higher or a corresponding content of KOH or alkali mixtures, with which it is possible to operate fairly well and to obtain good results.

According to the invention, however, it is found that the range of contents of free NaOH being much lower than 0,6%, offers great advantages for the spinning. For it has appeared that by decreasing the content of free alkali to below 0,5% or preferably below 0,3%, with for the rest the same method a textile product having in general a remarkably better quality is obtained, particularly with a view to the strength which by a decrease of the content of free alkali from 0,5% to 0,2% showed an improvement of 15–20%. Also other properties, such as the resistance to boiling, are improved. This improvement is lasting by lowering the content of free alkali below 0,1%, even as much that no more free alkali is present or even a deficiency in bound alkali occurs.

Though in general protein solutions by the aging tend to become still more viscous till coagulation occurs, this tendency appears to be already very small for 0,2% of free alkali and for 0,1% of free alkali the remarkable phenomenon occurs that the viscosity decreases during the aging, as the following table shows.

Free NaOH	After 3 hours	After 12 hours	After 22 hours	After 48 hours
+0.2%	53	66	66	65
+0.1%	95	72	62	43
0.0%	188	72	47	22

Though it is true that solutions having a very low content of free alkali or even a deficiency in bound alkali, sometimes can be prepared and treated less easily than those with a very much higher content of alkali, this partly depending from the protein used (which rather causes differences of the viscosity), according to the invention this can be met by suitable measures. In case e. g. operating with protein solutions containing 0,1% or less of free alkali would cause difficulties by the high starting viscosity, these difficulties can be overcome by adding to the solution small amounts of a substance having no or an extremely weak alkaline reaction and which in large amounts can dissolve protein being not neutralised, e. g. urea, thiourea and the like. E. g. the viscosity of a casein solution containing only 0,05% or less of free alkali, will be lowered to half its value or less by addition of 1-5% of urea.

If, therefore, a content of free alkali below 0,1% or even a deficiency in bound alkali, that is to say, if proteins being neutralised incompletely, have to be dissolved, would cause difficulties, the use of these substances being not or extremely weakly alkaline is a suitable manner of meeting the difficulties. The possibility of the growth of bacteria, however, increases, but this can be met in the ordinary manner by using one of the many preserving means, e. g. thymol, phenol, cresol, β-naphtol, hypochloric salts, salicylic aldehyde, salts of heavy metals, etc.

The solutions may also be pasteurised or sterilised immediately after their preparation, which preferably is carried out by momentaneous heating. It is a particular property of these casein solutions with a low alkali content that they can withstand this, since by this operation the solutions having a higher alkali content become unsuitable or less suitable for spinning purposes, probably by hydrolysis of the casein.

These protein solutions having a very low content of free alkali offer also in an other connection an important advantage, because practically they can be spun without aging. In case protein having a very low ash content, in which form e. g. casein can be obtained, is used hereby the solution with a very low content of free alkali or even lacking in bound alkali has a lower starting viscosity than solutions of proteins containing more ash.

The protein solutions according to the invention having a very low content of free alkali or even lacking in bound alkali, also cause difficulties by the filtration as a consequence of their high starting viscosity. As a matter of fact the protein solutions having a rather high free alkali content have a rather low starting viscosity which, however, increases during the aging, as the following table shows.

Per cent free NaOH	3 hours	12 hours	22 hours	46 hours
+0.9	8	12	12	16
+0.6	12	17	17	21
+0.4	23	32	31	36
+0.3	29	38	39	41
+0.2	53	66	66	65
+0.1	95	72	62	43
+0.0	188	72	47	22
−0.1	(1)	(1)	60	43
−0.2	(1)	(1)	83	58

[1] Too viscous.

According to the invention it has been found further that spinning solutions having a low alkali content are very well resistant to increased temperatures, so that their viscosity can be sufficiently decreased by heating, in order to obtain solutions which can easily be filtered. The remarkable fact thereby is that the heating has only a very small influence on the starting viscosity, but that the starting viscosity lasts longer. This is clearly shown by the following table, which relates to spinning solutions prepared from two samples of casein, one part of the solutions having been kept at 25° C and another part having been first heated at 80° C during some time and thereupon having been kept also at 25° C. The viscosity was determined with the falling sphere viscosimeter at several times after the preparation.

Sample	Temp.	1 day	2 days	3 days	5 days	6 days
	Degrees					
B	25	62	21	10	2	1
B	80	63	65	64	45	42
C	25	25	10	4	1	1
C	80	34	35	37	28	25

It has been found that the duration of the heating may vary between some minutes and some hours and that the temperature may be increased to at least 60° C, preferably, however, to a temperature above 80° C. The surprising fact is that the spinning solutions according to the invention are not coagulated and/or decomposed at the high temperatures, such in contradistinction to the spinning solutions having a high content of free alkali.

By way of example, but not as a limitation of the invention, the following examples are given.

Example 1

(*a*) 100 kg spinning solution is prepared from 16,7 kg of casein (dry matter content 95,6%, acid number 8,7), 81,9 kg of water, 0,382 kg of NaOH and 1,0 kg of urea.

16% casein
1% urea
−0,2% free alkali
or 0.3 mol./Kg casein
} viscosity=18.

(*b*) 100 kg spinning solution is prepared from 16,7 kg of the same casein, 82,9 kg of water and 0,382 kg of NaOH.

16% casein
−0,2 free alkali
} viscosity=24.

Example 2

(*b*) 100 kg spinning solution are prepared from 16,7 kg of casein (dry matter content 95,6%, acid number 8,7), 82,5 kg of water and 0,782 kg of NaOH.

16% casein
+0,2% free alkali
or +0.3 mol/Kg casein
} viscosity=29.

(*b*) 100 kg spinning solution are perpared from 16,7 kg of casein of the same casein, 79,5 kg of water, 0,782 kg of NaOH and 3 kg of urea.

16% casein
+0,2% free alkali
3% urea
} viscosity=9.

These viscosities are determined with the falling sphere viscosimeter.

Obviously the invention is not limited to the examples given, but the data mentioned may vary according to the circumstances, particularly there exist several substances having a dissolving action and satisfying the exigencies.

Various changes may be made in the details disclosed in the foregoing specification without departing from the invention or sacrificing the advantages thereof.

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