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HARDENING CASEIN ARTIFICIAL FIBERS WITH TITANIUM, ZIRCONIUM OR TIN SALTS

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8 Claims. (Cl. 8—127.6)

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This invention relates to a process for treating artificial fibers and filaments formed with casein, and to the products produced. In particular, this invention is directed to a method for producing filamentous structures formed from casein which are curly and wool-like, and which in addition have improved chemical and physical properties.

In the manufacture of artificial filaments and fibers formed from casein, the ordinary process comprises the steps of dissolving a casein material in an alkali solution, extruding the dissolved casein through a spinneret into an acid coagulating bath to form a plurality of filaments, thereafter passing the bundle, i. e., "tow," through subsequent baths which may contain formaldehyde, and finally subjecting the tow to prolonged curing or hardening in a formaldehyde hardening bath. The hardened filaments are then thoroughly washed to remove excess formaldehyde, acid, salts, and the like, and then dried. If desired, they may be cut to a predetermined length to form staple fibers. Casein filaments and fibers produced in this manner have not been entirely satisfactory because they have been found to have very poor resistance to hot dilute acid and alkali solutions such as those encountered in the after-treatment of textiles, such as treatments involving dyeing, scouring, laundering, and the like. Other filaments and fibers have the further disadvantage in that they take up dye from a dye bath solution too rapidly, which makes the dyeing operation very difficult and sometimes actually impossible to control, resulting in the formation of uneven and streaky yarns and fabrics.

Many attempts have been made to overcome these disadvantages but such attempts have not proven entirely satisfactory. Many of the proposed treatments do not improve the boil resistance to a satisfactory degree. Other treatments, while they may impart satisfactory resistance to hot dilute acid and alkali solutions, at the same time introduce other objectionable characteristics, such as loss of strength and "tendering." Still other treatments result in a darkening or other permanent discoloration which prohibits the use of the fiber in the formation of textiles having white or light shades. Furthermore such treatments often produce a harsh or objectionable hand; or sometimes may involve the use of expensive or dangerous chemicals. For example, it has been suggested that the resistance of casein fiber to acid and alkali boil treatments may be improved by subjecting the fiber to an acetylation step. In this treatment, the casein fiber is first

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dried, then treated with ketene or acetic anhydride at elevated temperatures for a period of several hours. Although this treatment may enhance the boil resistance and dyeing properties of the fiber, a substantial percentage of the fiber strength is lost, the fiber becomes yellow, dull and lifeless, and takes on an undesirable scroop. The use of acetic anhydride in the treatment of casein fibers at elevated temperatures is also undesirable because a recovery process is required, and from the operational standpoint elaborate precautions have to be taken to avoid exposure to the irritating and poisonous fumes. In addition, an extra washing and drying step is required, which adds to the cost of processing such fibers.

The use of sodium nitrite or nitrous acid has also been suggested as a means for improving the boil resistance of casein fiber. This process is unsatisfactory in that the fiber becomes brown in color and also results in a loss in fiber strength.

The use of chromium salts has also been suggested for the after-treatment of casein fibers. Although this process ordinarily produces fibers which have satisfactory boil resistance without loss in strength, it imparts a permanent blue-green color to the fiber which is difficult and usually impossible to mask or neutralize. Such fiber is, therefore, suitable for forming textiles having dark or black shades only.

Other processes for improving the boil resistance and dyeing characteristics of fiber have been suggested, but these have been found either to be ineffective in accomplishing their purpose, impractical, or resulting in an adverse effect upon the physical and chemical properties of the fiber.

From the physical standpoint, the prerequisites of an ideal artificial filament of fiber formed from casein, such that the finished product may be advantageously used in the manufacture of yarns, fabrics, textiles and the like, are as follows: (*a*) the filament or fiber should be substantially white in color; (*b*) such filament or fiber should have high resistance to attack by acids when boiled in dilute acid solution; (*c*) moreover, such filament or fiber should have high resistance to attack by alkalies when boiled in dilute alkali solution; (*d*) the filament or fiber should have a relatively high tensile strength; (*e*) finally, such filament or fiber should have a rate of dye takeup substantially comparable to that of wool. All of these prerequisites must be met in order to provide artificial casein fibers and filaments having real commercial value. Thus, in accordance with the present invention,

the final product after processing, comprising the artificial filaments and fibers formed from casein. must be subjected to and pass these standards, hereinafter called "the pentafold test."

It is, therefore, a general object of the present invention to provide a process for treating artificial filaments and fibers formed from casein in order to produce products having improved physical and chemical properties, thereby overcoming the disadvantages heretofore encountered in the prior art.

It is a further object of this invention to provide a method for treating artificial casein filaments and fibers to produce a final product having enhanced characteristics, including a high resistance to hot dilute acid and alkali solution, improved rate of dye takeup, retention of a substantial part of the tensile strength of the original fiber, white color, a soft feel, and which final product after treatment acquires a good crimp with little or no scroop.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The pentafold test which has been adopted in order to establish a set of standard requirements for the product of the present invention, is as follows:

(1) *Acid boil resistance*

A sample of fiber to be tested is placed in an acid bath buffered to a pH of 2.5, the bath then being brought to boiling and maintained at boiling temperature for 1½ hours. At the end of this period the fiber is removed from the bath, washed free of acid and salt and dried overnight at room temperature. The fiber is then examined for changes such as color, tendering, harshness and tack and is then assigned a number from 1 to 10 based on a combination of such properties. A No. 1 rating is given a fiber which shows no sign of deterioration of any sort during the acid boil. A No. 10 rating is assigned to a fiber which disintegrates to a hard, horny mass after being subjected to this test. Nos. 2 through 9 are assigned to those fibers which show a gradual variance in properties from an unchanged to a completely disintegrated fiber.

(2) *Alkali boil resistance*

This is conducted in a manner similar to that of the acid boil resistance test, except that the test solution is buffered at a pH of 8.6, and the time of boil is 1 hour instead of 1½ hours. Ratings are assigned to the washed, dried fiber in a manner identical to those assigned in the acid boil resistance test.

(3) *Color*

The finished fiber is evaluated for color by visual inspection. If the fiber retains a substantially light color which is capable of being dyed to a pastel shade, especially when commingled with other fibers such as rayon, wool and the like, then the finished product is passed as satisfactory.

(4) *Tensile strength*

The tensile strength of the fiber after treatment is determined by comparison with the fiber prior to such treatment. The treated fiber is considered to be a satisfactory product if the tensile strength is not less than 80% of the fiber prior to such treatment.

In testing for strength the fibers are first conditioned at 70° F. and 65% relative humidity. They are then prepared for testing by the standard A. S. T. M. method, 1946 A. S. T. M. Standards, part 3 (a) "Nonmetallic Materials," "Standard Method for Testing Rayon Staple . . . Tensile Strength Part A," preferred method flat bundle, pages 640–643, sections 24–31 inclusive, except that the bundle is made smaller so that it will be suitable for testing in the Scott IP–2 Tester. Samples for wet strength testing are soaked for 30 minutes in distilled water at room temperature prior to testing. The strength figures are reported as grams per denier.

(5) *Dye takeup*

The rate of dye takeup is determined by preparing a dye bath ordinarily used for dyeing wool fibers and an equivalent amount of the final product, after treatment in accordance with this invention, is immersed in this bath. The rate of dye takeup is then determined by observing the time at which the dye bath becomes exhausted, and comparing this with the rate of dye takeup on wool. The appearance of the dyed fiber also gives a good indication of the rate of dye take up since, if the dye takeup is too high, the fiber will be uneven and mottled in appearance.

We have now found that these objects may be attained by treating filamentous structures consisting of artificial casein filaments and fibers, after coagulating such structures but prior to drying, by inserting a step comprising subjecting said structure to treatment in an aqueous solution of a salt of a metal selected from the group consisting of zirconium, titanium, and tin. In addition to providing a product having enhanced chemical and physical characteristics, it was found that such structures, as a result of such treatment with these particular metal salts, became curly and acquired wool-like properties.

In the now preferred embodiment, the filamentous casein structures are subjected to treatment by the metal salt solutions of the class described at elevated temperatures of between 120° F. and 200° F., preferably for a period of from 1 to 24 hours, at a pH of 0.8 to 3.0. The treatment may be conducted either on uncut strands, with or without tension, or on the staple fiber. If desired, there may be added to the treating bath other salts, such as sodium chloride, sodium sulphate and the like; hardening agents such as formaldehyde; and if necessary, sufficient acid or acid salts to control the pH within the range of 0.8 to 3.0. The ratio of fiber to bath, including solids, is on a weight basis, preferably in a ratio of from one part of filament or fiber to between 15 to 20 parts of the bath.

The amount of the metallic salt which may be used is within the range of from a 0.5% solution up to saturation. Poor results are obtained using solutions containing less than 0.5% salt concentration. The amount of metallic salt preferably employed in the treating bath was found to be within the range of from 2% to 10% of said salt on a weight basis. Among the zirconium salts which may be used are, for example, zirconium sulphate, sodium zirconyl sulphate, potassium zirconyl oxylate, ammonium zirconyl sulphate, and the like. Among the titanium salts which may be employed are titanium basic sulphate, titanium tetrachloride and the like. Among the tin salts which have been found to be satisfactory are stannic chloride, stannic sulphate, stannous chloride, and the like.

Best results have been attained by carrying

out the treatment of the casein fiber in the metal salt bath at elevated temperature, within the range of 120° F. and 200° F. The effectiveness of the reaction of the metallic salt on the protein was found to increase very rapidly with an increase in the temperature, and the necessary time of treatment in the bath greatly shortened as the temperature increased. For example, at room temperature the full effectiveness of the treatment is not realized even when the fiber is left in the metallic salt bath for a period of 48 hours. Full effectiveness is attained at 150° F. after a period of treatment of 3 to 4 hours in the bath; and if the temperature is raised to 175° F., the treating time is reduced to 2 to 2½ hours. At temperatures higher than 200° F., although very satisfactory boil resistance is attained, the strength and other properties of the fiber are adversely affected, probably due to the partial degradation of the protein at such temperatures.

As aforementioned, the pH range must lie within 0.8 to 3.0 in order to attain best results in the final product. The optimum pH range has been found to lie within a range of 1.0 to 2.5. If the pH of the bath is lower than 0.8, the tensile strength of the resulting fiber is reduced. If the pH be raised to higher than 3.0, a precipitation of the metallic salt may occur and in any event the full degree of resistance of the fiber to hot dilute acid or alkali solution is not realized.

The following examples are given by way of illustration. Unless otherwise stated, the parts herein recited are in parts by weight.

Example 1

Acid precipitated casein was dissolved with the aid of 2.1% of caustic soda to a solids content of about 20% and then extruded through a spinneret into a sulfuric acid-sodium sulphate coagulating bath, and the bundle of filaments then passed through a saline setting bath with concurrent stretching, and thereafter hardened overnight in a bath containing sodium sulphate and formaldehyde. The hardened filaments were then squeezed to remove excess hardening bath, stapled to ¾'' length, and the unwashed stapled fiber treated in the following bath for 2¾ hours at 165° F. with a bath-to-fiber ratio of 17:1 by weight based upon the dry weight of the fiber, at a pH of 1.6:

	Per cent
Sodium zirconyl sulphate	5.7
Formalin	5.7
Water	88.6
	100.0

After treating, the fiber was centrifuged to remove excess liquid, washed thoroughly, oiled with a sulphonated oil solution and dried. When tested for acid and alkali boil resistance, the alkali rating was found to be in the range of 2 to 3 and the acid rating between 1 to 2. Fiber made in a similar manner but omitting the final treating bath, gave a boil resistance rating in the range of between 8 and 9 for both the alkali and the acid boil tests. The finished fiber was white in color, soft and wooly to the touch, and had good crimp.

Example 2

An acid precipitated casein was dispersed with the aid of 2.3% of caustic soda to a solids content of about 20%, and then extruded through

a spinneret into an acid-salt coagulating bath. The bundle of filaments was then passed through a saline setting bath with concurrent stretching, and then hardened for 3 hours in a bath containing sodium sulphate and formaldehyde. The hardened filaments were then squeezed between rolls to remove excess hardening bath, stapled to 2'' length, and the staple fiber then treated in the following bath for 2¾ hours at 170–175° F., at a pH of 1.1:

	Per cent
Stannic chloride	6.3
Formalin	6.3
Water	87.4
	100.0

After treating, the fiber was extracted, washed, oiled, and dried. When tested for acid and alkali boil resistance, the alkali rating was 3, and the acid rating was 2. Fiber made in a similar manner, but omitting the final treating bath, gave boil resistance ratings in the range of 8 to 9 for both the alkali boil and the acid boil tests. The finished fiber was substantially white in color, soft and wooly to the touch, and possessed excellent crimp.

Example 3

Casein fiber was prepared, extruded and treated in a manner similar to Example 2, except that the bath containing the stannic chloride was replaced by the following bath. The pH of this bath was 1.3, and the temperature was approximately 160° F. for 3 hours:

	Per cent
Basic titanium sulphate	6.3
Formalin	6.3
Water	87.4
	100.0

The titanium sulphate was in excess of the amount which would dissolve in the bath. After treating, the fiber was centrifuged, washed, oiled and dried. When tested the fiber was found to have an alkali boil rating of 3 and an acid boil rating of 2. The finished fiber was substantially white in color, soft and wooly to the touch, and possessed excellent crimp.

Example 4

Casein fiber was prepared, extruded and treated in a manner similar to Example 2, except that the bath containing stannic chloride was replaced by the following bath, with sufficient sulfuric acid added to adjust the pH to 1.65:

	Per cent
Potassium zirconyl oxylate	6.3
Formalin	6.3
Water	87.4
	100.0

The fiber was treated in the bath at 170° F. for 2¾ hours. After treating, the fiber was centrifuged, washed, oiled and dried. When tested the fiber was found to have an alkali boil rating of 3, and an acid boil rating between 2 and 3. The finished fiber was substantially white in color, soft and wooly to the touch, and possessed excellent crimp.

Example 5

Casein fiber was prepared, extruded and treated in a manner similar to Example 2, except that

the bath containing stannic chloride was replaced by the following bath having a pH of 1.7:

	Per cent
Sodium zirconyl sulphate	5.7
Formalin	5.7
Water	88.6
	100.0

The fiber was treated in the bath at 135° F. for 7 hours. After treating, the fiber was centrifuged, washed, oiled and dried. When tested the fiber was found to have an alkali boil rating of 3, and an acid boil rating of 2. The finished fiber was white in color, soft and wooly to the touch, and had good crimp.

Example 6

Casein fiber was prepared, extruded and treated in a manner similar to Example 2, except that the bath containing stannic chloride was replaced by the following bath having a pH of 2.0.

	Per cent
Ammonium zirconyl sulphate	1.25
Formalin	6.25
Water	92.50
	100.00

The fiber was treated in the bath for 3 hours at 170° F. After treating, the fiber was centrifuged, washed, oiled, and dried. When tested, the fiber was found to have an alkali boil rating of 3, and an acid boil rating of 3. The finished fiber was white in color, soft and wooly to the touch, and had good crimp.

Example 7

Casein fiber was prepared, extruded, and treated in a manner similar to Example 2, except that the bath containing stannic chloride was replaced by the following bath having a pH of 2.3:

	Per cent
Stannous chloride	6.3
Formalin	6.3
Water	87.4
	100.0

The fiber was treated in the bath for 3 hours at 170° F. After treating, the fiber was centrifuged, washed, oiled, and dried. When tested, the fiber was found to have an alkali boil rating of 3, and an acid boil rating of 3. The finished fiber was white in color, soft, and wooly to the touch, and had good crimp.

The advantages flowing from the present invention are considerable, some of the advantages being as follows:

The novel metallic salt treatment may be made on fiber in the wet state without the necessity of pre-drying. Furthermore, such treatment, being an aqueous treatment, does not necessitate the use of expensive or dangerous organic chemicals and solvents, nor is there any necessity for a recovery system. The resultant fiber is substantially white in color. The finished product retains a substantial part of its original strength and there is relatively no scroop resulting from such treatment. A wool-like effect is always obtained. The fiber is comparatively resistant to dilute acid and alkali solutions, especially when boiled. Finally, the dyeing properties are enhanced in that the fiber possesses a slower rate of dye takeup, thus enabling the dyeing plant to obtain bright, uniform, level shades, either alone or in admixture with other types of fibers.

Other advantages will be evident from the various applications and uses to which such filaments and fibers may be put.

Since certain changes in carrying out the above process, and certain modifications in the article which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

We claim:

1. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of a salt of a metal selected from the group consisting of titanium, zirconium, and tin in a concentration within the range between 0.5% and saturation, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

2. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of a titanium salt in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

3. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of a salt of a metal selected from the group consisting of titanium, zirconium, and tin in a concentration within the range between 0.5% and saturation, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F., and thereafter dyeing the filament to a light color.

4. a process for producing an artificial filament

from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of titanium sulfate in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

5. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of basic titanium sulfate in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

6. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, wtihout intermediate drying, by the application thereto of an aqueous solution of stannic chloride in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

7. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkaline liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of a zirconyl sulfate in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

8. A process for producing an artificial filament from casein having high resistance to hot acid and alkali treatment, light color, good tensile strength, and even dyeing properties, utilizing the initial steps of dissolving casein in an alkali liquid, delivering a stream of the said casein solution into an acid coagulating bath, and hardening the coagulated casein in a second bath containing at least formaldehyde, comprising the inventive step of treating the coagulated and hardened fibers from the hardening bath, without intermediate drying, by the application thereto of an aqueous solution of sodium zirconyl sulfate in a concentration within the range between 2% and 10%, at a bath pH within the range between 0.8 and 3 and at a temperature between 120° F. and 200° F.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,717,483	White	June 18, 1929
2,294,384	Champion	Sept. 1, 1942
2,316,057	Doser et al.	Apr. 6, 1943
2,328,431	Doser et al.	Aug. 31, 1943
2,339,408	Jacokes et al.	Jan. 18, 1944

FOREIGN PATENTS

Number	Country	Date
4,457	Great Britain	1915

Certificate of Correction

Patent No. 2,567,184 **September 11, 1951**

JOHN F. CORWIN ET AL

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 2, for "with" read *from*; line 30, for "Other" read *Such*; column 2, line 38, for "of", second occurrence, read *or*; column 9, line 44, for "wtihout" read *without*; column 10, lines 20 and 21, for "alkali" read *alkaline*; and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of December, A. D. 1951.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.