

UNITED STATES PATENT OFFICE

2,204,535

FIBER

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ington, D. C.; dedicated to the free use of the
People in the territory of the United States

No Drawing. Application May 28, 1938,
Serial No. 210,790

1 Claim. (Cl. 28—1)

(Granted under the act of March 3, 1883, as
amended April 30, 1928; 370 O. G. 757)

This application is made under the act of
March 3, 1883, as amended by the act of April
30, 1928, and the invention herein described and
claimed, if patented, may be manufactured and
used by or for the Government of the United
States of America for governmental purposes
without the payment to us of any royalty thereon.

We hereby dedicate the invention herein de-
scribed to the free use of the People in the terri-
tory of the United States to take effect on the
granting of a patent to us.

Our invention pertains to fibers composed es-
sentially of casein and containing a relatively
high percentage of metallic salts.

The object of our invention is to produce com-
positions, suitable for spinning into fibers, com-
prising casein and metallic caseinates in soluble
form, and containing a high percentage of metal-
lic compounds. Thus the strength, water-resist-
ance, and elasticity of said fibers are greatly in-
creased. Other objects will become apparent in
the course of the following teachings.

In forming dispersions containing casein, suit-
able for spinning into fibers, it is difficult to in-
corporate more than a comparatively small
amount, as about 3% (based on the weight of the
casein), for instance, of strengthening and water-
resisting salts, such as calcium chloride, without
causing precipitation of calcium caseinate. This
prevents the spinning of the dispersion. If, how-
ever, sulfated or sulfonated (preferably to a con-
siderable degree) aliphatic or aromatic com-
pounds, as for example, a sulfated vegetable oil,
are incorporated with the dispersion much larger
amounts of metallic compounds may be blended
into the composition without the precipitation
of the corresponding caseinate. If sodium hex-
ametaphosphate, pyrophosphate, or a mixture of
these is added to the casein composition, even
larger amounts (20-30%) of the metallic com-
pounds may be mixed with the dispersion without
the separation of insoluble metallic caseinates.

Inorganic bisulfites, such as those of sodium
and ammonium, are often useful in obtaining
smooth casein dispersions of high metallic con-
tent. In the presence of these bisulfites, non-
sulfated oils, such as oleic acid, are often com-
patible with the spinning solution.

If the metallic compound used is calcium hy-
droxide, careful filtration is required to avoid
plugging the spinnerette holes. Comparatively
large amounts of amphoteric compounds, such
as sodium aluminate, may be incorporated with-
out a too great increase in viscosity if the spin-
ning dispersion comprises the previously men-

tioned high-percentage sulfur trioxide-contain-
ing compounds and/or phosphates. Without
these compounds, the addition of sodium alu-
minate, for instance, in increasing amounts above
2%, results in a rapidly increasing viscosity of
the solution so that it cannot be easily spun.
Barium hydroxide is one of the most satisfactory
of the metallic compounds to use because of its
greater solubility and because the fiber retains
a high proportion of its barium while in the
precipitating bath.

The following examples are given to illustrate
some preferred methods for insuring the com-
patibility of large amounts of metallic caseinates
with spinning solutions. Proportions are given
in parts.

EXAMPLE I

Spinning solution

Casein-----	24	
Water-----	100	20
A highly sulfonated vegetable oil (or its sodium salt)-----	3.6	
A mixture of sodium hexametaphosphate and pyrophosphate-----	1.5	
Barium hydroxide [Ba(OH) ₂ ·8H ₂ O]-----	4.42	25
Water-----	106.48	

The 24 parts of casein are soaked in the 100
pts. of water for 15-30 minutes. The sulfated
oil and the phosphates are then added and the
mixture warmed until the casein is largely dis-
solved. The barium hydroxide is then dissolved
in the remaining quantity of water, and the solu-
tion stirred mechanically into the casein com-
position. Thus a smooth dispersion is obtained,
free from lumps of insoluble caseinate.

The temperature of both the spinning solution
and the precipitating bath was 50° C. However,
other temperatures varying from room to 80°
C. may be used.

The sulfated oil serves also as a plasticizer.
If even softer fibers are desired, the amount of
the oil may be increased, or the fibers may be
subjected to an after treatment with oil, glycerol,
or similar softening material.

The bath composition is:

	Parts	
Sulfuric acid-----	8	
Formaldehyde-----	5	
Dextrose-----	20	50
Water-----	67	

This bath composition may, however, be varied.

The above procedure for incorporating large
amounts of metallic compounds into the spinning

solution results in fibers of greater strength and water resistance.

The following example illustrates the use of a sulfonated aromatic product, and of a high percentage of a calcium salt.

EXAMPLE 2

Casein	24
Water	160.5
Sodium hydroxide solution (2N)	8
Calcium cymene sulfonate	7.5

Additional plasticizers may be added if a softer product is desired or the fibers may be after treated with oils.

Example 3 illustrates the use of a high percentage of sodium aluminate. Such solutions are ordinarily too viscous to spin, but in this case, the sulfated oil and hexametaphosphate present enable this to be done.

EXAMPLE 3

Casein	24
Water	125
Sodium hydroxide solution (2N)	8
A highly sulfated vegetable oil (or its sodium salt)	4.8
Sodium hexametaphosphate	1.5
Sodium aluminate	3.6
Water	99.1

Casein may be sulfonated directly by the action of chlorosulfonic acid whereby the insolubility of the metallic caseinates may be increased. The chlorosulfonic acid is stirred directly into the dry casein; allowed to react for a short time, 15 minutes, for example, and water is then cautiously added. The alkali should be added promptly to minimize the effect of the hydrochloric acid liberated by the reaction.

EXAMPLE 4

Casein	24
Chlorosulfonic acid	2.0
Water	100
Oleic acid	3.6
Sodium hexametaphosphate	1.5
Sodium hydroxide solution (2N)	15
Barium hydroxide $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$	4.42
Water	89.48

If the amount of chlorosulfonic acid is increased, the sodium hexametaphosphate may be omitted.

Example 5 illustrates the use of a sulfated higher alcohol in increasing the compatibility of the metallic compounds with the casein composition.

EXAMPLE 5

Casein	24
Water	100
Sodium oleyl sulfate	3.6
Sodium hexameta- and pyrophosphate mixture	2.4
Barium hydroxide $[\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}]$	6.64
Water	103.36

The bath composition and temperatures are the same for Examples 2-5, inclusive, as those given under Example 1.

The flexibility of these fibers may be improved by incorporation of an oil or fat with the sodium oleyl sulfate or by after treatment with oils or glycerin.

It will be understood that our invention is not limited to the above examples as proportions, constituents, and substitutes may be varied over a wide range. It is also possible at some concentrations to omit certain ingredients, such as, for instance, the mixture of phosphates. The amounts of metallic compounds may particularly be varied, and similar amphoteric compounds may be substituted for the sodium aluminate.

The general procedure is the same in the case of all the examples, i. e., the spinning solutions are extruded through any type of spinnerette normally used in the rayon industry into precipitating baths of the indicated compositions.

Having thus described our invention, what we claim for Letters Patent is:

As an article of manufacture, a fiber comprising casein, sulfonated casein, salts of sulfonated casein and of casein as its essential components; and fat acids.

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