

March 8, 1949.

G. HEBERLEIN ET AL
PROCESS FOR PRODUCING FIBROUS
MATERIAL AND THE PRODUCT

2,463,618

Filed Sept. 12, 1944

2 Sheets-Sheet 1

Fig. 2.

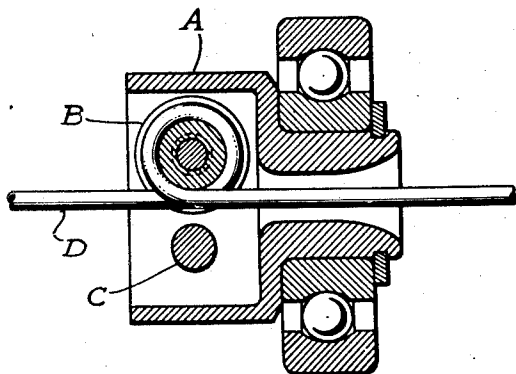


Fig. 1.

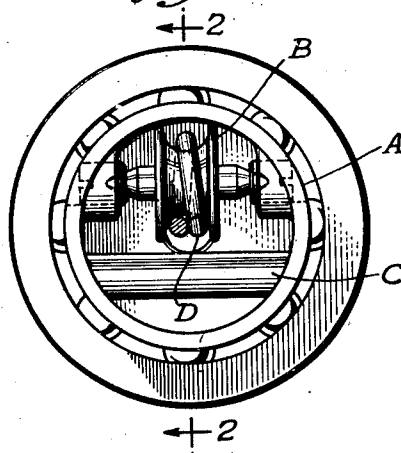


Fig. 3.

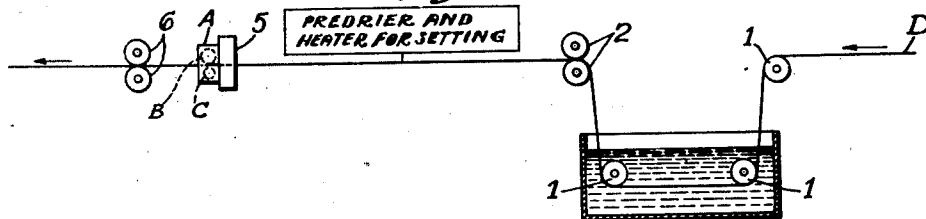
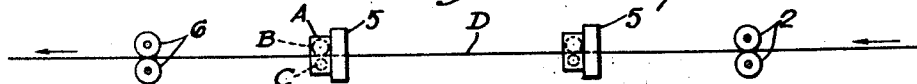


Fig. 4.



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Fig. 7.

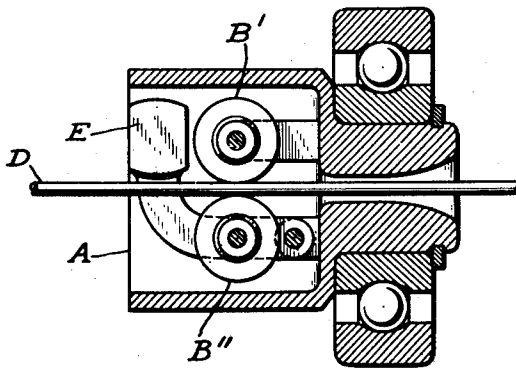


Fig. 6.

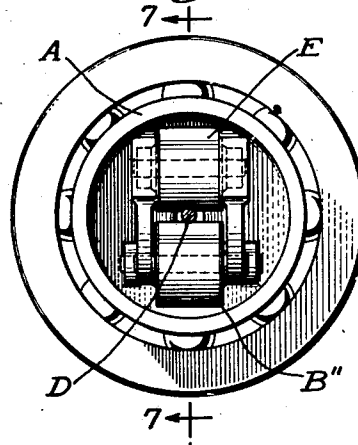
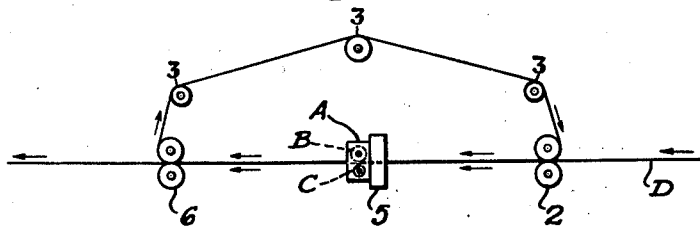


Fig. 5.



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UNITED STATES PATENT OFFICE

2,463,618

PROCESS FOR PRODUCING FIBROUS
MATERIAL AND THE PRODUCT

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Application September 12, 1944, Serial No. 553,694
In Switzerland October 18, 1943

11 Claims. (Cl. 57—157)

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This invention relates to the improvement of artificial fibers, natural and regenerated cotton yarns, and certain natural nitrogenous fibers such as natural silk, and especially to the production of woollike fibers therefrom. It intends to produce fibers which are fundamentally different from the original material and which can be designated as a new starting material for the textile industry. It intends further the production of those fibers by means of a special time- and room saving method.

The new textile material is characterized by its high and permanent curliness combined with a distinct woolly feel and a high insulating property. It may be worked into pullovers, stockings and knitted goods as well as woven into dress goods or cloakings. A further valuable property of the new textile material is its reduced swelling capacity and an affinity to acid dyestuffs together with an increased affinity to substantive dyestuffs, when prepared by following certain methods, in accordance with our invention.

According to the U. S. Patents 2,019,185 and 2,019,183 a wool-like artificial silk results by supertwisting a normal twisted or not twisted artificial silk yarn, setting the twist therein for instance by moistening and drying it on bobbins at an elevated temperature and afterwards untwisting the yarn, giving to it preferably a light twist in the opposite direction. In the second patent a further improvement consists in the fact that the yarn after untwisting it, is exposed to a wet heated atmosphere in a loose i. e. untensioned state. It was further known to combine this process with a formaldehyde treatment in the presence of acid reacting catalysts at temperatures of preferably 90–160° C. Such a treatment seemed to be necessary when using artificial silk from regenerated cellulose as starting material, because the high swelling capacity of this material was an unfavorable factor and it was applied directly before the last finishing that is to say after untwisting. Such treatments to make such material resistant against swelling in water are known per se, see for instance French Patents 844,361, 883,547, 879,919, 882,150, and 885,218. They may not be confounded with the ordinary artificial resin treatments consisting in a so-called deposition of artificial resins on the

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fibers, which also effects a reduction of the swelling capacity but which is not permanent, because the artificial resins can easily be washed out. Contrary to this mechanical deposition of artificial swelling resistant resins on or into the fibers, the above mentioned formaldehyde treatments cause a permanent modification of the fibers which render them more resistant to swelling in aqueous mediums.

It has now been found that it is advantageous to make the fibers permanently resistant against swelling whilst they are in a high twisted condition. When working according to this method of invention, steaming or treating with a swelling agent in the high twisted state will not be necessary. Thus an improved process to produce a permanent, strongly creped and swelling-resistant fiber material by overtwisting and untwisting of smooth textile yarns consists therein that the yarns are subjected to a swelling resistant treatment known per se, whilst they are in high twisted condition. Until now the swelling-resistant treatment has been applied only after the untwisting, that is, after the creping of the fiber.

As mentioned above the woolly character obtained following the improvement will be more permanent and all treatments to render it otherwise permanent as for instance the well known steaming or treatment with strong swelling agents in the high twisted state will be unnecessary. On the contrary the permanence of the creping will be not at all inferior following the improvement instead of first steaming for one hour with steam of 3 atmospheres, untwisting and stabilizing thereafter by treating with a swelling reducing agent such as e. g. formaldehyde.

As starting material for the improved process there may be used smooth fibrous yarns which are susceptible to a swelling reducing treatment such as for instance rayon yarns from regenerated cellulose, staple fibre yarns from regenerated or native cellulose e. g. cotton, linen or cottonized bast-fibers, yarns from albuminous fibers such as silk which are known to be susceptible to a formaldehyde treatment. Also mixed twists or mixed spun yarns may be used.

The overtwisting and untwisting may be carried out on bobbins. There are also known

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means to insert a false twist, see British Patents 424,880, 442,073, 464,981 and French Patent 884,965, which describe the transitory overtwisting of a running yarn followed by the untwisting. A supplementary twisting operation was necessary following this method if one wished to untwist beyond the zero point in the opposite direction. It has now been found that a supplementary twisting operation can be avoided if the supertwisting takes place with the false twisting installation opposite to the original twist direction and beyond the zero point. It has been also found in accordance with our invention that yarns made from staple fibers may be twisted beyond the zero point when using at least two staple fiber yarns together i. e. side by side or in form of a twist. When using a false twisting device it is also possible to use an endless supporting yarn which may be in the gray condition or an endless metallic string to twist staple fiber yarns beyond the zero point. In both cases staple fiber yarns are prevented from falling into pieces or becoming non-cohesive when passing the zero point.

It is common to all of our above mentioned processes for producing swelling resistance, that the yarn is impregnated with certain agents for instance with solutions of formaldehyde and a catalyst or formaldehyde yielding substances and with hexamethylene-1,6-diethylene urea or derivatives of ethylene-urea together with ammonium poly-acrylate. Or one may use aliphatic or aromatic di-isocyanates such as hexamethylene-1,6-di-isocyanate. All of the above are representatives of setting agents. The expression "setting agent" as used in the claims is intended to cover such agents herein disclosed and similar agents. It includes not only formaldehyde mentioned above, but also substances which yield formaldehyde, as stated, and particularly monomeric formaldehyde under the reaction conditions herein described.

Other materials that may be used for this purpose are: Quaternary salts of methyl halogen-compounds with tertiary bases which give real solutions, that is to say, highly dispersed aqueous solutions which are able to penetrate into the micelles. They are used for the swelling-resistance process. After impregnation with such material, the yarn is then heated above 100° C. after drying and high twisting. Suitable quaternary salts are the quaternary salts with chloro- or bromo-methyl ethers or esters of low molecular aliphatic, aromatic or mixed poly-hydric alcohols; also corresponding derivatives of phenols and the quaternary salts of halogen-methyl-compounds with a —NH— or —NR— group instead of the —O— group, for instance, of chlor-methyl amides and of secondary or tertiary chlor-methyl amines. Methods of preparation for the enumerated compounds are known per se.

Analogous halogen methyl ethers and halogen methyl amides or amines of high molecular aliphatic compounds such as fatty alcohols or amines or fatty acid amides with more than 10 carbon atoms, which are transformed into quaternary salts with pyridine and applied as emulsions are used in the textile industry to make fabrics water-repellent.

In contrast thereto, relatively low molecular compounds are used in accordance with our improvement which give highly dispersed aqueous solutions, when transformed into quaternary salts. Such compounds have been proposed in the form of organic solutions to animalize cellulosic fibers

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(to give such fibers dyeing characteristics like wool and silk). But it has been unknown heretofore that these compounds when used in aqueous solutions and heated on the fibers after drying will, at the same time animalize the fibers, and give a higher affinity for direct dyestuffs and an enhanced resistance against swelling.

To make the halogen methyl compounds soluble in water, that is, to transform them into quaternary salts, pyridine is preferably used as tertiary base.

It is an important feature of the improved process employing such quaternary ammonium compounds that in spite of the reduction of the swelling capacity, an enhanced affinity for direct and acid dyestuffs results, whilst the methods to reduce the swelling capacity known heretofore, i. e., with formaldehyde, reduce at the same time the affinity for dyestuffs, nor does the treatment with high molecular quaternary ammonium compounds to render the fibers water-repellent as above produce a reduction of the swelling capacity or change the affinity of the fiber towards acid or substantive dyestuffs.

Impregnation, in accordance with our process, can take place on bobbins or the single yarn may be impregnated. The latter is the case, when operating as a continuous process. After the impregnation, the goods, may be predried, if desired. The predrying can take place on bobbins or with the single yarn. After the predrying a condensation or reaction between the fiber and the reagents brought upon the fiber takes place, by heating or baking advantageously at higher temperatures, e. g. at 100° C. and above. This reaction which renders the fibers swelling resistant must take place while the material is in the high twisted state, that is to say for instance on bobbins after the high twisting, or immediately after the high twisting when working with single yarns, for instance during the winding on a second bobbin in the high twisted state, or when working with a false twisting device immediately before the untwisting takes place. If desired the high twisted state may be kept up during the condensation by using a second false-twisting head driven at the same speed as the first.

The drying and the condensation is accomplished preferably by means of hot air. Other suitable methods of heating can be used, for instance heating with infra-red rays.

After the condensation, the yarns are untwisted, if desired beyond the zero point in the opposite direction. They may be also cut into staple fibers which can be further treated e. g. spun into yarns.

A special form suitable for being further treated is represented by the so-called "flyer yarn." On treating same following the improved process, for instance with hexamethylene-diisocyanate in the high twisted state and untwisting afterwards they will become animalized at the same time and will therefore be very suitable to produce mixed wool goods.

In the attached drawings forming part of this application and showing apparatus forming part of our invention and on which we prefer to carry out the process of our invention,

Figure 1 is an embodiment of a false twisting device in front view;

Fig. 2 is a longitudinal section on the line 2—2 of Fig. 1. A shows a tube which is driven and runs on ball bearings, in which there is supported a small roller B with guide groove arranged on a

shaft perpendicular with respect to the axis of the tube inserted in the tube in such a manner that its periphery is tangent to the axis of the tube. C is a counterweight for instance a bracket for the weight balancing of the small roller supported eccentrically in the tube. The yarn D enters approximately centrally in the direction of the axis of the tube into the device; it is wound around the small roller and leaves it in the same direction, approximately centrally. On account of this central guiding any fluttering of the yarn is excluded.

Fig. 3 shows diagrammatically the arrangement of a false twisting device: The thread passes over the guide rollers 1 through the impregnating trough 4 and is temporarily high twisted between the fixed points 2 and 6, for instance pairs of rollers by means of the false twisting device 5. Between 2 and 5 the condensation takes place; if desired the preliminary drying of the material can be effected in front of 2. If desired the condensation can also be effected between two false twisting devices 5, 5' running at the same speed, in accordance with the diagrammatic sketch shown in Fig. 4. Here the yarn, as can easily be understood, retains its twist between 5 and 5'.

Fig. 5 shows diagrammatically the arrangement when using a so-called gray backing material. Here 2 and 6 are the fixed points, 3 the guide rollers for the endless backing material and 5 the false twisting device. Another embodiment of the device for the temporary high twisting of a yarn passing between two fixed points is shown in Fig. 6 which is a front elevation and Fig. 7 which is a section on the line 7-7 of Fig. 6.

In these Figs. 6 and 7, A shows a tube which is driven and runs on ball bearings in which there are arranged two small rollers B' and B'' contacting each other on the axis of the tube and supported parallel with respect to each other and perpendicular with respect to the axis of the sleeve, one of which (B') is stationary while the other (B'') is supported to swing in the tube and in connection with which the swingably supported roller is connected with the centrifugal weight E in such a manner that the rollers upon the rotation of the tube, are pressed against each other.

Also with this mechanism a rectilinear guidance of the yarn during the high twisting between two fixed points is obtained and fluttering of the yarn avoided. This is of importance because fluttering would cause great difficulties in view of the high speed of rotation and the wet state of the yarn.

The following expressions used in the examples and elsewhere herein are defined as indicated below in accordance with well-understood usage in this art:

Den. means denier—a measure of the size of the yarn.

T/m S means turns per meter of S twist, and T/m Z means turns per meter of Z twist, in accordance with the 1941 Supplement to A. S. T. M. Standards, page 152—

"Twist, Direction of.—A yarn or cord has S twist if, when held in a vertical position the spirals conform in direction of slope to the central portion of the letter 'S', and Z twist if the spirals conform in direction of slope to the central portion of the letter 'Z'."

Engl. means English.

The following examples serve to explain the invention showing some embodiments of it.

Examples

I. Viscose artificial silk yarn of 450 den. with 60 single fibers and a twist of 70 T/m S is conducted through a bath composed of

	Cubic centimeters
Formaldehyde conc. technic 40% aluminium rhodanide solution	100
17° Bé	40
Water	860
	1000

After complete impregnation the yarn is pressed out and predried in an air current at 60-70° C. Subsequently the yarn is twisted temporarily to 1400 T/m Z by means of a false twisting device. Between the delivery rolls 2 and the twisting head the yarn is heated at 150° C. during 1 minute. For this heating the length of the twisting path and speed of yarn must be taken into consideration. Having left the false twisting device the yarn is reeled and steamed as skeins during 10 minutes without excess pressure. A woollike yarn results the single fibers of which are very strongly creped. The effect is substantially fast to washing. The swelling capacity of the fibrous material in water is reduced, the material equalling wool in this respect.

II. Viscose artificial silk yarn of 1800 den. with 150 single fibers and a twist of 40 T/m S is impregnated at 30° C. with an aqueous solution containing per liter 50 g. hexamethylene-1,6-diethyl-ene-urea. Thereupon the yarn is predried in an air-current heated to 60-70° C. and subsequently twisted on a false twisting device to 750 T/m Z. Between the delivery rollers and the twisting head the yarn is heated at 165° C. during 2 minutes. After the false twisting device the yarn is cut into staple fibers and preferably made loose on an opener. A strongly creped flock material is obtained which can be dyed with acid dye-stuffs. The swelling capacity in water is reduced compared with that of the usual rayon. The material may be spun separately or together with other natural or artificial staple fibers.

III. A cupramonium artificial silk yarn 360 den. (single fiber about 1.3 den.) and 120 T/m S is impregnated with an aqueous solution containing per liter.

	Grams
Condensation product of formaldehyde and formamide	130
Aluminium hydrochloride	10

and predried at temperatures between 40° and 60° C. Thereupon it is twisted on a ring-twisting machine to 1600 T/m S and heated in the high twisted state, in the form of skeins if desired, during 15 minutes at 110° C. It is then untwisted on a second twisting machine beyond the zero point in the opposite direction to 70 T/m Z, suitably reeled and slightly steamed in form of skeins. A woollike yarn is obtained with strongly curled single fibers. The creping is practically fast to washing and the swelling capacity of the fiber material reduced.

IV. A yarn 20/1 metric number with a twist of 400 T/m Z from viscose staple fibers of 4 den. and a length of 120 mm. and a yarn from viscose artificial silk 450 den. (single fiber ca. 4 den.) and a twist of 200 T/m Z are twisted together to

150 T/mS. The twist obtained is impregnated in an aqueous solution containing per liter:

Formaldehyde conc-----cc--	150
Zinc chloride-----grams--	20
Potash alum-----do-----	10

and predried at an air temperature of 60° C. Subsequently the twist is supertwisted temporarily on a false twisting device to 1000 T/mS. The false twisting device has two twisting heads rotating with the same velocity and between these twisting heads the yarn is heated in a hot air canal at 125° C. during 2 minutes. Having left the false twisting device the yarn is reeled and steamed in form of skeins in untensified state. A woollike twist is obtained. The woollike shape does not change by washing. The swelling capacity of the fibrous material is reduced.

V. A kierboiled cotton twist consisting of two yarns 24/1 Engl. number with 350 T/mZ and a twist of 100 T/mS is treated during 2 minutes with caustic soda of 30° Bé.; the twist having preferably been allowed to shrink during this treatment. Thereupon the caustic soda is washed out with water, the water being displaced by alcohol and the latter by trichloroethylene. The twist is then soaked during several hours with a 5% solution of tetramethyl di-isocyanate in trichloroethylene, centrifuged and dried at an air temperature of 65° C. Thereupon it is overtwisted to 1200 T/mS on a suitable mechanism i. e. on a ring twisting machine. The material is heated at 100° C. during 5 hours in the high twisted state and untwisted to 100 T/mS. The twist has become voluminous. It resembles wool not only in appearance but also in its behaviour to dyestuffs. The affinity for substantive dyestuffs is remarkably increased and dyeing with acid dyestuffs is possible. The single fibers show an enhanced creping.

VI. A yarn of 300 den. of natural silk non-soured is twisted to 1600 T/mS on a ring twisting machine. The high twisted yarn material is then soaked in a bath containing per liter 2 cc. formaldehyde 40% during 10-12 hours at a temperature of 25-30° C. Thereupon the yarn is dried at an elevated temperature and untwisted to 70 T/mZ, reeled, slightly pressed (centrifuged) and preferably hung in a steam atmosphere. A silk yarn is obtained which is strongly curled. The effect is permanent to washing.

VII. Viscose artificial silk yarn 450 den. with 60 single fibers and a twist of 70 T/mS is conducted through a cold aqueous solution containing per liter 100 g. ethyloxymethyl pyridinium chloride pressed out and twisted on a false twisting device temporarily to 1400 T/mZ. Along the twisting path that is to say before the twisting head, the yarn is dried by heating with an air current at a temperature of 185-190° C. and having left the false twisting device, reeled and steamed without excess pressure in the untensioned state. A voluminous yarn is obtained with strongly curled single fibers. The character of the yarn is not altered by washing or dyeing operations. The treated fibrous material shows a characteristic affinity for acid dyestuffs and a raised affinity to direct dyestuffs.

VIII. Viscose artificial silk yarn 300 den. with 60 single fibers and a twist of 50 T/mS is conducted through a cold aqueous solution containing per liter 50 g. of a quaternary ammonium salt, prepared from the trichloromethyl ether of glycerol and a corresponding quantity of pyridine. The trichloromethyl ether has been prepared on

introducing hydrochloric acid into a mixture of glycerol and an excess of trioxymethylene. After complete impregnation of the artificial silk yarn it is pressed out and subsequently twisted to 1700 T/mZ on a false twisting device. Between the delivery rollers and the twisting head the yarn is dried and heated for a short time at 190° C. For this purpose the yarn is conducted preferably through an insulated tube and dried in this tube by an air-current heated to 190-195° C. The length of the tube is calculated so that the effect of the hot air continues for about ½ minute and drying is effected when the yarn has passed through about half of the twisting path. The further treatment and result are similar to those in the preceding example.

IX. Viscose artificial silk yarn 300 den. with 60 single fibers and a twist of 50 T/mS is impregnated with an aqueous solution of 80 g. of acetamido-methyl-pyridinium chloride per liter prepared for instance following the British Patent 475,170. Two such impregnated yarns are twisted together with 1250 T/mS and heated at 180° C. during 1 minute in high twisted state. Subsequently the yarn is untwisted beyond the zero point to 60 T/mZ, reeled and slightly steamed in form of skeins without tension. A voluminous twist is obtained of a wool-like character which can be dyed with acid and direct dyestuffs. The swelling capacity of the fibrous material is reduced by this treatment.

X. Viscose artificial silk yarn 300 den. with 44 single fibers and a twist of 100 T/mS is overtwisted to 1700 T/mZ on a false twisting device. During the overtwisting that is to say before untwisting takes place, the yarn is steamed. Having left the false twisting device, the yarn is more voluminous and the fibers are characteristically curled. The yarn has a wool-like character.

XI. Two yarns of spun-matte viscose artificial silk each of 450 den. and 60 single fibers and a twist of 70 T/mS are temporarily twisted together to 1000 T/mZ by means of a false twisting device. Before untwisting takes place, it is steamed. The yarns are best reeled separately. They show a pronounced creping.

XII. A rayon staple fiber yarn 30/1 metric number (single fiber 2.75 den. length of staples 50 mm.) and with a twist of 450 T/mZ and a viscose artificial silk yarn 300 den. with 100 single fibers and a twist of 80 T/mZ are twisted together temporarily at 1300 T/mS. Before untwisting takes place, the twist is steamed and thereafter reeled separately. By this treatment the viscose yarn is transformed into a strongly curled woollike material. The rayon staple fiber yarn becomes more voluminous at the same time.

XIII. A yarn consisting of acetate artificial silk of 360 den. 70 single fibers and a twist of 60 T/mS is twisted on a false twisting device to 1500 T/mZ. Before untwisting takes place, it is steamed by conducting it through a tube. A yarn is obtained which is characteristically curled and shows a wool-like character.

XIV. A yarn consisting of fibers from superpolyamides of 1000 den. and 250 single fibers and a twist of 50 T/mZ is supertwisted on a false twisting device to 950 T/mZ. Before untwisting the yarn is steamed with superheated steam. It shows a strong curliness and is very suitable to replace wool.

XV. Two cotton yarns each 30/1 metric number with a twist of 350 T/mZ are twisted to 1100 T/mS on a ring twisting machine. The yarn is then steamed in high twisted state at 3 atmos-

phers during 1 hour, dried and untwisted to 100 T/mS, reeled and hung for some time without substantial tension. A voluminous twist is obtained the fibers of which show an increased curliness.

XVI. A cotton twist combined from 2 raw yarns 20/1 engl. number and 350 T/mZ with a twist of 100 T/mS is swelled with caustic soda solution of 32° Bé., to which has been added 20 cc. per liter of a wetting agent, at temperatures of 10–20° C. during ½–1 minute. The twist is conducted through the bath without substantial tension, so that it can easily shrink. It is then hydroextracted and twisted temporarily on a false twisting device to 1200 T/mS and delyed in this state with boiling water. This can be done suitably between two false twisting heads rotating at the same speed. Having left the false twisting device the thread is acidified, washed out and dried without substantial tension. A twist is obtained of woollike character. The single separated fibers are stronger and more regularly curled than the raw cotton fibers.

XVII. Instead of a cotton twist mentioned in Example XVI a mixed twist from cotton and cottonized flax is used. The treatment remains the same as in Example XVI.

XVIII. Two cotton flyer yarns 12/1 english number preformed in Z-direction are impregnated at 70–80° C. with a hot caustic soda solution of a specific gravity of 30° Bé. at 15° C. and pressed out. Thereupon the two flyer yarns are twisted together on a false twisting device to 1000 T/mZ and delyed in high twisted state with boiling water. Having left the false twisting device the yarns are acidified, washed out and dried without substantial tension. Flyer yarns are so obtained with strongly curled cotton fibers. They are very suitable to the manufacture of voluminous and soft twisted yarns.

XIX. Viscose artificial silk yarn 900 den. with 150 single fibers and a twist of 70 T/mS is conducted through caustic potash of 18° Bé. at room temperature and pressed out between a pair of rollers which is driven. The strongly swelled yarn is then twisted transitorily on a false twisting device to 900 T/mZ. It is thereupon deswelled in the high twisted state with boiling water. The yarn which leaves the false twisting device with slightly alkaline reaction is reeled as much as possible without tension. It is then washed to the neutral point in form of skeins, hydroextracted and dried without tension. After drying it is preferably steamed without pressure during 5–10 minutes. A woollike yarn is obtained, the individual fibers showing a distinct curliness.

XX. Two rayon staple fiber yarns each of No. 20/1 (metric number) and fibers of 4 den., a staple fiber length of 120 mm. and a twist of 400 T/mZ are impregnated with caustic soda of 30° Bé. at 80° C. and subsequently twisted on a false twisting device to 1100 T/mS. Immediately before untwisting takes place the swelling of the yarn is removed by a solution of 40 cc. concentrated sulfuric acid and 50 g. sodium sulfate per liter. After the false twisting device the yarns are reeled separately and without tension. The skeins are then washed to the neutral point, hydroextracted and dried without tension. A woollike yarn is so obtained.

XXI. Two yarns made from spun-matted viscose artificial silk each of 450 den. and with 60 single fibers and a primary twist of 80 T/mS are twisted together on a ring twisting machine to 40 T/mZ. The twist is then impregnated at a

temperature of 80° C. with a solution of caustic potash of 16° Bé. (at 15° C.), slightly pressed out and temporarily twisted to 1000 T/mZ on a false twisting device. Immediately before untwisting takes place i. e. in the maximum state of twist the swelling is removed with hot water. After the false twisting device the material is reeled as much as possible without tension. The skeins are washed to the neutral point with warm water, dyed in the usual way with direct dyestuffs, hydroextracted and dried without tension. Subsequently the twist is soaked in the form of skeins during 10 minutes in an aqueous solution containing per liter

	Cubic centimeters
Formaldehyde 40%-----	100
Solution 17° Bé. of aluminium rhodanide----	40

centrifuged, predried at 60–70° C. and heated at 120° C. during 15 minutes. Finally the yarn is steamed during 10 minutes without pressure. The material thus obtained resembles wool closely as concerns appearance, swelling property in water and insulating property. The curliness of the fiber material is very distinct and permanent against laundering.

XXII. A spun rayon yarn 30/1 metric number, with single fibers of 2.75 den. and a twist of 450 T/mZ and a yarn of viscose artificial silk 300 den. with 100 single fibers and a twist of 80 T/m are twisted together at 50 T/mS. The twist thus obtained is conducted through a bath containing 30% by weight of zinc chloride at a temperature of 90–95° C. and subsequently super-twisted to 1200 T/mS on a false twisting device. In the maximum state of supertwist it is washed out with warm water containing sodium chloride; after the false twisting device, the twist is reeled with a minimal tension and washed out until it is free from sodium chloride. This may be carried out by spraying the material which is being moved on reels. The skeins thus obtained are hydroextracted, dried in a loose state and steamed without pressure during 10 minutes. A voluminous twist is obtained with single fibers which show a distinct curliness.

XXIII. Viscose artificial silk yarn 900 den. with 150 fibers and a primary twist of 30 T/mS is impregnated with a caustic soda solution of 16° Bé. (determined at 15° C.) at a temperature of 60° C. and subsequently supertwisted to 1000 T/mZ on a false twisting device with two twisting heads rotating at the same speed. Between the two twisting heads i. e. in the state of maximum twist swelling is removed with boiling water. After the second twisting head the yarn is treated with diluted sulfuric acid of 1–2° Bé. When the yarn has left the false twisting device, it is cut to the desired length of staples and washed to the neutral point. After drying the fibrous material is made loose on a box opener. A highly curled flock material is thus obtained which may be spun itself or mixed with natural fibers.

XXIV. A cuprammonium artificial silk of 360 den. with single fibers of about 1.3 den. and a twist of 80 T/mS and predyed with vat dyes is temporarily twisted to 1650 T/mZ on a false twisting device. Before the high twisting, the yarn is conducted through a caustic potash solution of 14° Bé. (determined at 15° C.), which is heated at a temperature of 70° C. A wetting agent may be added to the caustic potash solution. In the high twisted state the swelling of the yarn is removed with hot water and after untwisting, reeled and acidified, washed out, soaped at 40 to

50° C., rinsed, hydroextracted and dried without tension in form of skeins. A voluminous wool-like yarn is obtained with single fibers of a distinct curliness.

XXV. A cotton twist, made from two raw yarns 20/1 metric number and a twist of 350 T/mZ, with a twist of 100 T/mS is impregnated with a caustic soda solution of 15° Bé., at a temperature of 10-20° C. To the solution a wetting agent may be added. The twist is then pressed out and supertwisted on a false twisting device to 1200 T/mS, a considerable tension being applied in the longitudinal direction. Along the twisting path, the twist is dried by means of hot air. After the false twisting device it is reeled with a minimum of tension and delyed in a loose state with hot water in form of skeins, acidified, washed out, hydroextracted and dried. A voluminous soft twist is obtained with a wool-like character. Separated single fibers show a higher and more regular curliness than the corresponding raw cotton fibers.

XXVI. Two cotton flyer yarns 2.7 den. pre-twisted in Z direction are impregnated with a caustic soda solution of 20° Bé. A wetting agent may be added to this solution. Subsequently the two flyer yarns are twisted together on a false twisting device to 500 T/mS. Along the twisting path the yarn is dried by hot air, so that it is just dry when reaching the state of maximum twist.

After leaving the false twisting device, it is washed with diluted sulfuric acid, to which Glauber salt is preferably added. The washing is carried out in a loose state. Thereupon the yarn is acidified, washed to the neutral point and dried without tension. The curliness of the cotton fiber material is considerably enhanced and it is especially suitable for the manufacture of voluminous, soft twisted yarns.

Apparatus described but not claimed herein is claimed in our copending divisional application Serial No. 9,484, filed February 19, 1948.

The expression "fibrous material" as employed in the claims is intended to refer to various forms of natural fibers of cotton, silk and synthetic materials capable of having its swelling capacity reduced by treatment with formaldehyde, low molecular weight quaternary ammonium chloromethyl compounds, diethylene urea or diisocyanates, herein described as agents for reducing such swelling capacity, and their equivalents.

The "setting agents" herein employed each contains a radical selected from the group consisting of methylene and oxymethylene radicals containing groups rendering the agent capable of reacting bifunctionally with hydroxy groups of cellulose.

We claim:

1. A process for treating cellulosic yarn to produce a wool effect which comprises, impregnating the yarn with formaldehyde capable of reacting bifunctionally with hydroxy groups of cellulose and an acid catalyst, supertwisting the fibrous yarn, baking the supertwisted impregnated yarn at about 100° C. or above, and then detwisting the cellulosic yarn to produce a wool effect which is substantially fast to washing.

2. A process for treating cellulosic yarn to produce a wool effect which comprises, impregnating the yarn with an alkylene diethylene urea compound capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the fibrous yarn, baking the supertwisted impreg-

nated yarn at about 100° C. or above, and then detwisting the cellulosic yarn to produce a wool effect which is substantially fast to washing.

3. A process for treating cellulosic yarn to produce a wool effect which comprises, impregnating the yarn with a di-isocyanate capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the fibrous yarn, baking the supertwisted impregnated yarn at about 100° C. or above, and then detwisting the cellulosic yarn to produce a wool effect which is substantially fast to washing.

4. A process for the improvement of artificial fibrous material which comprises, impregnating the fibrous material with a setting agent containing a radical selected from the group consisting of methylene and oxymethylene radicals containing groups rendering that agent capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the fibrous material, baking the supertwisted impregnated material and then detwisting the fibrous material to produce a wool effect which is substantially fast to washing.

5. A process for the improvement of artificial fibrous material which comprises, impregnating the fibrous material with a setting agent containing a radical selected from the group consisting of methylene and oxymethylene radicals containing groups rendering that agent capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the fibrous material, baking the supertwisted impregnated material and then detwisting the fibrous material beyond the zero point to give it a reverse twist to that of the supertwist to produce a wool effect which is substantially fast to washing.

6. A process for the improvement of artificial fibrous material which comprises, impregnating the fibrous material with a setting agent containing a radical selected from the group consisting of methylene and oxymethylene radicals containing groups rendering that agent capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the yarn past the zero point in the opposite direction to that of the primary twist, baking the supertwisted impregnated yarn and then detwisting the yarn to produce a wool effect which is substantially fast to washing.

7. A process for treating cellulosic yarn to produce a wool effect which comprises, impregnating the yarn with hexamethylene-1,6-diethylene urea capable of reacting bifunctionally with hydroxy groups of cellulose, supertwisting the fibrous yarn, baking the supertwisted impregnated yarn at about 100° C. or above, and then detwisting the cellulosic yarn to produce a wool effect which is substantially fast to washing.

8. A textile material having a high and permanent curliness substantially fast to washing combined with a distinctly woolly feel and a high insulating property containing fiber prepared in accordance with the process of claim 4.

9. A textile material having a high and permanent curliness substantially fast to washing combined with a distinctly woolly feel and a high insulating property containing yarn prepared in accordance with the process of claim 3.

10. A textile material having a high and permanent curliness substantially fast to washing combined with a distinctly woolly feel and a high insulating property containing yarn prepared in accordance with the process of claim 1.

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11. A textile material having a high and permanent curliness substantially fast to washing combined with a distinctly woolly feel and a high insulating property containing yarn prepared in accordance with the process of claim 2.

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REFERENCES CITED

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

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Certificate of Correction

Patent No. 2,463,618.

March 8, 1949.

GEORGES HEBERLEIN ET AL.

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

Column 3, line 30, strike out the word "with"; column 6, lines 8 to 13, inclusive, for

Formaldehyde conc. technic 40% aluminium	
rhodanide solution-----	100
17° Bé-----	40
Water-----	860

1000

read

Formaldehyde conc. technic 40%-----	100
Aluminium rhodanide solution 17° Bé-----	40
Water-----	860

1000

column 7, line 15, for "untensified" read *untensioned*; column 11, line 39, following the word and period "yarns." insert the following paragraph:

The expression "cellulosic material" as used herein is employed to define natural cellulose such as cotton, and regenerated cellulose such as viscose and cuprammonium materials in the form of yarns, threads, and like forms.;

same column, line 40, beginning with the words "Apparatus described" strike out all to and including "February 19, 1948." in line 42, and insert the same paragraph after "cellulose." in line 58;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 16th day of August, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.