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CONTINUOUS MANUFACTURE OF VISCOSE RAYON

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Fig. 2.

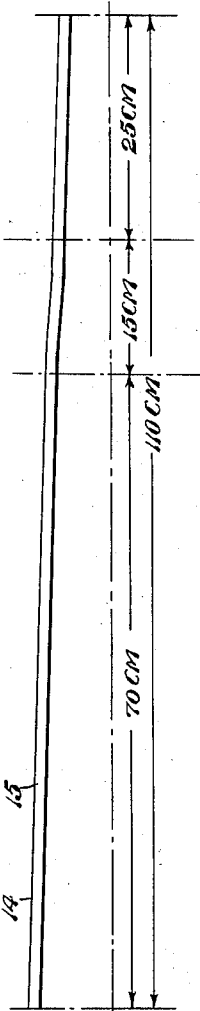
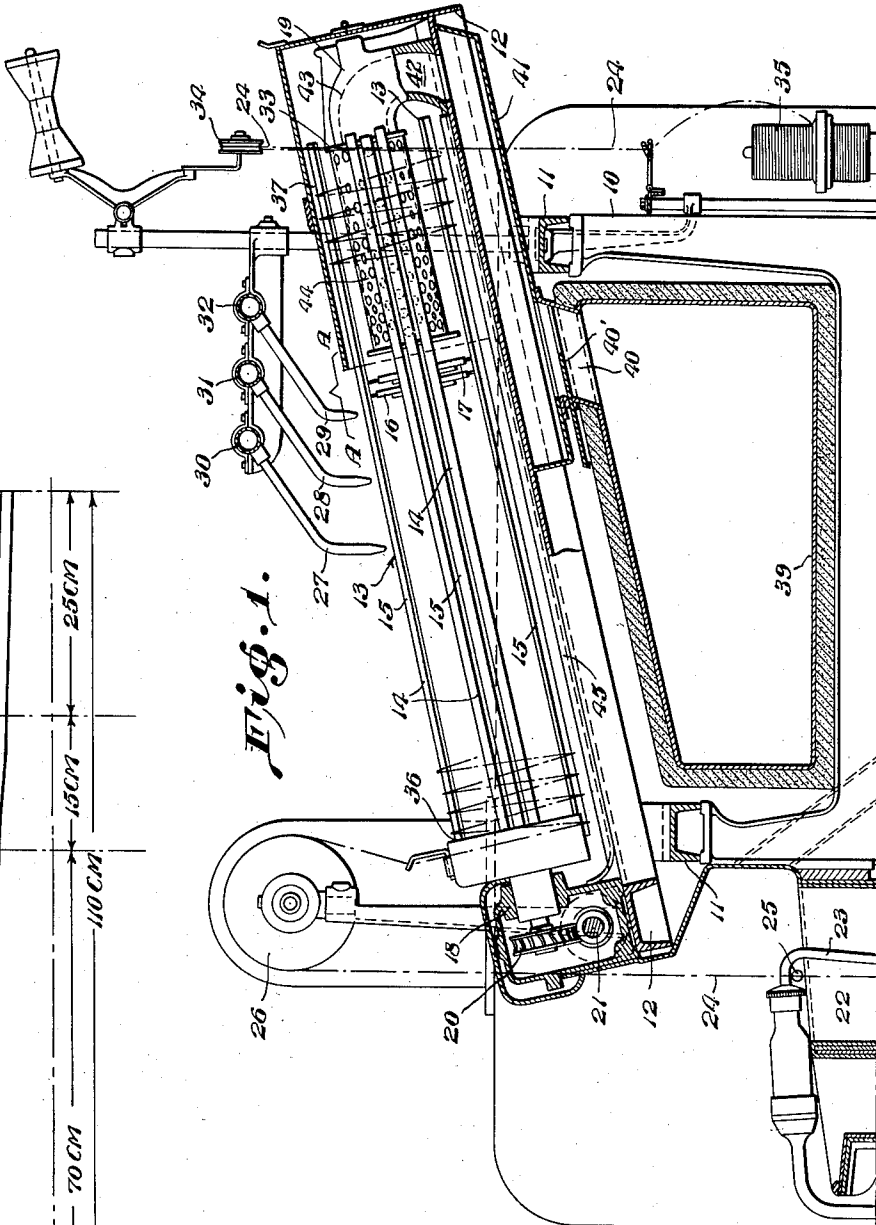


Fig. 1.



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UNITED STATES PATENT OFFICE

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CONTINUOUS MANUFACTURE OF VISCOSE RAYON

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12 Claims. (Cl. 18—54)

This invention relates to the manufacture of viscose rayon and particularly to its continuous production.

In the manufacture of rayon yarn by the continuous process according to the cuproammonium method, the freshly precipitated thread emerging from an alkaline coagulating bath is automatically conveyed from the lower to the upper end of a unitary inclined drum composed of two interleaving cages of bars, which, by rotating around individual, relatively eccentric and angled axes, effect a forwardly progressing movement of the thread. This drum constitutes a unitary thread storage device.

As the thread mounts the drum, it is successively subjected to the various treatments necessary for setting, washing, avivifying and drying, while centrifugal force, evolved by the revolutions of the drum, adhesion and gravity, acting jointly on the treating liquids, are kept balanced in a manner that the liquids are caused to stay on the exterior surface of the drum and, in response to its slant, to travel gradually downward to its lower end. By reason of their counterflow with respect to the ascending thread, the action of the fluids is singularly effective and economical and permits the condensation of these treatments together with precipitation on the one end and twisting on the other end, into one single, continuous operation.

For the preparation of artificial fibres according to the viscose method an equally simple process has not heretofore existed. The share which the viscose method takes in the total production of artificial fibres being many times larger than that of the cuproammonium method, the commercial advantages of such a process for viscose are proportionately greater. They are duly stressed by the many suggestions that have been made for the solution of the problem. None of them proved practicable. Many lacked the requisite mechanical means such as the counterflow spinning drum above described or other equivalent unitary thread storage devices, but, even after these had been developed, all efforts of utilizing them for producing viscose fibres by a process of the character described for the cuproammonium method, have been futile.

This failure can be accounted for by the impracticability of adjusting the customary finishing methods of manufacture now composed of several separate and individual steps to the peculiarities of processing upon the spinning drum. The typical manner in which the latter functions to counterflow treating liquids, pre-

cludes such separation. The treating liquids collectively, slowly descending along the surface of the drum, represent one coherent unit and they freely intermingle in their counterflowing.

To make this clear, let us assume that the same means that are now commonly applied for desulphurizing the thread after washing, like solutions of sulfides, sulphites, weak alkalines, etc. be tried for this purpose on the spinning drum. It will then happen that the free acid at the lower part of the drum decomposes the polysulphides or thiosulphates as well as the excess of the desulphurant, regenerating sulphur which will again be carried upward by the ascending thread. These and similar reactions arising from treatment intermingling through counterflow or otherwise, are adverse reactions which render the continuous process impracticable and inoperative. For similar reasons none of the customary agents for bleaching and avivifying are applicable.

Thus it becomes apparent that development of a continuous process for viscose, which will compare in simplicity with that described for the cuproammonium method, is dependent on a drastic revision of present practices for finishing viscose threads. Without such revision, one has to take recourse to an elaborate system of drums at the sacrifice of the very benefits most expected from continuity in production including simplicity and low cost of equipment, simplicity and ease of operations, economy of labor, and maintenance.

The primary object of this invention consists in developing a process for the continuous production of viscose rayon which is practical.

According to my invention I effect all treatments following precipitation of a viscose thread or aggregate of threads (called in the following and in the claims often collectively "thread") and necessary for the complete regeneration of cellulose therefrom, in one continuous operation by substituting for the treatment means commonly applied (such as those above outlined), means that can in the sequence of their use, intermingle upon the unitary storage device (as the drum) without consequentially interfering with each other by adverse reactions.

Further I desulphurize a moving viscose thread or aggregate of threads by treatment means which, without disturbing preceding and subsequent treatments, will act so quickly that removal of sulphur is accomplished in a relatively narrow zone and in the speed at which the thread moves.

Adaptation of the above-mentioned quick and non-interfering treatment methods to the operation of the preliminary described spinning drum or similar devices (which as it rotates advances the threads on its surface in form of an inclined coil from the lower end toward the higher end) I effect by treatment means applied in counterflow to the axial direction of advancement of the thread.

This performance on the drum is linked together with prior precipitation of the threads in the spinning bath and with their subsequent drying and twisting, to combine all into one single, uninterrupted operation.

I localize the effect of the desulphurant to a determinate zone on the unitary storage device.

It is my discovery that the kation active emulsifiers for desulphurizing the thread afford the most outstanding advantageous embodiment of my invention. This desulphurant is characterized both by relative inactivity when intermingled with the precipitant acid or salt on the thread, and by relatively great activity upon the sulphur of the acid-free thread.

The element of speed in desulphurizing constitutes a very important factor in the continuity of operations wherein only a limited period of time and a limited zone can be allowed for completing the necessary reactions. It has been proven by my tests that kation active emulsifiers, especially if employed as acidified solutions, have great merits as desulphurants. Their action greatly exceeds in speed and effectiveness, that of the anion active types, among which latter the emulsifiers generally recommended for desulphurizing, like soaps, sulphonated oils or fatty alcohols, condensation products of fatty acids, such as are known as Gardinol, Igepon, Tytrovon, etc., have to be classified. To my knowledge, no mention or use has ever been made of this distinction.

Kation active emulsifiers are aryl- or alkyl substituted amines, pyridin derivatives, etc., which contain the effective group for reaction with the sulphur in the electro-positive part of the molecule. Their superior utility as desulphurants I attribute to a neutralization of negative electrical charges of the sulphur molecules which takes place simultaneously with the emulsion of sulphur, which results in its precipitation together with an equivalent amount of the kation active agent. This reaction proceeds more promptly in the presence of a small amount of an organic acid.

If the effective group of such kation active emulsifiers contains, in addition, a fatty acid radical, the resulting products are, moreover, possessed of avivifying properties as is, e. g., the case with "Soromin AFZ," "Sapamin," etc. (fatty acidic-amids of the asymmetric diethyl-diamino-ethane group).

Desulphurizing by such treatment means permits the carrying out of washing, desulphurizing, avivifying and, if necessary, bleaching of the viscose thread in an extremely simple and economical manner. Treatment of the thread as progressed on a unitary storage device, first for washing by a solution of hot water, second for desulphurizing by a solution of a kation active emulsifier acidified by an organic acid, and third (when desired) by a bleaching agent acidified (if desired) by an organic acid, which bleaching treatment leaves no or an indifferent residue, achieves this purpose. Acidifying the desulphurant improves its efficiency of reaction. Inci-

dentally, acidifying the emulsifier also lowers its solubility and aids in improving the fibre.

According further to my invention, I divide the space available on the storage device into zones, the widths of which are adequate for completion of the proceeding chemical reactions under the counterflow treatment and keep the zone widths constant by an accurate placement and dispensation of the treating means along the storage device and by maintenance of the flow, temperatures and concentrations most favorable to the reactions.

For a viscose thread, spun either according to the customary direct method or to the stretch spinning method, one example of this part of my invention consists of the following distribution of treatment means upon a spinning drum storage device such as that initially described herein. Such cage and the means for applying the treatment fluid is illustrated in the attached drawing in which:

Figure 1 is a side elevation of the cage and adjacent parts of the spinning equipment, partly in section along the axis of the cage; and

Figure 2 is a diagrammatical showing of the form and arrangement of one of the bars of which the cage is composed.

10 and 11 constitute the supporting structure for a bank of cages. 12 is a structure supported by the structure 10, 11, which in turn serves for supporting the individual unitary thread storage device 13 shown in the drawing. The device 13 is in the form of a cage composed of two groups of bars 14 and 15. Each group of bars is supported by discs 16 and 17, respectively. The discs belonging to different groups of bars are rotatable about axes which are eccentric with respect to each other and which are oppositely inclined with respect to the longitudinal middle line of the cage as a whole. The discs are supported by beams or shafts which are supported from bearing brackets 18 and 19 from opposite ends of the structure 12. The cage is driven by a worm gear 20 from a worm shaft 21.

The yarn is spun in a bath 22 from a spinneret (not shown), which is fed at the bottom of the bath from a supply pipe 23, is progressed upwardly from the bath as indicated at 24 and through suitable tensioning guides indicated diagrammatically at 25 over the Godet wheel 26 which may be supported in any suitable manner from the frame of the machine, and down upon the unitary storage device cage 13 at substantially the same circumferential speed as the cage revolves.

Reaching the cage, the latter progresses the yarn spirally from its lower to its upper end.

At a distance, e. g., about 50 cm., from the lower end of the drum, water of 90-95° C. (195-203° F.) is dropped from a drip 27 on the thread in counterflow and is followed above, at a distance of, e. g., 2-5 cm., by the acidified solution of the emulsifier dropped on from a desulphurizing drip 28 at 70-75° C. (158-167° F.). If bleaching is desired, the drip 29 for the bleaching agent applied at about 25° C. is placed a distance still farther above of, e. g., 8-10 cm. Said drips being supplied respectively from the three treatment mains 30, 31, 32. In the open end of the cage is located a drying device 33.

Each individual bar 14 or 15 as the case may be is inclined toward the axis of its group as outlined in Fig. 2 illustrating a bar for a 110 cm. length of storage device. The bar from the leading-in end 36 to a point approximately 70 cm.

therefrom approaches the axis at a substantially uniform rate. For the next 15 cm. the rate is an accelerated one, first increasing markedly then decreasing and once more assuming the rate applying to the initial 70 cm. of length. For the remaining 25 cm. of length, the inclination is the same as on the initial 70 cm. of length as may be noted from the parallel lines. For the spinning of viscose yarn of from 100 to 300 denier, I have found such proportioning of the inclination to be most excellent.

Coaction of the drying device in conformance to the determinate circumferential variations of the turns of yarn is afforded through the supply of compressed air from a longitudinally through running main 39 within the main frame of the machine by a branch duct 40 having a slide regulating valve 40' which feeds the conduit comprised by the channel 12 and closing in header 41, to carry air through an aperture 42 in the top of the channel 12 to the hollow of supporting head 43 from whence it is distributed to the interior of the cage 13 through a perforated head 44. The perforations in this head distribute the air in conformance with the tendency requirements of the yarn itself for greatest shrinkage in length in the 15 cm. zone illustrated in Fig. 2. The temperature, quantity and humidity of the air are adjusted to the values found most suitable. I have found that air at 85° C. has an ability to absorb as much as 30 grams of water per cubic meter. The quantity of air may be adjusted to the quantity of moisture to be removed on this basis to obtain satisfactory results.

The flow of the treating liquids is proportioned to their concentration and to the amount of spinning bath liquor (usually sulphuric acid and salt liquor) which the thread carries to the drum. Taking the latter to be 10 and adhering to the concentrations given below in the several examples, the approximate proportions of the treating liquids used in succession are as 10:22:5:4. Under the counterflow action, the bleaching solution joins the emulsifier solution and the two in turn join the hot water, each with the resultant products of their several reactions.

Under these conditions, the ascending thread passes first through a zone under wash water which has been lowered near to room temperature, where the concentration of acid and salt is still sufficiently high to complete decomposition of the xanthogenate, and is then gradually decreasing.

In the succeeding zone also under wash water lowered near to room temperature, the thread is freed by water from mineral acid, salt and soluble and suspended impurities excepting sulphur, which remains finely divided on the thread. The temperature of the rinse water in this and the preceding zone is relatively low, having been reduced by the thread and cage temperatures, substantially to room temperature (as attained by cage rotation).

Desulphuration is initiated in the next zone (still within the 50 cm. distance to the water drip) by the thread absorbing in its further progress along the drum, increasing quantities of the emulsifier and the organic acid contained therein, as entered into solution with the hot wash water. The desulphurizing reaction progresses with rising temperature of the rinse and becomes complete near the water drip where the temperature is relatively high. Particles of sul-

phur carried eventually beyond that point are removed or backwashed to the desulphurizing region by the descending emulsifier solution of the next zone.

In the zone between the rinse water drip 27 and desulphurant drip 28, the desulphurized thread is given an opportunity to absorb such additional quantities of the desulphurizing emulsifier as are needed for the purpose of lubrication. Proportional dispensation of the amounts of emulsifier for the one or other of its two functions (desulphurizing and avivifying) is adjusted by the width of the zone between the two drips, the avivifying action being proportioned to width of the zone.

The bleaching solution is dropped on from the drip 29 at a point where the thread has again cooled to room temperature. The emulsifier distributed on the thread for avivifying, protects the thread and tends to level and to stabilize the bleaching action. It does not interfere in any way with the bleaching reaction.

It has been found advantageous to use an emulsifier which, at a given acidity, is soluble in hot water, but loses this solubility more or less completely at room temperature. Free diffusion of excess emulsifier (there is often used considerable excess of treatment solutions over and above the exact amounts required for chemical reactions on the thread content) into the descending liquid of the counterflow would produce a lowering of the surface tension in the lowermost zones of the cylinder causing the liquids to be thrown off by the drum prematurely. Lowering of the temperature as the emulsifier descends into the rinse water checks and stops its solubility and affords an effective protection against diffusion, and, moreover, aids its thorough utilization in the two following directions:

In conjunction with the rapid cooling of the liquids under the influence of the rotation of the drum, it causes a flocking out of the excess emulsifier, setting thereby a local limitation to its zone of action and rendering it accessible to recovery together with its already precipitated portion and the separated sulphur. In such condition it is relatively still more inactive as respects the thread and the acid precipitant carried by it in the lowermost zones of the drum.

By similar reactions in the upper sections of the drum the absorbed emulsifier is kept from dissolving during the bleaching operation, but will, as the temperature rises, toward the drying device 33 assume its then function as avivifier preventing the filaments from adhering during drying and imparting to them the pliability and smoothness indispensable for the subsequent twisting.

Underneath the cage 13 is arranged trough 45 in which the desulphurant and precipitant fluids are collected as waste liquor. The liquid may thereafter be withdrawn and the excess precipitant and the treatment chemicals may be recovered from the waste liquor.

Obviously, there will be a number of ways of carrying out my invention.

Having in the premises explained its general nature, I give below several concrete examples for its practical execution:

Example

1. Primary material is a well filtered and de-aerated viscose solution made from semi-aged pulp and containing 6% cellulose, 7% caustic

soda, 2% sulphur and 1.7% neutral sulphite, corresponding to 0.85% sulphur dioxide. It is spun with a ripening number of 6.3 according to the Hottenroth count corresponding to 15 of the new count and a viscosity of 105 measured by the falling sphere method. Spinning speed is 77 yards per minute. Pump and spinnerette are fitted to the production of 150 dr. yarn with 90 filaments.

The spinning bath contains 10% sulphuric acid and 15% sulphate of soda. It is heated to 113° F. (45° C.) and circulates at a rate of 300 cc. per spinning head per minute.

The dipping length is 8 inches (20 cm). The thread, emerging from the spinning bath, is guided to a Godet wheel which is rotating at the same or a somewhat higher speed than the drum so that the thread enters the latter without tension.

For the unitary thread treatment storage device I prefer a spinning drum as herein first described of a length of 1110 mm. (40"), set under an angle of 13°, as being adaptable to the production of all sizes of yarn below and up to 300 dr. At the entrance point of the yarn, the drum cage has a diameter of 190 mm. (7½"). It rotates with 118 revolutions per minute and holds about 170 yards of yarn in 255 turns.

To compensate for its shrinkage during processing the drum is tapered, so that the thread is at no place exposed to strain or tension.

20 inches (52 cm.) above the lower end of the drum the drip for water of 195–200° F. (90–95° C.) is mounted and set to a delivery of 55 cc. per minute. Solution of the emulsifier, containing 1.35 grs. "Soromin AFZ" and 2.5 grs. of acetic acid per liter, at a temperature of 170° F. (75° C.) follows above at a distance of 1¾ inches (4½ cm.) or at 22¾ inches (56½ cm.) from the lower end of the drum. Its flow is 12 cc. per minute. Halfway between the emulsifier drip and the entrance to the drying zone, the bleaching solution is administered substantially at room temperature. It contains 0.06 gr. hydrogen peroxide and 2 grs. of acetic acid per liter and runs at a rate of 10 cc. per minute.

Drying completes operations on the drum. From the drying zone the thread is guided from there over a wheel to a down-draft twisting spindle. The spindle rotates with 7000 revolutions per minute imparting to the thread a twist of 2½ turns per inch. The receiver spool holds approximately one pound of yarn.

The 150 dr. thread has the following physical properties:

Breaking load, dry	grs.	292.8
Breaking load, wet	grs.	142.3
Elongation, dry	per cent.	16.3
Elongation, wet	do	24

Example

2. In the majority of cases bleaching can be dispensed with. Treatment on the drum is then further simplified.

The following are detailed figures concerning preparation of a 300 dr. unbleached yarn from a semi-aged viscose solution containing 7% cellulose, 6.3% caustic soda, 1.97% sulphur and testing for polymerization:

Hottenroth number	7.7
Corresponding new number	19.4
Viscosity (falling sphere method)	114
Pump delivery	cc. per minute 21
Wash water	do 90
Emulsifier solution	do 20

The hot water drip is placed at a distance of 23½" (60 cm.) from the lower end of the drum; and the emulsifier solution follows above at an interval of 2½ to 3¼ inches (6–8 cm.).

Otherwise procedure is the same as detailed under Example 1, except that the bleaching treatment is omitted.

Example

3. Bleached pulp containing 95–96% alpha cellulose is converted in the usual manner into alkal cellulose and subjected to the normal ageing process. It is then xanthated and reduced to a viscose solution containing 6.75% cellulose, 7.62% alkali, 2.35% sulphur and 0.1% sulphur dioxide. The solution is spun if it has matured to a Hottenroth number of 6.3, corresponding new number of 15 and a viscosity of 95.

For the manufacture of 100 dr. yarn with 60 filaments accessories are set for the following rates of flows:

Pump delivery of spinning solution

cc. per minute	9.75
Wash water	do 40
Emulsifier solution	do 10

Distance between water and emulsifier drips is 1¼–1¾ inches (3–4 cm.).

Otherwise procedure is the same as described under Example 2.

Reference to figures given in the preceding practical illustrations will show that the quantities of water and chemicals used for finishing the thread on the spinning drum are considerably below those required by now practiced methods for viscose spinning. Also the rates of additional manufacturing expenses for treatment according to my invention are essentially lower than with prior methods, as the following table indicates:

Per lb. of yarn	dr.	150	300	100
Power in k. w. h.		1.4	0.8	2.1
Steam in lbs.		42	26	56
Men hours		0.173	0.098	0.238

Further the floor space necessary is reduced. For a manufacturing unit of 6400 spindles and a daily capacity of 22,000 lbs. of 150 dr. yarn, with exclusion of buildings for preparatory or auxiliary operations but with liberal allowances for working space and transportation, the floor space is estimated at 16,700 square feet. In such a unit the manufacture of yarn is condensed into one single room with great reduction of manual labor accompanied by benefit to the quality of the material. Under customary methods there needs be provided special buildings, equipment and organizations for spinning, washing, drying and conditioning, twisting or coning, and there is necessitated a number of manipulations detrimental to the quality of the yarn.

Commercial superiority of the new method is accordingly predicated not only on substantial current economies in chemicals and labor, but also on a considerably lower initial investment for manufacturing units of equal capacity.

Those steps of my method which have to do with the employment of a unitary storage device for carrying out the successive treatments desired, are subject to modification in accordance with the type of unitary storage device employed. That to which the specific examples apply, consisting of a unitary spinning drum of the cage type on which the treatments are progressed in counterflow to the progress of the thread upon it, is subject as the examples them-

selves show to modification in the widths of the zones of the treatment in accordance with the denier of the thread, and the specific properties of the viscose solution employed. Such zone widths may be very considerably increased for deniers lying far above three hundred denier and perhaps reaching into the thousands. The length of the cylinder would be correspondingly increased. Similar increases of zone widths of treatment would be brought about through a lowering of the flows, concentrations, and temperatures, given in the several examples and in the general description of my invention, and conversely. The flows, concentrations, and temperatures given are those I have found most efficient in the practice of my invention on the deniers and spinning speeds chosen, and as deriving for the invention the advantages claimed, but they may be lowered or raised somewhat without departing from my invention.

From the foregoing examples it will have been observed that in round figures the viscose solution spun contains approximately 6% to 8% cellulose, 6% to 7.75% alkali, and 1.9 to 2.5% sulphur, the precipitant of the spinning bath contains approximately 8 to 15% sulphuric acid and 10 to 25% sulphate of soda, the precipitant removal treatment comprises rinse water, the desulphurant comprises a kation active emulsifier introduced in solution containing approximately 1-3 grams of the emulsifier and 2-3 grams of acetic acid per liter, approximately 80 yards of thread are progressed ascendingly upon the storage device approximately from 20 to 25 inches of length of the storage device per minute, and there is used rinse water of a flow of from $\frac{1}{3}$ to $\frac{1}{2}$ cc. per denier of thread, and desulphurant of a flow of from $\frac{1}{4}$ to $\frac{1}{2}$ cc. per denier of thread counterflowed upon the thread at the rate of from 20 to 25 inches of length of the storage device per minute.

In short the quantities of the rinse water and the desulphurant are increased in accordance with the increase in the denier of the thread or yarn from 100 to 300 denier while the rate of counterflow of the introduced quantities of the treatment means is increased by increasing the distance between the point of introduction of the treatment means and the lower end of the drum, for such increases and decreases are to be made when the denier is raised above 300 denier, perhaps in the instance of yarn spun for cord tires or staple being increased so far as necessary according to the same proportion, although these proportions will not truly hold because of the increased widening and flattening of the yarn as its denier is increased.

There are features of my invention involving the unitary storage device, which are not to be restricted in form to those forms necessarily resultant from the employment of counterflow, or spinning drums of the cage type. Desulphurants having the characteristics of the desulphurant of my invention, and applied according to the steps of my invention, may also be combined with methods of thread progression employed on other types of drums. Among such other types of storage devices are, for example, those in which the thread is progressed in a spiral formed by loops about rolls whose axes lie in parallel planes, but are inclined to each other, with or without counterflow application of treating fluids, and such are single or multiple drums or rolls which progress the threads spirally, but without such axis inclination as would produce counterflow.

Wherever successive treatments may become intermingled, those features of my invention having to do with rapidity of action, sharpened zones of application and the boundaries thereof, and the attainment of relative inactivity of the treatments and the products of their reactions, will be found useful.

Even where the treatments and the products of their reactions do not intermingle, such steps as the acidifying of the kation active emulsifier and the simultaneous desulphurizing and avivifying through the desulphurant itself, and, if desired, the subsequent bleaching in the presence of the absorbed avivifier, will be found useful. I contemplate such modifications of my invention as will permit such utilization.

As is apparent from the examples given, I prefer to apply a flow of desulphurant which is very considerably in excess of that precisely required to react completely with the sulphur of the thread. The excess of this treatment means, together with the products of its reaction without sulphur, by reason of the abrupt reduction of its relatively high temperature of application to the relatively low room temperature, becomes insoluble in the rinse water. Moreover, they are both relatively inactive as respects the thread or the precipitant acid or salt adhering to the thread as it emerges from the spinning bath to such a degree that there is no reaction between them while the treatment fluids are on the spinning drum. Even where the desulphurant is capable of mild activity, the relative rates of progression of the thread in one direction on the drum, and the counterflow of treatment fluids in the opposite direction, is such as to prevent any reaction which might otherwise take place. On the other hand, reaction between the precipitating acid or salt of the spinning bath, as washed from the thread, and the combined rinse water and treatment fluids for desulphurizing and bleaching, is permitted after they leave the spinning drum and become waste liquor. The chemicals used for the various treatments are recovered from the waste liquor after such reaction as may occur during the removal and storage of the waste liquor, has occurred. This is also according to my invention. Irrespective of whether the desulphurant may have a capacity for long-time reaction with other treatments as they are commingled as waste liquors, or may be absolutely free of reactive capacity, the desulphurant on the spinning drum is relatively inactive as respects the other treating fluids, jointly or severally by virtue of its set-forth character, the controlled concentrations, rates of flow, and temperature, and the relative rate of progression of the thread and the counterflow in opposite directions.

Instead of applying the desulphurant considerably in excess of that precisely necessary for chemical combination with the sulphur, I may especially in those forms of my invention in which I also use the desulphurant as an avivifying agency, supply but the quantity sufficient for desulphurizing and avivifying with substantially no excess. That absorbed for avivifying then becomes a guarantee of complete sulphur removal.

In instances where I do not simultaneously utilize the application of desulphurant to avivify, I may introduce the desulphurant along with the rinse water at its relatively high temperature. The outstanding desulphurizing action takes place, I believe where the desulphurant in counterflow becomes admixed in the relatively high

temperature rinse water. In such case I avivify the thread by an independent application of an avivifier introduced between the desulphurant introduction and the drying with or without an intermediate bleaching treatment. It is anticipated that bleaching on the unitary storage device will be done only in exceptional cases as the use of unbleached yarn is steadily increasing, and as bleached material is now preferably obtained by starting from prebleached pulp.

While "Soromin" and "Sapamin" are both to be found among the now very numerous means which it has been heretofore proposed to use as desulphurants, and while Sapamin is known to me to have been patented (see German Patent No. 622,403 of 1935 perhaps among others) no one prior to my invention recognized those characteristic features of kation active desulphurants in general which I have recognized in effecting my invention, or combined them with the process steps involved in the unitary storage device method of operation. In the German patent there were discerned and utilized in the old time cake spinning wheel process those limited properties only which the concept of the inventor combined with the steps of that method.

It has also been known (see the German patent) that desulphurants, such as "Soromin" and "Sapamin," possess an avivifying property, and it has been proposed to use them as avivifiers both independently of and jointly with desulphurizing use. I do not claim discovery of these uses broadly. I do claim a new method of application of this combined desulphurizing and avivifying action through which it and the ensuing bleaching are effected without adverse reactions or interferences, and at maximum efficiency and economy.

The kation active emulsifiers I use may or may not possess the avivifying properties of "Soromin" or "Sapamin," and in such case I would modify my method by introducing a subsequent avivifying treatment either before or after bleaching.

Still other modifications of my invention will be made from time to time by those skilled in the art. Irrespective of the influence of terminology (necessarily circumstantial) utilized in the specification and the claims, it is intended that all such modifications whatsoever which fall within the generic spirit of my invention, shall be covered by the appended claims.

The illustrated and described embodiment of a cage for carrying out the invention is also described and illustrated in applicant's copending application Serial No. 344,947, filed July 11, 1940, Rayon spinning and drying cage, in which certain features, not covered by the present application, are claimed.

What is claimed is:

1. The method of manufacturing viscose rayon which consists in precipitating the thread in a spinning bath, in progressing the thread upon a common and unitary thread storage device in one direction, establishing upon the storage device in the direction of the progression of the thread at a distance from its leading-in end a zone of storage in which the thread is substantially free from adhering spinning bath precipitant by applying to the thread on the storage device in counterflow to the progression of the thread a precipitant-removal fluid which substantially completely removes adhering precipitant in advance of said zone, and in the desulphurizing within this zone the cellulose of the thread substantially completely through counter-

flow treatment by an aqueous solution of a kation active desulphurant fluid whose reaction with the sulphur takes place substantially completely within said zone, the desulphurant being of such a nature that the products of the desulphurizing treatment are at least within the time during which those products remain on said storage device substantially inactive as respects the thread and its adhering precipitant met with by the combined counterflow as it flows beyond the boundary of said zone toward the lead-in end of the device and leaves the storage device as waste fluid.

2. The method according to claim 1 in which a greater amount of the desulphurant is introduced than the amount theoretically necessary for combining with all the sulphur so that the products of the desulphurizing treatment include the desulphurant combined with sulphur and an excess of desulphurant free and uncombined.

3. The method according to claim 1 in which the desulphurant is a fatty acid amid of the asymmetric diethyl-diamine-ethane group and in which the aqueous solution contains in the neighborhood of 1.35 grams of desulphurant and 2.5 grams of acetic acid per liter.

4. The method according to claim 1 in which the viscose solution spun contains approximately 6% to 8% cellulose, 6% to 7.75% alkali, and 1.9 to 2.5% sulphur, the precipitant of the spinning bath contains approximately 8% to 15% sulphuric acid and 10% to 25% sulphate of soda, the precipitant removal treatment comprises rinse water, the desulphurant comprises a kation active emulsifier introduced in aqueous solution containing approximately 1-3 grams of the emulsifier and 2-3 grams of acetic acid per liter, approximately 80 yards of thread are progressed upon the storage device approximately from 20 to 25 inches of length of the storage device per minute, and there is used rinse water of a flow of from $\frac{1}{3}$ to $\frac{1}{2}$ cc. per denier of thread, and desulphurant of a flow of from $\frac{1}{15}$ to $\frac{1}{10}$ cc. per denier of thread counterflowed upon the thread at the rate of from 20 to 25 inches of length of the storage device per minute.

5. The method according to claim 1 in which the desulphurant is comprised of a solution having also an avivifying action on the thread, and is flowed on to the thread approximately in that quantity only adequate for the desulphurizing reaction plus that needed for avivifying, and is initially applied in a zone beyond the zone of desulphurizing reaction; and the width of said application zone being such that the thread has time to absorb that quantity of the solution needed for avivifying.

6. The method according to claim 1 in which the desulphurant is possessed of an avivifying as well as a desulphurizing property, is applied to the storage device and the thread in a zone beyond the said zone of desulphurizing reaction to permit the thread to absorb that quantity desired for avivifying, and a bleaching treatment having the property of being capable of penetrating the absorbed desulphurant without reacting therewith, is applied in a zone immediately succeeding said zone of avivifying absorption of the desulphurant.

7. The method according to claim 1 in which the desulphurant is soluble in the water only above a predetermined temperature and in which the temperature in the desulphurizing zone is maintained above said predetermined tempera-

ture and the temperature of desulphurant is maintained below the said predetermined temperature prior to its entry into the desulphurizing zone, whereby the desulphurant is undissolved prior to the entry thereof into the desulphurizing zone and dissolves when it enters into said zone.

8. The method according to claim 1 in which the desulphurant is reacted with the sulphur in the thread in its admixture with water serving as precipitant-removal fluid approximately at 200° F., and in which said temperature is reduced to room temperature immediately following in the direction of the travel of the thread, the desulphurizing reaction.

9. The method according to claim 1 in which said treatment for the removal of the precipitant and the establishment of said zone for desulphurizing free from the precipitant is a rinse water treatment, in which the desulphurant is introduced already admixed with the rinse water; so that the mixture of desulphurant and rinse water acts on the thread at first that is near the lead-in end of the device as precipitant-removal but exerts at a distance from and between the lead-in end and the point of supply of the mixture its desulphurizing action and in which, in a zone of said common unitary thread storage device following in the direction of the travel of the thread the zone of introduction of the desulphurant, an

avivifying treatment is applied and independently of the desulphurant.

10. The method according to claim 1 in which the desulphurant is an emulsifier having the property of being soluble at relatively high temperatures i. e. substantially above room temperature and insoluble at lower temperatures, and is applied at such a high temperature at which the emulsifier is in solution, and a counterflow bleaching fluid is applied to the thread on the same storage device in the zone immediately following the zone in which the desulphurant is applied to the thread, said bleaching fluid being applied at such a low temperature that the temperature of the desulphurant adhering to the thread is reduced to a point where the desulphurant is rendered insoluble.

11. The method according to claim 1 comprising the application of the desulphurant in an acid aqueous solution.

12. The method as claimed in claim 1 comprising the use of a kation active desulphurant which has both desulphurizing and avivifying properties and which is applied to the thread or threads in a manner permitting the emulsifier to carry out the additional function of avivifier for the thread.

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