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3,851,036

## METHOD OF MAKING HOLLOW FIBERS

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No Drawing. Continuation of abandoned application Ser. No. 851,284 Aug. 19, 1969. This application Sept. 13, 1971, Ser. No. 180,227

Int. Cl. D01f 7/00

U.S. Cl. 264—182

13 Claims

### ABSTRACT OF THE DISCLOSURE

A method of producing synthetic fibers having tough outer skins and hollow or semi-hollow cores which comprises spinning said fiber and subjecting the spun fiber to sequential coagulation treatments whereby the outer core is coagulated to a tough shell, whereas the inner core is incompletely coagulated and collapses. The fibers may be used in conventional textile materials and in dialysis cells.

This is a continuation of Ser. No. 851,284, filed Aug. 19, 1969, and now abandoned.

This invention relates to synthetic fibers, particularly to polyacrylonitrile homopolymers, copolymers, or inter-polymers in fibrous form. More specifically, the invention relates to a method of producing such fibers with hollow cores.

The production of hollow filaments has been the subject of considerable inquiry since these fibers have been found to be particularly susceptible to treatment with coloring materials such as dyes, flame retardants, anti-static materials, etc., while retaining structural stability and flexibility.

Hollow filaments have generally been prepared by melt spinning a polymeric material using a complicated spinnerette. Typically, the spinnerette orifices are provided with nozzles adapted to insert pressurized gas into the center of the uncoagulated fiber to thereby displace the core material. Additionally, a laminating technique has been used wherein C-shaped orifices separately extrude sections of the fiber which are laminated while still in a flowable condition prior to coagulation. These spinnerettes are bulky and expensive, and it is therefore desirable to devise a process adapted for use with conventional circular hole spinnerettes. The spinning process can be applied, however, to any existing system without modification of the spinnerette even to non-circular hole spinnerettes. With respect to acrylonitrile fibers, internal cavities have been produced by such methods as solution spinning from organic solvents into an aqueous coagulation bath as disclosed in 3,180,845 and 3,088,188 or solution spinning from nitric acid into a coagulation bath containing nitric acid as disclosed in U.S. 2,907,096. The former methods require collapsing the voids which form while the latter must avoid the collapse of the voids.

The use of certain coagulating baths is undesirable in treating synthetic fibers since it is found to detract from the physical properties of the ultimate fibers, such as the flexibility and extensibility. Additionally, the conditions upon which coagulation occurs are found to produce variable characteristics in the fibers so that a coagulating bath which works satisfactorily under some conditions is unsatisfactory when those conditions are varied or when the concentration is changed. This invention provides treatments which give useful fibers having the requisite strength.

It has now been discovered that wet spun semi-hollow synthetic fibers, particularly acrylonitrile fibers, can be produced having partially or wholly collapsed cores which are cheesy but which retain a structural integrity due to the tough outer shell, adapting them for use in conducting

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fluids by capillary action, by a sequential coagulation treatment conducted under such conditions as to produce a strong skin and weak collapsible core.

It is a primary object of this invention to provide a method which is adapted to produce synthetic polymer fibers having a hollow or semi-hollow core by extruding from conventional circular orifices.

A further object is to produce the subject fibers having improved properties, particularly flexural rigidity and affinity for coating materials.

These and other objects and advantages of the invention will be apparent from a consideration of the following drawings and description. In the drawings, FIGS. 1-7 are photomicrographs showing fibers produced by the present invention.

FIG. 8 is a schematic diagram illustrating a process for producing the fibers of FIGS. 1-7.

The method of the present invention may be described generally as comprising the steps of wet-spinning polymeric acrylonitrile material from an aqueous medium containing an inorganic salt or from an organic medium through orifices of circular cross-section, passing the filament into a weak first coagulation bath containing a solvent or salt corresponding to the solvent or salt present in the spinning dope, which bath contains 35-95% coagulant and is maintained at a temperature of -20° to +25° C., preferably 0° C., for a residence time of 13-40 seconds, optionally stretching the fibers therein, passing the initially coagulated fiber into a harsh second coagulation bath containing a like solvent or salt in an amount of less than 35%, preferably less than 10%, which bath is maintained at a temperature of 30°-120° C., preferably 25°-100° C., for an average residence time of 1-15 seconds, washings, stretching, collapsing the uncoagulated inner core by drying or cooling the filaments followed by drying without tension. Fibers thus produced have a cheesy inner core which is partially or wholly collapsed but is capable of conducting fluids by capillary action. This capillary action can be used directly as when the fibers are incorporated in dialysis cells for water purification or other microfiltration operations or indirectly in enabling them to absorb coating materials prior to incorporation in carpets and other textiles.

Reference to FIG 8 shows a schematic flow diagram wherein spin dope 3 is extruded initially to produce fibers 6 which are drawn from a spinnerette (1) through a first bath 2 wherein first coagulation bath 4 is provided. The fibers are drawn across adjustable roller 8 onto a series of rollers 10 adapted to maintain tension on the fibers into second bath 12 containing heating coil 14 and second coagulation bath 16. Following this treatment, the fibers are washed in tank 18 wherein guide rollers 20 keep the fibers submerged in wash liquid 22, generally comprising water. After washing a cold stretching treatment is provided by passing over moveable rolls 24 and then a hot stretching treatment is provided using a boiling liquid such as water maintained in tank 26. Finally, the fibers are dried in an oven (not shown). These steps are conventional in producing fibers and those skilled in the art will be aware of variations of this treatment which may be utilized depending upon the particular polymer being treated. For example, the stretching operations can be modified to provide more than one cold stretching operation and/or more than one hot stretching operation. Likewise, the washing treatment may occur in more than one stage.

In collapsing the inner core according to this invention, the essential point is stretching of the properly coagulated fibers. The fibers must be in a suitable state when they are stretched and dried, and this state can be produced by the specific coagulation techniques of this invention. To collapse the inner core, alternate treat-

ments are available; e.g., this is achieved by icing the fibers prior to drying and/or by subjecting the fibers to an acetone treatment to displace the solvent in the fibers, prior to drying. In some cases, drying may be used prior to stretching to collapse the core. Drying under tension is not required and will frequently destroy the voids completely or will unduly disrupt the structure integrity of the core. Generally, when drying temperatures above 90° C. are used, it is desirable to impregnate with a low surface tension liquid except where the fibers have been given a total hot stretch above 2:1. In this latter case, impregnation is not essential.

More specifically, the process of this invention comprises spinning a solution of an acrylonitrile containing polymer through a circular hole spinnerette. The term "acrylonitrile polymer" as used in this invention includes homopolymers, copolymers, and in terpolymers of acrylonitrile wherein the acrylonitrile is present in the polymer in a quantity of approximately 80% by weight or more. Suitable comonomers for preparation of copolymers useful in this invention include vinyl monomers such as acrylic and methacrylic acid esters, particularly the lower alkyl esters, other suitable vinyl compounds are vinyl acetate chloride, vinyl bromide, and vinyl pyridine, and sulfo-containing vinyl compounds such as ethylene sulfonic acid, mineral salts thereof, sulfoethyl acrylate or methacrylate compounds and salts thereof. Additional comonomers and methods of preparation will be apparent to those skilled in the arts.

While acrylonitrile polymers are preferred, other polymers can be used provided the rate of coagulation is slow enough to allow a two-stage treatment. Likewise, the fibers can be formed by blending the acrylonitrile polymer with minor (2-5%) proportions of compatible polymers, e.g. polyethylene glycol or different acrylonitrile polymers. Spinning dope is formed by dissolving the polymer in a suitable carrier, or by solution polymerizing the monomers in the spinning solvent, e.g., an aqueous solution carrier containing an inorganic salt or an organic solvent, or both. An aqueous zinc chloride solution may be utilized. Other aqueous saline solutions, that is, solutions containing an ionizable salt, may be used, which contain mixed inorganic salts such as zinc chloride, sodium chloride, calcium chloride, magnesium chloride, etc. Generally, any highly water-soluble salt may be utilized and this further includes the alkali metal thiocyanates, alkali earth metal thiocyanates, ammonium thiocyanate, guanidine thiocyanate, lithium bromide, lithium iodide, sodium iodide. The aforementioned systems may be termed "inorganic solutions"; however, the invention should be understood to include organic spinning dopes wherein the polymer is dissolved in, or formed by solution polymerization in, e.g., dimethyl acetamide or other organic spinning liquids. Mixed organic and inorganic systems may be used wherein the solvent system consists essentially of water containing at least one water-miscible, aliphatic liquid containing one alcoholic hydroxyl group and not more than six carbon atoms in the molecule, and at least one highly water-soluble salt as described above. For example, a system which has been used with satisfactory results comprises 48% zinc chloride, 28% water, and 24% methyl alcohol (weight percents are used). These and other systems are adequately described in the art as exemplified by U.S. Pats. 2,648,646 and 3,284,555.

The coagulation baths comprise a coagulation medium, generally water, and an organic solvent such as dimethyl acetamide or inorganic salts such as zinc chloride, or mixed organic-inorganic solutions containing water, alcohol, and inorganic salt. The specific bath depends upon the spinning dope and generally the bath should contain ingredients corresponding to those in the spinning dope. Naturally the compositions and temperatures will vary.

In the first coagulation bath, relatively weak coagulation conditions are used, e.g., the temperature is maintained at -20° to +25° C., preferably -10° to 0° C.,

and the spun fibers are allowed a dwell time of 13-40 seconds, preferably 15-40 seconds. When the bath comprises an aqueous inorganic system, the inorganic salt or mixture of salts should be present in a weight quantity of 20-50%, preferably 25-45%, given from 50-80% coagulant. When a mixed inorganic-organic system or an organic system is used, the organic component should be present in a quantity of 5-60%, giving 40-90% coagulant. In the first coagulation bath, rapid coagulation of the outer skin only is desirable and, therefore, tension and temperature extremes should be avoided since these tend to increase the rate of complete coagulation of the fibers. Thus, the low temperatures and low tension should be maintained throughout the fiber travel through the first bath.

When the fibers are introduced in the second bath, the outer skin will be coagulated; however, the dwell time and conditions in the first bath will have been insufficient to allow migration of the coagulation medium to the inner core of the fiber. Thus, the inner core will remain soft and uncoagulated. In the second bath, it is desirable to increase the migration of coagulating mediums to the inner portion of the core. To accomplish this purpose, high temperatures and concentrations of coagulant are utilized in a coagulating bath having greater proportion of coagulant than the first bath. For example, the second bath should contain (in organic systems) approximately 0-10% of the organic medium and in inorganic systems, approximately 0-35% of the inorganic salt. The temperature in the second bath should be maintained at 30-120° C., preferably about 100° C. It is generally unnecessary to apply tension to fibers in the second bath since high temperature accomplishes sufficient coagulation to yield the desired hollow or semi-hollow fibers. A dwell time in the second bath should be maintained at approximately 1-15 seconds, preferably 1-10 seconds, which will depend upon the exact conditions and ingredients used. This time is generally less than used in the first bath.

While excessive stretching should generally be avoided in the coagulation baths, it is possible and sometimes desirable to apply tension in and between the baths and after the second baths. Thus, for example, a stretch may be applied to the fibers in the first bath at a ratio of 1-3:1, between the first and second baths, up to a 3.0:1 ratio, and after the second bath, the fibers can be stretched up to 10:1 ratio or can be shrunk, depending upon the ultimate product desired. This stretching can be accomplished in a series of stretching steps by conventional techniques: for example, a three-stage stretch wherein a stretch ratio of approximately 2:1 is applied in each step. Stretching also orients the fiber molecules and increases the strength of the fibers in coagulated fibers. A stretch ratio of 1:1 indicates no elongation of fibers was produced and a ratio of less than 1:1 indicates shrinkage.

Following the second bath, the fibers are washed to eliminate the coagulating medium and any remaining solvent. Washing is generally accomplished in hot water at about 20-50° C. and can be a sequential stage-like treatment or a one-bath treatment.

In order to collapse without destroying the weak cheesy inner core of the fibers, alternate techniques are available. Essentially, the inner walls remain weak, while the outer skin is relatively tough due to the different rates of coagulation. To collapse the inner walls, the fibers can be dried without stretch, or can be cooled almost to freezing and/or impregnated with a liquid medium having low surface tension such as acetone. After this treatment, the fibers are dried in an oven, e.g. a hot air (100-150° C.) type oven.

The invention will be more fully understood by reference to the following illustrative examples. In the examples, parts and percentages are by weight unless otherwise indicated.

## 5 EXAMPLE 1

A homopolymer of acrylonitrile was spun from a zinc chloride solution through a 60-hole spinnerette having circular holes 6 mils in diameter into a first coagulation bath containing a 32% zinc chloride aqueous solution maintained at  $-8^{\circ}\text{C}$ . The spinnerette pressure drop was 76 p.s.i.g., and the polymer temperature issuing from the spinnerette was  $70^{\circ}\text{C}$ . While passing through the first bath, a 1.82:1 stretch was applied by conventional adjustable driven rollers and the fibers were led to a second bath maintained at  $100^{\circ}\text{C}$ . and containing 32% zinc chloride aqueous solution. The residence time in the first bath was approximately 10.4 seconds, while in the second bath, the residence time was about 1 second. The fibers were washed at  $30^{\circ}\text{C}$ . and removed from the wash bath and subjected to a 3-stage stretching operation, the first stage being on cold rollers at a ratio of 4:1, the second and third being in boiling water at ratios of 0.8:1 and 1:1 respectively. Following the stretching, the fibers were dipped in ice water ( $0^{\circ}\text{C}$ .), followed by an immersion in an acetone bath maintained at room temperature and passed through an oven wherein hot air at approximately  $130^{\circ}\text{C}$ . was blown over the fibers until dry. The dried fibers produced a cross-section corresponding to the microphotograph of FIG. 1 wherein the cores shrink and collapse to one side of the core. The fibers were 165 denier, and upon subsection to the conventional testing techniques, the elongation was 2%, the tenacity was 0.73 grams per denier and the elastic modulus was 39.

## EXAMPLE 2

The procedure of Example 1 was repeated using a spinnerette having 60 holes of 15 mil diameter and having a pressure drop of 23 p.s.i.g. wherein the polymer temperature was  $35^{\circ}\text{C}$ . at the orifice. The fibers were stretched in the first baths at a ratio of 2:1 and after the second bath in a 3-stage treatment comprising one cold and two hot stretches, all at a ratio of 1:1. Residence time in the first bath was 35 seconds and in the second bath was 2.9 seconds. The fibers were treated in boiling water before washing. The fibers produced are shown in FIG. 2 and were 454 denier with an elongation of 2%, tenacity of 0.16 grams/denier, and an elastic modulus of 13.

## EXAMPLE 3

Procedure of Example 2 was repeated with the temperature in the first bath being  $-6.5^{\circ}\text{C}$ . and a total stretch ratio, after the second bath, of 6:1 at  $80^{\circ}\text{C}$ . This produced the fibers shown in FIG. 3 which are 98 denier with an elongation of 33%, a tenacity of 1.6 grams/denier, a yield strength of 1.2 grams/denier, and an elastic modulus of 41. When looped, the tenacity was 1.1 grams/denier, and the elongation was 16%.

## EXAMPLE 4

The procedure of Example 2 was repeated using a first bath temperature of  $0^{\circ}\text{C}$ . with a residence time in the first bath of 17.4 seconds and in the second bath of 10 seconds. The fibers were not stretched, washed, or dried. The unstretched fiber had a very distinct difference in structure between the inner and outer fiber zones, as shown in FIGS. 4 and 5. In fact, when the fiber of FIG. 4 was cross-sectioned, the core fell out due to the lack of adhesion to the wall.

## EXAMPLE 5

The procedure of Example 3 was repeated using first bath temperature of  $0^{\circ}\text{C}$ . and a second bath residence time of 2.5 seconds and stretching ratios after the second bath of sequentially 1:1, 2:1 and 0.8:1. The fibers produced are shown in photomicrograph of FIG. 6, and were 60 denier, with an elongation of 24%, a tenacity of 1.7 grams/denier, a yield strength of 1.0 grams/denier, and an elastic modulus of 3.7. When looped, the elongation was 23% and the tenacity was 0.38 grams/denier.

## 6 EXAMPLE 6

The procedure of Example 5 was repeated using sequential stretch ratios after the second bath of 1:1, 1.5:1, and 1.5:1. This produced the fibers shown in FIG. 7 which were 60 denier with an elongation of 29%, a tenacity of 1.8 grams/denier, a yield strength of 0.97 grams/denier, and an elastic modulus of 31. When looped, the tenacity was 0.42 grams/denier, and the elongation 25%.

## EXAMPLE 7

An acrylonitrile homopolymer dissolved to 10% solids in a 50–60% aqueous sodium thiocyanate solution was spun through a spinnerette having 15 holes of 8 mil diameter wherein a pressure drop of 10 p.s.i.g. occurs. These fibers were led into a first bath containing a 10% sodium thiocyanate and maintained at  $0^{\circ}\text{C}$ . for a dwell time of 15.6 seconds. The fibers were passed without stretching to a second bath containing 10% sodium thiocyanate maintained at  $100^{\circ}\text{C}$ . and a dwell time of 6 seconds was experienced. Following the second bath, the fibers were washed at  $30^{\circ}\text{C}$ ., then cooled in ice water and stretched at a ratio of 1:1, followed by hot stretching in boiling water at a ratio of 8:1. After stretching, the fibers were conducted to an oven wherein air at  $125^{\circ}\text{C}$ . was blown across the fibers until dried. Fibers produced were 110 denier and correspond in structure to those shown in FIG. 6.

## EXAMPLE 8

An acrylonitrile terpolymer containing a combination of methylacrylate and methyl methacrylate in a total quantity of less than 20% was dissolved to 25% solids in 100% dimethyl acetamide. This solution was spun through a spinnerette having 15 holes of 8 mil diameter into a first bath containing 55% dimethyl acetamide maintained at  $0^{\circ}\text{C}$ . for a dwell time of 15.6 seconds. The fibers were conducted without stretching to a second bath containing 10% dimethyl acetamide maintained at  $100^{\circ}\text{C}$ . for a residence time of 4 seconds. The fibers were then washed at  $30^{\circ}\text{C}$ ., and the fibers were then conducted to boiling water where they were stretched at 3.33:1 ratio and then cooled in ice water prior to being dried at an oven temperature of  $125^{\circ}\text{C}$ . to produce 89 denier filaments having structure corresponding to that shown in FIG. 6.

## EXAMPLE 9

An acrylonitrile homopolymer dissolved in dimethyl sulfoxide to 25% solids was spun through a spinnerette having fifteen 8 mil holes into a first bath containing 50% dimethyl sulfoxide maintained at  $20^{\circ}\text{C}$ . for a dwell time of 15.6 seconds. The fibers were conducted to a second bath containing boiling water for a residence time of 6 seconds. The fibers were then washed at  $30^{\circ}\text{C}$ . and stretched at a 1:1 ratio, then conducted to boiling water and stretched at a 4:1 ratio. After cooling in ice water, they were dried at  $125^{\circ}\text{C}$ ., 110 denier filaments were produced corresponding in structure to those of FIG. 6.

## EXAMPLE 10

Procedure of Example 9 was repeated, substituting dimethyl formamide for the dimethyl sulfoxide and using a dwell time in the second bath of 4 seconds with 10% dimethyl formamide in the second bath and a hot stretch ratio of 3:1. Fibers were 100 denier and correspond to those of FIG. 6.

## EXAMPLE 11

A spinning solution is prepared using 15% of a copolymer containing 90% acrylonitrile and 10% methyl acrylate (M.W. about 100,000) and dissolved in a solution consisting of 35% sodium thiocyanate dissolved in 65% of a mixture of 20 parts water and 80 parts methyl alcohol.

Fibers produced by this invention are highly flexible and show high affinity for fluids conducting the fluids by

capillary action through the semi-hollow, inner core. They are useful in all lengths and in all diameters although diameters beyond the initial range of 5-20 mils are difficult to coagulate properly.

The testing procedures used on the fibers of this invention are conventional and are available from such sources as *Encyclopedia of Polymer Technology* (John Wiley & Sons, 1960) or the American Society for Testing and Materials and the American Association of Textile Chemists and Colorists.

Having described the invention, what is desired to be protected is as follows:

1. In the known process comprising solution spinning polyacrylonitrile homopolymers or copolymers containing at least 80% by weight acrylonitrile and up to 20% by weight of one or more vinyl monomers through a round orifice into a first bath to superficially coagulate the fiber; passing the superficially coagulated fiber into a second bath; washing the fiber; stretching the fiber; and drying the fiber; wherein the spinning solution and said first and second baths all contain a member selected from the group consisting of an aqueous saline solvent, an aqueous saline solvent containing an aliphatic alcohol containing less than 6 carbon atoms; dimethyl acetamide, dimethyl formamide, and dimethyl sulfoxide; the improvement which comprises forming hollow fiber without the addition of foaming agents by spinning said solution into said first bath wherein the concentration of the selected member is maintained in an amount of 5 to 65% by weight in 95 to 35% by weight water and the temperature of said first bath is maintained at -20 to +25° C., and maintaining the fiber in said first bath for from about 13 to about 40 seconds and thereafter passing the superficially coagulated fiber into said second bath wherein the concentration of said selected member is maintained in an amount less than that in the first bath and less than 35% by weight in more than 65% water and the temperature of said second bath is maintained at 30 to 120° C. and maintaining said fiber in said second bath from about 1 to 15 seconds.

2. The method of Claim 1 wherein an acrylonitrile copolymer is used which contains comonomers in an amount less than 20% by weight selected from the group consisting of acrylic acid lower alkyl esters, methacrylic acid lower

alkyl esters, vinyl acetate, vinyl chloride, vinyl bromide, vinyl pyridine, and sulfo-containing vinyl monomers.

3. Method of Claim 1 further comprising impregnating the fibers with acetone prior to drying.

4. Method of Claim 3 comprising cooling the fibers at about 0° C. before drying.

5. Method of Claim 4 wherein the fibers are impregnated with acetone after cooling to about 0° C. and before drying.

6. Method of Claim 1 wherein drying occurs before stretching.

7. Method of Claim 1 wherein polymer is acrylonitrile homopolymer.

8. Method of Claim 1 wherein solvent is dimethyl acetamide.

9. Method of Claim 1 wherein solvent is dimethyl formamide.

10. Method of Claim 1 wherein solvent is dimethyl sulfoxide.

11. Method of Claim 1 wherein an aqueous saline solvent is used.

12. Method of Claim 11 wherein the inorganic salt is  $ZnCl_2$ .

13. Method of Claim 1 wherein the salt is a lower alcohol and the salt  $ZnCl_2$  are used.

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JAY H. WOO, Primary Examiner

U.S. Cl. X.R.

161—178; 264—209, 210 F

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,851,036 Dated November 26, 1974

Inventor(s) L. S. Tzentis Page 1 of 4

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Insert the drawings as part of Letters Patent 3,851,036,  
as shown on the attached sheets.

Column 1, line 5, delete "No Drawing".

Column 2, line 33, "washings" should read -- washing --.

Column 3, line 24, after "acetate" insert -- , vinyl --.

Signed and Sealed this

*thirteenth* Day of *April* 1976

[SEAL]

*Attest:*

**RUTH C. MASON**  
*Attesting Officer*

**C. MARSHALL DANN**  
*Commissioner of Patents and Trademarks*

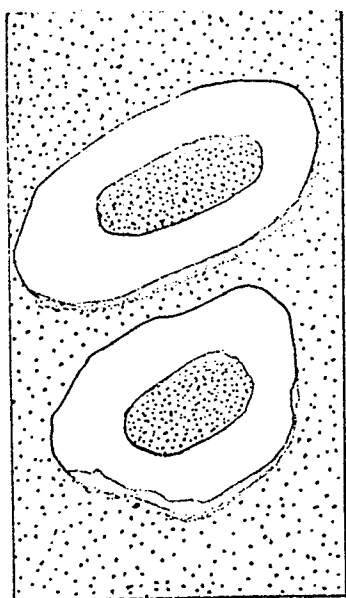


FIG. 1.

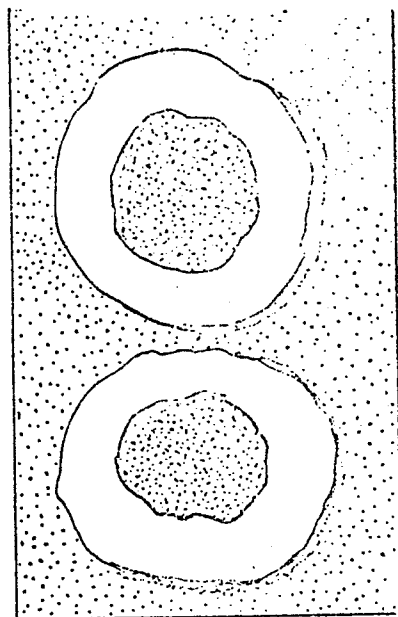


FIG. 3

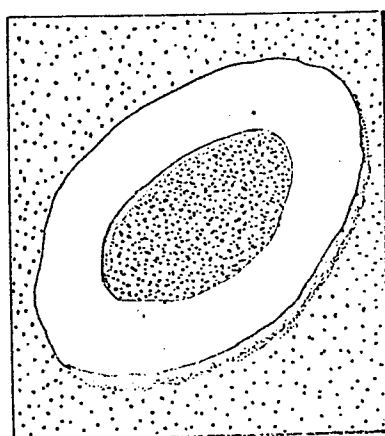


FIG. 2

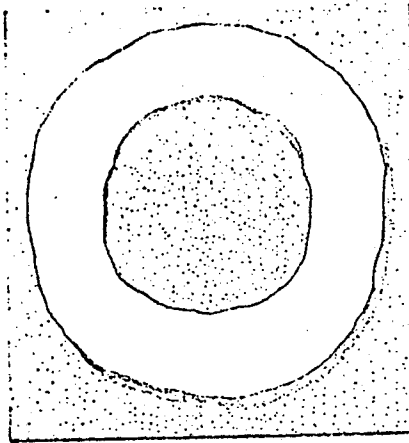


FIG. 4

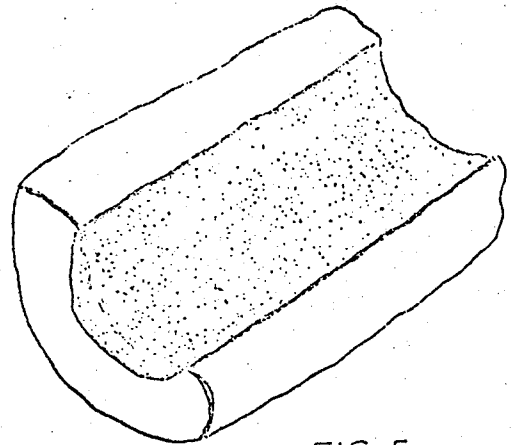


FIG. 5

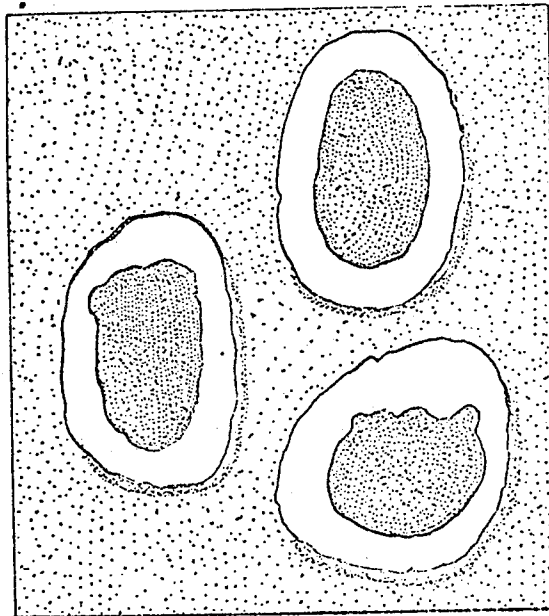


FIG. 6

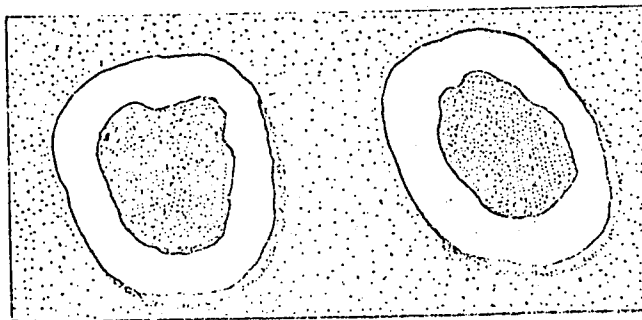


FIG. 7

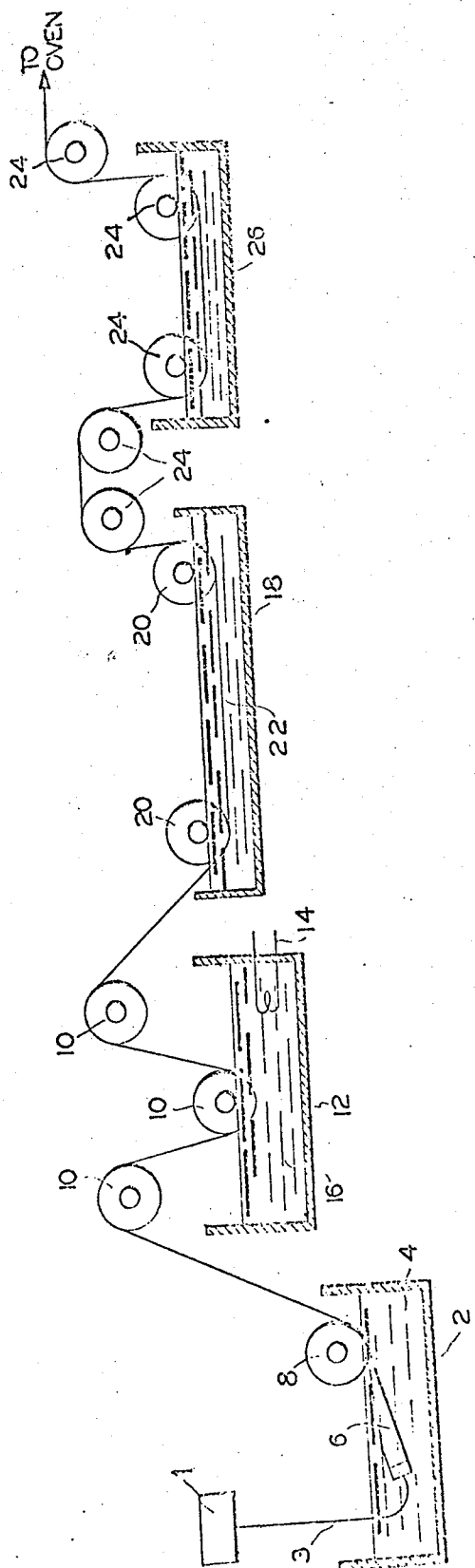


FIG. 8