

May 12, 1959 **W. N. SELLERS** **2,886,403**
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FILAMENTARY MATERIAL
Filed Jan. 31, 1956 3 Sheets-Sheet 1

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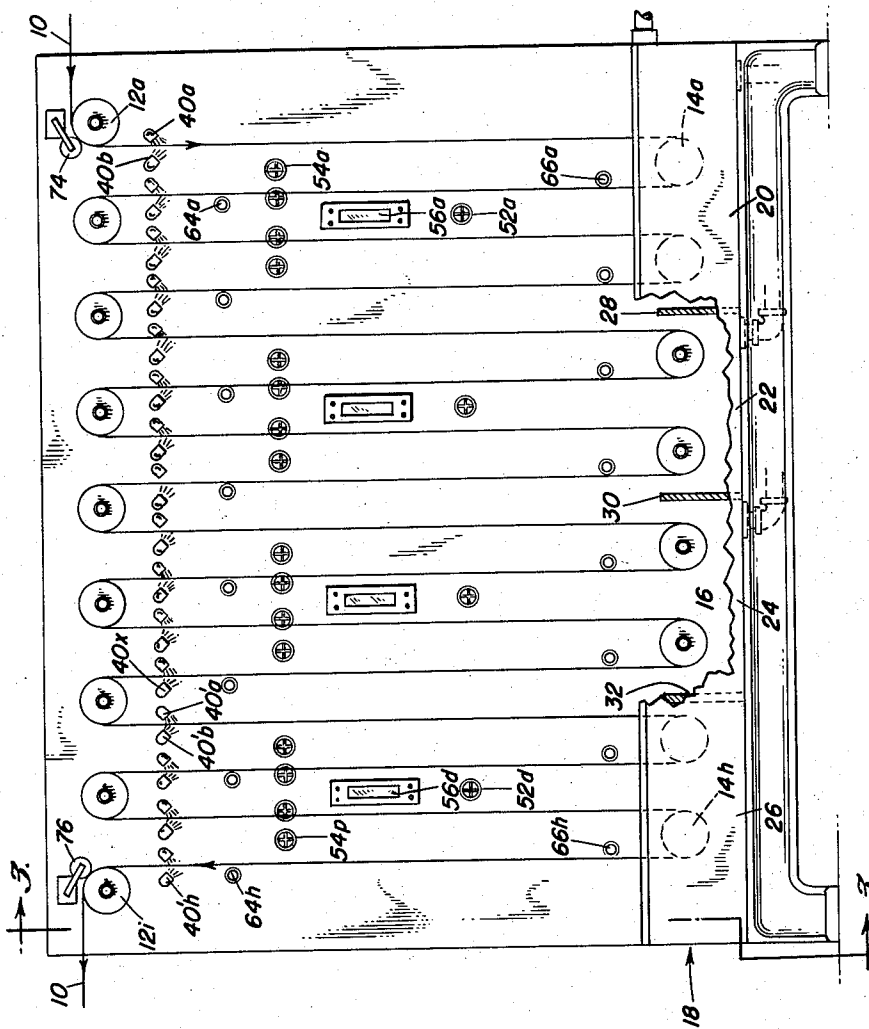
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3 Sheets-Sheet 2



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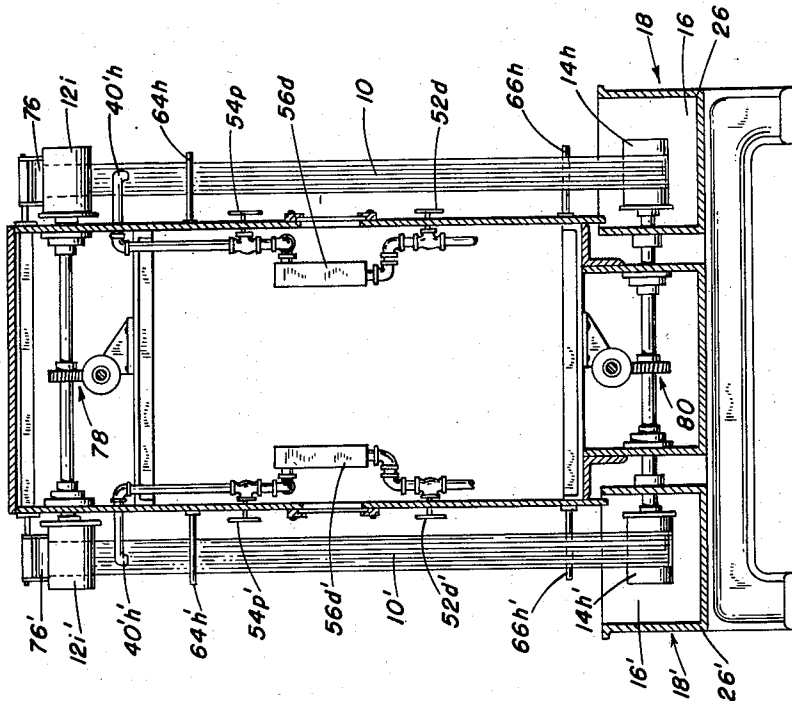


Fig. 3.

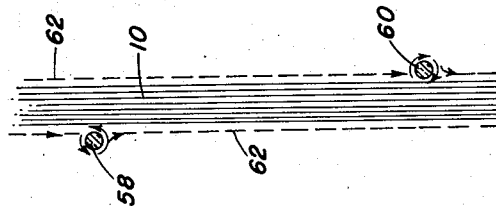


Fig. 4.

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1

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METHOD FOR THE LIQUID TREATMENT OF CONTINUOUS FILAMENTARY MATERIAL

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9 Claims. (Cl. 8—151.2)

This invention relates to certain new and useful improvements in a method for the liquid treatment of continuous "filamentary material" (including ribbons and slivers of continuous length as well as parallel bands of continuous filaments). More particularly, it is concerned with a method that is especially adapted for use in continuously treating (especially washing) continuous filamentary material in gelled state, e.g., a gelled tow (bundle of continuous filaments) comprised of a synthetic polymer, specifically a polymer of acrylonitrile. The filamentary material may be either a monofilament or a multifilament, and it may be of either natural or synthetic origin.

In certain processes of manufacturing synthetic articles in flexible, elongated (continuous) form, e.g., threads, tows, etc., of indefinite lengths, it is frequently desirable to wash or otherwise treat the freshly spun or formed material. One type of apparatus that has been used for this purpose involves a plurality of spaced, generally superimposed, thread-advancing reels upon each of which the thread progresses bodily along the length of the reel, in a generally helical path, from the point where it is wound thereupon to a discharge point, where it is unwound from the reel and led to the next reel. An arrangement of this kind and the use of the apparatus in the production of viscose rayon are described in, for example, U.S. Patent No. 2,225,640. Another type of thread-advancing device that has been employed for the wet treatment or washing of continuous lengths of synthetic yarn or thread comprises a pair of spaced, converging rolls about which the yarn is wound and over which it advances in a helical path from the feed-on end to the take-off end. During the passage of the advancing helices of thread over the converging rolls, or plurality of converging rolls, the thread is treated with a liquid, for example, by means of a jet through which the liquid is sprayed upon the roll and upon the thread advancing thereupon. Such apparatus and processes of treating a thread are described in, for example, Hartmann et al. U.S. Patent No. 2,194,470 and Gram U.S. Patent No. 2,294,902.

In treating gelled, synthetic filamentary material with liquid chemicals or chemical solutions, or with water or other solvent in order to remove extractables therefrom, considerable difficulties are often encountered in securing rapid and effective penetration of the treating liquid into the gelled material. In the known continuous, countercurrent extraction or washing methods, the coagulated or gelled filaments are passed through one or more baths containing a solvent that is miscible with the solvent employed in the spinning solution or in the coagulating bath in order to free the coagulated article from residual spinning solvent and/or coagulant. An increase in the efficiency of such extractions or washings is highly desirable in order to reduce the quantity of wash liquid required, the power required for pumping such liquid and the size of the extraction tanks. Where it is possible to recover the spinning solvent or coagulating liquid, an improved extraction process is additionally desirable in order to reduce the cost of the concentration or recovery of such materials from the wash liquid and to minimize the quantity of solvent or coagulant required for make-up.

2

One solution to the problem briefly described in the preceding paragraph is disclosed and claimed in the copending application of Thomas H. Robertson and Percival W. Cummings, Jr., Serial No. 397,161, filed December 9, 1953, now Patent No. 2,790,698, dated April 30, 1957. The invention therein disclosed and claimed is particularly applicable, as is the present invention, to the treatment of a gelled tow of a polyacrylonitrile (homopolymeric acrylonitrile or a copolymer of acrylonitrile) with water or other aqueous or other solvents to remove extractables therefrom.

The present invention is a different solution to the same problem described above and with considerable apparatus and method advantages thereover. Briefly described, the apparatus features of the present invention comprise, in combination, a series of spaced, cantilevered, rotatable, upper and lower rolls over which the continuous filamentary material is adapted to pass continuously in a serpentine or undulating path. Suitable means are provided for driving the upper and lower rolls at a desired speed. A compartmented trough also is provided, this trough being adapted to receive a treating liquid, e.g., water, and also the aforesaid lower rolls, and to permit the positioning of the latter at a point therein where they will be at least partly and preferably completely submerged in the treating liquid. Spray means are positioned adjacent the path of upward and downward travel of the continuous filamentary material. Means also are provided for continuously withdrawing liquid from compartments of the aforesaid trough and for conducting the said liquid to the spray means positioned above the individual compartment.

In a preferred embodiment of the apparatus of the present invention, the compartmented trough is constructed so as to permit, when in use, the flow of treating liquid therethrough countercurrent to the movement of the continuous filamentary material that is being treated. Squeeze rolls also advantageously are provided; for instance, the incoming filamentary material may be passed between one set and/or the outgoing filamentary material passed between another set when the apparatus is in use. Either or both sets of such squeeze rolls may be omitted as desired or as may be required, depending upon the preceding and subsequent treatments, if any, and other influencing factors; or, if desired or required, additional squeeze rolls may be included in the apparatus. The apparatus of the present invention also may include liquid wipers positioned to contact, during operation of the apparatus, the liquid film on the upwardly traveling sections of the continuous filamentary material.

The present invention also provides a new and improved method of continuously treating continuous filamentary material, e.g., a gelled tow (bundle of continuous filaments) formed of a polymer of acrylonitrile, with a liquid, e.g., water. Briefly described, the method comprises causing such a filamentary material to travel continuously in an upward and downward serpentine or undulating path and to enter a compartmented, liquid-treating bath at the base of its path of travel. The other essential steps of the method also include continuously directing a treating liquid against the sides of the upwardly and downwardly moving sections of the continuous filamentary material at supply points near the apexes of the said sections; continuously withdrawing liquid from compartments of the said treating bath; and continuously conducting the liquid that has been withdrawn from individual compartments to the corresponding supply points positioned above the individual compartment.

In a preferred embodiment of the method of the invention, the liquid in the compartmented liquid-treating bath flows countercurrent to the path of travel of the

continuous filamentary material. Also, in the preferred method of the invention, positive localized recirculation of the liquid film adhering to the upwardly traveling sections of the continuous filamentary material is effected. As has been indicated hereinbefore, the preferred continuous filamentary material is a tow of a polyacrylonitrile filamentary material, especially a gelled tow of such a material, and the treating liquid is an aqueous treating liquid, e.g., water alone.

It is a primary object of the present invention to provide improved apparatus and an improved method for continuously treating continuous filamentary material with a liquid.

Another object of the invention is to provide apparatus and a method for liquid treatment of continuous filamentary material that will result in less entanglement of the filaments, less crossovers between individual filaments and which also will reduce building space requirements for equipment by reducing the length of the process line.

A further object of the invention is to provide apparatus having cost advantages over apparatus heretofore commonly employed to effect a similar result.

Other advantages of the invention will be apparent to those skilled in the art from the following more detailed description and the accompanying drawing illustrating the invention.

The novel features that are characteristic of my invention are set forth in the appended claims. The invention itself, however, will best be understood as the description of the invention proceeds with reference to the accompanying drawing in which:

Fig. 1 is a somewhat schematic view of apparatus embodying the invention and of method features thereof;

Fig. 2 is a front elevation of apparatus embodying the invention;

Fig. 3 is an end elevation in section taken along the line 3—3 of Fig. 2; and

Fig. 4 is an enlarged, somewhat schematic view of a portion of continuous filamentary material having a film of liquid thereon and of liquid wipers adjacent thereto, and illustrative of a specific aspect of the invention.

The apparatus of the present invention may be used, for example, in continuously washing continuous filamentary material to remove extractables therefrom; and/or to treat such filamentary material with liquid solutions of one or more chemicals or other additives; and/or to apply a finish to continuous filamentary material.

The invention is preferably practiced in washing wet-spun, gelled filamentary material, more particularly such material that has been made either from homopolymeric acrylonitrile or form acrylonitrile copolymers containing a major proportion by weight of combined acrylonitrile, and especially those copolymers which contain in the molecules thereof an average of at least about 80% by weight of combined acrylonitrile. These acrylonitrile polymerization products are prepared by methods well known to those skilled in the art. I prefer to liquid-treat continuous filamentary material comprised of polymeric or copolymeric acrylonitrile having an average molecular weight within the range of about 15,000 to about 300,000, more particularly about 40,000 or 50,000 to about 150,000 or 200,000, and still more particularly those having an average molecular weight within the range of about 60,000 to 90,000, as calculated from viscosity measurements, using the Staudinger equation (reference: U.S. Patent 2,404,713).

Illustrative examples of monomers that can be copolymerized with acrylonitrile to yield a copolymer containing a major proportion by weight of combined acrylonitrile are compounds containing a single $\text{CH}_2=\text{C}<$ grouping, for instance the vinyl esters (e.g., vinyl acetate, etc.), the acrylic esters (e.g., methyl acrylate, etc.), acrylamide, a vinylpyridine (e.g., 2-methyl-5-vinylpyridine), methacrylonitrile and others of the kind mentioned in Cresswell U.S. Patent No. 2,558,730, dated July 3, 1951, and

in Cresswell et al. copending application Serial No. 214,616, filed March 8, 1951, now Patent No. 2,777,751, dated January 15, 1957.

The preferred, wet-spun thread or tow which is treated, specifically washed, in accordance with the present invention is one which has been prepared in the manner described in the aforesaid Cresswell et al. copending application and which involves extruding an aqueous solution of an acrylonitrile polymerization product containing a major proportion by weight of combined acrylonitrile through a shaped orifice into a liquid coagulating bath comprising an aqueous solution containing from about 3% to about 25%, by weight, of a water-soluble thiocyanate which yields highly hydrated ions in an aqueous solution, said coagulating bath being at a temperature not exceeding $+10^\circ \text{C}$. and said acrylonitrile polymerization product being dissolved in a concentrated aqueous solution of the same water-soluble thiocyanate which is a component of the said liquid coagulating bath.

With reference to the accompanying drawing and especially to Fig. 1 thereof, a tow of continuous filamentary material 10, and which, for purpose of ease of description, may be assumed to be a tow of continuous gelled polyacrylonitrile filaments, is led over a series of upper rolls 12a, 12b, 12c, 12d, 12e, 12f, 12g, 12h and 12i, inclusive, and lower rolls 14a, 14b, 14c, 14d, 14e, 14f, 14g and 14h. The lower rolls are at least partly immersed, and as shown in the drawing, are completely submerged in a liquid 16, specifically an aqueous liquid, contained in a compartmented trough 18. This trough is divided into sections 20, 22, 24 and 26 by means of baffles or adjustable wiers 28, 30 and 32. In the preferred embodiment of the invention, the compartmented trough is so constructed or positioned that the liquid therein flows counter to the path of travel of the tow 10; also, the lower rolls are preferably submerged in the trough 18 so that the top of each roll is a short distance, e.g., from 1 to 3 inches, below the surface of the liquid. In operation, the rapid raising of the tow from the liquid acts as a "rope pump," causing a column of liquid to rise with the rising tow. The rising and falling of this column causes a localized recirculation at each point where the tow emerges from the surface of the liquid, thereby aiding in more rapid and complete penetration of the liquid into the gelled tow and providing increased efficiency in washing or other liquid treatments.

Sections or compartments 20, 22 and 24 are each connected through conduits to recirculation pumps 34, 36 and 38 and by means of which liquid is drawn from the individual compartment and delivered to the sprays 40a to 40x, and 40'a to 40'h, inclusive. The sprays 40'a—40'h are supplied with treating fluid, e.g., water alone, from the vessel 42 through the indicated conduits. The treating fluid enters the vessel 42 through the conduit 44 from a supply source (not shown).

In some cases it is desirable that the treating fluid (e.g., water for washing certain flexible, filamentary or other elongated materials) be at a reduced temperature, e.g., $35^\circ\text{--}55^\circ \text{F}$., or any other temperature below normal for the particular liquid treating fluid. In this event, the vessel 42 is provided with cooling coils 46. The inlet line 48 to the cooling coils carries a suitable refrigerant and is provided with a valve 50 which is actuated when the temperature of the water or other treating fluid in the vessel 42 is above a desired point. The outlet line 51 carries the refrigerant from the discharge end of the cooling coils.

The vessel 42 serves to provide a constant head pressure on sprays 40'a to 40'h, inclusive; and, as has been indicated hereinbefore, also serves as a heat-exchanger for refrigeration when the treating liquid is to be introduced to the system at a desired low temperature. It also can serve as a mixing chamber when the liquid supplied to the sprays 40'a—40'h is one which contains a chemical or other additive that is to be applied to the filamentary material (in tow or other form) that is undergoing treat-

ment; and, also, when effluent from the sump tank 53 is to be admixed with fresh treating liquid being fed to the system.

Valves 52a, 52b, 52c and 52d, and valves 54a to 54p, inclusive, provide effective means for regulating the amount of wash liquid that is carried to the aforementioned sprays. Flow meters 56a, 56b, 56c and 56d also are provided for measuring the total flow of liquid to each set of sprays connected to the individual flow meter.

In Fig. 4 there are shown liquid wipers 58 and 60 and the manner in which the film of liquid indicated by 62 passes over these wipers. Such wipers provide additional localized washing or recirculation of the liquid and preferably are so positioned that they touch the film encasement of the rising tow but do not physically contact the tow itself. Similar wipers are also indicated at 64a to 64h, inclusive, and at 66a to 66h, inclusive.

The liquid 16 in the compartmented trough 18 flows through this trough as indicated and leaves the trough through the trough outlet 68, being thence conducted to the sump tank 53 through the conduit 72. From the sump tank 53 the effluent may be returned to the vessel 42, mixed with fresh wash water (or other fresh make-up liquid as may be required in the particular case), and subsequently applied to the rising tow or bundle of filamentary material through the sprays 40'a to 40'h, inclusive; or it may be led to a recovery system if its composition and concentration are such that it would be economical to do so; or it may be discharged to waste.

The elements of the double-sided unit shown in Figs. 2 and 3 (of which the front of one unit only is shown in Fig. 2) are essentially the same as those described in Fig. 1, and the same or similar designations have been used thereon wherever possible; for instance, the elements of the back side (i.e., the side opposite that shown in Fig. 2) bear the same general designations as the corresponding elements of the front side plus a prime (') mark. Fig. 2 also shows the pinch roll 74 resting on the feed-on roll 12a, thereby forming squeeze rolls between which the incoming tow passes; and the pinch roll 76 resting on the squeeze roll 12i, thereby forming squeeze rolls between which the outgoing tow passes.

Fig. 3 shows an end elevation in section taken along the line 3-3 of Fig. 2. This view shows more clearly the drive means 78 and 80 by which the upper and lower rolls, respectively, of the series are driven. The degree of tension on the continuously moving filamentary material, e.g., a tow of continuous filaments of a hydrogel (or hydrogel-alcogel) of a polymer of acrylonitrile, may be adjusted by changing the number of teeth in the sprockets which drive the rolls.

In washing some filamentary materials, for example, a gelled tow of polyacrylonitrile filaments that have been given a partial stretch to orient the molecules along the fiber axis, optimum washing efficiency results and apparatus design advantages accrue when the peripheral speeds of the rolls are such that the tow is under little or no tension as it passes over the rolls.

The apparatus may be one-sided, but preferably it is double-sided as shown in Fig. 3 so that the rolls can be driven from a common drive shaft, thereby assuring high capacity and ease of thread-up. The constructional and operating advantages of a double-sided unit will be apparent to those skilled in the art.

Various modifications of the invention will be apparent to those skilled in the art from the foregoing description and the accompanying drawing.

I claim:

1. In the processing of unfabricated, continuous, filamentary material, the method of continuously treating, with a liquid filamentary material wherein all of the filaments thereof are parallel and are of continuous length, said method comprises causing said filamentary material to travel continuously in an upward and downward serpentine path and to enter a compartmented, liquid-treating

bath at the base of its path of travel; continuously directing a treating liquid against each side of each of the upwardly and downwardly moving sections of the continuous filamentary material at supply points near the apexes of the said sections; continuously withdrawing liquid from compartments of the said treating bath; and continuously conducting the liquid that has been withdrawn from individual compartments to the corresponding supply points positioned above the individual compartment.

2. In the processing of unfabricated, continuous, filamentary material, a method as in claim 1 wherein the liquid in the compartmented liquid-treating bath flows countercurrent to the path of travel of the continuous filamentary material.

3. In the processing of unfabricated, continuous, filamentary material, a method as in claim 1 which additionally includes effecting positive localized recirculation of the liquid film adhering to the upwardly traveling sections of the continuous filamentary material.

4. In the processing of unfabricated, continuous, filamentary material, a method as in claim 1 wherein the continuous filamentary material is a tow of a polyacrylonitrile filamentary material and the treating liquid is an aqueous treating liquid.

5. In the processing of unfabricated, continuous, filamentary material, the method of continuously washing a gelled tow of filamentary material with an aqueous liquid which comprises causing said tow to travel continuously in an upward and downward serpentine path and to enter a compartmented, aqueous-treating bath at the base of its path of travel; continuously directing an aqueous wash liquid against each side of each of the upwardly and downwardly moving sections of the said tow at supply points near the apexes of the said sections; effecting positive localized recirculation of the liquid film adhering to the upwardly traveling sections of the said tow; continuously withdrawing aqueous liquid from compartments of the said aqueous treating bath, the aqueous liquid in the said bath flowing countercurrent to the path of travel of the said tow; and continuously conducting the aqueous liquid that has been withdrawn from individual compartments of the said bath to the corresponding supply points positioned above the individual compartment.

6. In the processing of unfabricated, continuous, filamentary material, a method as in claim 5 wherein the gelled tow is squeezed to remove excess liquid therefrom immediately prior to causing it to travel continuously in an upward and downward serpentine path.

7. In the processing of unfabricated, continuous, filamentary material, a method as in claim 5 which includes the additional step of squeezing excess wash liquid from the washed tow after it has completed its travel in an upward and downward serpentine path.

8. In the processing of unfabricated, continuous, filamentary material, a method as in claim 5 wherein the gelled tow is squeezed to remove excess liquid therefrom immediately prior to causing it to travel continuously in an upward and downward serpentine path, and the excess aqueous wash liquid is squeezed from the washed tow after it has completed its travel in an upward and downward serpentine path.

9. In the processing of unfabricated, continuous, filamentary material, a method as in claim 5 wherein the gelled tow is a gelled tow of a polyacrylonitrile filamentary material.

References Cited in the file of this patent

UNITED STATES PATENTS

1,037,280	Matter	Sept. 3, 1912
1,497,075	Elliott	June 10, 1924
1,866,153	Dreyfus	July 5, 1932
2,485,957	Cresswell	Oct. 25, 1949
2,558,735	Cresswell	July 3, 1951
2,714,052	Wizon	July 26, 1955
2,729,537	Lasley	Jan. 3, 1956

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,886,403

May 12, 1959

William N. Sellers

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 67, for "correspsond-" read -- correspond-; column 3, line 51, for "form" read -- from --; column 4, line 12, for "aqueons" read -- aqueous --; line 39, for "raising" read -- rising --; column 5, line 71, after "liquid" insert a comma; line 73, for "comprises" read -- comprising --.

Signed and sealed this 1st day of September 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents