

Patented Feb. 17, 1942

2,273,071

UNITED STATES PATENT OFFICE

2,273,071

HOSIERY AND METHOD FOR PRODUCING THE SAME

Edward W. Rugeley and Theophilus A. Feild, Jr.,
Charleston, W. Va., assignors to Carbide and
Carbon Chemicals Corporation, a corporation
of New York

No Drawing. Application October 27, 1939,
Serial No. 301,616

17 Claims. (Cl. 66—178)

This invention relates to knitted fabrics made from synthetic textile fibers, and it is especially directed to the formation of seamless and full-fashioned hosiery from textile fibers made from certain vinyl resins.

In the manufacture of hosiery, it is customary to employ a knitted fabric inasmuch as it is more elastic than woven materials. However, in order to obtain a knitted fabric having satisfactory wearing qualities, such as strength and elasticity, a highly resilient fiber must be employed. In addition, the fibers must be capable of being set in a predetermined shape by some process such as boarding, and when so set the bent threads must retain their shape under all conditions of wear. At the present time, real silk is the only commercially available textile fiber which fulfills these requirements and which can be fashioned into "form-fitting" hosiery which is truly satisfactory. Stockings prepared with commercially available artificial yarns, such as the cellulose derivatives, have a tendency to wrinkle at the knee and ankle and have a tendency to slip over the skin in adjusting to movements of the leg, instead of following the skin as does a real silk stocking.

Even when silk was used, it has been necessary to knit the stocking in the shape of the leg to have an article which will be completely free from tendencies to wrinkle or bag at the places surrounding the wearer's joints. Therefore the most desirable hosiery has been made in a flat piece, with each section of the stocking fashioned to fit the corresponding part of the wearer's leg, the flat piece then being sewn together along one edge. This type of hosiery is known as "full-fashioned" because of the fidelity with which it conforms to and clings to the wearer's leg, and such hosiery is characterized by a seam running from the toe, along the bottom of the foot, and up the back of the leg portion. Seamless-fashioned hosiery is much less costly to produce than is full-fashioned hosiery inasmuch as it is knitted entirely in one piece on circular knitting machines, and it acquires its shape by change of stitch, assisted by boarding. However, seamless hosiery, sufficiently good to compete with the full-fashioned hosiery in fitting qualities and in retention of shape, has never been made from the commercially known textile fibers. In fact, the difference is so marked that on seamless hose there is usually formed a dummy "seam" stitched in the rear of the stocking so that it may, in respect of outward appearance, resemble full-fashioned hosiery.

This invention provides knitted articles, particularly hosiery, which have properties of elasticity, resiliency, tensile strength, resistance to wear and retention of shape equivalent to, or more than, those prepared from natural silk, and

in many respects these knitted fabrics are superior to silk hosiery. A characteristic peculiar to the fabrics of this invention is their ability to be preformed into any desired shape by a process of controlled shrinkage, and the yarn, once set in this manner, will retain its dimensions with great accuracy, although remaining highly elastic and retaining its high tensile strength during the life of the fabric and in spite of hard wear and repeated launderings. This peculiar property, which is not present to any appreciable degree in any artificial or natural textile fibers heretofore known, enables seamless stockings to be made and then permanently formed into the desired shape, thus producing permanently fashioned hosiery from a seamless stocking.

The new fibers from which the articles of this invention are knitted, are formed from vinyl resins such as may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, and which have an average macromolecular weight of at least about 15,000. (Molecular weights referred to herein are those calculated by means of Staudinger's formula from viscosity determinations of solutions of the resins.)

Briefly, the fibers are formed by spinning a solution or dispersion of the vinyl resin into filaments. These filaments may be formed into fibers of the desired size by twisting and doubling operations as desired, and thereafter the fibers are stretched to yield products suitable for use in the present invention. This stretching operation is a vital feature in the production of useful textile fibers from the vinyl resins, and it serves the dual purpose of greatly increasing the tensile strength, and of conferring on the fibers the unusual property of high true elasticity. By means of the stretching operation, the two highly important properties of tenacity and elongation may be varied and controlled almost at will.

As has been indicated, the vinyl resins from which the new fibers are prepared must have special characteristics. The class of resins useful in this invention are those such as are described in Patent 1,935,577 to E. W. Reid, and these resins may be made by the processes described in that patent or by other means, such as the process described in Patent 2,064,565 to E. W. Reid. Of these conjoint polymers of vinyl halides with vinyl esters of aliphatic acids, the preferred resins are those which contain from about 70% to about 95% by weight of the halide in the polymer. Within this range, those resins formed from vinyl chloride and vinyl acetate which contain in the polymer about 80% to about 95% by weight of vinyl chloride are especially desirable.

The resins must have an average macromolecular weight of at least 15,000, and the upper

value is limited only by the solubility of the resins in suitable liquids to yield spinnable solutions or dispersions. Vinyl resins, as ordinarily prepared, consist of a mixture of polymeric aggregates of different molecular sizes. These resins may be freed from polymers having excessively low molecular weights by various extraction procedures, such as those described in Patent 1,990,685 to C. O. Young and S. D. Douglas, or by similar methods of partial dissolution or precipitation, or both. The resin after such treatment must be completely dispersible in warm dry acetone, or in other liquids from which the filaments may be formed in the spinning operation. By "dry" acetone is meant that substance which contains less than about 0.60% by weight of water. It has been found that, when the acetone used contains water in excess of this amount, the quality of the resin dispersion is materially impaired, and solutions made from such solvents can be filtered and spun only with great difficulty. The concentration of the vinyl resin in the spinning solution is dependent upon and varies inversely with the macromolecular weight of the resin, but the resin content ordinarily employed, using acetone as the solvent, is 30% or less by weight.

The spinning, or filament extrusion, operation may be carried out in equipment customarily employed for so-called "dry-spinning" of other types of filaments. A bobbin-type thread take-up may be employed, or the filaments may be given a twist at the point of spinning by employing a "cap-type" mechanism.

The next step in the yarn processing is that of stretching, and this step is one of paramount importance in the production of the new fibers. The amount of stretch imparted to the yarn may vary considerably up to about 600%. The extent of stretch used is determined by the polymer size (average macromolecular weight) of the resin, and by the characteristics desired in the finished yarn. The actual stretching of the yarn can be accomplished by any means which will effect the necessary extension, and it can be conveniently carried out by transferring the yarn from the spool on which it is contained to a second spool positively driven at a higher peripheral speed. Where the yarn is stretched in excess of about 200%, particularly where it is stretched in a single stage, it is necessary to conduct the stretching at an elevated temperature. In general, this may be conveniently done by stretching the yarn in an atmosphere of steam because the steam not only maintains the yarn at the desired temperature, but it also keeps the yarn sufficiently surface-wetted to prevent breakage. Where the yarn has been stretched at a temperature of less than about 100° C., it is necessary to subject it to a "setting" treatment because for a period after the yarn has been stretched it shows a marked tendency to contract. The setting of the stretch in the yarn may be accomplished in several ways; for example, by prolonged aging of the extended yarn under tension, or by subjecting the tension-stretched yarn to elevated temperatures which greatly accelerate the rate of setting. However, where the yarn is stretched at a temperature in excess of about 100° C., as is desirable where it is to be stretched as much as 600%, the tendency of the yarn to contract at moderate temperatures after the stretching treatment is so slight that the setting treatment may be eliminated. The process of producing

yarn from the conjoint polymerization product of a vinyl halide with a vinyl ester of an aliphatic acid which is suitable for use in this invention is disclosed in United States Patent No. 2,161,766, issued June 6, 1939, to E. W. Rugeley, T. A. Feild, Jr., and J. F. Conlon.

In the production of seamless-fashioned, or circular-knitted, hose, as well as full-fashioned hosiery, from the previously described vinyl resin textile fibers, the stretching of the fibers is essential not only because it imparts high tensile strength and elasticity to the fibers, but because a portion of the stretch imparted to the yarn is utilized in making the finished stocking conform to the desired shape by a process of controlled shrinkage. If the untensioned, stretched yarn is heated to a temperature in excess of that at which it is "set," or if no setting operation was employed, to an elevated temperature (for example, above about 65° C.), the yarn will shrink due to a release of the internal strains developed in the stretching operation. Therefore, if the stocking is placed over a form or mold and heated to the required temperature, the stocking will shrink so that it fits the form with exactness. Upon cooling the stocking and removing it from the form, it will retain this shape, along with the natural resiliency and elasticity of the fibers regardless of wear or laundering, provided the stocking is at no time subjected to a temperature in excess of that to which it was heated in the shrinking operation. Although this is the preferred technique, the desired shrinkage may be accomplished by other means than heat. For example, the stocking may be subjected to limited or controlled action of a solvent for the resin. Acetone, which is a solvent for these resins, may be employed by diluting it sufficiently with a non-solvent, such as water, so that the internal strains in the fibers may be released to the desired extent without causing disintegration or coalescence of the fibers, such as would occur if pure acetone were used. When the stocking is shrunk by means of solvents or softening agents, the stocking will retain its shape unless heated to a temperature near the softening point of the resin. Where this method is employed to produce fashioned hosiery, it is desirable to knit the stocking with a slightly looser stitch at those parts which will shrink the most, such as the ankle, so that in the finished article, the stitch size will be approximately uniform.

It is possible to produce stockings in accordance with this invention which contain other fibers in admixture with the vinyl resin fibers described. For example, the vinyl resin fibers may be mixed with other continuous artificial or natural textile filaments, such as silk and the various cellulose derivatives and regenerated silk and cellulose. However, the most desirable hosiery is made entirely of the vinyl resin fibers since they possess a very high strength by comparison with other textile fibers. Also, because their strength is virtually the same whether they are wet or dry, they may be knitted in either wet or dry condition. These fibers are resistant to impairment by water, have true elasticity, resistance to chemical, bacterial and fungal attack, they are thermoplastic and will not support combustion. Furthermore, the stockings of this invention are essentially crease-proof under ordinary conditions, but retain creases introduced by heat, such as by steam. In other words, they hold their boarded form, and this invention

therefore represents the first truly successful seamless-fashioning stocking.

Although the vinyl resin fibers described are peculiarly suited to the knitting of seamless-fashioning hosiery, they are also well suited to the manufacture of full-fashioning hosiery, and the various operations incident to the preparation of full-fashioning hosiery from these fibers are illustrated by the following typical examples.

EXAMPLE 1

The yarn

A vinyl resin prepared by the conjoint polymerization of vinyl chloride with vinyl acetate, containing about 90% by weight of vinyl chloride in the polymer and having an average macromolecular weight of about 21,000, is spun into filaments. The filaments are stretched 453% in an atmosphere of steam and gathered into yarns of 18 and 36 denier, with 20 and 40 filaments respectively. An emulsifiable mineral oil is used as a lubricant in packaging the yarn for subsequent operations.

EXAMPLE 2

Throwing

Single ends of the 18 denier yarn from Example 1 are given a left twist of 35 turns per inch, and then two ends of the twisted yarn are plied with a right twist of 50 turns per inch, to produce the yarn employed in knitting the leg of the hose. The welt yarn is prepared by giving a left twist of 15 turns per inch to single ends of the 36 denier yarn and plying two ends of this twisted yarn with a right twist of 20 turns per inch.

With the compensated twist described, the yarns serve excellently as a knitting supply which is not subject to thread kinking, and in which it is not necessary to set or condition the twist.

Instead of knitting the hose from a yarn having a compensated twist, it has been found practical to use a yarn twisted in one direction and the twist set by subjecting the yarn, under tension, to an elevated temperature. The yarn is preferably exposed to a relatively high temperature for a very limited period of time, such as transferring the yarn from one positively driven spool to another through an intermediate steam chamber, although the twist may be set satisfactorily by subjecting the spooled yarn to a temperature of about 65° C. for a comparatively prolonged period. In the case of a single direction twist, the maximum practical twist from the standpoint of the twist setting is about 30 turns per inch.

EXAMPLE 3

Knitting

The thrown yarns can be readily knitted on all types of full-fashioning hosiery machines, and the yarn can be knitted with equal ease in either wet or dry condition. A typical hose construction is as follows:

Welt:

2 ply 35 denier yarn, 15-15/20 twist, 38 courses per inch.

Leg:

2 ply 18 denier yarn, 35-35/50 twist, 48 courses per inch.

Splicing:

2 ply 35 denier yarn, 15-15/20 twist.

On a 48 gauge machine, an overall length of 32 inches is generally used and the hose foot size is ordinarily knitted one-half size larger than

that desired in the finished hose, to compensate for shrinkage in subsequent operations.

The hose is looped with a 200 denier thread and seamed with a 120 denier thread using 18 stitches per inch.

EXAMPLE 4

Scouring, dyeing and forming

In all of these operations, except forming, it is necessary to take precaution that a maximum temperature of 65° C. is not exceeded lest the untensioned fabric shrink excessively.

The ease of scouring is obviously determined by the type of knitting lubricant employed. It has ordinarily been found sufficient to use a scour of soap and soda ash for removal of both lubricants and contamination. In extreme cases of contamination, an emulsified petroleum naphtha bath may be advantageously used.

The dyeing of the hose is accomplished in a standard dyeing machine generally employing the procedure described in copending application Serial No. 290,198, filed August 15, 1939.

In the manufacture of hosiery, it is standard practice to subject the finished stocking to a forming or pressing treatment before packaging, in order to eliminate any distortion which may have occurred in the prior operations and to improve the appearance of the stocking. Heretofore, it has been necessary to subject the hosiery to a preforming treatment prior to the dyeing and finishing treatments because of the fact that the forming operation often has had an undesirable effect on the finish of the hosiery, if it is performed in a single operation. This has necessitated subjecting the stocking to two forming or boarding operations. Although a similar procedure may be followed in the preparation of the hosiery described in this invention, the properties of the vinyl resin fibers are such that the entire forming operation may be satisfactorily accomplished after the scouring, dyeing and finishing treatments, inasmuch as the forming operation has no deleterious effect on the color or finish of the hosiery. The forming, or boarding, of the hose is accomplished by drying on standard forms at a temperature between about 60° and 70° C. The preferred method is to employ a form slightly narrower than the standard for silk hosiery, since hosiery made from the vinyl resin fibers described contracts less on being removed from the form.

Many special uses and adaptations of the materials of this invention will be apparent to those skilled in the art. The procedures by which the new materials are made can be varied in many of their details, and such modifications are included within the invention as defined by the appended claims.

We claim:

1. A knitted stocking containing textile fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, and having an average macromolecular weight of at least about 15,000.

2. A stocking knitted from yarn containing textile fibers in admixture with fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least about 15,000.

3. A stocking knitted from yarn containing textile fibers in admixture with fibers made from vinyl resins resulting from the conjoint polymerization of vinyl chloride with vinyl acetate, containing from about 80% to about 95% by weight of the chloride in the polymer and having an average macromolecular weight of at least about 15,000.

4. A full-fashioned stocking knitted from yarn containing stretched textile fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of vinyl halide in the polymer and having an average macromolecular weight of at least about 15,000.

5. A circular knitted seamless stocking knitted from yarn containing stretched textile fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of vinyl halide in the polymer and having an average macromolecular weight of at least about 15,000.

6. A seamless-fashioned stocking knitted from yarn containing stretched textile fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least about 15,000; said stocking having been shrunk into the desired shape, and characterized by its resistance to creasing, elasticity, and retention of shape during wear and repeated laundering.

7. A full-fashioned stocking knitted from yarn containing textile fibers mixed with fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least about 15,000, said textile fibers having been stretched up to about 600%.

8. A circular knitted seamless stocking knitted from yarn containing textile fibers mixed with fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least about 15,000, said textile fibers having been stretched up to about 600%.

9. A seamless-fashioned stocking knitted from yarn containing stretched textile fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing from about 70% to about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least about 15,000; said fibers having been stretched up to about 600%; said stocking having been shrunk into the desired shape, and characterized by its resistance to creasing, elasticity, and retention of shape during wear and repeated laundering.

10. A seamless-fashioned stocking knitted

from yarn containing textile fibers made from vinyl resins resulting from the conjoint polymerization of vinyl chloride with vinyl acetate, containing between about 80% and 95% by weight of vinyl chloride in the polymer and having an average macromolecular weight of at least about 15,000; said fibers having been stretched up to about 600%; said stocking having been shrunk into the desired shape, and characterized by its resistance to creasing, elasticity, and retention of shape during wear and repeated laundering.

11. A full-fashioned stocking knitted from yarn containing textile fibers made from a vinyl resin resulting from the conjoint polymerization of vinyl chloride with vinyl acetate, containing between about 80% to about 95% by weight of vinyl chloride in the polymer and having an average macromolecular weight of at least 15,000; said fibers having been stretched up to about 600%; said stocking having been formed into the desired shape, and characterized by its resistance to creasing, elasticity and retention of shape during wear and repeated laundering.

12. Process for making stockings which comprises knitting them from yarn containing fibers of resins substantially identical with those which result from the conjoint polymerization of vinyl halides and vinyl esters of aliphatic acids, and having an average macromolecular weight of at least about 15,000, and shrinking the stocking to a desired shape.

13. Process for making seamless-fashioned hosiery which comprises knitting yarn containing stretched fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing between about 70% and about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least 15,000; placing the knitted stocking on a form and causing it to shrink until the stocking has assumed the shape of the form.

14. Process for making stockings which comprises knitting yarn containing stretched fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing between about 70% and about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least 15,000; scouring, dyeing, and finishing the knitted stocking, and thereafter placing the knitted stocking on a form and causing it to shrink until the stocking has assumed the shape of the form.

15. Process for making stockings which comprises knitting yarn containing stretched fibers made from vinyl resins substantially identical with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing between about 70% and about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least 15,000; scouring, dyeing, and finishing the knitted stocking, and placing the knitted stocking on a form and heating it until the stocking has assumed the shape of the form.

16. Process for making stockings which comprises knitting yarn containing stretched fibers made from vinyl resins substantially identical with those which may result from the conjoint

polymerization of vinyl halides with vinyl esters of aliphatic acids, containing between about 70% and about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least 15,000; scouring, dyeing, and finishing the knitted stocking, and placing the knitted stocking on a form and subjecting it to the controlled action of a solvent until the stocking has assumed the shape of the form.

17. Process for making stockings which comprises knitting yarn containing stretched fibers made from vinyl resins substantially identical

with those which may result from the conjoint polymerization of vinyl halides with vinyl esters of aliphatic acids, containing between about 70% and about 95% by weight of the halide in the polymer and having an average macromolecular weight of at least 15,000; scouring, dyeing, and finishing the knitted stocking, and placing the knitted stocking on a form and subjecting it to the action of steam until the stocking has assumed the shape of the form.

EDWARD W. RUGELEY.
THEOPHILUS A. FEILD, JR.