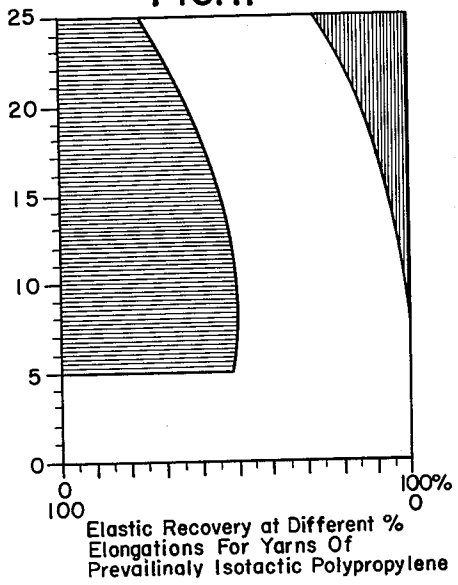
March 20, 1962 B. BEGHELLI 3,025,689

HOSIERY ARTICLES KNITTED FROM POLYPROPYLENE YARN

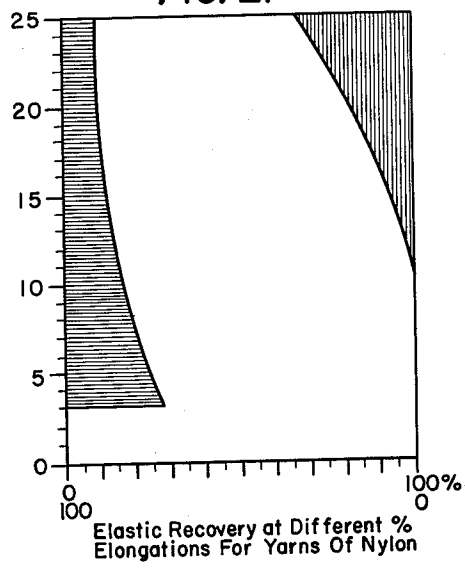
Filed Sept. 16, 1957

FIG. 1.



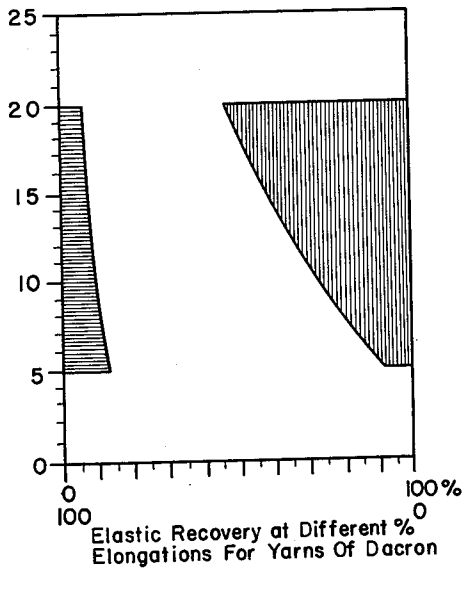
Elastic Recovery at Different % Elongations For Yarns Of Prevailinaly Isotactic Polypropylene

FIG. 2.



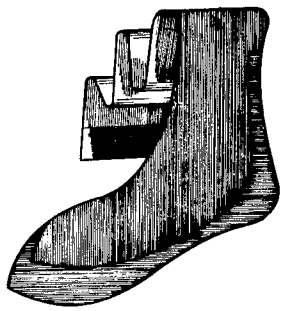
Elastic Recovery at Different % Elongations For Yarns Of Nylon

FIG. 3.



Elastic Recovery at Different % Elongations For Yarns Of Dacron

FIG. 4.



INVENTOR

BENITO BEGHELLI

BY Taulmin & Taulmin

ATTORNEYS

United States Patent Office 3,025,689 Patented Mar. 20, 1962

3,025,689

HOSIERY ARTICLES KNITTED FROM POLYPROPYLENE YARN

Benito Beghelli, Terni, Italy, assignor to Montecatini, Società Generale per l'Industria Mineraria e Chimica, Milan, Italy

Filed Sept. 16, 1957, Ser. No. 684,079
Claims priority, application Italy Sept. 27, 1956
3 Claims. (Cl. 66—202)

This invention relates to fabrics knitted from yarns formed of textile fibers at least the major proportion of which are fibers of polypropylene consisting prevailingly of isotactic macromolecules. More particularly, the invention is concerned with seamless and full-fashioned hosiery.

Knitted fabrics, being generally more elastic than woven fabrics, are preferred for hosiery. From the practical viewpoint of knitting the hosiery, the fibers and yarns used should have optimum properties of regularity, flexibility, smoothness, mechanical strength and elasticity. The mechanical strength and flexibility of the fibers and yarns are of special importance in the knitting operation because of the stresses and strains to which the fibers and yarns are subjected during their sinuous path through the needles of the knitting machines. Other important factors are the capacity of the fibers and yarns to withstand setting of the knitted fabric in a predetermined shape by some process such as boarding and to retain their pre-set shape under all conditions of wear.

The mechanical strength and elasticity of the hosiery is of paramount importance because only a strong stocking having good elastic recovery can be worn for any length of time without "laddering" or "running."

Up to the present time, fibers and yarns of nylon and "Dacron" (polyethylene terephthalate) have been regarded as the best available for use in stockings due to their high tenacity and good elastic properties.

The present invention provides knitted articles, particularly hosiery, which have properties of elasticity, resiliency, tensile strength, resistance to wear and retention of shape, as well as high thermal insulating capacity, resistance to creasing, to moths and micro-organisms and to chemicals, which are all combined in a stocking for the first time, and which are superior in all, or in most all respects to nylon and "Dacron" hosiery.

The new fibers from which the hosiery of this invention is knitted are formed from high molecular weight, linear, head-to-tail isotactic polymers of propylene.

Recently, G. Natta and his co-workers have disclosed new, normally solid, linear, head-to-tail polymers of the alpha-olefines CH_2=CHR in which R is a hydrocarbon radical including polymers of propylene (see, e.g., Natta et al. J.A.C.S., March 20, 1955), which polymers are of two different steric configurations by virtue of which the polymers are crystallizable or non-crystallizable. The crystallizable (or crystalline) polymers consist of macromolecules in which substantially all of the asymmetric tertiary main-chain carbon atoms of adjacent monomeric units have, on the same chain section, the same steric configuration and the main chain of the macromolecules, if presumed fully extended in a hypothetical plane, shows substantially all of the R groups bound to the teritiary carbons of the monomer units making up said chain section on one side of the plane and all of the hydrogen atoms bound to said tertiary carbon atoms on the opposite side. These crystallizable polymers were termed "isotactic" polymers by Natta, and that term has since been adopted in the art.

The amorphous, non-crystallizable polymers consist essentially of macromolecules in which tertiary asymmetric carbon atoms of the main chain having the same steric configuration have substantially a statistical distribution, and the main chain of the macromolecules, if presumed fully extended in the hypothetical plane, shows the R groups and the hydrogen atoms bound to the tertiary carbon atoms substantially in random distribution on the two sides of the plane. These amorphous polymers were termed "atactic" polymers by Natta.

The two different types of polymers made up, respectively, of the sterically differentiated macromolecules are present in the polymerizate obtained by polymerizing the alpha-olefine with the aid of a catalyst prepared from a compound, e.g., a halide, of a transition metal of groups IV to VI of the periodic table and a metallorganic compound of a metal of the 1st to 3rd groups of the periodic table, and can be separated from the polymerizate by selective solvent extraction on the basis of their different steric configurations. As has also been disclosed by Natta et al., by selection of the specific transition metal and organometallic compounds used in preparing the catalyst, the polymerization of the alpha-olefine can be oriented to the production of a polymerizate which consists predominantly to substantially of isotactic polymers, or to the production of predominantly to substantially atactic polymers.

The new fibers from which the hosiery of this invention is knitted are formed from polypropylene consisting prevailingly of isotactic macromolecules, as defined.

Briefly, the fibers and yarns can be formed by melt-extrusion of the polymer to form filaments, by dry-spinning a solution of the polymer into an evaporative atmosphere for the solvent or by wet-spinning the solution into a liquid setting bath which extracts the spinning solvent from the extruding stream of solution to leave the polymer in the filament form. The filaments may be stretched and then knitted as mono-filament yarns to produce stockings or, more generally, are either formed into yarns of the desired denier by twisting and doubling operations as desired, which are then stretched prior to being knitted into seamless or full-fashioned hosiery, or are disrupted into staple fibers which, alone or in admixture with other fibers, are formed into spun yarns that are knitted. The stretched yarns may be set or stabilized by heating them in a free-to-shrink condition or they may be knitted and then heat-stabilized in the stocking for purposes explained hereinbelow.

The filaments can be formed by extrusion or spinning of a mixture of isotactic polypropylene and atactic polypropylene and the atactic polymer may be allowed to remain in the formed filaments or may be removed therefrom by extraction with a solvent therefor which leaves the isotactic polymer intact.

The polypropylene filaments and yarns have in combination all of the properties required for a superior hosiery and to a greater extent than filaments and yarns known heretofore. Because of the particular structure of the polypropylene comprising the filaments and yarns, in which the crystalline areas are separated by amorphous very flexible areas, the filaments and yarns have both a high tenacity and a high elongation, while the finishing processes for the hosiery, such as boarding and setting operations, favor a high crystallization of the polymer and thus increase the inherently good elastic properties of the filaments and yarns and of the hosiery knitted therefrom.

The elastic properties of the polypropylene yarns are superior to the elastic properties of both nylon and "Dacron." This is shown by comparative tests the results of which are shown in the diagrams given in the attached drawing, in which the elastic recovery is shown as a function of the percent elongation, that is, of the initial strain imparted to the yarn.

In the drawing:

FIGURE 1 is the diagram showing the elastic recovery, at different percent elongations, for polypropylene;

FIGURE 2 is the diagram showing the elastic recovery, at different percent elongations, for nylon; and

FIGURE 3 is the diagram showing the elastic recovery, at different percent elongations, for "Dacron."

FIGURE 4 shows an article of hosiery knitted from the improved yarn of my invention.

In the diagrams, the horizontally hatched areas designate the percentage of instantaneous elastic recovery, the unhatched areas the percentage of delayed elastic recovery, and the vertically hatched areas the permanent strain.

It is evident, from a study of the diagrams of FIGURES 1–3, that the polypropylene yarn is less susceptible to being permanently strained than are similar yarns of either nylon or "Dacron." Put another way, it can be said that, the total elastic recovery of the three types of yarn being equal, the polypropylene yarns are distinguished by having the highest percentages of instantaneous recovery.

The above comparison is between the polypropylene yarn from which the present hosiery is knitted and the two yarns which have been regarded as the best, most up-to-date hosiery yarns.

Other tests performed on the polypropylene yarns for determining the resistance thereof to repeated stresses show that the yarns neither harden (which would result in decrease in the elastic elongation and tenacity of the yarn under stress) nor retain strain to any appreciable extent. The same tests were performed on similar yarns of nylon (6,6) and of "Dacron." From the results of the tests, which are shown below, it is clearly apparent that the polypropylene yarns are superior hosiery yarns.

POLYPROPYLENE

	Starting Property	Property after 100 Cycles Between—		Property after 1,000 Cycles Between—
		0 and 2.5 g./den.	0 and 5 g./den.	0 and 2.5 g./den.
Residual strain, percent	----------	+0.6	+2	+2
Elongation at break, percent	28	27	25	25
Tenacity, g./d.	6.5	6.5	6.6	6.8

NYLON (6,6)

Residual strain, percent	----------	+1.4	the filaments during the 67 cycles test.	+3.2
Elongation at break, percent	30	25		23
Tenacity, g./d.	5.5	5.6		5.5

"DACRON"

Residual strain, percent	----------	3	the filaments break during the 41 cycles test.	+9
Elongation at break, percent	16	13		11
Tenacity, g./d.	5.2	5.5		5.7

An outstanding advantage of the polypropylene filaments and yarns in the present hosiery is the capacity thereof to absorb a very large amount of work without breaking and to return a high proportion of the work, thus minimizing the phenomenon of elastic hysteresis. As an index of this last-mentioned property, the following ratio is used.

$$X=\frac{Lr}{Ld}\cdot 100$$

where Lr is the elastically recovered work and Ld is the strain work.

The values for 10% and 20% elongations of a polypropylene yarn used in making hosiery in accordance with this invention are reported in the following table and contrasted with the values for similar yarns of nylon and "Dacron."

	Polypropylene	Nylon	"Dacron"
Toughness	0.91	0.84	0.41
X for an elongation of 20%---percent	53	38	25
X for an elongation of 10%---do	80	78	35

The hosiery of the invention may be made on any suitable type of knitting machine, either straight or circular. We have found that, due to the exceptional regularity and extraordinary mechanical properties of the polypropylene yarns, the knitting proceeds so smoothly and rapidly, regardless of the type of knitting machine used, that the hosiery can be made at considerable savings in costs as compared to the cost of hosiery knitted from other yarns.

Until the stretched filaments and yarns of polypropylene are set after being heated in a free-to-shrink condition they possess a residual shrinkage capacity due to the release of the internal strains developed in the stretching operation. Advantage may be taken of this tendency to shrink in finishing the full-fashioned or seamless hosiery of the invention. The stocking as it comes from the knitting machine may be placed over a form and heated to the required temperature (about 140° C.) during which treatment it shrinks to fit exactly the form on which it is supported. When the stocking so shaped is cooled and removed from the form, it retains the shape of the form, along with the high inherent resiliency and elasticity of the polypropylene filaments or yarns, during wear and laundering.

The polypropylene hosiery is hydrophobic and has, therefore, the added advantage of rapid drying after laundering which is a present-day requirement for satisfactory hosiery.

The following example is given to illustrate the invention and the advantages of the polypropylene stockings as determined by various practical tests.

Example

Mens' socks were knitted on a circular Komet type knitter, using a polypropylene yarn having a metrical titer of 1/32,000, a tenacity of 6.7 g./den., an elastic elongation of 30%, and a specific gravity of 0.9.

Wear-resistance tests were carried out on the socks in comparison with nylon and wool socks, produced on the same knitting machine from yarns having the same titer.

A worker wore a wool sock on one foot and a 100% polypropylene sock on the other for each successive day of a 60-day period. During that time, the wool sock had to be replaced eight times because of holes, whereas the same polypropylene sock was worn for the entire 60 days and at the end of that time was entirely unaltered. The test was repeated, except that instead of a wool sock, a nylon sock was worn. The nylon sock had holes after 40 days; the polypropylene sock remained unimpaired at the end of the 60-day period.

Tests have established that dirt adheres to the surface of the polypropylene hosiery without being absorbed by the fibers, and the hosiery is therefor washed very easily. The soiled polypropylene socks were washed effectively in a few seconds with cold water and soap.

The polypropylene hosiery is not stained by the brown liquid normally dissolved out of shoe leather by perspiration, and which is absorbed by and remains permanently fixed in other stockings. The polypropylene hosiery has been proved to be absolutely refractory to absorption of the brown color.

An additional important advantage of the polypropyl-

ene hosiery is that the polymer does not decompose when exposed to chemicals and therefore does not yield decomposition products that can induce skin irritations or allergy symptoms. This is in contrast to the decomposition of nylon and other types of fibers used in making hosiery which is known to occur for instance under the influence of certain gases present in the air.

The hosiery of this invention can be knitted entirely of the polypropylene filaments or yarns, or from mixtures of polypropylene fibers with other kinds of fibers, e.g., natural fibers including silk, wool and cotton, fibers of other synthetic resins including nylon, "Acrilan" and "Dacron," and artificial fibers such as regenerated cellulose and cellulose acetate fibers, the other fibers being present in the yarns in amounts from 5% to 95% by weight, usually from 5% to 50% by weight. However, the most desirable hosiery is definitely that which is knitted entirely from the polypropylene filaments or yarns. The low density of the polypropylene filaments and yarns permits of the manufacture of articles of high covering power coupled with light weight.

The polypropylene hosiery may be of any of the known types, from extremely sheer to what is known in the trade as "service weight" and may be dyed any desired color.

When the atactic polypropylene is permitted to remain in the filaments, the proportion thereof present is preferably not in excess of about 20% so that the filaments consist for at least 80% of polypropylene which is not extractable with boiling n-heptane, and the non-extractable portion of which is made up of the isotatic polypropylene.

The polypropylene used to produce the filaments to be knitted into hosiery as described herein has an intrinsic viscosity which may be from 0.3 to 2 or even higher.

Since changes and variations may be made in practicing this invention without departing from the spirit thereof, it is intended to include in the scope of the appended claims all such modifications in details as are apparent to those skilled in this art.

What is claimed is:

1. As a new article of manufacture, hosiery comprised of knitted yarns of polypropylene having an intrinsic viscosity between about 0.3 and about 2.0 and consisting essentially of isotactic macromolecules and distinct and separable linear, regularly head-to-tail atactic macromolecules, the isotactic macromolecules constituting at least 80% by weight of the polypropylene and the atactic macromolecules constituting up to 20% by weight of the polypropylene, said hosiery having high inherent elasticity, being resistant to staining by discoloring substances dissolved out of shoe leather by perspiration, characterized in that it does not induce skin irritations or allergy symptoms, and having longer wearing properties, under the same conditions of wear, than hosiery of like weight knitted from nylon yarns.

2. A full-fashioned stocking according to claim 1.

3. A seamless stocking according to claim 1.

References Cited in the file of this patent

UNITED STATES PATENTS

2,313,058	Francis	Mar. 9, 1943
2,615,231	Little	Oct. 28, 1952
2,777,310	Comer	Jan. 15, 1957
2,816,883	Larchar et al.	Dec. 17, 1957
2,821,457	Erlich	Jan. 28, 1958
2,832,125	Knohl	Apr. 29, 1958
2,882,263	Natta et al.	Apr. 14, 1959

FOREIGN PATENTS

538,782	Belgium	Dec. 6, 1955

OTHER REFERENCES

New High MP Polymers, "Chemical and Engineering News," 33 July 11, 1955.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,025,689 March 20, 1962

Benito Beghelli

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

Column 3, in the table, lines 49 to 56, under the heading "NYLON (6,6)", fourth column thereof, for "the filaments during the 67 cycles test" read -- the filaments break during the 67 cycles test --.

Signed and sealed this 28th day of August 1962.

(SEAL)
Attest:

ESTON G. JOHNSON
Attesting Officer

DAVID L. LADD
Commissioner of Patents