

1

3,060,550

TREATMENT OF POLYAMIDES

Robert D. Smith, Enka, N.C., assignor to American Enka Corporation, Enka, N.C., a corporation of Delaware

No Drawing. Filed Mar. 27, 1959, Ser. No. 802,301
26 Claims. (Cl. 28—76)

This invention relates to synthetic linear polymers, and more particularly to a process for improving the properties of shaped articles prepared from fiber-forming synthetic linear polyamides.

The shaped articles may be filaments, yarns, fabrics, or other shaped articles formed from synthetic linear polyamides. Examples of these fiber-forming synthetic linear polyamides are those obtainable from polymerizable monoaminomonocarboxylic acids and their amide-forming derivatives, including caprolactam and those obtainable from the reaction of suitable diamines with suitable dibasic carboxylic acids or their amide-forming derivatives. To facilitate discussion, these synthetic linear polyamides may be referred to as nylon.

Some of the properties of nylon articles that are affected by the process of this invention are snag resistance, seam slippage, luster, and dye affinity. Other property changes will become apparent from the following detailed description.

This application has particular usefulness to nylon hose because it is desirable that snag resistance be improved, that the fabric have a reduced luster and that its affinity for certain dyes be increased. It is to be understood that any nylon article can be treated by the process of this invention.

It has been proposed in East German Patent No. 10,574, dated October 15, 1955, that a roughened surface and dulled polyamide article may be produced by treating the article with a concentrated aqueous solution of zinc chloride. This is followed by a water wash. There are certain difficulties with this process. The concentration required, namely, 45–65%, is too expensive, results in too harsh a treatment, and is highly toxic. In addition, a precipitate is formed which is undesirable.

It is accordingly an object of this invention to overcome the difficulties of the prior art and to provide a satisfactory and economical process for improving the properties of polyamide articles.

Another object of this invention is to improve the properties of synthetic linear polyamide shaped articles.

It is a further object of this invention to alter the surface characteristics of polyamide articles.

A still further object of this invention is to increase the snag resistance of nylon hose.

It is a further object of this invention to reduce the luster of nylon hose.

Other objects, such as increased dye affinity and reduced seam slippage in fabrics which corresponds to snag resistance in hosiery will become apparent from the following detailed description.

It has been found that these and other objects may be accomplished by treating the polyamide article with an aqueous solution containing hydrochloric acid and one or both of zinc chloride and an organic compound selected from the group consisting of ethyl alcohol, n-propanol, isopropanol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, isobutylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, pentaerythritol, formic acid, butyric acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid and acetic acid. This treatment is followed by a water wash.

In carrying out this invention the polyamide article is immersed in the above-described aqueous solution for a sufficient time for it to act on the surface of the article

2

but insufficient to appreciably affect the strength of the article. This will usually be from a few seconds to several hours with the preferred time being forty-five minutes. The time of treatment will vary with the concentration of the treating solution and temperature of the treatment. The temperature of this immersion solution will vary according to the boiling point of the compound added and will normally range from room temperature to 190° F. The aqueous solution must be removed from the polyamide article before it is subjected to further processing. This is accomplished by washing with water containing a small amount of dilute hydrochloric acid for a short period of time, preferably five minutes, and at a temperature of about 100° F. This is followed by a second water wash of approximately the same duration as the first water wash but at room temperature. The second water wash is not critical to the successful operation of this invention, however, it is preferred to insure that all of the treating solution be removed from the treated article. In addition, it is not necessary but preferable that hydrochloric acid be added to the first water wash. This is added to prevent precipitation of any zinc oxychlorides and subsequent contamination of the yarn.

This treatment may be carried out at any time in the processing of the filament, yarn, or fabric. When treating hose, the chemicals are preferably added to the scour bath thereby eliminating the necessity for an additional process step. In this case the scouring agents must be compatible with the zinc chloride, the hydrochloric acid and the organic compound. Preferably the scour bath should contain only non-ionic scouring agents and should not contain any chelating agents which might react with the zinc chloride. When treating hose it may also be used before or after the scouring and after dyeing or even on the completely finished article. Since this composition is removed from the surface of the article, the article may be subjected to any further processing steps that are desirable, such as dyeing and finishing for hosiery. Further processing of the articles does not reduce the beneficial effects of this process.

The concentration of zinc chloride in the aqueous solution may be from 0.1–20% with the preferred concentration being 5%. The preferred way is to use the lower concentrations because to use the high concentrations would make the process unsound economically. The organic compound may be in concentrations of 0.1–10.0%. The hydrochloric acid added to the treating solution and water wash is dilute acid, preferably 3 N. The amount of acid added to the treating solution is determined by adding the acid until the solution is clear. This will usually be a small amount, as for example, 0.01–1.0%. The amount of acid added to the water wash is 0.01–1.0%. When only zinc chloride or the organic compound is added to the treating solution, the hydrochloric acid is concentrated acid if the best results are to be obtained, and a higher percentage is used, namely 1–2%. It is possible to accomplish the desired results by the use of the organic compound alone, but the results are not too good.

This treatment will greatly increase the snag resistance of hosiery. It will also deluster the hose or other article, this delustering being particularly desirable in hosiery. In addition, the affinity for red dyestuff is increased with the result that the hose dyes to a more desirable color. This process may also change the treated article's affinity for other dyes. In addition, this process has little effect on the strength of the article treated.

These improvements are thought to be the result of the roughened surface of the articles. It is evident by microscopic examination that this treatment produces severe pitting on the surface of the filaments, which may be varied considerably by the intensity of the treatment. A comparison of cross sections of treated and untreated

3

filaments shows very little difference in the core of the filaments. This indicates that the alteration of the polyamide occurred only in the surface layer and in this respect the treated filaments differ materially from the untreated filaments.

The above-described improved properties are determined by well known and standard tests. Snag resistance is determined by the method described in ASTM Designation: D115-54T. Reduced luster is determined by Contrast Gloss Measurements using the Hunter Multipurpose Reflectometer (3 filter system), and dye affinity by visual observations.

The following examples illustrate the various applications of this invention, but are not intended to be restrictive but rather merely illustrative of this invention.

EXAMPLE I

Several semi-dull, 15 denier two filaments, polycaprolactam, seamless, greige hose, having been knitted and pre-boarded in a conventional manner, were immersed in aqueous solutions at 175° F. whose compositions are shown in Table I, and allowed to remain there for a period of forty-five minutes. The aqueous solutions are maintained at a ratio of forty parts bath to one part hose by weight and the volume was 1000 ml. The hose were removed and subjected to a water washing for five minutes at 100° F., which was followed by a second water wash at room temperature for five minutes. These hose were then hydroextracted and dried on a heated hosiery board. The thus treated hose were subjected to the snag resistance test and the following Table I illustrates the results. It will be noted that the compositions used to treat the hose are given in this table. It is to be understood that each class represents a separate treatment of several hose. Hose from groups A, D and E were dyed in a conventional dye bath and the dye affinity was determined by visual observation. It was observed that the welt of hose D and E dyed redder than did the leg of hose D and E, and that both the welt and leg of these hose dyed redder than did the control.

Table I

Hose	Composition	Snags per sq. in.
A.....	Control (not treated).....	8.0
B.....	1% ZnCl ₂	7.5
B.....	2.0 ml. 3 N HCl.....	
C.....	2% ZnCl ₂	6.0
C.....	3.4 ml. 3 N HCl.....	
D.....	3% ZnCl ₂	4.9
D.....	4.9 ml. 3 N HCl.....	
E.....	4% ZnCl ₂	4.4
E.....	7.9 ml. 3 N HCl.....	
F.....	5% ZnCl ₂	3.3
F.....	10.0 ml. 3 N HCl.....	

The above table illustrates the improvements obtainable by the use of zinc chloride and hydrochloric acid, however, the following tables will illustrate that this result is improved by the addition of the organic compound as well as by the use of concentrated hydrochloric acid.

EXAMPLE II

Hose of the same type as used in Example I were immersed in a conventional nylon hosiery scour bath containing non-ionic scouring agents to which were added the compositions shown in Table II, maintained at 190-200° F. The bath volume was 1000 ml. The hose were treated in this manner for forty-five minutes. This was followed by a five minute water wash at 100° F. and another water wash at room temperature. These hose were then subjected to hydroextraction and board drying. The hose were then subjected to the snag resistance test and Table II illustrates the results, which table was prepared in the same manner and represents the same methods used in Table I. Hose from groups A, D and E were dyed in the same manner and with the same result as in Example I.

4

Table II

Hose	Composition	Snags per sq. in.
A.....	Control (No ZnCl ₂).....	8.0
B.....	1% ZnCl ₂	7.2
B.....	6 ml. 3 N HCl.....	
C.....	2% ZnCl ₂	6.0
C.....	8 ml. 3 N HCl.....	
D.....	3% ZnCl ₂	5.8
D.....	9 ml. 3 N HCl.....	
E.....	4% ZnCl ₂	4.7
E.....	11 ml. 3 N HCl.....	
F.....	5% ZnCl ₂	5.2
F.....	13 ml. 3 N HCl.....	

EXAMPLE III

Hose as in Example II were immersed in the same type scour bath but the bath contained the compositions shown in Table III and had a volume of 1500 ml., and the first water wash contained about 0.1% hydrochloric acid. The hose were treated and tested in the same manner as in Example II. Table III represents the results of this treatment and was prepared in the same manner as Table II. Hose from groups A, E, I, K and M were dyed in the same manner and with the same results as in Example I.

Table III

Hose	Composition	Snags per sq. in.
A.....	Control.....	6.4
B.....	2% HCl (conc.).....	2.8
B.....	5% ZnCl ₂	
C.....	10 ml. 3 N HCl.....	5.4
C.....	0.5% HCl (conc.).....	
D.....	5% ZnCl ₂	2.7
D.....	3 ml. 3 N HCl.....	
E.....	2% formic acid.....	4.4
E.....	5% ZnCl ₂	
F.....	9 ml. 3 N HCl.....	3.1
F.....	2% acetic acid.....	
G.....	5% ZnCl ₂	3.1
G.....	9 ml. 3 N HCl.....	
H.....	1.0% Chloroacetic acid.....	5.4
H.....	9 ml. 3 N HCl.....	
I.....	0.2% Trichloroacetic acid.....	2.8
I.....	5% ZnCl ₂	
J.....	9 ml. 3 N HCl.....	2.4
J.....	2% n-propanol.....	
K.....	5% ZnCl ₂	2.8
K.....	10 ml. 3 N HCl.....	
L.....	2% Allyl alcohol.....	5.0
L.....	5% ZnCl ₂	
M.....	9 ml. 3 N HCl.....	2.1
M.....	1.5% ethylene glycol monomethyl ether.....	
N.....	5% ZnCl ₂	5.9
N.....	9 ml. 3 N HCl.....	
O.....	2% Isobutylene glycol.....	3.7
O.....	5% ZnCl ₂	
O.....	10 ml. 3 N HCl.....	
O.....	5% Isobutylene glycol.....	
O.....	7% Chloroacetic acid.....	

EXAMPLE IV

A new batch of hose, being 15 denier, monofilament, were treated in the same manner as in Example III, and the results are given in Table IV.

Table IV

Hose	Composition	Snags per sq. in.
A.....	Control.....	4.8
B.....	1% HCl (conc.).....	2.6
B.....	5% ZnCl ₂	
C.....	10 ml. 3 N HCl.....	1.8
C.....	1.5% HCl (conc.).....	
D.....	5% ZnCl ₂	2.2
D.....	10 ml. 3 N HCl.....	
E.....	2% Pentaerythritol.....	1.8
E.....	5% ZnCl ₂	
E.....	13 ml. 3 N HCl.....	1.8
E.....	2% Isopropanol.....	
E.....	5% ZnCl ₂	1.8
E.....	13 ml. 3 N HCl.....	

EXAMPLE V

Several semi-dull, 15-denier, monofilament, polycaprolactam, full-fashioned, greige hose, having been knitted and pre-boarded in a conventional manner, were immersed in a conventional nylon hosiery scour bath maintained at 190–200° F. and which contained non-ionic scouring agents. The compositions shown in Table V and 50 ml. concentrated hydrochloric acid were added to this scour bath which had a total volume of 20,000 ml. The hose were treated in this manner for forty-five minutes and then hydro-extracted. Immediately the hose were subjected to a five minute water wash of 20,000 ml. at 100° F. and a second five minute water wash of 20,000 ml. at room temperature. These hose were then hydro-extracted and air dried in a conventional manner. The hose were divided into two lots, the first was post-boarded and tested at this point. The second lot was dyed, finished and post-boarded in a conventional manner. The second lot was subjected to the same tests as the first. In addition to the snag resistance, luster and dye affinity tests previously described, both lots were subjected to the ball burst strength test described in ASTM Designation: D231–46 and the standard hosiery stretch test described in ASTM Designation: D1058–51. Table V represents the results of this treatment and the foregoing tests.

Table V

Hose	Composition	Snags per sq. in.		Contrast Gloss, Lot I
		Lot I	Lot II	
A.....	Control.....	4.0	3.3	1.16
B.....	5% ZnCl ₂	1.8	2.8	1.02
C.....	2% chloroacetic acid.....	1.3	1.5	1.07
	5% ZnCl ₂			
	2% n-propanol.....			

	Strength lbs. per sq. in.				Stretch (scissors) inches			
	Welt		Leg		Welt		Ankle	
	Lot I	Lot II	Lot I	Lot II	Lot I	Lot II	Lot I	Lot II
A.....	113	114	22.9	24.1	11	11½	7¼	7¼
B.....	112	115	21.3	23.5	10¾	11	7¼	7¼
C.....	112	116	20.7	24.5	10¾	11	7¼	7¼

In the welt and leg portions the dye affinity was very similar for all of these hose as compared with the control. The foregoing example illustrates that the differences in strength and stretch between hose A, B and C are minor and well within acceptable limits for commercial hosiery. Snags and luster were both desirably reduced by this treatment. No luster test was conducted on the dyed and finished hose because the luster will be covered by the dyeing.

The foregoing examples illustrate the application of this invention to hosiery made from polycaprolactam. It will be apparent that other articles may similarly be treated. Examples of other articles are filaments, yarn, fabric and ribbons. Also the polyamide articles treated may, if desired, contain modifying agents such as pigments, dyes, antioxidants, plasticizers, oils, and resins.

It will be apparent from the foregoing examples that this treatment may be applied at any stage in the processing of the polyamide article without departing from the spirit and scope of this invention. For example, the filaments may be immersed in the treating solution or the unfinished, semi-finished, or finished fabric may similarly be treated.

The examples show that zinc chloride, or the organic compound, when used alone with hydrochloric acid will improve snag resistance, but the greatest improvement is obtained when they are used in combination. Thus this

treatment greatly improves the snag resistance of polyamide articles, particularly hosiery, and it roughens the surface of the article, thereby improving seam slippage and delustering the yarn. In addition, dye affinity, particularly for red dyes, is increased.

Since it is obvious that many changes and modifications can be made in the details of the invention above set forth, it is to be understood that the invention is not to be limited except as set forth in the appended claims.

What is claimed is:

1. A process for improving the properties of nylon filaments and yarns which comprises treating said filaments and yarns with an aqueous solution containing 1 to 2% of hydrochloric acid and 0.1 to 10% of an organic compound selected from the group consisting of ethyl alcohol, n-propanol, isopropanol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, isobutylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, pentaerythritol, formic acid, butyric acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid and acetic acid, for a period of time sufficient to impart snag resistance thereto, washing said filaments and yarns to remove said aqueous solution and knitting said filaments and yarns into a textile fabric.
2. A process according to claim 1 wherein the organic compound is chloroacetic acid.
3. A process according to claim 1 wherein the organic compound is isobutylene glycol.
4. A process according to claim 1 wherein the organic compound is pentaerythritol.
5. A process according to claim 1 wherein the organic compound is n-propanol.
6. A process according to claim 1 wherein the organic compound is formic acid.
7. A process for improving the snag resistance of a nylon knitted fabric which comprises treating said knitted fabric with an aqueous solution containing 1 to 2% of hydrochloric acid and 0.1 to 10% of an organic compound selected from the group consisting of ethyl alcohol, n-propanol, isopropanol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, isobutylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, pentaerythritol, formic acid, butyric acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and acetic acid, for a period of time sufficient to impart snag resistance to said knitted fabric, followed by a water wash containing dilute hydrochloric acid and then by a water wash.
8. A process according to claim 7 wherein the organic compound is chloroacetic acid.
9. A process according to claim 7 wherein the organic compound is isobutylene glycol.
10. A process according to claim 7 wherein the organic compound is pentaerythritol.
11. A process according to claim 7 wherein the organic compound is n-propanol.
12. A process according to claim 7 wherein the organic compound is formic acid.
13. A process for improving the properties of nylon filaments and yarns which comprises treating said filaments and yarns with an aqueous solution containing 0.1 to 20% of zinc chloride, 0.01 to 1.0% hydrochloric acid, and 0.1 to 10% of an organic compound selected from the group consisting of ethyl alcohol, n-propanol, isopropanol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, isobutylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, pentaerythritol, formic acid, butyric acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and acetic acid, for a period of time sufficient to impart snag resistance thereto, washing said filaments and yarns to remove said aqueous solution, and knitting said filaments and yarns into a textile fabric.
14. A process according to claim 13 wherein the organic compound is chloroacetic acid.

7

15. A process according to claim 13 wherein the organic compound is isobutylene glycol.

16. A process according to claim 13 wherein the organic compound is pentaerythritol.

17. A process according to claim 13 wherein the organic compound is n-propanol.

18. A process according to claim 13 wherein the organic compound is formic acid.

19. A process for improving the snag resistance of a nylon knitted fabric which comprises treating said nylon knitted fabric with an aqueous solution containing 0.1 to 20% zinc chloride, 0.01 to 1.0% hydrochloric acid, and 0.1 to 10% of an organic compound selected from the group consisting of ethyl alcohol, n-propanol, isopropanol, allyl alcohol, ethylene glycol, diethylene glycol, triethylene glycol, isobutylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, pentaerythritol, formic acid, butyric acid, chloroacetic acid, dichloroacetic acid, trichloroacetic acid, and acetic acid, for a period of time sufficient to impart snag resistance to said knitted fabric, followed by a water wash containing dilute hydrochloric acid and then by a water wash.

20. A process according to claim 19 wherein the organic compound is chloroacetic acid.

21. A process according to claim 19 wherein the organic compound is isobutylene glycol.

8

22. A process according to claim 19 wherein the organic compound is pentaerythritol.

23. A process according to claim 19 wherein the organic compound is n-propanol.

24. A process according to claim 19 wherein the organic compound is formic acid.

25. A process according to claim 19 in which the zinc chloride is in the concentration of 5%.

26. A process according to claim 19 in which the aqueous solution treatment is carried out at a temperature of 190° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,480,775	Ryan	Aug. 30, 1949
2,730,479	Gibson	Jan. 10, 1956
2,734,001	Mecklenburgh	Feb. 7, 1956
2,889,611	Bedell	June 9, 1959

FOREIGN PATENTS

555,490	Great Britain	Aug. 25, 1943
568,092	Great Britain	Mar. 19, 1945
479,262	Canada	Dec. 11, 1951
1,060,059	France	Nov. 18, 1953

OTHER REFERENCES

Rayon and Synthetic Textiles, May 1950, page 91.