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MIXED SHRINKAGE YARN

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No Drawing. Continuation-in-part of applications Ser. No. 743,320, July 9, 1968, and Ser. No. 667,095, Sept. 12, 1967. This application Dec. 11, 1968, Ser. No. 783,151

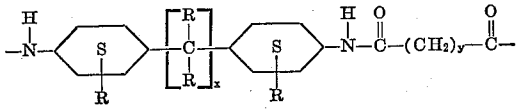
Int. Cl. D02g 3/02; C08g 41/44

U.S. Cl. 57—140

6 Claims

ABSTRACT OF THE DISCLOSURE

Mixed-shrinkage yarns consisting of a first group of continuous oriented filaments of a polyamide wherein at least 50 mol percent of the polymer repeating units are of the formula



wherein x is 1 or 2, y is an integer in the range of 7–14, R is H or methyl and a second group of continuous filaments having a lower shrinkage than said first group of filaments and consisting essentially of a polymer selected from cellulose esters, synthetic linear aliphatic polyamides, silk, rayon polyesters and acrylic polymers, the yarn being further characterized by a difference in filament length between the two groups of filaments of at least 2% when subjected to boiling water which difference increases to at least 3% when subjected to heat-setting.

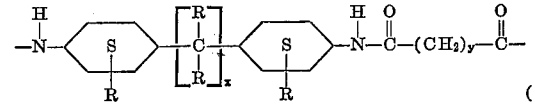
This application is a continuation-in part of applications Ser. No. 743,320, filed July 9, 1968, now abandoned, and Ser. No. 667,095, filed Sept. 12, 1967, now U.S. Patent No. 3,416,302; which is in turn a continuation-in-part of Ser. No. 608,281, filed Jan. 10, 1967, now abandoned.

BACKGROUND

In recent years the introduction of synthetic yarns such as those from polyamides has led to fabrics having high strength, improved resistance to wear and, in some cases, improved launderability. In order to attain improved aesthetics with continuous filament yarns, mixed-shrinkage yarns have been developed. When a fabric produced from such a yarn is heated, e.g. with hot or boiling water, some of the filaments shrink more than the others, thus giving the fabric an improved hand. It is difficult to obtain a mixed-shrinkage yarn which has a desirable balance of properties, i.e. a relatively high shrinkage differential between the high-and low-shrinkage filaments, relatively low total yarn shrinkage, freedom from tendency to form filament loops as initially produced for ease of processing into fabric and good functional properties. The prior art discloses mixed-shrinkage yarns which, by virtue of carefully regulated processing conditions, may possess a reasonable difference in shrinkage among the filaments and, at the same time, be free from objectionable loopiness when removed from the package for processing into fabric. However, heat-setting of such yarn, e.g. at temperatures of 170–180° C., produces no substantial increase in bulk or differential shrinkage of the yarn over that obtained in boiling water. Consequently, the differential shrinkage obtained on fabric finishing is not as great as might be desired and, in addition, considerable care must be taken in heat-setting the fabric to prevent loss in differential shrinkage.

SUMMARY OF THE INVENTION

The yarn of the present invention consists essentially of a first group of continuous oriented filaments of a polyamide wherein at least 50 mole percent of the polymer repeating units are of the formula



(I)

wherein x is 1 or 2, y is an integer in the range of 7–14, R is the same or different member of the class consisting of hydrogen and methyl and a second group of continuous oriented filaments having a lower shrinkage than said first group of filaments, said second group of filaments consisting essentially of a polymer selected from the group consisting of cellulose esters, synthetic linear aliphatic polyamides, polyesters, silk, rayon and acrylic polymers, the yarn being further characterized by a difference in filament length (DFL) between the two groups of filaments when subjected to boiling water of at least 2%, the DFL increasing to at least 3% when subjected to heat-setting as described below.

The diamino portion of Formula I, due to its carbocyclic nature, is a mixture of isomers having trans-trans (tt), cis-trans (ct) and cis-cis (cc) configurations. Hydrogenation conditions employed in preparing the diamines used in the polymer synthesis results in a mixture of isomers, different conditions of hydrogenation producing a different isomer distribution as shown in U.S. 2,494,563 and U.S. 2,606,924.

In one embodiment, the first group of filaments consists essentially of a homopolymer having the repeating units of Formula I.

In another embodiment, the first group of filaments consists of a copolymer containing 50–95 mole percent of the repeating units of Formula I and 5–50 mole percent of another polyamide unit prepared from a member of a class consisting of (1) the same diamine as employed for production of the Formula I repeat unit with a different dicarboxylic acid, and (2) the same dicarboxylic acid as employed for production of the Formula I repeat unit with a different diamine. Preferably, the copolymer contains 75–95 mole percent of the repeating units of Formula I.

The tt isomer content of the polymer used to prepare the first group of filaments, i.e. the high shrinkage filaments, is preferably at least 40% by weight.

The second group of filaments in the yarn of this invention consists of filaments which are selected and processed to have a lower shrinkage than the first plurality of filaments. Filaments for this purpose may, for instance, be selected from the cellulose ester filaments which are well known in the art and which are commercially available. Cellulose triacetate filaments are preferable for this purpose. Commercial cellulose acetate filaments typically have a lower shrinkage than filaments of the compositions employed in the preparation of the first group of filaments. Polyester filaments, i.e. synthetic polymer filaments composed of at least 85% by weight of an ester of a dihydric alcohol and terephthalic acid may be employed. Polyethylene terephthalate or other polyester fibers as are readily available commercially are suitable. Filaments prepared from synthetic linear aliphatic polyamides such as 66 and 6 nylon may be employed. Acrylic filaments, i.e. filaments prepared from a long-chain synthetic polymer composed of at least 85% by weight of acrylonitrile may be used. Polyacrylonitrile and other acrylic filaments are commercially available and well known in the art. The modacrylic filaments which are commercially available may also be employed.

The shrinkage of the first group of filaments is normally adjusted to a level within the range desired for the commercial preparation of fabrics. This is usually 12% or somewhat lower. This may be accomplished, for instance, by suitable adjustment of the severity and duration of heat-treatment of the yarn following the drawing operation. Similarly, if the shrinkage of the second group of filaments is not sufficiently low to give the desired difference when the filaments are produced by the normal commercial procedure, appropriate shrinkage treatments, as are well known to those skilled in the art, may be employed.

In order to obtain the improvements of this invention in substantial measure, the yarn should contain at least 25% by weight of the higher shrinkage filaments and preferably at least about 50% are present. At least 25% by weight of the lower shrinkage groups should preferably be present to offer sufficient bulking.

The yarn of this invention has surprisingly good recovery properties as evidenced by resistance to wrinkling and laundering in spite of the presence of a substantial number of filaments which exhibit relatively poor recovery. In addition, these yarns have relatively low yarn shrinkage so that greige fabric shrinkage is not excessive while retaining a good level of differential shrinkage under the restraints imposed by the fabric finishing procedure and by fabric structure. Thus, these yarns yield attractive fabrics of excellent bulk and covering power. Furthermore, the aesthetics of fabrics prepared from these yarns may be varied to a considerable degree due to the unisue high temperature response of the yarn. By regulation of the degree of restraint on the fabric in conventional heat-setting procedures, the bulk and hand of the fabric may be varied over a considerable range. Also, even if the fabric scouring or other finish step prior to heat-setting is carried out in such manner as to inhibit the development of bulk (and this is true with certain conventional fabric finishing procedures), the desired bulk can be achieved later in the heat-treating operation. It should be realized, of course, that in fabric heat-setting procedures fabrics may as a matter of choice be held under tensions high enough to prevent the increase in DFL in the yarn but, in this case, tendency to increase in DFL will help prevent or minimize a loss in DFL which would otherwise occur. These advantages have not been attainable with prior art mixed-shrinkage yarns.

The filaments may be of round or non-round shapes as may be desired. They may contain suitable heat stabilizers, antioxidants, light stabilizers, ultraviolet light absorbers, delustrants, pigment, dyes, and the like. Other polymer additives may be present to improve dyeability, wickability, static propensity or melting point of the fiber.

The expression "relative viscosity" as used herein signifies the ratio of the flow time in a viscometer of a polymer solution relative to the flow time of the solvent by itself. Measurements of relative viscosities as referred to herein and as measured in the examples is determined from a solution of 3.7 grams of polyamide in 50 ml. of a 1:1 mixture of 98–100% formic acid and phenol at 25° C., unless otherwise noted.

In the examples, the shrinkage of the yarns is determined on skeins of measured length as follows: A skein of about 1500 denier is prepared by winding an appropriate number of turns of about 110 cm. length per turn, on a reel. For 60 denier yarn, 25 turns are used. The skein is tied at two diametrically opposed points before removal from the reel. The length of the collapsed skein (appr. 55 cm.) is measured accurately under a load of 4 mgd. (milligrams per denier) based on the denier of the collapsed skein, i.e. about 3000. A water bath is heated to boiling over a ½ hour period. When the temperature reaches 50° C., the skein, with a suspended weight at one of the tie points amounting to 4 mgd., is hung (immersed) in the bath and remains there for 10 minutes after the boiling point is reached. It is then removed and air dried

with the weight attached. The length is then determined again and the percent shrinkage calculated from the equation

$$\text{Percent Shrinkage, } S=\frac{100(L_0-L_1)}{L_0}$$

where L_0 equals length of skein before boiling, L_1 equals length of skein after boiling.

The percent difference in filament length (DFL) between the high- and low-shrinkage filaments is determined as follows: A strand of yarn containing both high- and low-shrinkage filaments is separated from a similarly boiled and dried skein as above and cut adjacent each tie point so as not to include the tie. If loops in the longer (low-shrinkage) filaments occur near the upper tie point (suspension point) as a result of the boiling, the strand, before cutting, should be pinched firmly at the tie point and gently stroked to force the loops away from the tie point so that the cut yarn strand may be knotted above the point at which loops are present. The cut yarn is then doubled and the free ends tied together to form a loop. The free ends above the knot are taped to a meter rule and the length of the high shrinkage filaments in the loop is measured while a 0.6 g. paper clip is hanging in the loop. The length of the low shrinkage filaments is measured by pulling the paper clip downwardly until substantially all the filaments appear to be straight and determining the length of the extended loop. The percent DFL is calculated from the following equation:

$$\text{Percent DFL}=\frac{100(L_2-L_3)}{L_3}$$

where L_2 is the length of the longer filaments and L_3 is the length of the shorter filaments.

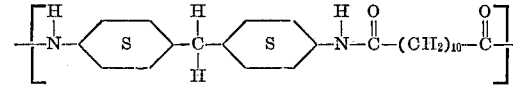
The DFL after exposure to heat-setting temperature is measured by hanging a boiled-off, air-dried skein in an oven at 177° C. for 2 minutes under the same total load as was used in boil-off and then determining the DFL as described above for the boiled-off skein.

The high- and low-shrinkage filaments may be combined in any suitable fashion. The different filaments may be combined by extrusion from the same spinneret; however, generally it will be more convenient to combine the separately prepared filaments at a later stage. For instance, two yarns made up of the desired filaments may be combined by passage through an interlacing jet of the type described by Bunting & Nelson in U.S. 2,985,995. Other methods of combining the two filament bundles as are well known in the art may be employed.

EXAMPLE I

A polymer is prepared in an autoclave containing by weight 40 parts of water and 60 parts of the salt of bis-(4-aminocyclohexyl)methane and dodecanedioic acid. The diamine consists of 70% of the tt isomer and about 5% of the cc isomer.

As a viscosity stabilizer, 0.2 mole of acetic acid are added for each mole of the polyamide salt. The solution also contains 0.0046% manganous hypophosphite, based on the weight of the salt. This solution is heated to 300 p.s.i.g. (21.4 atmospheres) and maintained at this pressure for 2 hours and the temperature is raised to 300° C., a sufficient amount of 20% aqueous slurry of finely-divided kaolinite being added when the temperature reaches 200° C. to provide a concentration of 1% by weight of the kaolinite in the final polymer. The pressure is then reduced to atmospheric while the temperature is raised to 305° C. The polymer having the following repeating units



is held under steam for 20 minutes. It is then extruded and cut to flake. The relative viscosity of the flake is 56.5.

The flake is melted in a screw melter and fed to a spinneret where it is extruded, as described in U.S. 2,939,-201, to form 36 trilobal filaments. The face of the spinneret is blanketed with steam from a supply source at 35 p.s.i.g. (3.4 atmospheres). The filaments are quenched with cross flow air in the conventional manner, passed over a finish roll where a lubricating finish is applied, then passed around a pair of feed rolls rotating at a peripheral speed of 1900 y.p.m. (1737 meters/min.). The yarn is then passed around a pair of draw rolls rotating at peripheral speed of 3000 y.p.m. (2743 meters/min.). then to a pair of rolls heated at 170° C. and rotating at a peripheral speed of 2800 y.p.m. (2560 meters/min.). The yarn then passes to a pair of unheated rolls rotating with a peripheral speed of 2820 y.p.m. (2579 meters/min.), then interlaced to a low degree by passage through an interlacing jet as described in U.S. 2,985,995, and finally to a windup rotating at 2774 y.p.m. (2537 meters/min.). The yarn is given 6–8 passes around the various pairs of rolls mentioned above. The denier of the yarn is 60.

A bobbin of yarn prepared as above is placed on a draw winder together with a bobbin of commercial 60 denier, 17 filament cellulose triacetate yarn. The two yarns are then interlaced by passing the yarns simultaneously through an interlacing jet of the type referred to above and wound into a package. When tested as previously described, the shrinkage of the yarn after boil-off is found to be 5.7% and this increases to 8.6% when the yarn is boiled-off and heat-set at 177° C. The DFL of the yarn is found to be 4.9% after boil-off, and this increases to 7.0% when the yarn is boiled-off and heat-set at 177° C. Knit tubing (A) was prepared from this yarn.

Knit tubing (B) was prepared by interlacing two ends of the 60 denier triacetate yarn used above. Knit tubing (A) and (B) were scoured and (A) was found to be distinctly superior in recovery properties as evidenced by good wrinkle resistance. The yarns used for preparing the knit tubing were twisted 5 turns per inch before knitting.

EXAMPLE II

A copolymer is prepared from a solution containing 60 parts of the salt of bis-(4-aminocyclohexyl)methane and a mixture of dodecanedioic and isophthalic acids and 40 parts of water. The mixed acids contain 8.7% by weight of isophthalic acid which is sufficient to provide 10% by weight or 12.3 mole percent of the isophthalic polymer units in the final polymer. The diamine contains 70% of the tt isomer and about 5% of the cc isomer. As a viscosity stabilizer, 0.64 gram of acetic acid per kilogram of dry salt are added. The salt solution is heated in an autoclave for a period of 2 hours while the pressure increases to 300 p.s.i.g. (21.4 atmospheres). When the pressure reaches 200 p.s.i.g. (14.6 atmospheres), sufficient 20% solution of potassium phenyl phosphinate is added to provide approximately 1 gram per kilogram of dry salt. When the temperature reaches 200° C., a sufficient amount of a 20% aqueous slurry of finely-divided kaolinite is added to provide a concentration of 2% by weight of kaolinite in the polymer. The pressure is maintained at 300 p.s.i.g. (21.4 atmospheres) by bleeding off steam and heating is continued for 2.5 hours until the temperature reaches 300° C. at which time the pressure is reduced to atmospheric pressure over a period of 90 minutes and the temperature is increased to 305° C. The polymer is then held at atmospheric pressure under steam for 1 hour. It is then extruded and cut to flake. The relative viscosity of the flake is 39. The flake is melted in a screw melter and fed to a spinneret where it is extruded to form 18 trilobal filaments. The face of the spinneret is blanketed with steam from a supply source at 30 p.s.i.g. (3.4 atmospheres). The filaments are quenched in the conventional manner and passed over a finish roll where a lubricating finish is applied. The filaments are then passed around a pair of feed rolls rotating with a peripheral speed of 2300 y.p.m. (2103 meters/min.). From the feed rolls the yarn passes to a pair of draw rolls rotating at a peripheral speed of 2996 y.p.m. (2740 meters/min.) then to a pair of heated rolls at 175° C. rotating at a peripheral speed of 2907 y.p.m. (2658 meters/min.). The yarn then passes to a pair of unheated rolls rotating at a peripheral speed of 2926 y.p.m. (2676 meters/min.) and finally to a windup at 2903 y.p.m. (2655 meters/min.). The yarn is given 6–8 passes around each pair of rolls mentioned above. The denier of the yarn is 30.

Two ends of the 30 denier, 18 filament yarn prepared as above are plied together and the resulting yarn combined with one end of 60 denier, 17 filament commercial triacetate yarn by passage through an interlacing jet as described previously, the shrinkage is found to be 5.6% after boiling and 11.1% after boiling and heat-setting. The DFL of the yarn is found to be 3.6% after boiling and 10.9% after boiling and heat-setting.

When the yarn is knit into tubing as described in Example I and compared with tubing knit from triacetate yarn alone, the results are essentially the same as found in Example I.

EXAMPLE III

A copolymer is prepared from bis-(4-aminocyclohexyl)-methane and a mixture of dodecanedioic and isophthalic acids containing 8.7% by weight of the isophthalic acid, and a 30–denier, 18-filament yarn is prepared from the copolymer following the general procedure of Example II.

Three ends of the above 30–18 yarn are plied without twist to form a 90–54 yarn which is then combined in an interlacing jet, as described in Example I, with a 100–48 commercial polyacrylonitrile yarn. When tested as previously described, the shrinkage of the yarn after boil-off is found to be 4.5%, and this increases to 11.5% when the yarn is boiled off and heat set at 177° C. The DFL of the yarn is found to be 3.8% after boil-off, and this increases to 12.5% when the yarn is boiled off and heat set at 177° C.

The above yarn is twisted five turns per inch and knit into tubing. After scouring, the tubing is found to be much less wrinkled than tubing knit from acrylic yarn prepared by passing two ends of yarn through the above-described interlacing jet.

EXAMPLE IV

The ends of the 30–18 copolymer yarn of Example 3 are plied together without twist to form a 60–36 yarn. The 60–36 yarn is combined in an interlacing jet, as described in Example III, with a 75–30 commercial viscose rayon yarn. The resulting yarn has a shrinkage after boil-off of 3.2%, and this increases to 9.9% after boil-off and heat setting at 177° C. The yarn has a DFL of 5.2% after boil-off, and this increases to 8.6% after boil-off and heat setting at 177° C.

When the above yarn is twisted five turns per inch and knit into tubing and the tubing scoured, it is found to be much less wrinkled than tubing knit from viscose rayon yarn prepared by passing two ends of the yarn through the above-described interlacing jet.

EXAMPLE V

A 60–36 copolymer yarn is prepared as described in Example IV. A skein of 60–40 commercial polyethylene terephthalate yarn is prepared and the skein boiled in water, dried and then heated in an oven at 170–175° C. for 5 minutes. The skein is then wound into a cone. The 60–36 copolymer yarn and the boiled-off and heat-treated polyethylene terephthalate yarn are combined in an interlacing jet as described in Example III. The shrinkage of the yarn after boil-off is 4.4%, and this increases 10.4% after boil-off and heat setting at 177° C. The DFL of the yarn after boil-off is 3.8%, and this increases to 11.0% after boil-off and heat setting at 177° C. When the yarn is twisted five turns per inch and knit into tubing, and the tubing scoured, it is found to be much less wrinkled than

a similar tubing knit from polyethylene terephthalate yarn prepared by passing two ends of the yarn through the above-described interlacing jet.

EXAMPLE VI

A 60–34 commercial 66 nylon yarn is processed in the same manner as the polyethylene terephthalate yarn of Example V. It is then combined in an interlacing jet with a 60–36 copolymer yarn prepared as described in Example IV. The resulting yarn has a shrinkage after boil-off of 4.5%, and this increases to 11.2% after boil-off and heat setting at 177° C. The yarn has a DFL after boil-off of 2.5%, and this increases to 11.5% after boil-off and heat setting at 177° C. When the yarn is twisted five turns per inch and knit into tubing, and the tubing scoured, it is found to be much less wrinkled than tubing knit from nylon yarn prepared by passing two ends of the yarn through the above-described interlacing jet.

EXAMPLE VII

Three ends of 20-denier, 10-filament silk yarn are plied without twist to form a 60–30 yarn. This 60–30 silk yarn is then combined with a 60–36 copolymer yarn prepared as described in Example IV, using an interlacing jet of the type described in Example III. The resulting yarn has a shrinkage after boil-off of 5.0% and this increases to 12.1% on heating setting at 177° C. The DFL is 2.6% after boil-off, and this increases to 13.6% on heat setting at 177° C. When the yarn is twisted 5 turns per inch and knit into tubing, and the tubing scoured, it is much less wrinkled than tubing knit from silk yarn prepared by passing two ends of the 60–30 silk yarn through the above-described interlacing jet.

EXAMPLE VIII

Following the general procedure of Example I, a polymer is prepared from bis(4-aminocyclohexyl)methane and sebacic acid and processed into a 60-denier, 36-filament yarn. The diamine consists of 55% of the tt isomer and about 5% of the cc isomer.

The above yarn is combined in an air jet with a commercial 60-denier, 17-filament cellulose triacetate yarn following the procedure of Exampe I. The shrinkage of the yarn after boil-off is 5.5% and this increases to 8.8% when the yarn is boiled off and heat set at 117° C. The DFL of the yarn is 4.3% after boil-off, and this increases to 8.1% when the yarn is boiled off and heat set at 177° C.

This yarn is twisted 5 t.p.i. and knit into tubing and the tubing scoured. It is much less wrinkled then tubing knit from yarn prepared by interlacing two ends of the triacetate yarn.

EXAMPLE IX

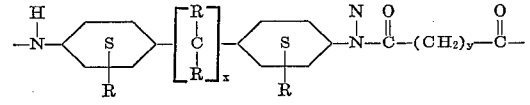
Following the general procedure of Example I, a polymer is prepared from bis(4-aminocyclohexyl)methane and azelaic acid and processed into a 60-denier, 36-filament yarn. The diamine consists of 55% of the tt isomer and about 5% of the cc isomer.

The above yarn is combined in an air jet with a commercial 60-denier, 17-filament cellulose triacetate yarn following the procedure of Example I. The shrinkage of the yarn after boil-off is 12% and this increases to 14% when the yarn is boiled off and heat set at 177° C. The DFL of the yarn is 9.2% after boil-off, and this increases to 14.9% when the yarn is boiled off and heat set at 177° C.

This yarn is twisted 5 t.p.i. and knit into tubing and the tubing scoured. It is much less wrinkled than tubing knit from yarn prepared by interlacing two ends of the triacetate yarn.

What is claimed is:

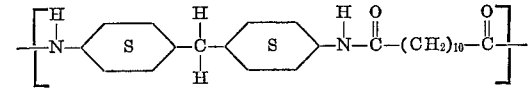
1. A mixed shrinkage yarn consisting essentially of a first group of continuous oriented filaments of a polyamide wherein at least 50 mole percent of the polymer repeating units are of the formula



wherein x is 1 or 2, y is an integer in the range of 7–14, R is H or methyl, the said polymer having a tt isomer content of at least 40% by weight, and a second group of continuous filaments having a lower shrinkage than said first group of filaments and consisting essentially of a polymer selected from the group of cellulose esters, synthetic linear aliphatic polyamides, silk, rayon polyesters and acrylic polymers, the yarn being further characterized by a difference in filament length between the two groups of filaments of at least 2% when subjected to boil-off at 4 mgd. load which difference increases to at least 3% when subjected to heat-setting at 177° C. for two minutes under the same total load.

2. The yarn of claim **1** wherein the second group of filaments consist essentially of cellulose triacetate.

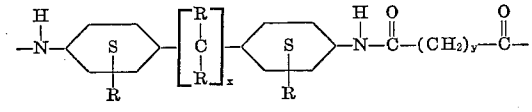
3. The yarn of claim **1** wherein the first group of filaments is of polymer having the following repeating units:



4. The yarn of claim **3** wherein the second group of filaments consist essentially of cellulose triacetate.

5. The yarn of claim **4** wherein the first and second groups of filaments are each present in an amount of at least about 25% by weight.

6. The yarn of claim **1** wherein the first group of filaments is of copolymer having between 50 and 95 mole percent of the following repeat units:



Formula I

wherein x is 1 or 2, y is an integer in the range of 7–14, R is H or methyl and between 5 and 50 mole percent of another polyamide unit prepared from a member of the class consisting of (1) the same diamine as employed for production of the Formula I repeat unit with a different dicarboxylic acid and (2) the same dicarboxylic acid as employed for production of the Formula I repeat unit with a different diamine.

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JOHN PETRAKES, Primary Examiner

U.S. Cl. X.R.

28—72; 260—78, 857

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(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,481,133 Dated December 2, 1969

Inventor(s) Robert H. Knospe

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

Column 3, line 30, "unisue" should be --unique--.

Column 6, line 46, "The", first occurrence, should be --Two--.

Column 7, line 45, "117°C." should be --177°C.--.

SIGNED AND
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JUN 2 1970

(SEAL)
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