ELASTOMERICALLY-REINFORCED POLYAMIDE STRAPPING AND METHOD

Filed Sept. 3, 1970

INVENTORS:
HERBERT MAMOK
RAINER HEJL
JOACHIM KÖRNER

Johnston, Root, Ckeffe, Heif, Thompson & Shultoff
ATT'YS
ELASTOMERICALLY-REINFORCED POLYAMIDE STRAPPING AND METHOD

Herbert Mamok and Rainer Hei, Wuppertal-Elberfeld, and Joachim Körner, Remscheid, Germany, assignors to Akasol, Incorporated, Asheville, N.C.

Filed Sept. 3, 1970, Ser. No. 69,261
Claims priority, application Germany, Sept. 17, 1969, G 69 36 419.8
Int. Cl. B52b 5/02, 27/28
U.S. Cl. 161—92

ABSTRACT OF THE DISCLOSURE

A flexible, load-bearing strapping article which consists essentially of an intertwined structure of continuous multifilament yarns of a fibrous polyamide, e.g. nylon 6 (poly- caprolactam) or nylon 6,6 (polyhexamethylene adipamide), which has been reinforced with an elastomeric copolymer of butadiene, styrene, acrylonitrile and methacrylic acid. The article is produced by impregnating and surface-coating the intertwined yarn structure with an aqueous emulsion of the copolymer and then heating to cross-link the copolymer onto the yarn.

Various strapping materials such as straps, belts, ropes, cords, nets and the like are widely employed as a load-bearing means, i.e. where they are partly or completely wrapped around an object and placed under a relatively high load. These strapping materials are most commonly used for lifting and transporting heavy objects or articles or as a means of holding heavy objects in place. If the strapping material is exposed to a strong abrasive or frictional load, it can easily become damaged and useless after only a short period of use. In many instances, a strapping material which is only slightly damaged must be discarded and replaced since any further use would tend to be quite dangerous.

Polyamide threads or yarns have been employed in the manufacture of various strapping articles, and although such polyamide materials offer satisfactory flexibility and tensile strength, they are not sufficiently abrasion-resistant to withstand constant friction or chafing under heavy loads. This is of course generally true of all fibrous strapping materials, regardless of their particular form or structure, i.e. as a strap, belt, rope, net or the like. With only a slight abrasion or wearing away of surface filaments, the strapping becomes substantially weaker and incapable of supporting its originally intended load. Of course, the original strapping article can be constructed to provide a high safety factor, i.e. so that its size and strength are several times larger than that required to support a given load. However, this represents a substantially greater cost per unit length of the strapping material, and the useful life of the strapping material may be only slightly extended, especially where the rubbing or abrasion may be constantly applied at a particular location along the surface of the strapping material.

One object of the present invention is to provide a flexible, load-bearing, heavy duty strapping article which exhibits a very high resistance to abrasion and which has a very long useful life in supporting, lifting or transporting all types of loads. Another object of the invention is to provide an improved strapping article which is relatively light in weight and which can have a relatively small safety factor. Yet another object of the invention is to provide an elastomERICALLY-reinforced strapping article requiring a relatively small proportion of an elastomeric copolymer and exhibiting good adhesion between the copolymer and a polyamide fibrous substrate. Still another object of the invention is to provide a method of producing the particular strapping article of the invention. These and other objects and advantages of the invention will become more apparent upon consideration of the following detailed specification.

It has now been found, in accordance with the invention, that an improved flexible, load-bearing strapping article having excellent resistance to abrasion is one which consists essentially of a plurality of intertwined continuous polyamide multifilament yarns having a tensile strength of at least 7 grams/denier, the intertwined structure being substantially completely impregnated and surface coated with approximately 15 to 30% by weight, with reference to the polyamide yarns, of a heat-crosslinked elastomeric copolymer of butadiene, styrene, acrylonitrile and methacrylic acid. It is to be emphasized that the filamentary structure is not only surface coated with the elastomeric copolymer but also contains this copolymer substantially impregnated or embedded in the hollow zones or open spaces located within the interior of the filamentary structure. It has further been found that the strapping material of the invention can be produced in a very advantageous manner by both impregnating and surface coating it with an aqueous dispersion of the elastomeric copolymer, e.g. by complete immersion in the aqueous dispersion, such that the strapping material takes up approximately 15 to 30% by weight of the copolymer, followed by heating the thus impregnated and surface-coated material at an elevated temperature above about 100° C. and for a period of time sufficient to cross-link the copolymer for adherence to the polyamide yarns. Surprisingly, this vulcanization takes place without the addition of catalysts or accelerators and at temperatures substantially below those which might otherwise damage the polyamide yarns or the elastomeric copolymer. Also, the flexibility of the strapping article is not excessively diminished by its content of the elastomeric copolymer which in itself retains a large degree of elasticity. At the same time, the resistance to abrasion or frictional rubbing and chafing is greatly enhanced.

The term “polyamide” is employed herein with reference to the well-known fiber-forming polyamides which are synthetic high molecular weight polymers having the characteristic—NHCO—recurring unit or linkage in a substantially hydrocarbon linear chain. Such yarns, threads or filaments are often referred to under the generic name “nylons” followed by a numeral to indicate the particular monomer from which the polyamide is prepared. Especially suitable polyamides are the polycaprolactams such as nylon 6, nylon 7, nylon 11 or nylon 12 and also polyhexamethylene adipamide which can be more briefly identified as nylon 6,6. For commercial purposes, nylon 6 and nylon 6,6 are readily available and most economical for preparing the nylon substrate for the strapping article of the invention. It is especially desirable to employ a multifilament polyamide or nylon yarn which has a tensile strength of at least 7 grams/denier, in order to provide the high strength normally required of strapping materials.

It is further desirable to employ a multifilament nylon yarn for the substrate of the strapping article wherein each yarn or thread is composed of a relatively large number of individual fibers or filaments, such that the substrate will absorb a relatively high proportion of the elastomeric copolymer from an aqueous emulsion or dispersion, e.g. with at least about 30% by weight of the total amount of the elastomeric copolymer being impregnated into the interior hollow zones or open spaces of the intertwined polyamide yarn structure. The remaining 70% by weight or less of the copolymer then remains as a surface-coating on the exposed yarn surfaces. Of course, there should be at least a thin film of the copolymer on
the exposed yarn surfaces, i.e. as so as to provide a thin covering film without necessarily providing a flat surface structure completely embedding the substrate within the copolymer. In general, the proportion of the elastic copolymer which is impregnated into the substrate as compared to that which is merely surface-coated thereon depends largely on the exact filamentary structure of the substrate, but in all cases, it is desirable to work within the above-noted limitation of at least 30% by weight of the copolymer being impregnated or embedded within the yarn structure while employing the preferred amount of 15 to 30% by weight of the elastomeric copolymer with reference to the weight of the polyamide yarns. This latter content of the copolymer with reference to the substrate, under specific circumstances, might be extended to about 10 to 40% by weight, for example where smaller amounts may improve flexibility somewhat and abrasion-resistance presents a less significant problem. On the other hand, excessively large amounts of the elastomeric copolymer should normally be avoided in order to maintain maximum flexibility as well as reducing the overall cost.

The polyamide or nylon substrate according to the invention can have a wide variety of shapes or structures as is common with all types of strapping articles. Thus, a strapping article may be in the form of a belt, strap, rope, cord or the like, exhibiting a cross-section varying from an approximately rectangular shape to a flat circular shape. Such strapping articles are also intended to include nets or similar structures having an open mesh, e.g. where individual threads or yarns are knotted at the points of intersection in a rectangular pattern or are woven to provide a similar open mesh structure. Where such a net-like structure is employed, it should be understood that no attempt is made to fill the large open spaces of the mesh with the elastomeric copolymer since this would generally require more than 50% by weight of the copolymer with reference to the individual polyamide threads or yarns. Instead, each thread or yarn in the net-like structure is both impregnated and surface coated individually so as to conform with the requirements of the invention.

In this same context, the term "intertwined" is employed herein in its broadest sense to include knotted yarn structures as well as woven, knitted or relatively highly twisted combinations of individual continuous yarns or threads. Such an intertwined structure is generally necessary to achieve the high tensile strength requirements of strapping materials which normally must support a large load in their linear direction. It is especially preferable to employ polyamide yarns which are intertwined into a flat belt or strap-like structure.

One preferred embodiment of a strapping article in accordance with the invention is illustrated in the accompanying drawing in which:

FIG. 1 is a partly schematic transverse cross-section of a woven belt or strap of continuous nylon yarns impregnated with the particular elastomeric copolymer of the invention.

FIG. 2 is a substantial enlargement of a small portion taken from FIG. 1 in order to better illustrate the manner in which the belt is impregnated and surface-coated.

As shown in FIG. 1, a number of warp threads or yarns 1 are distributed in regular staggered positions over the thickness of the woven structure, and may consist of a single of multi-ply yarn which extends continuously along the length of the belt. The interwoven weft or filling yarns 2 and 3 alternate above and below the warp yarns 1 in a single row or layer while another filling yarn 4 alternates above and below adjacent warp yarns to the topmost and bottommost rows of the woven structure. The resulting intertwined or interwoven structure, depending upon the size of the individual yarns, is quite suitable as a strapping material for handling very heavy loads. This is particularly true where the filling yarns 2, 3 and 4 run continuously back and forth over the width of the belt while extending longitudinally along each side of the belt at the reversal points. In other words, these filling yarns are also continuous throughout the entire structure while being intertwined with a minimum amount of the reinforcing elastomeric copolymer after the belt has been impregnated.

As shown in FIG. 2, the warp yarn 1 is made up of a large number of individual polyamide filaments which may be more or less tightly twisted together in the continuous yarn. This is also true of the filling yarns 2 and 3 as well as the filling or binder yarn 4, all of which are interwoven around the warp yarn 1. With the relatively tight weave of the illustrated nylon belt, there are only relatively small hollow zones or open spaces 5 between the individual yarns. These will be substantially filled by the impregnated copolymer, but it should also be understood that the copolymer will tend to completely permeate each individual yarn depending upon the number of individual filaments and the amount of twist in the individual yarns. In this respect, it is advantageous to employ warp yarns 1 with a relatively high degree of twist while employing filling yarns 2, 3 and 4 with a relatively low degree of twist. The warp yarns are then less saturated with the elastomeric copolymer so as to retain a high degree of longitudinal flexibility, while the filling yarns are more completely saturated and provide a more wear-resistant surface structure. It will also be noted that the exposed surfaces of the outermost filling yarns 2 have only a thin film of the elastomeric copolymer adhered to their surfaces. However, this outer surface-coating 6 of the elastomeric copolymer tends to follow the surface irregularities of the substrate and generally is not applied in a thick layer which completely obscures or covers the woven appearance of the belt.

It will be recognized that the invention is not limited to this illustrated embodiment since strapping articles may be provided wherein the polyamide yarn structure or substrate can be woven, braided, plaited, knitted, twisted or otherwise intertwined into a relatively strong belt, strap, cord or the like. It is quite critical, however, to employ a reinforcing elastomeric copolymer which will not only provide a highly improved abrasion-resistance but which will also strongly adhere to the polyamide or nylon yarns. Moreover, it is quite desirable to employ an elastomer which can be applied to the yarn from an aqueous emulsion or dispersion in relatively low concentrations so as to substantially completely permeate or impregnate the substrate. The method of producing the strapping article or material according to the invention is thus directed to the use of a particular type of elastomeric copolymer or so-called interpolymer which is composed predominantly of butadiene and minor amounts of styrene and acrylonitrile together with a significant proportion of methacrylic acid. All four of these components are considered to be essential for achieving the results of the present invention. Their proportions, however, may be varied within conventional limits so as to yield an elastomeric and at least potentially cross-linkable copolymer.

The elastomeric copolymer employed for purposes of the present invention is obtained by the conventional emulsion polymerization of the monomers within the following approximate proportions:

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Percent by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butadiene</td>
<td>55-65</td>
</tr>
<tr>
<td>Styrene</td>
<td>25-15</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>10-2</td>
</tr>
<tr>
<td>Methacrylic acid</td>
<td>10-18</td>
</tr>
</tbody>
</table>

Especially good results have been achieved with a commercially available elastomeric copolymer or interpoly-
mer identified as Perbunan-SN-Latex 15M, which is a copolymer of approximately 60% by weight of butadiene, 20% by weight of styrene, 5% by weight of acrylonitrile and 15% by weight of methacrylic acid. These approximate proportions are therefore particularly adapted to achieve the results of the present invention.

Such elastomeric copolymers can be readily dispersed in water for application to the filamentary polyamide substrate, e.g. by immersion in an aqueous bath. The concentration of the elastomeric copolymer in the aqueous bath can be adjusted so that the substrate will take up the required amount of the copolymer. In general, this concentration can range from about 10 to 30%, preferably about 15 to 22% by weight, depending upon the length of time during which the substrate is retained in the bath and its absorptivity for the emulsion. The individual polyamide yarns should become substantially completely impregnated or saturated with the aqueous dispersion of the elastomeric copolymer, and relatively small open spaces between adjacent yarns will also tend to become completely filled with the copolymer. Large open spaces, e.g. as in a net-like construction, will tend to remain free of the aqueous dispersion and copolymer, particularly after excess dispersion has been drained off from the substrate. Therefore, a substantially complete impregnation is achieved within the meaning of the present invention when the individual yarns have reached their saturation point.

The impregnated and surface coated substrate can initially be dried to remove a substantial amount of water, or the substrate is preferably immediately subjected to a heat treatment at an elevated temperature above 100°C., preferably about 110°-130°C., for a period of time sufficient to heat-vulcanize the copolymer and adhere it to the substrate. It is common to employ a cross-linking agent or accelerator such as zinc oxide for the purpose of vulcanizing or cross-linking this type of copolymer, it was surprisingly found that such additions are not necessary and in fact should be avoided for purposes of the present invention. The desired degree of cross-linking is achieved solely in the presence of the polyamide, and the resulting heat-crosslinked copolymer retains its elastomeric character, whereby indicating that only a partial cross-linking has occurred or that cross-linking takes place with the polyamide itself rather than between the molecules of the copolymer. It can be assumed that the free carboxylic groups contributed by the methacrylic aid to the copolymer take part in a cross-linking type reaction when the copolymer is exposed to elevated temperatures. However, the exact mechanism is not clearly understood except for the fact that the polyamide substrate has a definite influence on the cross-linking. Thus, the same results are not achieved if the elastomeric copolymer is merely heat-vulcanized in the absence of the polyamide or some cross-linking agent, and very substantially different results are achieved if a cross-linking agent such as zinc oxide is added to the copolymer.

The time required for the heat-treatment or heat-cross-linking step of the present invention is not critical although it requires a sufficiently long period of time to achieve a noticeable cross-linking. Higher temperatures naturally reduce the amount of time required while lower temperatures extend this period of time. The most efficient period of heat-treatment can thus be readily determined by a few routine tests.

The following example will further illustrate the invention without any intention of limiting the invention to this specific example.

**EXAMPLE**

The nylon or polyamide substrate is in the form of a belt consisting of several layers of interwoven continuous nylon 6,6 yarns with five plies or threads in each yarn. This belt is impregnated by immersion in a trough or tank which contains a 17-18% aqueous dispersion of a copolymer of butadiene, acrylonitrile, styrene and 15% methacrylic acid, as identified above under the trademark Perbunan-SN-Latex 15M (obtained from Farbenfabriken Bayer AG Leverkuren, Germany). The belt is drawn slowly through the trough until it is substantially completely saturated with the aqueous dispersion and is then drawn vertically out of the trough, thereby permitting excess dispersion to run off and the retained in the trough. Then, without any further addition of other substances to the impregnated belt, it is heated for about five to fifteen minutes at 110°C. to 130°C. This relatively short period of thermal treatment is sufficient to cross-link the applied copolymer and causes it to become firmly adhered to the nylon substrate. The belt then contains 18 to 20% by weight of the heat-crosslinked copolymer which is embodied within the interior of the belt as well as being coated as a thin film on its surface. Individual yarns within the treated belt also exhibit a high degree of saturation and surface-coating with the copolymer.

The resulting belt, produced in accordance with the invention, is then subjected to an abrasion test for comparison with a non-treated nylon belt of identical construction. In essence, this test is carried out by pressing each belt with equal force against a rotating rough concrete roller and separating the resulting rubbing or abraded particles by immersion of the roller in water.

In particular, the test apparatus includes a concrete roller with a circumference of 1 meter which is rotated at a speed of 30 revolutions per minute by means of any suitable drive means. The individual belt being tested is applied over an angle of 120° of the roller circumference while being held in a fixed position at one end and attached to a load of 8 kilograms at its opposite freely hanging end. Under these identical conditions, each belt is abraded on both sides, in each case with 500 revolutions of the roller. The rubbings or abraded particles are removed from the roller in a dipping tub positioned beneath the roller so that it passes partially through this tub. Upon completion of the test, the individual belts are visually inspected and subjected to a test for tensile strength as shown in the following table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength in tons (2,000 kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before abrasion</td>
<td>After abrasion</td>
</tr>
<tr>
<td>I. Belt treated with elastomeric copolymer</td>
<td>14.1</td>
</tr>
<tr>
<td>II. Non-treated belt</td>
<td>18.4</td>
</tr>
</tbody>
</table>

The difference in tensile strength on the two belts before the abrasion is attributed in part to the fact that the treated belt broke across the girth while the non-treated belt broke along the seam. After abrasion, both belts broke at the point of abrasion.

As can be seen from the foregoing table as well as the greater amount of rubbings or abraded particles taken from both belts, the belt according to the invention exhibits an abrasion resistance which is almost five times higher than the abrasion resistance of the non-treated belt. In addition to this improved abrasion resistance, there is also a substantial increase in the tensile strength of the loops located along both edges of the belt treated in accordance with the invention.

The non-treated belt used for purposes of comparison, is very strongly damaged at the point of abrasion. By comparison, the treated belt according to the invention exhibits only a very slight change in appearance so that one would not hesitate to continue its use as a strapping article.

The polyamide or nylon yarns do not require any special pretreatment either before or after they are incorporated into the interwoven continuous strapping material or substrate. The elastomeric copolymer adheres firmly to the yarns to provide a very continuous film coating on the exposed surfaces as well as impregnating the yarns so that individual filaments or fibers are con-
solidated or held firmly to one another. This in itself is quite surprising since many elastomers exhibit a poor adhesion on nylon without using an intermediate adhesive or bonding agent.

The initial polyamide yarns may contain conventional aqueous finishing agents or preparations in small amounts which are insufficient to have any noticeable effect upon the impregnation or application of the elastomeric copolymer from its aqueous dispersion. In this respect, conventional emulsifying agents may also be present, e.g. as normally used on nylon fibers or in elastomer emulsions. On the other hand, oily or hydrophobic preparations or finishing agents, e.g. mineral oil finishes or the like, should be avoided or removed before the nylon substrate is impregnated. More than about 1% by weight of such oily preparations on the initial nylon yarns would of course make it more difficult to achieve a complete impregnation with the aqueous dispersion of the elastomeric copolymer.

The considerable improvement in abrasion resistance of the strapping material depends upon the fact that the yarns or substrate are not only surface-coated or provided with just a film over the outer exposed surfaces but are also highly impregnated so as to consolidate and strengthen the entire structure. It is for this reason that the substrate must be substantially completely impregnated, i.e. at least to the minimum extent required by the invention. The resistance to rubbing or frictional abrasion is thus not limited to a surface phenomenon but continues even after the original surface has been worn away. Also, a loosening of individual filaments or fibers does not occur during abrasion, and a frayed effect with a tendency to cause further deterioration due to the rubbing of filaments against each other is considerably if not completely avoided.

If desired, the nylon substrate can also be colored or dyed at the same time that it is impregnated with the elastomeric polymer by incorporating suitable dyes or pigments in the aqueous emulsion. Pigment dyes are especially suitable for this purpose and may be employed in conventional amounts to achieve the desired coloration. Other essentially inert additives may be incorporated in the impregnation bath but are not required.

The reinforced strapping article or material of the invention has an exceptionally long useful life, even when subjected to extreme conditions of wear and tear, and therefore represents a substantial economy for all heavy duty industrial or commercial applications.

The invention is hereby claimed as follows:

1. A flexible, load-bearing, abrasion-resistant, elastomerically-reinforced strapping article consisting essentially of a plurality of intertwined continuous polyamide multifilament yarns having a tensile strength of at least 7 grams/denier, the intertwined structure being substantially completely impregnated and surface coated with approximately 15 to 30% by weight, with reference to the polyamide yarns, of a heat-crosslinked elastomeric copolymer which consists essentially of an emulsion copolymer of 55 to 65% by weight butadiene, 25 to 15% by weight styrene, 10 to 2% by weight acrylonitrile and 10 to 18% by weight methacrylic acid.

2. A strapping article as claimed in claim 1 wherein said polyamide yarns are composed of a polymer selected from the class consisting of nylon 6, nylon 7, nylon 11, nylon 12 and nylon 6.6.

3. A strapping article as claimed in claim 1 wherein said elastomeric copolymer is composed of approximately 60% by weight of butadiene, approximately 20% by weight of styrene, approximately 5% by weight of acrylonitrile and approximately 15% by weight of methacrylic acid.

4. A strapping article as claimed in claim 1 wherein said polyamide yarns are interwoven into a flat belt.

5. A strapping article as claimed in claim 1 wherein at least 30% by weight with reference to the total amount of said elastomeric copolymer is impregnated into the interior open spaces of the intertwined polyamide yarn structure while the remainder is surface-coated on the exposed yarn surfaces.

References Cited

UNITED STATES PATENTS

3,582,446 6/1971 Stolki 161—89
3,577,310 5/1971 Torii et al. 161—88
2,929,795 3/1960 Reid et al. 260—80.7 X
3,070,583 12/1962 Uranick et al. 260—80.7 X
3,118,854 1/1964 Hess et al. 260—80.7 X

WILLIAM J. VAN BALEN, Primary Examiner
M. A. LITMAN, Assistant Examiner

U.S. Cl. X.R.

117—138.8; 161—95, 255; 260—80.7