United States Patent Office 3,248,258
Patented Apr. 26, 1966



3,248,258

# NYLON YARN TREATED WITH A FINISHING COMPOSITION

Fred Haden Coats, Jr., Chattanooga, Tenn., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Feb. 10, 1965, Ser. No. 431,730
3 Claims. (Cl. 117—138.8)

This application is a continuation-in-part of copending application Serial No. 253,272 filed January 23, 1963, now abandoned.

This invention relates to the production of tire cord structures and, more particularly, to improved finishing compositions therefor.

In the production of filamentary material, it is customary to apply a finish composition to the freshly spun filaments to act as a lubricant for the yarn during subsequent processing and in its end use. For ease of application and economics, the finish is customarily applied as an aqueous emulsion or dispersion.

When cord structures prepared from polyhexamethylene adipamide (6–6 nylon), polycaproamide (6 nylon) or other known nylons, or from copolymers thereof, are to be used as reinforcements in rubber products such as tires, it is common practice to dip the cord structure in an aqeous latex dispersion prior to its incorporation in the tire carcass. This promotes better adhesion with the rubber stock. Due to the aqueous nature of latex dip dispersions, aqueous finish compositions of the type mentioned above are stripped from the yarn in the dip bath to an extent that the amount of lubricant remaining is not sufficient to maintain proper interfilament frictional properties. This insufficiency contributes to early flex fatigue.

The object of this invention is to provide filamentary structures which not only can be treated to insure good adhesion to rubber but also exhibit improved fatigue resistance when used as reinforcements in rubber products.

This and other objects are attained in this invention in a nylon filamentary yarn, the filaments of which contain from 1 to 3 percent by weight of a finish composition comprising 3 to 10 parts of a liquid, oil-insoluble, non-ionic surfactant selected from the class consisting of (a) partial esters of long-chain aliphatic acids having between 12 and 20 carbon atoms per molecule and the condensation product of one mol of a hexitol with at least about 30 mols of ethylene oxide and (b) the condensation product of one mol of an alkylphenol with at least about 15 mols of ethylene oxide, dispersed in 90 to 97 parts of an ester lubricant selected from the class consisting of natural and synthetic glyceryl triesters having a melting point below 25° C. and being free from strongly polar groups.

The lubricants suitable for use in the present invention are natural or synthetic glyceryl triesters which are liquid at room temperature, and which contain no strongly polar group, e.g., hydroxy, amine or carboxylic acid group. Examples of such compounds include coconut oil, glyceryl triacetate and glyceryl trioleate. Compounds which are similar in structure to the above-mentioned esters but which have a melting point higher than about 25° C. and/or contain strongly polar groups produce a surprising and deleterious effect on adhesion.

The finish compositions of the invention also include a surfactant. The type of surfactant used in conjunction with the lubricant is critical. It is esssential that the surfactant be a non-ionic, oil-insoluble material. The unsuitability of oil-soluble, non-ionic surfactants alone is believed to be due to insufficient wetting of the cords by the aqueous dip, thus interfering with dip application and causing a loss in adhesion. By the term oil-insoluble is



indicated lack of substantial solubility at the usual temperature at which finishes are formed and applied.

The amount of non-ionic surfactant used with the lubricant must be within the range of 3 to 10 percent by weight, based on the combined weight of the lubricant and surfactant if a suitable increase in fatigue resistance is to be achieved. To promote wetting of the cords by the aqueous dip and to minimize static, it has been found that a minimum of about 3 percent by weight must be added to the lubricant. However, if more than about 10 percent by weight is used, the surfactants promote emulsification of the lubricant, as when the cord is passed throug the dip bath, to an extent that flex life is seriously impaired. In general, about 4 to 6 percent of surfactant is the preferred range.

If desired, small amounts of other non-ionic surfactants, including those soluble in the lubricant, may be used in the compositions of this invention for particular purposes, as to increase the stability of the non-aqueous emulsion or to aid in the repression of static. When employed, such materials should not exceed about 3 percent of the total weight nor should the total weight of surfactant (oil-soluble and oil-insoluble) exceed 10 percent of the weight of the composition. In general, the use of such secondary materials will be neither necessary nor desirable. In addition, small amounts of bactericides, antioxidants and the like may also be added as required.

The amount of finish to be applied to the yarn lies within a relatively narrow range. Below this range, insufficient lubrication results in reduced flex life, while above this range, adhesion and processability are adversely affected. While the amount of finish on the fibers may vary from about 1 to 3 percent of the weight of the fibers, optimum results are obtained when the amount of finish is within the range of about 1.5 to 2.8 percent of the weight of the fibers.

While this invention is primarily concerned with non-aqueous systems the objects to this invention may be achieved by employing the more conventional aqueous route. This may be accomplished by using a minimum amount of surfactant commensurate with emulsion stability and emulsifying the lubricant to form an aqueous emulsion, and applying the minimum amount to the yarn consistent with acceptable processing requirements. In this manner there may be obtained a cord having 0.5 percent by weight of finish ingredients of which 15 percent by weight is emulsifier. The cord is then given a second pass through pure lubricant to add and additional 1.3 percent by weight giving a cord which contains a total of 1.8 percent by weight of finish of which 4 percent is emulsifier. Cords prepared in this way show good adhesion and the flex life is markedly superior to control yarns and approaches the level achieved by the non-aqueous route. The lower flex life is believed due to the reduced uniformity of the finish resulting from the necessary two-step application. The aqueous emulsions with their abnormally low emulsifier content require the best known art of emulsification in order to be operable, and even then an on-line emulsifier is required to minimize the problems attendant to low emulsion stability. For these and other reasons, the non-aqueous emulsions of this invention are preferred.

The finish compositions of this invention may be applied to the continuous multifilament yarn in any known suitable manner, for example by passing the yarn through a bath of the finish. The treated yarns are then processed to cord structures suitable for the reinforcement of rubber goods by methods well known in the art. There are many variations in the conditions selected for twisting, plying, latex dipping, stretching, etc., which will depend upon the initial properties of the cord, its ultimate

use, the choice of rubber stock and other factors, and these form no part of the present invention.

For any given conditions of treatment, the amount of latex or other adhesive solids remaining on the cords after coating will vary somewhat along the length of the cord, and since low solids levels tend to give low adhesion levels, a higher solids value is generally used than otherwise might be the case. On the other hand, excessive adhesive solids must be avoided since this condition also leads to low adhesive strength levels. For nylon cords, the dip is conventionally applied to give 4 to 6 percent adhesive solids, at which level adhesion measured at room temperature, of the cord to rubber stocks used for tire construction will often be so great that failure is due to stock tear rather than to insufficient adhesion.

In certain instances, a lower level of adhesive pick-up, as occurs along the length of a cord where the dip solid content falls below the 3 to 4 percent level, is not deleterious. For example, in addition to a very noticeable improvement in fatigue resistance, it has been discovered that cords finished with a composition of the invention containing a particular ester of a condensate of sorbitol and about 30 mols of ethylene oxide exhibit significantly improved adhesion characteristics at low levels of dip (adhesive) pick-up. This ester is obtained by esterifying the above condensate with a mixture of oleic and lauric acids, preferably in a ratio of 4 mols of oleic acid to 1 mol of lauric acid; 5 mols of the acid mixture are used for each mol of the condensation product. Compositions containing this ester are a highly preferred embodiment of this invention.

In the examples that follow, except where noted, the finish composition, in which the parts stated are by weight, is applied to freshly spun, 840 denier, 140 filament, 6–6 nylon yarn by advancing the yarn over a roller running in a finish trough positioned between a convergence guide and draw zone. After being finished and drawn, the yarn is given 13 turns per inch of Z-twist. Two of these Z-twisted strands are then plied together with 13 turns per inch of S-twist to form a cord having a final denier of about 1900. A latex dip mixture is applied by running the cord through a dip bath, and the treated cords are then at 300° F. for 2.2 minutes under 2 percent applied stretch. The amount of solids deposited on the cords should be at least 1 percent, and preferably from 3 to 7 percent. After drying, the cord is hot-stretched by applying 11 percent stretch at 380° F. for 0.3 minute.

The latex dip is an aqueous mixture of a resorcinol-formaldehyde resin and a copolymer comprising butadiene and vinyl pyridine ("Gen-Tac"); the resin is prepared by adding 13 parts of 0.5 N sodium hydroxide and 1.9 parts of resorcinol to 2.8 parts of 37% formaldehyde. After allowing the resulting solution to stand six hours at room temperature, 42.8 parts of 40% "Gen-Tac" and 39.4 parts of water are then added to the resorcinol-formaldehyde condensate. This aqueous mixture may then be diluted as desired or applied to the cord as prepared. The dip should be prepared fresh at the time of use since the viscosity increases with time.

Samples of nylon cords which have been treated as described above are molded into H-block specimens, using a natural rubber tire carcass stock. Similar results are obtained with SBR or natural —SBR stocks. After removal from the mold, adhesion of the cord to rubber in each block is determined by measuring the force required to separate the cord from the rubber. The measurement may be carried out at room temperature or at an elevated temperature, e.g., 121° C. Cord fatigue life is determined by the test described in ASTM Method D–885; in this test, the cords are subjected to alternating compression and tension forces to the point of failure.

## EXAMPLE I

A finish composition of the present invention is prepared by adding 5 parts of the product obtained by esterifying the condensation product of 30 mols of ethylene oxide and 1 mol of sorbitol with 5 mols of a 4:1 (mols) mixture of oleic and lauric acids to ninety-five parts of coconut oil. The finish is then applied to nylon yarn.

After finishing, yarn containing 2.5% by weight of the above dispersion is twisted, plied and passed through a 5 percent latex dip to give cord A, through a 10 percent latex dip to give cord B and through a 15 percent latex dip to give cord C. Samples of cords A, B, and C are used to prepare H-block and fatigue test specimens.

For purposes of comparison, additional cord samples D–I are prepared and incorporated into H-blocks. Samples D, E and F are similar to samples A, B and C except for the use of an aqueous finish which is prepared in stable form by emulsifying coconut oil. A 20% emulsion containing coconut oil and emulsifier in a ratio of 7 to 3 is used. The yarn contains 2.5 percent of the finish, based on the weight of the yarn.

Samples G, H, and I are similar to Samples A, B, and C except for the use of an alternative but closely related esterified ethylene oxide condensation product. The alternative product is a condensation product of sorbitol with 40 mols of ethylene oxide which has been esterified with a relatively high percentage of oleic acid in order to give a material insoluble in water. A composition containing 5 percent of this product and 95 percent of coconut oil is applied to the nylon yarn as described above. The finished yarn contains 2.5 percent of the finish composition, based on the weight of the yarn.

*Table I*

| Cord | Percent Dip Solids | H-Block Adhesion pounds | C.T. Fatigue, Kilocycles to Failure |
|---|---|---|---|
| A | 1 | 24.6 | |
| B | 2.5 | 27.0 | |
| C | 4 | Stock Tear | 1,642 |
| D | 1 | 22.0 | |
| E | 2.5 | 25.2 | |
| F | 4 | Stock Tear | 1,204 |
| G | 1 | 17.8 | |
| H | 2.5 | 23.0 | |
| I | 4 | Stock Tear | 1,546 |

From the results, is is apparent that yarns of this invention (A, B and C) provide reinforcement cords which exhibit not only an improved level of fatigue resistance but also a high level of adhesive strength at dip solids contents as low as 1 percent.

## EXAMPLE II

In this example the surfactant of Example I is used with a range of lubricants to further illustrate the invention. This example also shows that the use of lubricants having (1) a melting point above 25° C. and/or (2) strongly polar groups results in a loss of adhesion. Five parts of the surfactant used for Samples A, B and C of Example I are used with 95 parts of the lubricants shown in Table II. The cords are prepared and tested as in Example I except that the cords contain 5 percent dip solids and adhesion is measured at 121° C.

*Table II*

COMPARISON OF TIRE YARN FINISH LUBRICANTS

| Lubricant | Melting Point, ° C. | Static Adhesion (lbs.) | C.T. Fatigue Life (kc.) |
|---|---|---|---|
| Coconut Oil | 22–25 | 23 | 1,534 |
| Glyceryl Triacetate | −78 | 23 | 1,621 |
| Glyceryl Trioleate | −17 | 23 | 1,560 |
| Glyceryl Trilaurate | 46.4 | 12 | 1,530 |
| Glyceryl Trioleate/Glyceryl monooleate 50/50 | <25 | 17 | 1,410 |

## EXAMPLE III

This example illustrates the use of alkylphenolethylene oxide condensates in the practice of this invention. Five parts of the surfactant are used with 95 parts of coconut oil. In Sample J, the surfactant used is prepared by condensing 1 mol of nonylphenol with 6 mols of ethylene oxide; the condensate dissolves in the lubricant to give a solution. In Sample K, the surfactant used is prepared by condensing 1 mol of nonylphenol with 15 mols of ethylene oxide; the condensate is not soluble in the lubricant and the admixture is a two-phase system. Cords are prepared and tested for adhesion as in Example I except that the cords contain 2 to 2.5 percent dip solids. Sample K has an adhesion level of 25.1 lbs. while that for Sample J is only 21.6 lbs.

It will be appreciated by those skilled in the art that variations from the details given can be made without departing from the scope of the present invention.

What is claimed is:

1. Nylon filamentary yarn, the filaments of which are treated with from 1 to 3 percent by weight of a finish composition consisting essentially of 3 to 10 parts of a condensation product of an alkylphenol and at least 15 mols of ethylene oxide dispersed in 90 to 97 parts of a



member selected from the group consisting of coconut oil, glyceryl triacetate and glyceryl trioleate.

2. Nylon filamentary yarn, the filaments of which are treated with from 1 to 3 percent by weight of a finish composition consisting essentially of 3 to 10 parts of the pentaester of a 4:1 mixture of oleic and lauric acids and the condensation product of a mol of sorbitol and at least 30 mols of ethylene oxide dispersed in 90 to 97 parts of coconut oil.

3. Nylon filamentary yarn, the filaments of which are treated with from 1 to 3 percent by weight of a finish composition consisting essentially of 3 to 10 parts of the condensation product of nonylphenol and at least 15 mols of ethylene oxide dispersed in 90 to 97 parts of coconut oil.

**References Cited by the Examiner**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 1,803,869 | 5/1931 | Ruff | 117—139.5 |
| 2,418,752 | 4/1947 | Brown | 117—139.5 |
| 2,810,694 | 10/1957 | McLean et al. | 252—8.8 |
| 2,876,127 | 3/1959 | Willis | 117—139.5 X |


WILLIAM D. MARTIN, *Primary Examiner.*