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[54] **SYNTHETIC YARN COATED WITH A SPIN FINISH AND PROCESS FOR PRODUCING THE SAME**
9 Claims, No Drawings

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ABSTRACT: Spin finish for yarns to be bonded to rubber includes polyvinyl alcohol and microcrystalline or emulsifiable polyethylene wax. The wax has a melting point of at least 50° C. and a penetration at 77° F. of between 1 and 10 in accordance with ASTM test method D-1321-55T.

SYNTHETIC YARN COATED WITH A SPIN FINISH AND PROCESS FOR PRODUCING THE SAME

This application is a continuation-in-part of my copending application Ser. No. 838,001, filed June 16, 1969, which in turn was a continuation of application Ser. No. 523,970, filed Feb. 1, 1966, which in turn was a continuation-in-part of application Ser. No. 332,837, filed Dec. 23, 1963, now all abandoned.

The present invention relates to yarn coated with a spin finish formulation, the yarn being particularly useful in the construction of laminated articles such as tires, rubber belts, etc., and to methods for making such yarns.

Melt spun polymers such as nylon are commonly treated with a spin finish applied shortly after the molten filaments solidify and are gathered into a yarn bundle, and before the yarn is drawn. The spin finish is added to improve the ease of processing of the yarn, and adds several desirable characteristics to the yarn. A primary function of the spin finish is to lubricate the yarn in the subsequent drawing operation. Other characteristics which are imparted to some degree by the spin finish include improvement in the hand of the yarn, reduction of static electricity, and an increase in abrasion resistance. According to the present invention, inclusion of specific concentration ranges of certain components in the spin finish imparts a significant increase in tensile strength to the yarn, which is particularly advantageous in applications wherein the yarn is used as a reinforcement in laminated articles, such as automotive tires or rubber belts. In addition, the finish imparts increased durability to articles incorporating the yarn.

Accordingly, a primary object of the invention is to provide a yarn treated with a novel spin finish formulation which provides an increase in durability and tensile strength of the yarn, the finish being capable of application to the yarn as an aqueous emulsion. A further object is to provide a yarn having an increased tensile strength, and products made of such yarn. A further object is to provide a method for making yarn of increased tenacity, which bonds well to rubber.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

It has been discovered that a substantial and marked increase in yarn breaking strength and flex life is achieved by treating the freshly spun yarn with a spin finish so as to apply to the yarn between 0.0075 and 0.25 percent waxoidal lubricant, between 0.005 and 0.2 percent polyvinyl alcohol, between 0.02 and 0.875 percent of liquid lubricant, all based on the weight of the yarn, together with sufficient emulsifier to disperse these components in water for ease of uniform application to the yarn.

The term "polyvinyl alcohol" as used herein is used in its accepted trade sense, and refers to the water-soluble polyalcohol normally prepared by partially saponifying polyvinyl acetate. Particularly useful and preferred are those polyvinyl alcohols wherein from 70 to 100 percent of the acetate groups have been replaced by hydroxyl groups, and wherein the molecular weight is such as to give a viscosity in 4 percent aqueous solution (at 20° C.) from 2 to 60 centipoises. Especially preferred is the viscosity range between 4 and 6 centipoises.

Suitable low-temperature lubricants or oils according to the present invention include the many known yarn lubricants which are liquid at room temperature. The oils may be of vegetable, marine, or of petroleum origin. Among the vegetable oils, there may be mentioned linseed, soybean, corn, peanut, castor, rapeseed, and olive oils. Suitable marine oils are menhaden oil, whale oil and sperm oil. Applicable mineral oils are those whose viscosities vary between the kerosenes and the heavy motor oils with a highly refined, colorless mineral oil being preferred. Mineral oils having Saybolt viscosities of from 30 to 180 seconds at 100° F. are considered of especial advantage. Various of the so-called synthetic lubricants may also be used to advantage. Among the synthetic lubricating oils which can be suitably employed are the various polyalkylene glycols, commercially available from the Carbide and Carbon Chemical Company and known commercially as

Ucons. In addition, the fatty acid esters can be used to advantage. The esters may be either mono-, di-, triesters, etc., or mixtures thereof. The fatty acid portion of the ester can contain anywhere from one to about 22 carbon atoms; and may be derived from such fatty acids as acetic, propionic, lauric, myristic, palmitic, stearic, adipic, azelaic, benzoic, citric, abietic, fumaric, phthalic, oleic, ricinoleic, sebacic, succinic, tartaric, etc. The alcohol portion may be derived from either monohydric or polyhydric alcohols which contain from one to three hydroxyl groups. Suitable examples are methanol, ethanol, 2-methyl 1-propanol, 1-pentanol, heptanol glycerol, and many others. Among specific examples of suitable esters are isopropyl palmitate, butyl stearate, isopropyl myristate, isobutyl laurate, methyl abietate, dibutyl adipate, diisooctyl adipate, di-2-ethylbutyl azelate, glycerol monoacetate, glycerol tripropionate, di-n-butyl maleate, n-propyl oleate, amyl oleate, isopropyl palmitate, isooctyl palmitate, dimethyl phthalate, butyl octyl phthalate, di (2-ethyl-hexyl) phthalate, isobutyl ricinoleate, glycerol monoricinoleate, dioctyl sebacate, n-butyl stearate, octyl stearate, dibutyl succinate, diethyl tartrate, etc. A particularly advantageous class of fatty acid esters is mixed triglycerides which may be represented by the following formula:



wherein R designates saturated or unsaturated aliphatic radicals. Either one or two of the R groups contain from one to five carbon atoms having at most one double bond while the remaining R group or groups may contain from 12 to 22 carbon atoms with from zero to five double bonds. The location of the shorter carbon chain aliphatic radicals with respect to the glyceryl radical is not of critical importance, i.e., it may be in either the alpha, beta or gamma position. Some examples of suitable compounds of this type are glycerol monoricinoleate diacetate, glycerol monolinoleate, diacetate, glycerol monolinolenate diacetate, glycerol monoacetate dilinoleate, glycerol monoacetate diricinoleate, glycerol monolaurate dibutyrate, glycerol monolaurate divalerate, etc. Various phosphoric acid derivatives may also be suitably employed. Examples of such compounds include triethyl phosphate, tributyl phosphate, triphenyl phosphate, tri-(2-ethylhexyl) phosphate, tributoxyethyl phosphate, tricresyl phosphate, cresyl diphenyl phosphate, tri-dimethylphenyl phosphate, diphenyl mono-o-xenyl phosphate, tri-p-tertbutylphenyl phosphate, diethyl ethylphosphonate, dibutyl butylphosphonate, bis (2-ethylhexyl) phosphonate, tris (2-chloroethyl) phosphite, etc.

The liquid lubricant is added to the finish formulation primarily to lubricate the yarn during further processing, such as drawing the yarn, twisting, etc. and should constitute between 0.02 and 0.875 percent of the weight of the yarn to provide adequate drawing performance with a minimum number of filament breaks.

The term "waxoidal lubricant" as employed in the specification and claims means either or both of microcrystalline waxes and emulsifiable polyethylene, which materials may be oxidized or nonoxidized, and must have a melting point of at least 50° C. and a penetration at 77° F. of between 1 and 10 in accordance with ASTM test method D-1321-55T. The preferred emulsifiable polyethylene is commercially available from Tennessee Eastman Company as Epolene E-10. Best results are achieved with microcrystalline waxes, which have a finer, less apparent crystalline structure than paraffin wax, and comprise a solid hydrocarbon mixture of molecular weight averaging higher than paraffin wax. These waxes possess plastic properties and are obtainable from crude petroleum fractions. All microcrystalline waxes are said to be of about the same molecular weight and to be composed of hydrocarbon chains of twice the length of those of the paraffin waxes.

Commercially available products are exemplified by Crown Wax 23, Crown R50, Bareco Wax C-7500 and C-6500 of the Petrolite Chemical Corporation, and Cardis 320, Mekon Y-20 and Fortex of the Warwick Wax Company.

Other known wax types are generally unsatisfactory because of unsatisfactory durability in tires constructed using the yarn, or because of unsatisfactory adhesion to rubber, or both. Microcrystalline wax is preferred over the emulsifiable polyethylene wax because of superior durability.

Any of the known emulsifying agents, which are capable of dispersing the lubricants in an aqueous medium to form an emulsion which is stable over extended periods of time and at elevated temperatures, may be employed in the practice of this invention. While a number of available emulsifiers can be employed, the amine soaps are particularly suitable. The amine soap may be derived from a fatty acid containing at least about eight carbon atoms with from about 12 to 22 carbon atoms being preferred. Oleic acid is highly suitable, but such fatty acids as lauric, palmitic, myristic, stearic, behenic and the like may be used if desired either in whole or in part. Animal, marine and vegetable oils are suitable sources for the fatty components of these soaps. Any water-soluble aliphatic amine may be employed in forming the soap, but the lower alkylamines are preferred as exemplified by the primary, secondary, and tertiary amines of ethanol, propanol, isopropanol and the several butanols. Triethanolamine and 2-amino 2-methyl 1-propanol are particularly outstanding for this purpose. Other suitable amines include the various primary, secondary and tertiary methyl, ethyl, propyl, isopropyl and butyl amines and morpholine. The amine soaps may be either prepared in advance or in situ by the addition of the amine and an appropriate fatty acid to the aqueous vehicle.

It is often desirable to include a nonionic surface action agent as a part of the emulsifying system in that these materials tend to suppress the accumulation of static during the drawing operation in addition to providing increased emulsion stability. Among agents of this type which may be employed are the polyoxyethylene ethers of a long chain fatty alcohol or thiol and the polyoxyethylene esters derived from long chain fatty acids. The long chain fatty alcohols and long chain fatty acids from which these materials are formed may contain from about 12 to 40 carbon atoms in their alkyl chains and these chains may be straight or branched. The fatty acids and fatty alcohols may be commercially pure single compounds or mixtures of such single compounds of one type, i.e., acids or alcohols, or they may be mixtures that are obtained from naturally occurring products. Suitable long chain fatty alcohols are, for example, dodecyl alcohol, tridecyl alcohol, cetyl alcohol, myristyl alcohol, linoleyl alcohol and the mixture of alcohols derived from sperm oil. The alkylated phenols such as octyl phenol and nonyl phenol may also be employed. Suitable long chain acids are, for example, lauric acid, oleic acid and the mixture of acids derived from coconut oil. In producing the polyoxyethylene ethers and esters, ethylene oxide may be permitted to act directly on the long chain fatty alcohols and long chain fatty acids. Alternatively, the long chain fatty acids and long chain fatty alcohols may be reacted with a polyethylene glycol. The length of the polyethylene oxide chain may be varied over a considerable range, satisfactory results having been obtained with chain lengths of from about 2 to 50 ethylene oxide units. A particularly effective nonionic emulsifier of this type is the adduct formed by reacting 1 mol of tridecyl alcohol with an average of 9 mols of ethylene oxide.

The amount of the waxoidal lubricant finally selected is determined by a compromise between an increase in tire flex life durability and a simultaneous decrease in adhesion to rubber. Table I generally illustrates the effect of addition of microcrystalline wax as a finish component of nylon tire yarn, wax content being expressed as percent of the weight of the yarn.

TABLE I

Wax Content

	0%	0.065%	0.13%	0.195%
Tire Durability, Miles*	1,000	2,500	3,000	3,300
Core-to-Rubber Adhesion Strip Test, Pounds**	33	29	17	9

* (Tire run at 150 percent overload, inflated at 50 percent of proper pressure, and run at 45 miles per hour until failure. Number indicates miles run before failure of the tire.)

** (Cord formed into fabric and laminated in rubber. Number indicates pounds force required to separate given area of rubber from fabric.)

As may be seen, incremental addition of the wax to the finish composition increases tire flex life markedly at low wax concentrations, and then becomes less effective as the wax approaches 0.25 percent of the weight of the yarn. However, the cord-to-rubber adhesion, while affected only to a small extent at low wax concentrations, rapidly deteriorates as the wax concentration approaches and surpasses 0.25 percent of the weight of the yarn. An optimum range of wax concentration would therefore be between approximately 0.01 and 0.25 percent of the weight of the yarn.

It has been discovered that the addition of between 0.005 and 0.20 percent polyvinyl alcohol (based on the weight of the yarn) to the yarn having wax in the ranges noted above provides a substantial and unexpected increase in tenacity. Thus the addition of 0.033 percent polyvinyl alcohol to the yarn containing 0.065 percent microcrystalline wax in table I above increases the tenacity of the subsequently drawn yarn from 9.0 grams per denier to approximately 9.3 grams per denier. Polyvinyl alcohol in this concentration range improves the drawing performance of the yarn, and does not adversely affect either tire durability or adhesion of the yarn to rubber. If less than about 0.005 percent polyvinyl alcohol is used, tenacity is not significantly enhanced, while if more than about 0.20 percent is used, the finish tends to flake from the yarn and unduly build up on the drawpin, yarn guides and associated equipment.

The following is a specific example of the preferred spin finish composition according to the present invention, as compared to a control finish formulation:

TABLE II

	Control	Test
Polyvinyl Alcohol (88% hydrolysis, 4-6 centipoises in 4% aqueous solution at 20° C.)	0%	5%
Microcrystalline Wax M.P. 100°-105° C.	10	10
Glycerol Monoacetate	25	25
Surfonic TD-90	48	43
Oleic Acid	10	10
Aminomethylpropanol	7	7

In these formulations, the last three components serve as the emulsifier. Surfonic TD-90, a proprietary composition, is believed to be the reaction product of 1 mol of tridecyl alcohol and 9 mols of ethylene oxide. Each formulation was dispersed in about 7 volumes of water and applied to nylon-66 continuous filament yarn before the yarn was drawn at an application rate yielding 0.65 percent of the weight of the dried yarn as the finish formulation.

Table III illustrates the substantial and unexpected increase in breaking strength (B.S.) in the test yarn of table II and in tire cord made from this yarn as compared to yarn treated with the control formulation of table II.

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TABLE III

	Control	Test
Drawn Yarn Denier	840	840
Drawn Yarn B.S., gms.	7500	7800
Drawn Yarn Elongation, %	18.0	18.3
Greige Cord (840/2) B.S., lb.	32.3	34.3
Processed Cord B.S., lb.	32.5	34.9

Thus the addition of 0.03 percent polyvinyl alcohol to the yarn as part of the finish according to the invention produced a 3 percent increase in breaking strength of the yarn and a 7 percent increase in breaking strength of the finished tire cord.

In the presently preferred embodiment of the invention, the glycerol monoacetate in table II is replaced by an equal amount of glycerol monoricinoleate diacetate.

The desirable increase in yarn breaking strength is achieved when the finish constitutes between 0.25 and 1.75 percent of the weight of the yarn, the optimum finish level being about 0.65 to 1.3 percent of the weight of the yarn. The finish is applied most conveniently as an aqueous emulsion wherein the finish constitutes between 6 and 23 percent by weight of the total emulsion, the preferred concentration of the finish being about 12 percent of the emulsion.

Best results are achieved when the yarn has a substantially uniform coating including microcrystalline wax constituting between 0.0075 and 0.25 percent of the weight of the yarn, and polyvinyl alcohol constituting between 0.005 and 0.21 percent of the weight of the yarn. The presence of the low-temperature lubricant or oil is not believed to be essential in the final product and much or all of it may be evaporated or otherwise lost during further processing, such as during the hot-stretching step in the manufacture of pneumatic tires. However, the oil reduces the number of filaments broken during the drawing operation, and is therefore normally desirable.

Yarn treated with the finish according to the present invention readily accepts latex or similar coatings and displays excellent adhesion to rubber, both natural and synthetic. These properties, together with the increased durability and breaking strength noted above, are well suited for yarns used in laminated articles such as pneumatic tires or reinforced rubber belts or hose.

Although for the sake of simplicity the invention has been described herein with a greater particularity in connection with filaments, yarn cord structures, etc. formed from a polyhexamethylene adipamide polymer, the invention is applicable to filamentary materials which comprise a wide variety of synthetic polymeric substances. These include, for example, a full range of polycarbonamides, e.g. polyhexamethylene adipamide, polyhexamethylene sebacamide, polyoctamethylene adipamide, polyoctamethylene sebacamide, the self-polymerization product of 6-amino-caproic acid and also omega-amino-undecanoic acid, polypyrrolidone and others in addition to the many copolymers thereof; the synthetic linear polyesters, e.g., polyethylene terephthalate and the polyester derived from the reaction of terephthalic acid and trans-bis-1,4-(hydroxymethyl) cyclohexane, and various modified polyesters; the hydrocarbon polymers, e.g. polyethylene, polypropylene, the vinylidene and styrene polymers; the acrylonitrile polymers and copolymers thereof, e.g., the copolymers of acrylonitrile and vinyl acetate; the polyurethanes; the polycarbonates; the polyvinyl alcohols and many others. Yarn made of melt blends of diverse polymer types, such as blends of polyesters and polycarbonamides, are specifically contemplated.

It should be particularly noted that the present invention relates to a spin finish formulation for continuous filament industrial or tire yarn, which should not be confused with a formulation for use as a textile yarn size. A spin finish is applied to melt spun yarn almost immediately after the filaments

solidify, and before the yarn is drawn. By way of contrast, textile denier yarns (those having a total denier less than about 600) frequently are further coated with a sizing composition after the drawing operation, which sizing coating forms a continuous film about the individual filaments and binds the filaments together. The amount of polyvinyl alcohol in the present formulation is insufficient to provide substantial filament-to-filament adhesion, and thus does not constitute a size.

In the above specification and in the accompanying claims, all references to proportions or percentage compositions refer to parts by weight where not otherwise specified.

It is to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described my invention, what I claim as new and desire to secure by Letters Patent is:

1. An article of manufacture, comprising in combination:
 - a. a yarn composed of a plurality of continuous filaments,
 - b. and uniformly deposited on said yarn:
 1. a waxoidal lubricant constituting between 0.0075 percent and 0.25 percent of the weight of said yarn,
 2. and polyvinyl alcohol constituting between 0.005 percent and 0.22 percent of the weight of said yarn.
2. The article of manufacture defined in claim 1, further comprising a rubber mass bonded to said yarn, whereby said yarn reinforces said rubber mass.
3. The article of manufacture defined in claim 1, wherein said article is a pneumatic tire.
4. The article of manufacture defined in claim 1, wherein said waxoidal lubricant is microcrystalline wax.
5. An article of manufacture, comprising in combination:
 - a. a yarn composed of a plurality of continuous filaments,
 - b. and a substantially uniform coating on said yarn, said coating including:
 1. a waxoidal lubricant constituting between 0.0075 percent and 0.25 percent of the weight of said yarn,
 2. polyvinyl alcohol constituting between 0.005 and 0.22 percent of the weight of said yarn,
 3. a liquid lubricant constituting between 0.02 and 0.875 percent of the weight of said yarn, and
 4. sufficient emulsifier to disperse said polyvinyl alcohol, said waxoidal lubricant, and said liquid lubricant in water.
6. A method for making high-tenacity yarn with increased flex life comprising in combination:
 - a. applying uniformly to a freshly spun continuous filament yarn, based on the weight of said yarn,
 1. between 0.005 percent and 0.22 percent polyvinyl alcohol and
 2. between 0.007 percent and 0.25 percent waxoidal lubricant,
 - b. and elongating the yarn.
7. The method defined in claim 6, wherein between 0.0075 percent and 0.875 percent low-temperature lubricant, based on the weight of said yarn, is applied to said yarn before said yarn is drawn.
8. The method defined in claim 7, wherein said waxoidal lubricant includes microcrystalline wax.
9. A method for making high-tenacity yarn with increased flex life comprising in combination:
 - a. applying uniformly to a freshly spun continuous filament yarn, based on the weight of said yarn,
 1. between 0.005 percent and 0.22 percent polyvinyl alcohol,
 2. between 0.007 percent and 0.25 percent waxoidal lubricant,
 3. between 0.02 percent and 0.875 percent liquid lubricant, and
 4. sufficient emulsifier to disperse said polyvinyl alcohol, said waxoidal lubricant, and said liquid lubricant in water, and
 - b. drawing the yarn.