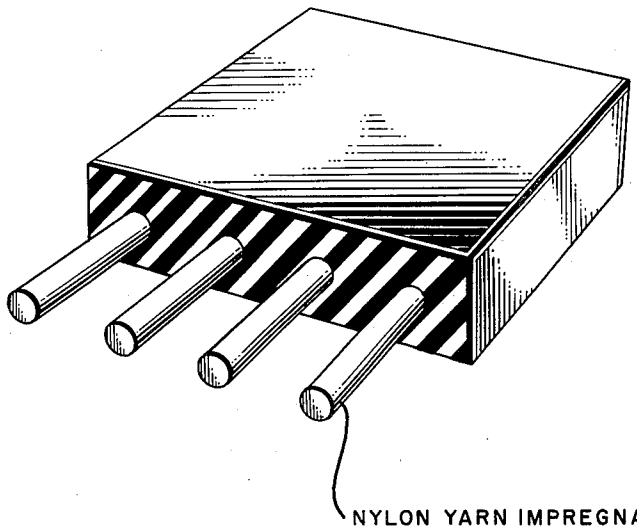
Nov. 16, 1965 V. V. SKEEN ETAL 3,218,222

RUBBER ARTICLE REINFORCED WITH NYLON FILAMENTS

Original Filed June 9, 1960



NYLON YARN IMPREGNATED WITH CERTAIN TRIGLYCERIDES AND REINFORCING A RUBBER ARTICLE.

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United States Patent Office 3,218,222 Patented Nov. 16, 1965

3,218,222

RUBBER ARTICLE REINFORCED WITH NYLON FILAMENTS

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Original application June 9, 1960, Ser. No. 34,863, now Patent No. 3,160,511, dated Dec. 8, 1964. Divided and this application Feb. 7, 1962, Ser. No. 171,738

5 Claims. (Cl. 161—92)

This invention relates to a rubber article reinforced with nylon filaments.

Nylon filaments have made a substantial penetration into the tire cord market and other markets of similar rubber-fabric composite articles. In the main, the entry of nylon filaments in these fields of applications has been at the expense of cellulosic filaments and resulted because of the many superior physical properties of nylon filaments. At present virtually all airplane and large off-the-road equipment tires are reinforced with nylon cord. Furthermore, a substantial portion of replacement passenger tires today contain nylon cord. Noteworthy is the fact that virtually all of the premium passenger car tires are reinforced with nylon cord.

One of the former drawbacks to the use of nylon cord-containing tires was the tendency of such tires to increase undesirably in size during normal use conditions. However, during the past few years "hot-stretch" processes and apparatus have been developed and used to reduce the growth tendency of nylon cord tires significantly. These means have eliminated to a great degree the problem of tire dimensional growth. Another drawback of nylon cord-containing tires at a time past was the somewhat low rubber-to-cord adhesion. This latter problem has been solved by the use of certain bonding agents applied to the nylon cord prior to the time the nylon cord is incorporated in the rubber. Unfortunately, the hot-stretch procedures have given rise to certain concomitant problems. One of these problems is that the finishing compositions normally applied to nylon filaments to improve their pliability and to impart the desired lubricity thereto tend to deteriorate during the hot-stretching operation. This tendency is quite objectionable in that it causes adverse effects in the filaments and results in decomposition of the finishing compositions and attendant liberation of obnoxious smoke and fumes. In other words, the heretofore known finishing compositions for nylon filaments do not perform satisfactorily during hot-stretching of such filaments.

Most, if not all, of the nylon filaments today are manufactured by the melt spinning process. In such process the nylon polymer is heated to the molten or plastic state but below the decomposition temperature thereof. The molten or plastic mass is extruded at a constant rate and under pressure through small orifices in the face of a spinneret to form molten streams of polymer. The molten polymer streams are cooled and solidified into individual filaments. The filaments are then brought together, and a finish composition is applied to the filaments. At this stage in their production the nylon filaments are not highly oriented and have relatively low tensile strength. To orient the nylon filaments and thereby to increase greatly the strength thereof, they are stretched in one or more stages to a desired extent by attenuating them by means of thread advancing devices such as two godets operated at a predetermined speed differential therebetween. It is quite advantageous to localize the point of drawing by the employment of a yarn braking device, for example, a snubbing pin, located between the godets. In one hot-stretching procedure, the nylon filaments while traveling between the snubbing pin and second godet are heated, such as by passing them

across the surface of a heater plate maintained at a suitable elevated temperature. At this point the deterioration of the known finishing compositions is manifest by the visible, offensive smoking and fuming of the compositions, giving rise to very serious processing problems. After being hot-stretched the filaments are collected, twisted; and a plurality of ends are plied into cord. Before being incorporated in rubber, the nylon cord usually is passed through a "hot-dip" bath containing a dispersion of latex and a bonding agent such as a mixture of a dihydric benzene and formaldehyde. The thus impregnated cord is stretched a relatively small extent and dried under tension. Prior art finishing compositions for nylon filaments tend to induce foaming of the "hot-dip" bath.

An object of the invention is to provide articles of manufacture embodying nylon filaments impregnated with said composition, whether in the form of cords, fabric, and rubber articles reinforced with such nylon filaments.

Other objects will appear more fully hereinafter.

The drawing is a perspective view illustrating a nylon yarn impregnated with triglycerides and reinforcing a rubber article.

According to this invention there is prepared a new and useful composition comprising an aqueous emulsion of a particular class of fatty acid esters defined below or a mixture of such esters in the presence of a suitable emulsifying agent. Nylon filaments are impregnated therewith and the impregnated filaments are dried. Advantageously the impregnation is carried out during the manufacture of the filaments and prior to the stage in their manufacture at which they are stretched to impart increased molecular orientation therein. The impregnated filaments are rendered more tractable in textile handling operations and particularly can be effectually hot-stretched at elevated temperatures of above 140° C. but below the sticking point of the filaments. When incorporated in rubber articles for reinforcing the same, the articles exhibit high flexural strength and accordingly have a longer service life. The improvement is especially noteworthy where the article is repeatedly flexed under elevated temperature conditions, as a pneumatic tire would be during use.

The class of fatty acid esters employed in the practice of the instant invention are mixed triglycerides and can be represented generally by the following formula

$$\begin{array}{l} RCOOCH_2 \\ | \\ RCOOCH \\ | \\ RCOOCH_2 \end{array}$$

wherein R designates saturated or unsaturated aliphatic radicals. Two of the aliphatic radicals contain 1 to 5 carbon atoms and at most one ethylene unsaturation. The other aliphatic radical contains 12 to 22 carbon atoms and from 0 to 5 double carbon to carbon bonds. The lower acyl groups may be located in γ, β, or α, γ positions with respect to the glyceryl radical, the location of the respective acyl groups not being critical to the present invention.

Among these defined esters or mixed triglycerides are diaceto-laurin, diaceto-myristin, diaceto-palmitin, diaceto-stearin, diaceto-arachidin, diaceto-behenin, diaceto-lignocerin, diaceto-laurolein, diaceto-myristolein, diaceto-palmitolein, diaceto-olein, diaceto-gadolein, diaceto-erucin, diaceto-ricinolein, diaceto-linolein, diaceto-linolenin, diaceto-elaeostearin, diaceto-licanin, diaceto-arachidonin, and diaceto-clupanodonin. Of the just mentioned triglycerides the preferred compounds are diaceto-ricinolein, diaceto-linolein, and diaceto-linolenin, as well as mixtures of these three compounds. As indicated above the lower fatty acid substituents can be either in the alpha, beta, or the alpha, gamma positions.

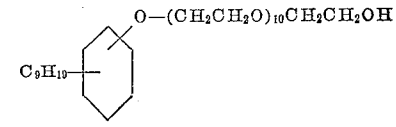
Other suitable triglycerides include dipropiono-laurin, dipropiono-myristin, dipropiono-palmitin, dipropiono-stearin, dipropiono-arachidin, dipropiono-behenin, dipropiono-lignocerin, dipropiono-laurolein, dipropiono- myristolein, dipropiono-palmitolein, dipropiono-olein, dipropiono-gladolein, dipropiono-erucin, dipropiono-ricinolein, dipropiono-linolein, dipropiono-linolenin, dipropiono-elaeostearin, dipropiono-licanin, dipropiono-arachidonin, and dipropiono-clupanodonin; dibutyro-laurin, dibutyro-myristin, dibutyro-palmitin, dibutyro-stearin, dibutyro-arachidin, dibutyro-behenin, dibutyro-lignocerin, dibutyro-laurolein, dibutyro-myristolein, dibutyro-palmitolein, dibutyro-olein, dibutyro-gadolein, dibutyro-erucin, dibutyro-ricinolein, dibutyro-elaeostearin, dibutyro-licanin, dibutyro-arachidonin, and dibutyro-clupanodonin; divalero-laurin, divalero-myristin, divalero-palmitin, divalero-stearin, divalero-arachidin, divalero-behenin, divalero-lignocerin, divalero-laurolein, divalero-myristolein, divalero-palmitolein, divalero-olein, divalero-gadolein, divalero-erucin, divalero-ricinolein, divalero-linolein, divalero-linolenin, divalero-elaeostearin, divalero-licanin, divalero-arachidonin, and divalero-clupanodonin; dicapro-laurin, dicapro-myristin, dicapro-palmitin, dicapro-stearin, dicapro-archidin, dicapro-behenin, dicapro-lignocerin, dicapro-laurolein, dicapro-myristolein, dicapro-palmitolein, dicapro-olein, dicapro-gadolein, dicapro-erucin, dicapro-ricinolein, dicapro-linolein, dicapro-linolenin, dicapro-elaeostearin, dicapro-licanin, dicapro-arachidonin, and dicapro-clupanodonin; dicrotono-laurin, dicrotono-myristin, dicrotono-palmitin, dicrotono-stearin, dicrotono-arachidin, dicrotono-hehenin, dicrotono-lignocerin, dicrotono-laurolein, dicrotono-myristolein, dicrotono-palmitolein, dicrotono-olein, dicrotono-gadolein, dicrotono-erucin, dicrotono-ricinolein, dicrotono-linolein, dicrotono-linolenin, dicrotono-elaeostearin, dicrotono-licanin, dicrotono-archidonin, and dicrotono-clupanodonin and others corresponding to the above structural formula. In general, methods for producing these mixed triglycerides are known and involve conventional triesterification of glycerol with the selected fatty acids.

The finishing composition of the present invention is an aqueous emulsion, and hence a suitable emulsifying agent normally is employed as an ingredient thereof for rendering the emulsion more stable. While a number of emulsifying agents can be employed and are within the scope of the general disclosure, the non-ionic surface active agents are the preferred class of materials. Of the non-ionic surface active agents the polyethers are the preferred emulsifying agents, including alkylaryl polyoxyethylene ethanols, alkyl polyoxyethylene ethanols, alkylaryl polyoxypropylene ethanols, alkyl polyoxypropylene ethanols, etc. In general these polyether compounds are prepared by reacting a suitable monohydric or polyhydric alcohol with suitable amounts of alkylene oxide. Ethylene oxide is the most often used alkylene oxide in view of its attractive price, but propylene oxide may be used in whole or in part with ethylene oxide.

Suitable primary alcohols reactable with ethylene oxide and the like for preparing the emulsifying agents employed herein include dodecyl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, palmitoleyl alcohol, oleyl alcohol, linoleyl alcohol, carnaubyl alcohol and others. The long chain aliphatic radical of these alcohols may have from 10–24 and higher carbon atoms in the chain and 0 to 2 double bonded carbons. The preferred alcohols are C_{14}–C_{20} compounds. The primary alcohols of the just described type are condensed with 5 to 30 moles of ethylene oxide or the alkylene oxide.

As indicated alkylaryl polyoxyalkylene alcohols are also useful as emulsifying agents. These compounds are generally prepared by reacting 8 to 30 moles of an alkylene oxide such as ethylene oxide with alkyl substituted phenols. The alkyl group or groups substituted on the benzene ring contain 2 to 20 carbon atoms in each chain and preferably from 5 to 7 carbon atoms. Trade names

of these alkylaryl polyoxyalkylene alcohols include Igepol CA, Igepol #300, Igepol CO, Antarox A–400, Triton X–10, Emulphor DDT, and are believed to have the formula:



Suitable polyhydric alcohols condensed with alkylene oxide include, for example, sorbitan monolaureate polyoxyethylene condensate (20 moles of ethylene oxide), sorbitan monopalmitate polyoxethylene condensate (40 moles of ethylene oxide), sorbitan monostearate polyoxyethylene condensate (60 moles of ethylene oxide), sorbitan monooleate polyoxyethylene condensate (80 moles of ethylene oxide), and the like. Again the preferred alkylene oxide is ethylene oxide, however as previously indicated, propylene oxide is known to be an equivalent therefor in some instances.

The ratio of emulsifying agent to the triglyceride ester component can be varied within rather wide limits, the requirement being that enough emulsifying agent be employed so that the emulsion is stable. However, it has been found that in order to prepare stable emulsions of the esters above defined and essential to the present composition, the percentage of emulsifying agent, based on the weight of the ester plus the emulsifying agent, can be about 10 percent to about 50 percent. The preferred percentage is about 30 to about 40 percent by weight.

In order to obtain the benefits of the treatment of this invention, it is generally necessary that the triglyceride compound remain in or on the nylon filaments at the time the filaments are hot-stretched and at the time they are employed in a rubber composite article in an amount from about 0.05 to about 3.0 percent based on the weight of the filaments.

For convenience, the finishing composition of the present invention is applied to a longitudinally traveling bundle of filaments by employment of a roller partly immersed in the composition or a wick material partly immersed in the composition, the traveling filaments coming into contact therewith. In place of such manner of application, the finishing composition can be impregnated in the nylon filaments in any other suitable manner, such as by immersion in a bath of the composition or by spraying or brushing the composition on the filaments.

The relative concentration of the triglyceride ester component in the finishing composition can be varied considerably in obtaining impregnation of the ester on the filaments in the above-mentioned amounts. The concentration will depend, among other things, on the particular method of impregnation employed, and on the form of filaments treated. Emulsions ranging from about 0.5 to about 20 percent or higher of the triglyceride ester component based on the weight of the finishing composition are quite suitable for impregnating commercial nylon filaments.

The new and useful filament finishing composition can be prepared in the following manner. The selected triglyceride ester component and emulsifying agent therefor are intimately agitated together with the desired quantity of water at temperatures of about 25° C. to 50° C. In one excellent way of preparing an emulsion of good stability, the ingredients are agitated in a high shear liquid blender or mill, such as a Waring Blendor. Generally, an agitation time of about 5 to 30 minutes at temperatures from 0° to 100° C. is sufficient to prepare emulsions exhibiting good stability. It is preferred, however, that the new finishing compositions be prepared by blending the triglyceride component with the emulsifying agent at a temperature of about 40° C. to 45° C., subsequently adding the required amount of water and thereafter vigorously agitating the emulsion for about 20 to 30 minutes

at about 15° C. to 30° C. Where desirable, the emulsion is cooled by suitable means during the agitation period.

Nylon, as is well known, is a high molecular weight linear polymer which contains recurring carbonamide groups as an integral part of the main polymer chain separated by at least two carbon atoms. Broadly speaking, nylon polymers are of two general types. One type of nylon is obtainable from polymerizable monoamino-monocarboxylic acids and their amide-forming derivatives, for example ε-caprolactam and α-pyrrolidone, known generically in their polymerized form as nylon-6 and nylon-4, respectively. The other type of commercial nylon is obtainable from suitable primary or secondary diamines and suitable dicarboxylic acids or amide-forming derivatives thereof. Among the latter type are polymers formed by the reaction of tetramethylene diamine, pentamethylene diamine, hexamethylene diamine and the like with adipic acid, suberic acid, sebacic acid and the like. The polymerization product of hexamethylene diamine and adipic acid has the generic name of nylon-66.

The manner in which the foregoing aspects of the invention are attained will appear more fully from the following example, in which reference is made to typical and preferred procedures in order to indicate more fully the nature of the invention, but without intending to limit the invention thereby. In the example all parts and percentages are by weight unless otherwise indicated.

Example

Eighteen parts of diaceto-ricinolein was combined with 2 parts of an emulsifier composed of a mixture of myristyl alcohol, cetyl alcohol, stearyl alcohol, arachyl alcohol, palmitoleyl alcohol, oleyl alcohol, and linoleyl alcohol having been condensed with 20 moles of ethylene oxide per mole of alcohol. The mixture of triglyceride ester component and emulsifying agent was homogenized with 180 parts of water to form a stable emulsion. The emulsion was applied to a bundle of 140 nylon-66 filaments having an ultimate total denier of 840 between the spinneret employed in the melt-spinning of the filaments and the point of first take-up in an orderly manner on a spin bobbin. The filaments were hot drawn on a conventional draw-twist machine employing two sets of rolls, a drawing pin in the yarn path between said rolls, a heated plate in the yarn path between said pin and said second set of rolls, and a ring twister take-up assembly. Between the two sets of rolls, the filaments are stretched about 5 times. The filaments attained a temperature of about 180° C. during the operation.

The finishing composition showed no signs of decomposition and was completely stable at the temperature employed.

When a finish heretofore known and composed in the main of sulfonated peanut oil and mineral oil was applied to the filaments in the same manner as stated above in place of the triglyceride ester, offensive smoke and fumes were given off during the processing.

The filaments containing the novel finishing composition and those containing the heretofore known finish were separately processed into tire cord, and the cord incorporated into a pneumatic tire by standard and conventional procedures. The nylon filament cord containing the triglyceride ingredient processed well in the "hot-dip" bath and exhibited improved and more uniform adhesion characteristics with respect to the rubber of the tire as compared with cord containing the heretofore known composition. The nylon filament cords were used as the reinforcing textile fabrics in pneumatic tires by standard procedure. The tires were of the type used in high speed racing vehicles. Tire failure occurred in the tires containing the heretofore known finish long before failure occurred in the tires impregnated with the triglyceride ingredient.

When other triglyceride ester materials of the defined class are emulsified with other non-ionic emulsifying agents, similarly excellent results are obtained in the production of nylon-66 and nylon-6 tire cord.

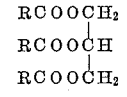
Thus nylon filaments treated with the new finishing compositions above described are especially adapted for use in the rubber-fabric composite articles since they may be hot-stretched efficiently without the occurrence of obnoxious smoking and fuming. In addition to rendering the filament more amenable to hot-stretching, the new finishing compositions have numerous other advantages such as providing increased adhesion between the rubber and filaments and increased resistance of the rubber-fabric composite articles to heat deterioration upon repeated rapid flexing, as in the case of pneumatic tires.

It is to be understood that the foregoing description is given merely by way of illustration and that many variations may be made therein, without departing from the spirit of the invention.

This application is a divisional application of pending application Serial No. 34,863, filed June 9, 1960, the latter application being a continuation-in-part application of application Serial No. 797,014, filed March 4, 1959, which is now abandoned.

What is claimed is:

1. A rubber article reinforced with nylon cord, the filaments of which are coated with a mixed triglyceride having the structural formula:



wherein R designates aliphatic radicals, two of which having 1 to 5 carbon atoms and at most one double carbon to carbon bond and one of which having 12 to 22 carbon atoms and at most 5 double carbon to carbon bonds in an amount of about 0.05 to about 3.0 percent by weight of the filaments.

2. The article of claim 1 wherein the nylon filaments are made of nylon-66 polymer.

3. The article of claim 1 wherein the nylon filaments are made of nylon-6 polymer.

4. The article of claim 2 wherein the triglyceride is diacetoricinolein.

5. The article of claim 3 wherein the triglyceride is diacetoricinolein.

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EARL M. BERGERT, *Primary Examiner.*