

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Tire Cord

We, THE GOODYEAR TIRE & RUBBER COMPANY, a corporation organized under the laws of the State of Ohio, United States of America, of 1144 East Market Street, Akron, Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to improved polyester cord and cord fabric for the reinforcement of pneumatic tires, their preparation and a tire containing the same.

It is generally recognized that the cooler a pneumatic tire remains in use the longer its life will be, because high temperatures decrease the life of a tire. This invention relates to a polyester fabric and the method of processing it to minimize the heat generated when a tire containing it is used.

It is well known in the art to process thermo-stretchable ply-reinforcing materials prior to incorporation in tires to optimize their various physical properties, such as tenacity and tire growth. It has now been found that the processing of polyester tire cord and cord fabric to bring out their best properties requires different processing conditions from those used for the processing of other thermo-stretchable reinforcing materials, and the processing of polyester tire cord and cord fabric can be controlled to minimize heat generating characteristics of the tire, as well as to give them high tenacity and low tire growth. The heat generated by a tire is inter-related with its elongation and heat shrinkage, and it has been found that by maintaining the elongation measured at 2.0 grams per denier (referred to herein as gpd)

of a polyester tire cord between 6.5 and 9.0 per cent and its heat shrinkage 45 between 2.5 and 5.75 per cent, the heat generation is kept below 35 units, a heretofore unobtainable result with polyester tire cord fabric. (The "units" referred to are relative rather than absolute units, obtained by applying the equation for H_g given below, to a constant given instrument).

According to this invention, polyester tire cord and cord fabric are treated to 55 provide low heat generation in use, as well as other desirable properties. The reason the cord or fabric is treated is that the properties of thermo-stretchable materials, such as elongation, heat shrinkage and 60 heat generation are time dependent. It is therefore advisable to process the polyester in the form of cord or fabric shortly prior to incorporation into a tire. This is most conveniently done by treatment of a spool 65 of the cord or a fabric roll.

The polyester tire cord or fabric is processed on a multi-stage treating unit containing a series of time and temperature tension zones. Specifically, the cord or 70 fabric is first subjected to an extremely high temperature in the range of 440 to 490°F. for a very short exposure time of 35 to 70 seconds, and during this heat treatment the cord or fabric is subjected 75 to sufficient tension to stretch it substantially 2 to 7 per cent. The cord or fabric is thereafter, as the next stage in a continuous process, subjected to a treatment at a temperature which is a minimum of 80 ten degrees higher than that employed in the first stage—that is, 450 to 500°F. for a similar minimum time exposure of 35 to 70 seconds, during which the cord or 85 fabric is allowed to shrink 30 to 50 per cent of the stretch that has been applied in

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the first treatment stage. The cord or fabric is then cooled under sufficient tension to maintain the residual stretch.

The polyester to which the treatment is applied is essentially a linear terephthalate. It ordinarily is an alkylene terephthalate in which the alkylene group contains 2 to 6 or 8 carbon atoms, having an intrinsic viscosity in phenol/trichloroethane (60:40) at 30°C. in excess of 0.55, a tenacity in excess of 5.5 grams per denier, and a minimum melting point of 450°F. It may be an ester of cyclohexane dimethanol and terephthalic acid. As is known, the polyesters obtained from aromatic glycols, such as the linear polyester known as Kodel (Registered Trade Mark), have improved heat resistance and higher modulus due to the presence of ring structures in the linear molecule, and such polyesters, although more expensive than the polyethylene terephthalates, respond also effectively to the three-stage treatment here described.

The invention is further described in connection with the accompanying drawings which relate to the treatment of tire-cord fabric. Tire cord may be subjected to the same processing steps in suitable equipment.

In the accompanying drawings:

Figure 1 is a schematic elevation of equipment for the multi-stage treatment of tire-cord fabric according to this invention;

Figure 2 is a section through the finished tire made from the treated cord;

Figure 3 is a graph showing the effect of heat generation on the durability of a tire reinforced with polyester cord fabric; and

Figure 4 is a graph which shows the interrelation of elongation, heat shrinkage and heat generation of polyester tire cord fabric.

Referring to Figure 1, the treatment is here discussed as applied to a linear polyethylene terephthalate having an intrinsic viscosity of 0.65, a tenacity of 8.0 grams per denier and a melting point of 493°F. This polyester is produced in a size of 1100 denier yarn. Three of these yarns are twisted into a 1100/3 cord. A roll of fabric is constructed from these cords. This fabric consists of 1540 cords across its width.

The fabric is withdrawn from one of the two rolls 1 and 2 and passed through a storage compensator 4 which insures a continuous flow of the fabric through the equipment. The fabric is then passed through the adhesive container 6 and then through the pull rolls 8. From here the fabric goes through a series of ovens, the first oven 10 being a warm-up oven

maintained at about 260 to 300°F., in which the moisture from the adhesive is removed from the fabric so that when the fabric reaches the first stage of the treatment to which this invention relates it is 70 dry, or substantially dry. The time that the fabric remains in the third oven 12—that is, the time it takes for it to pass from the roll 13 to the roll 14—is 53 seconds. In the oven 12, the first stage of 75 this process is carried out. The temperature is 460°F. The fabric between the set of tension rolls 8 and the set of tension rolls 15 is maintained under a tension sufficient to stretch the cords 5 per cent. 80 Usually this will be in the range of 4000 pounds or 2.6 pounds per cord. The chamber 17 is usually maintained at about room temperature. The rolls 19 in this chamber are connected through a chain 85 and pulleys to the rolls 20 in the oven 12 so that the rolls 20 can be raised or lowered to maintain a particular residence time within the oven 12 and this is compensated for by moving the rolls 19 the same amount in the opposite direction. 90 Such a device is known in the industry as a Rollevator.

The cord fabric then may or may not pass through a second adhesive chamber 95 25 and may or may not be dried. It then passes into the oven 26 where the second stage of the heat treatment of this invention takes place. This oven is maintained at a temperature of 470°F. The residence time within this chamber is substantially 100 53 seconds, the same as in the oven 12. The fabric is under less tension between the tension rolls 15 and the tension rolls 28 so that during the time the fabric is 105 in this chamber 26 it shrinks 2 per cent of the length at which it enters oven 26. The rolls 30 in this oven 26 are connected with the rolls 31 by a Rollevator. The latter rolls are not enclosed, and between 110 the oven 26 and the cooling chamber 33 the fabric is exposed to atmospheric cooling.

The fabric then passes into the cooling chamber 33 and it eventually reaches substantially room temperature before passing through the rolls 28, after which it is no longer under tension. It then passes through another storage compensator 35 to the wind-up roll 40. 120

Although the fabric is under tension between the rolls 8 and 15, no substantial amount of stretching occurs until it reaches oven 12 where the high temperature plasticizes the polyester fabric sufficiently 125 to permit this stretching. Similarly, in the second tensioning zone between the tensioning rolls 15 and 28, it is only in the oven 26, and shortly after, that the fabric is at a sufficiently high temperature to 130

plasticize the fabric and allow it to shrink to any substantial extent.

The resulting fabric has a thermal shrinkage of substantially 3.4 per cent and an elongation at 2 grams per denier of 8.0 per cent. Our copending application No. 46138/67 (Serial No. 1110752) describes and claims a linear polyester cord reinforcement for a tyre, the cords of which have been permitted a thermal shrinkage of 2.5 to 5.75 per cent and the cords having an elongation at 2 grams per denier of between 6.5 and 9.0 per cent.

The fabric after being treated in this manner is ready to be coated with rubber and built into a tire. Figure 2 illustrates a typical tire. The reinforcing cords in the fabric of the carcass plies are cords of the type which have been subjected to the treatment just described. These cords may be radial or incorporated in the tire on the bias. The fabric of the invention may be used elsewhere in the tire, according to any known or novel tire construction.

EXAMPLE I

This example is based on the treatment just described.

A 1100 denier polyester yarn was twisted into a 1100/3 cord construction and these cords were woven into a tire fabric having 28 ends per inch cord count. This polyester tire cord fabric was processed through a multi-stage unit such as illustrated in Figure 1. This fabric was stretched 5 per cent with an exposure of 53 seconds at a temperature of 460°F. followed by a shrinkage of 2 per cent at an exposure of 53 seconds at a temperature of 470°F. The material processed in this manner has an elongation at 2.0 gpd of 8.0 per cent and a thermal shrinkage of 3.4 per cent. Heat generation per unit stress cycle of the polyester cord material was found to be 25.2 "units" at a test temperature of 200°F. which is a reduction of 30 per cent below the heat generation of fabric of the same polyester which has not been processed by this invention (the "units" used are the same relative units as described above).

Tires built from this fabric and tested for tire durability (on standard equipment described below) ran 4,680 miles before failure, which is 62 per cent better than tires built from polyester tire cord fabric 55 processed outside the scope of this invention.

EXAMPLE II

A polyester tire fabric similar to that described in Example I was stretched 7 per cent with an exposure of 35 seconds at 455°F., followed by a shrinkage of 3 per cent at an exposure of 45 seconds at a temperature of 465°F. The fabric had an elongation at 2 gpd of 7.5 per cent and a thermal shrinkage of 3.8 per cent. Heat generation of this fabric was found to be 29.5 "units" (relative units as above). Tires built from this fabric and tested for tire durability completed 3,890 miles prior to separation.

EXAMPLE III

A polyester fabric similar to that described in Example I was stretched 5 per cent with an exposure of 35 seconds at 470°F., followed by shrinkage of 2 per cent at an exposure of 35 seconds at a temperature of 480°F. Fabric properties showed elongation at 2.0 gpd of 7.0 per cent and a thermal shrinkage of 4.2 per cent. Heat generation of this fabric was found to be 29.6 "units" (relative units as above). Tires built from this fabric and tested for durability completed 3,357 miles prior to failure.

Polyester tire cord fabrics were processed under a range of conditions both within and outside of the scope of this invention. The results are summarized in Table I. Fabrics A, B and C of the foregoing examples. Fabrics D and E were processed under different conditions detailed in the table. The conditions are outside of the scope of those set forth herein, and the properties are inferior. These results show the effect of subjecting the same polyester tire cord fabric to different treatments.

TABLE I
POLYESTER TIRE-CORD FABRIC

	A	B	C	D	E
FIRST STAGE:	460	455	470	455	440
Temp. (°F.)	53	35	35	53	133
Time (Seconds)	5	7	5	5	5
Stretch (%)					
SECOND STAGE:	470	465	480	455	440
Temp. (°F.)	53	45	35	53	133
Time (Seconds)	2	3	2	1	1
Shrink (%)	3.4	3.3	4.2	5.8	2.3
Thermal Shrinkage (%)*	25.2	29.5	29.6	36.0	42.1
Heat Generation	8.0	7.5	7.0	6.3	20.
Elongation 2 g/denier (%)	4680	3890	3357	2283	2102
Tire Durability in miles	*Standards On Textile Materials: D885-62T (1963, 34th Ed.) Sect. 29 and 38, of The American Society for Testing Materials.				

Tire durability is determined by building the treated polyester into a tire and subsequently testing the tire by running it against a 67-inch Bureau of Standards dynamometer test wheel which has six cleats mounted across the face of the wheel. Each cleat is two inches wide by three-quarters inch high. The tire is tested at 2 pounds per square inch inflation pressure over the recommended inflation of the Tire & Rims Association and 120 per cent of the load recommended by Tire & Rims Association. The mounted and inflated tire is run against the cleated test wheel at 45 mph until tire failure occurs.

Figures 3 and 4 show the general relationship in a graphical manner between cord properties and tire performance.

The graph of Figure 3 shows the effect of heat generation on the durability or life of a tire reinforced with polyester cord or polyester cord fabric. The cord or fabric for these tires was processed in such a manner as to vary their heat generation characteristics. As can be seen from the graph, heat generation in excess of 35 units (relative units as above) causes a rapid decrease in tire durability.

In Figure 4 the interrelation of elongation, heat shrinkage and heat generation of polyester cords is shown. From Figure 3, it has been determined that a heat generation of less than 35 units is necessary for good tire performance. The fabric elongation and heat shrinkage necessary to give low heat generation and hence good tire performance are shown in Figure 4. It can be seen that there are minimum-maximum limits to elongation and heat shrinkage beyond which the heat generating characteristics of the fabric are undesirable. To be within these limits and have low heat generation, a polyester tire cord fabric must have a minimum elongation of 6.5 per cent and a maximum elongation of 9.0 per cent with a minimum thermal shrinkage of 2.5 per cent and a maximum thermal shrinkage of 5.75 per cent.

Heat generation per unit stress cycle, as described herein, was determined as set forth in MEASUREMENT OF THE DYNAMIC STRETCH MODULUS AND HYSTERESIS OF TIRE CORD by W. J. Lyon and Irvin Prettyman, JOURNAL OF APPLIED PHYSICS, Vol. 18, No. 6, June 1947. Resonance frequency of the system was maintained at 69 to 71 cycles per second (corresponding to frequency encountered in tire service) by adjustment of the vibrating mass. Then the current in the vibrating coil was adjusted to maintain strain cycles of 0.5 per cent elongation. The equations used in calculating heat generation (H_L) are:

$$\eta = k_1 \frac{dV}{Df_0 d}$$

$$E = k_2 \frac{mf^2}{D}$$

$$H_L = k_3 \frac{Df_0 \eta}{d E^3}$$

In these equations the terms used are defined as:

η = polymer intrinsic viscosity

d = yarn density in g/c.c.

V = Voltage required to maintain amplitude for a constant resistance

D = Yarn denier

f_0 = resonant frequency of yarn for a given vibrating mass

E = dynamic modulus of yarn

m = mass of vibrating systems

H_L = Heat generation per unit stress cycle per unit sample length

Elongation and thermal shrinkage are used herein with the meaning given them in Sections 29 and 38 of ASTM Standards On Textile Materials D885-62T (1963, 34th Edition.)

We believe that a reasonable explanation for the phenomenon encountered in this invention is found in the relation of the physical state of the fiber to its history.

The physical properties of any fiber are dependent on not only the chemical composition of the fiber but also its physical state, i.e. the degree of orientation, per cent crystallinity, size of crystallites, and the interaction of these factors with temperature.

In the case of polyester fibers, the rate and degree of crystallinity are very sensitive to temperature. The maximum rate of crystallization occurs at a temperature of about 350° F. Nylon, on the other hand, is much less sensitive and crystallizes over a much wider and lower temperature range. In addition, the rate of crystallization of polyester fibers is considerably lower than that of nylon.

Heat treatment of a fiber is desirable to plasticize the amorphous area which allows further crystallization and orientation, particularly where the fiber is under tension.

We have theorized that the use of high temperatures for carefully controlled periods of time is required with polyester for the proper combination of crystallization, crystallite size and orientation. However, when this is done, thermal strains are developed in the fiber. To alleviate these thermal strains, we have found it necessary to allow the fiber to shrink while maintained at a higher temperature than it was initially subjected to.

WHAT WE CLAIM IS:—

1. A process of treating polyester cord reinforcement for a tire, which process comprises subjecting the reinforcing material, in a first stage, at a temperature in excess of 440°F. to sufficient tension for a period of 30 to 70 seconds to stretch it by 2 to 10 per cent of its original length, and thereafter in a second stage subjecting the reinforcing material so treated to a temperature at least ten degrees F. higher than the temperature of said first stage and at said latter temperature, in the second stage, allowing the reinforcing material under a relaxed tension during 30 to 70 seconds to shrink 30 to 50 per cent of the amount that it has been stretched in the first stage, and then maintaining the residual stretch present after the second stage in which the reinforcing material is shrunk, without substantial change, while the reinforcing material is cooled to substantially room temperature.
2. A process according to Claim 1 in which the reinforcing material is polyethylene terephthalate and in the initial stage of the treatment the temperature is between 440 and 490°F.
3. A process according to Claim 2 in which the reinforcing material is stretched

5 per cent during an exposure time of 53 seconds at a temperature of 460°F. and then is shrunk 2 per cent during an exposure time of 53 seconds at a temperature of 470°F.

4. A process of treating polyester cord substantially as described in any of the foregoing examples, with the exception of those labelled D and E.

5. A process of treating polyester cord substantially as hereinbefore described with reference to, and as shown in, Figures 1 and 2 of the accompanying drawings.

6. Polyester cord when treated in accordance with any preceding claim.

7. Linear polyester cord reinforcement for a tire, the cords of which have been treated by a process according to Claim 1, said cords having a permitted thermal shrinkage of 2.5 to 5.75% and an elastic elongation at 2 gms. per denier of 6.5 to 9.0%.

8. A pneumatic tire which includes linear polyester cord reinforcement as set forth in Claim 6 or 7.

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