

PATENT SPECIFICATION

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(54) MODIFIED POLYESTER REINFORCING ELEMENTS AND RUBBER STRUCTURES MADE THEREFROM

(71) 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 an improved rubber structure reinforced with an improved polyester reinforcing fiber modified with a metal complex compound, a polycarbonate, or an isocyanate each alone or in any combination with each other, the modifier being present in the polyester prior to fiber formation.

Pneumatic tires are being subjected to increasingly severe operating conditions including high speeds and heavy loads. Rubber used in the tire is reinforced with such materials as rayon, nylon, polyester, wire, and glass fibers. Maximum reinforcement of the rubber is obtained with a given fiber when maximum adhesion is produced between the rubber and fiber. Polyethylene terephthalate tire cords are particularly desirable to use as reinforcing elements because of their excellent dimensional stability as shown by low growth or stretch during service. However, it has been observed that in the environment of the rubber of a pneumatic tire the heat generated under high speeds and heavy loads causes the polyester cord to lose tensile strength and ultimately adhesion to the rubber.

The chemical environment of the rubber of a tire is complex because many different chemicals are needed in its construction in order to obtain maximum tire performance. Because of this chemical complexity in the rubber and the severe heat developed during service, a variety of chemical reactions result in the degradation of the polyester cord and the adhesive bond between the cord and the rubber.

Many attempts have been made to minimize these destructive forces and the present invention is an advance in solving the problems created by these destructive forces. Prior attempts have been made by modifying the rubber. Other attempts have been directed toward the adhesive. The present invention is directed toward the polyester cord.

It has now been discovered that a more thermally stable pneumatic tire may be made when the rubber thereof is reinforced with a modified polyester cord described herein.

The thermally stable tire is made possible by the discovery that a polyester cord used in the construction of the pneumatic tire can be protected against tensile loss in the cord and degradation of the adhesive bond between the cord and the rubber by incorporating in the polyester prior to fiber formation a critically small amount of a modifier which (1) can be blended satisfactorily with the polyester; (2) is reactive with the polyester within the limitations of time and temperature existing in an extruder used in melt spinning; generally less than 10 minutes and preferably 1 to 4 minutes and between 10°C. to 60°C. above the melting point of the polyester at normal pressures; (3) has the proper melt viscosity to prevent dripping of the spun resin which may occur when the melt viscosity is too low and to prevent excessive pack pressure during extrusion which may occur if the melt viscosity is too high;

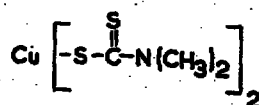
(4) is of such a nature that its degradation products will not be harmful to the polyester, otherwise a drop in tensile will occur; (5) allows good spinning and drawing of the polyester, control of which may be achieved by controlling the reaction during extrusion; otherwise, if no control is possible, then uncontrolled cross-linking may occur, and the resin will be difficult to properly draw; and (6) has a high melting point and a low vapor pressure, thereby imparting efficiency in the processing of the material being drawn.

Such a modifier has been discovered to be a polycarbonate, an isocyanate or a metal complex each used alone or in any combination with each other.

It has been observed that an exceptional increase in hot adhesion is obtained when a small amount of a polycarbonate alone or a small amount of an isocyanate alone is added with the metal complex or both the polycarbonate and the isocyanate are added with the metal complex to the polyester chips prior to fiber formation.

It is believed that certain desirable reactions take place between the polycarbonate when used alone, or the isocyanate when used alone or the metal complex when used alone and certain undesirable by-products present in the polyester to form a reaction product which is less detrimental to the polyester at elevated temperatures than are the by-products. Also, it is believed that the isocyanate alone provides adhesive sites on the surface of the formed polyester fiber which may account for the exceptionally desirable bonding. The polycarbonate may be used alone because it acts as a scavenger or protective agent for the polyester cord.

The metal complex compound used in the present invention is any complex the metal ion of which has an incompletely satisfied 'd' orbital and will further complex or coordinate with compounds containing atoms like N, O, P, S and halogens and has a stability (log k) constant for its ammonia and amine complexes of between 5 and 25. The metal ions preferred in the metal complex of this invention include Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, Th, and Pa. A preferred metal complex is copper dimethyldithiocarbamate having the formula



The metal complex may be used alone or in combination with other modifying agents of this invention in amounts from 0.001 part to 0.1 part by weight per 100 parts of polyester. Polycarbonate may be present in an amount from 0.1 part to 2 parts by weight per 100 parts of polyester. The isocyanate, which also includes isocyanate generating compounds, may be present in an amount from 0.01 part to 2 parts by weight per 100 parts of polyester, and preferably in an amount from 0.05 part to 0.2 part by weight.

It is preferred to add the metal complex as a powder to the polyester chips just prior to the introduction of the mixture into the extruder associated with the spinning of the resulting molten mixture into filaments. The polyester modifier may be blended with the solid polyester in a double cone dryer to form a master batch which is then fed to the extruder, or the materials may be supplied separately, in the correct ratio, to the throat of the extruder.

It is essential when the metal complex, the polycarbonate or the isocyanate is to be intimately blended with the polyester in the molten state, which occurs in the range from about 270°C. to about 310°C., that the molten blend be maintained under a pressure of about 800 lbs. per square inch for not more than 10 minutes, and preferably for from 1 to 4 minutes, and out of contact with oxygen, a condition present in melt spinning apparatus.

The improved fiber to be used in this invention is made as indicated above by adding the particular modifier to a polyester prior to fiber formation. The polyester is any fiber forming thermoplastic linear high molecular weight condensation polyester, and particularly polyethylene terephthalate as well as polymers of cyclohexanedi-methylene terephthalate. These polyesters, as well as copolymers of aromatic dicarboxylic acids, and particularly condensation products of ethylene glycol with a mixture of terephthalic acid and isophthalic acid, ethylene glycol with terephthalic acid and another dibasic acid such as sebacic or adipic acid or hydroxycarboxylic acids such as parahydroxy benzoic acid present in small amounts, are suitable. By linear terephthalic polyesters is meant a linear condensation polyester comprising recurring glycol

dicarboxylate structural units in which at least about 85% of the recurring structural units are units of the formula



wherein G represents a divalent organic radical containing from 2 to 8 carbon atoms which is attached to the adjacent oxygen atoms by saturated carbon atoms. The terephthalate radical may be the sole dicarboxylate constituent of the recurring structural units or up to about 15% of the structural units may contain other dicarboxylate radicals such as adipate, sebacate, isophthalate, 4,4' bibenzoate and hexahydroterephthalate. By high molecular weight is meant polyesters having an intrinsic viscosity of at least 0.4 and preferably greater than 0.6 and as high as 1.5 as measured in a 60/40 phenol/tetrachlorethane mixed solvent at 30°C. It is preferred that the polyethylene terephthalate and other similar polyesters have a high melting point which for polyethylene terephthalate is about 265°C. measured with a hot stage polarizing microscope. Generally the polyester fibers of this invention may be prepared in accordance with well-known procedures for melt extrusion and drafting.

The rubber component of the rubber structure of this invention may be any rubber that is a stretchable composition having a tendency to return to its approximate original shape after being vulcanized, and particularly any rubber that is used in the manufacture of tires and drive belts. Thus, the laminate of this invention may involve natural rubber otherwise known as Hevea Brasiliensis, or conjugated diene polymeric rubbers made by polymerizing butadiene-1,3, isoprene, 2,3-dimethyl butadiene-1,3, and mixtures of these conjugated dienes, or copolymers of these diene monomers with up to 50% of compounds which contain a $CH_2=C=$ group and which are copolymerizable with butadiene-1,3 where, for example, at least one of the valences is attached to an electronegative radical, that is a radical which increases the polar character of the molecule such as vinyl, phenyl, nitrile and carboxy radicals. Examples of the diene rubbers are polybutadienes including the stereospecifics, polyisoprenes including the stereospecifics, butadiene/styrene copolymers, also known as SBR, and butadiene/acrylonitrile copolymers also known as NBR.

The following examples disclose how an improved polyester cord may be made by adding a metal complex to polyester chips and then forming filaments therefrom. Parts are by weight unless otherwise specified, throughout the Examples.

EXAMPLE 1 (CMPE)

100 parts of dried polyethylene terephthalate (PE) chips are tumbled with .025 part of copper dimethyldithiocarbamate (C) until the mixture is substantially homogeneous. The resulting blend of the copper dimethyldithiocarbamate and polyester is melt spun at a temperature of 290°C. through a 190 hole spinneret at a spinning speed of 150 yards per minute to give a single spun yarn having a total denier of approximately 7800. The spun yarn is passed to a pair of rotating heated feed rolls and then passed around a pair of heated draw rolls rotating at a speed which imparts a draw ratio of about 6 to 1, to give a total denier of approximately 1300, and then wound on a bobbin. The modified polyester yarn (CMPE) has a tenacity of 7.9 grams per denier, a break elongation of 13%, an intrinsic viscosity of .785, a tensile strength of 24.3 lbs., and an elongation at 10 lbs. pull of 6.2%.

The yarn produced above is plied 8 turns per inch, and 3 of these plies are twisted in reverse direction 8 turns per inch to form the cord used in producing the improved rubber structure of this invention. The resulting cord has a break strength of 62.8 lbs., a 5% modulus (lase) of 12.6, a 10% modulus (lase) of 26.1, and an elongation at break of 19.7%. The resulting modified polyester cord is identified as cord sample A. The unmodified polyester was processed into filaments and a cord made in the exact manner described above and identified as cord sample B.

Both cord samples A and B were treated with an R/F/L adhesive made in the following manner. A 20% solids dispersion of a conventional R/F/L adhesive is made by adding 8.9 parts of resorcinol to 6.55 parts of a 37% solution of formaldehyde and 5 parts of a 10% solution of sodium hydroxide, and then adding this mixture to a latex mixture comprising 35.5 parts of a 39.5% solids latex of a 70/15/15 terpolymer of butadiene/styrene/vinyl pyridine and 64 parts of a 40.7% solids latex of a 70/30 copolymer of butadiene/styrene, the mixture being in 130.05 parts of water. Certain of the cords are passed through a dip tank containing this adhesive. The dipped cords are then dried at 450°F. and embedded in rubber compounded

as shown below, and then a peel adhesion test is made of a one-inch strip under static conditions at 250°F. Thermal stability of the cord is measured in terms of percent tensile strength retained by the air bomb (AB). Air bomb testing is done by heating the untreated cord embedded in the rubber compound as shown below for 2.5 hours at 350°F. under 80 psi air pressure. The data obtained is listed in Table 1.

EXAMPLE 2 (CTMPE)

100 parts of dried polyethylene terephthalate (PE) chips are tumbled with .015 part of copper dimethyldithiocarbamate (C) and 1.0 part of a polyester blocked polyisocyanate (T) resulting from the reaction of 100 parts of the hydroxyl polyester from the reaction of 11 mols of ethylene glycol and 10 mols of adipic acid, and 9 parts of 1,4-butanediol blocked with 40 parts of 4,4'-diphenylmethane diisocyanate having an HCl acidity of 0.017% and commercially available as "Texin" 192A ("TEXIN" is a registered Trade Mark) sold by Mobay, until the mixture is substantially homogeneous. The resulting blend (CTMPE) of the carbamate (C) and the polyester blocked polyisocyanate (T) and polyester is melt spun at a temperature of 290°C. through a 190 hole spinneret under the same conditions as described for Example 1. This yarn identified as (CTMPE) is then tested in the same manner as shown in Example 1 and the resulting data reported in Table 1.

EXAMPLE 3 (CTPCMPE)

Example 2 is repeated with the exception that 2 parts of a polycarbonate (PC) of the nature shown below and having an intrinsic viscosity of .5 is added along with the carbamate (C) and the polyester blocked polyisocyanate (T) to the dried polyethylene terephthalate (PE) chips, and mixed to form a homogeneous mixture. The resulting blend (CTPCMPE) is then melt spun at a temperature of 290°C. through a 190 hole spinneret under the same conditions described in Example 1. This yarn identified as (CTPCMPE) is then tested in the same manner as shown in Example 1 and the resulting data reported in Table 1. "Mallory Fatigue" is a heat durability test value, obtained by testing a rubber tube reinforced with the cord, in accordance with ASTM D-885-59T section 42. The values shown are kilocycles to failure.

TABLE 1

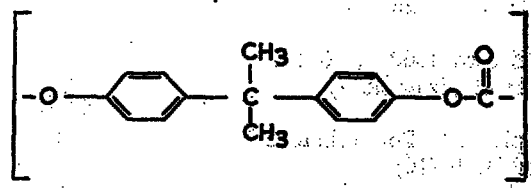
Test	Adhesive 1"		Mallory Fatigue KC	% Tensile Strength Retained
	Strip	Hot Static		
1. Control (PE cord sample B of Ex. 1 — 1300/3, 8/8)	100		100	100 AB
2. CMPE (Cord sample A of Ex. 1 1300/3, 8/8)	109		115	115 AB
3. CTMPE (Ex. 2 cord 1300/3, 8/8)	115		139	108 AB
4. CTPCMPE (Ex. 3 cord 1000/3, 10/10)	120		143	108 AB

The polycarbonate as a powder or fine particles is added to the polyester alone or together with the other modifying agent, usually in the form of chips or granules, and the mixture is then passed to a melting zone such as an extruder, and then forwarded by means such as gear pumps to a filter pack and a spinneret from which filaments are formed in a continuous manner. A number of these filaments are gathered into a yarn, which yarn is then twisted to form a ply, a number of which plies are then twisted to form a cord.

Any polycarbonate may be used as an additive or modifier or scavenger or protective agent in combination with the other modifier or scavenger or protective agents for polyester tire cord. Broadly, the polycarbonates may be any derived from 4,4'-dihydroxy-di(mononuclear aryl)-alkane and having a molecular weight between 15,000 and 80,000, a degree of polymerization between 10 and 400, and an intrinsic viscosity

between .46 and 1.2 as measured by dilute solution viscometry in methylene chloride at 25°C. These polycarbonates can be prepared in accordance with conventional methods including phosgenation in which phosgene is blown into the 4,4'-dihydroxy-di(mononuclear aryl)-alkane in the presence of an aqueous solution of a caustic alkali and a solvent. The ester-interchange method may also be used wherein a 4,4'-dihydroxy-di(mononuclear aryl)-alkane is reacted with a diester of a carboxylic acid and as more fully described in British Patent 772,627.

The polycarbonate preferably used in the present invention was a polyester of carbonic acid and bis phenol A known as [bis-(4-hydroxy phenyl)2,2,propane] and having the repeating unit structure



wherein n is a measure of the molecular weight and may be at least 10 and up to 400.

The following example discloses how an improved polyester cord may be made by adding polycarbonate to polyester chips and then forming filaments therefrom.

EXAMPLE 4

100 parts of dried polyethylene terephthalate (PE) chips are tumbled with 2 parts of the polycarbonate described above. When the molecular weight corresponds to an intrinsic viscosity of .5 measured at 25°C. in dichloromethane, as in this example, the polycarbonate is commercially available as "Merlon" Resin M 39 ("MERLON" is a registered Trade Mark) sold by Mobay. The mixture is tumbled until it becomes substantially homogeneous. The resulting polycarbonate blend polyester (MPE) is melt spun at a temperature of 290°C. through a 190 hole spinneret at a spinning speed of 150 yards per minute, to give a single spun yarn having a total denier of approximately 7800. The spun yarn is passed to a pair of rotating heated feed rolls and then passed around a pair of heated draw rolls rotating at a speed which imparts a draw ratio of about 6 to 1, to give a total denier of approximately 1300, and then wound on a bobbin. The polycarbonate modified polyester yarn has a tenacity of 7.9 grams per denier, a break elongation of 12.4%, an intrinsic viscosity of .790, a tensile strength of 23.3 lbs., and an elongation at 10 lbs. pull of 5.6%.

The yarn produced above is plied 8 turns per inch, and 3 of these plies are twisted in reverse direction 8 turns per inch to form the cord used in producing the improved rubber structure of this invention. The resulting cord has a break strength of 62.9 lbs., a 5% modulus (lase) of 14.3, a 10% modulus (lase) of 29.0, and an elongation at break of 17.8%. The resulting polycarbonate modified polyester cord is identified as cord sample C. The unmodified polyester was processed into filaments and a cord made in the exact manner described above and identified as cord sample D. Both cord samples C and D were treated with an R/F/L adhesive made in the same manner as described for cord samples A and B in Example 1. Thermal stability of the cord is measured in terms of percent tensile retained by the closed glass tube method (GT) or by the air bomb method (AB). Glass tube testing is done by heating the untreated cord for 48 hours at 300°F. Air bomb testing is done by heating the untreated cord embedded in the rubber compound as shown below for 2.5 hours at 350°F. under 80 psi air pressure. The following data were obtained.

TABLE 2

Test	Adhesive 1"		% Tensile Retained
	Hot	Static	
1. Control (PE cord 1300/3, 8/8) (sample D of Example 4)	100		100 AB
2. MPE (PE plus 2% Polycarbonate, cord 1300/3, 8/8) (sample C of Example 4)	145		107 AB
3. Control (PE cord 1000/3, 10/10) (sample D of Example 4)			100 GT
4. MPE (PE plus 2% Polycarbonate cord 1000/3, 10/10) (sample C of Example 4)			122 GT
5. MPE (PE plus 1% Polycarbonate cord 1000/3, 10/10) (sample C of Example 4)			107 GT

Typical isocyanates that may be used are:

Polymethylene polyphenylisocyanate —

sometimes referred by the
trademark "PAPI"

5 Triphenyl methane-triisocyanate
2,4-tolylene-diisocyanate and dimer —

sometimes referred to by the
trademark "Desmodur TT"
preparation for which see
British Patent No. 1,088,580.

2,6-tolylene-diisocyanate

10 Bitolylene diisocyanate

Dianisidine diisocyanate

m-Phenylene diisocyanate

1-alkyl-benzene-2,4-diisocyanate

1-alkyl-benzene-2,5-diisocyanate

15 2,6-dialkyl-benzene-1,4-diisocyanate

1-chlorobenzene-2,4-diisocyanate

Dicyclohexylmethane-diisocyanate

3,3-dimethoxy diphenyl methane-4,4'-diisocyanate

1-nitrobenzene-2,4-diisocyanate

20 1-alkoxy-benzene-2,4-diisocyanate

1-alkylbenzene-2,6-diisocyanate

m-Xylylene-diisocyanate

1,3-dimethyl-4,6-bis (β-isocyanatoethyl)-benzene-diisocyanate

Hexahydrobenzidine-4,4'-diisocyanate

25 Ethylene-diisocyanate

Propylene-1,2-diisocyanate

Cyclohexylene-1,2-diisocyanate

3,3'-dichloro-4,4'-biphenylene diisocyanate

2,3-dimethyl-tetramethylene diisocyanate

30 Cyclohexyl isocyanate

p,p'-Diphenylene diisocyanate

2-chlorotrimethylene diisocyanate

Butane-1,2,2-triisocyanate

Trimethylene diisocyanate

35 Tetramethylene diisocyanate

Propylene-1,2-diisocyanate

Butylene-1,2-diisocyanate

Ethylidene diisocyanate

Phenyl isocyanate



Polymethylene polyphenylisocyanate identified above by the trademark "PAPI" is also referred to as polyaryl polyisocyanate and is a dark amber, somewhat viscous liquid belonging to the aromatic polyisocyanate family as disclosed in a new product bulletin issued by The Carwin Company of North Haven, Connecticut, dated July 1956. "PAPI" is further described as containing both ortho and para substitution and composed of a family of low molecular weight polymers having an average composition of the trimer with n in the formula above having an average value of 1 and manufactured under United States Patent 2,683,730, the formula being shown therein.

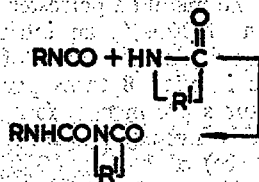
Typical isocyanate generating compounds are blocked isocyanates which include all reaction products of an isocyanate and a compound having a hydrogen reactive with the isocyanate group. Examples of the blocking compounds include monohydroxy compounds especially primary and secondary alcohols, details of preparation being disclosed in United States Patents 2,952,665 and 3,325,333, amines including urea, primary and secondary mono and polyhydric phenols including phenol and resorcinol, (when phenol is used to block "PAPI", the resulting compound is known by the trademark "Hylene MP" as more fully described in "Adhesives Age" 2 30-33 (1959)) amides, as well as lactams, details of preparation being disclosed in Belgian Patent 665,474, (when caprolactam is used to block "PAPI" the resulting compound is known by the trademark "Isonate" 123P) and resinous compositions which have an active hydrogen and will block an isocyanate. The preferred type of resinous blocking agent is made by reacting an aldehyde with a resin-forming component such as urea, or a phenol, preferably a polyhydric phenol, such as resorcinol. Suitable aldehydes that may be used in forming a resin include formaldehyde, acrolein, glyoxal, furfural, crotonaldehyde, aldol and benzylaldehyde. Suitable phenols that may be reacted with one of the aforementioned aldehydes include phenol, cresol, catechol, phloroglucinol, saligenin, dibeta naphthol, xyleneol, hydroquinone, resorcinol, orcinol, pyrogallol, beta-naphthol, amino-phenol, guaiacol. Urea and melamine may also be used. More detail of preparation is disclosed in United States Patent 3,268,467.

When the hydroxy compound is reacted with the isocyanate to form a blocked isocyanate, the isocyanate group is converted to a urethane group and the following general formula may be used to express this conversion:

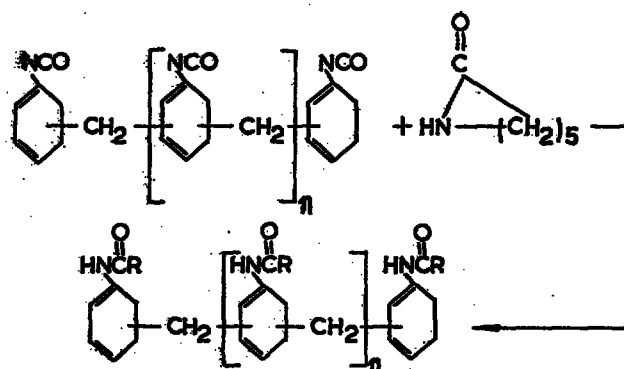


With a polyisocyanate the reaction may be expressed in terms of the following general formula: $ROH + OONR'NCO \rightarrow ROCONHR'NCO$ wherein R and R' represent mono and divalent organic radicals. Suitable hydroxy compounds include aliphatic, araliphatic and hydroaromatic alcohols such as methanol, ethanol, butanol, isobutanol, octyl alcohol, cyclohexanol, benzyl alcohol, xyleneols, cresols, resorcinol and phenol and mixtures thereof.

When a lactam is reacted with an isocyanate to form a blocked isocyanate the isocyanate group is converted to a urethane group. The following general formula may be used to express this conversion:



wherein R and R' are any organic radical having up to 8 carbon atoms. A more specific embodiment of a lactam blocked isocyanate is one involving the following reaction:



wherein when R is the lactam above and n is 1 the product is sometimes commercially referred to as "Isonate 123P" and is described in a bulletin dated September 1, 1966, published by The Upjohn Company Polymer Chemicals Division.

The amide blocked isocyanates are made in a manner similar to the manner described above for the amines and the ureas.

The term "isocyanate" as used herein includes both an isocyanate or polyisocyanate per se as well as an isocyanate generating agent.

It is preferred to add the isocyanate or isocyanate generating compound in pellet form to the polyester chips just prior to the introduction of the mixture into the extruder associated with the spinning of the resulting molten mixture into filaments. The solid polyester and modifier may be blended in a double cone dryer to form a master batch which is then fed to the extruder, or the materials may be supplied separately, in the correct ratio, at the throat of the extruder.

The following example discloses how an improved polyester cord may be made by adding an isocyanate to polyester chips and then forming filaments therefrom.

EXAMPLE 5 (PEBPIMPE)

100 parts of dried polyethylene terephthalate (PE) chips are tumbled with 1 part of a polyester blocked polyisocyanate (PEBPI) resulting from the reaction of 100 parts of the hydroxyl polyester from the reaction of 11 mols of ethylene glycol and 10 mols of adipic acid, and 9 parts of 1,4-butanediol blocked with 40 parts of 4,4'-diphenyl methane diisocyanate having an HCl acidity of 0.017% and commercially available as "Texin" 192A sold by Mobay, until the mixture is substantially homogeneous. The resulting blend (PEBPIMPE) of the polyester blocked polyisocyanate and polyester is melt spun at a temperature of 290°C. through a 190 hole spinneret at a spinning speed of 150 yards per minute to give a single spun yarn having a total denier of approximately 7800. The spun yarn is passed to a pair of rotating heated feed rolls and then passed around a pair of heated draw rolls rotating at a speed which imparts a draw ratio of about 6 to 1, to give a total denier of approximately 1300, and then wound on a bobbin. The modified polyester yarn has a tenacity of 7.9 grams per denier, a break elongation of 12.4%, an intrinsic viscosity of .790, a tensile strength of 23.3 lbs., and an elongation at 10 lbs. pull of 5.6%.

The yarn produced above is plied 8 turns per inch, and 3 of these plies are twisted in reverse direction 8 turns per inch to form the cord used in producing the improved rubber structure of this invention. The resulting cord has a break strength of 62.9 lbs., a 5% modulus (lase) of 14.3, a 10% modulus (lase) of 29.0, and an elongation at break of 17.8%. The resulting polyester blocked polyisocyanate modified polyester cord is identified as cord sample E. The unmodified polyester was processed into filaments and a cord made in the exact manner described above and identified as cord sample F.

Both cord samples E and F were treated with R/F/L adhesive made in the same manner as described for cord samples A and B of Example 1. Thermal stability of the cord is measured in terms of percent tensile retained by the air bomb (AB). Air bomb testing is done by heating the untreated cord embedded in the rubber compound as shown below for 2.5 hours at 350°F. under 80 psi air pressure. The data obtained is listed in Table 3.

EXAMPLE 6 (DTTMPE)

The dimer of 2,4-tolylene-diisocyanate (also known by the trademark Desmodur TT) is added in an amount of 0.1 part to 100 parts of dried polyethylene terephthalate (PE) chips and mixed to form a homogeneous mixture. The resulting blend

(DTTMPE) is then melt spun at a temperature of 290°C. through a 190 hole spinneret under the same conditions as described in Example 5. This yarn, made of (DTTMPE), is then tested in the same manner as shown in Example 5 and the resulting data reported in Table 3.

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EXAMPLE 7 (RFBPIMPE)

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A resorcinol/formaldehyde resin blocked polymethylene polyphenylisocyanate was prepared in the manner described in Examples 1 and 2 of the United States Patent 3,268,467 except that 20 parts of methyl butyl ketone was used in place of the 20 parts of water and water-free formaldehyde was used in place of the 37% formaldehyde in water. A solid product identified as (RFBPI) was obtained having a m.p. above 100° C. To 100 parts of dried polyethylene terephthalate (PE) chips was added 0.1 part of the product identified as RFBPI and this blend (RFBPIMPE) was then processed in the same manner described above in Example 5 of this invention and the resulting data reported in Table 3 below.

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EXAMPLE 8 (CLBPIMPE)

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A caprolactam blocked polymethylene polyisocyanate is added in an amount of 0.1 part to 100 parts of dried polyethylene terephthalate (PE) chips and mixed to form a homogeneous blend. The resulting blend identified as (CLBPIMPE) was then melt spun at a temperature of 290°C. in the same manner as described for the blend in Example 5. The resulting cord was then treated and tested in the same manner as described in Example 5 and the data reported in Table 3.

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Each of the Examples 5, 6, and 8 above was rerun except that in the case of Example 5, .5% of the PEBPIMPE was used and 2% of a polycarbonate was added at the same time to produce a thermally more stable cord as shown by the data reported in Table 4. In a rerun of Example 6, .1% of DTTMPE and 1% of polycarbonate were used, the results being reported in Table 4.

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TABLE 3

Test	(1) Adhesive 1" Strip Hot Static	(2) Mallory Fatigue KC	(3) % Tensile Retained
1. Control (PE cord sample F of Ex. 5 1300/3, 8/8)	100	100	100 AB
2. PEBPIMPE (Cord sample E of Ex. 5 1300/3, 8/8)	129	184	115 AB
3. DTTMPE (Example 6 cord 1300/3, 8/8)	102	158	107 AB
4. RFBPIMPE (Example 7 cord 1000/3, 10/10)	100	106	109 AB
5. CLBPIMPE (Example 8 cord 1000/3, 10/10)	123	314	108 AB

TABLE 4

Test	(1)	(2)	(3)
6. Control (PE + 2% polycarbonate cord 1300/3, 10/10)	100	100	100 AB
7. DTTMPE .1% plus 1% polycarbonate	130	139	98 AB
8. CLBPIMPE .1% plus 1% polycarbonate	123	98	102 AB
9. PEBPIMPE .5% plus 2% polycarbonate	149	116	103 AB

The polyester cords used in these examples were made by first twisting yarn 8 or 10 turns per inch and then twisting three of these singles 8 or 10 turns per inch to form a cord.

The modified polyester cord is embedded in rubber compounded in accordance with the following formula:

Ingredients	Parts by Weight	
	Amount Used	May be Used
1. Natural Rubber	70	0—100
2. OE/SBR 1778 (styrene/butadiene-1,3 23.5/76.5 copolymer) (plus 37½ parts oil per 100 parts SBR)	27.5	100—0
3. Cis 1,4-polybutadiene	10	0—50
4. Carbon Black (Reinforcing agent)	40	25—100
5. Zinc Oxide (Activator of cure)	4	2—10
6. Stearic Acid (Activator of cure)	2	1.5—3.0
7. Primary Accelerator (2,2'-dithiobisbenzothiazole)	1.25	.5—3.0
8. Pine Oil (Softener)	10	2—50
9. Secondary Accelerator (Tetramethyl thiuram disulfide)	.10	.05—1.0
10. Antioxidant	.60	.1—4
11. Sulfur (Vulcanizing agent)	2.5	1.0—5.0

In compounding the rubber stock in accordance with the formulation set forth above, a masterbatch of ingredients 1 and 2 is made with the carbon black and mixed on a mill to a temperature of about 110°C. and may be mixed at a temperature as high as 140°C. The resulting carbon black masterbatch is then cooled and the remaining compounds are mixed into the batch in the order indicated above to a temperature of about 70°C. and may be mixed at a temperature as high as 100°C.

The rubber structure of this invention may be prepared by first coating a reinforcing fabric with the rubber and then using the rubber coated fabric to make any desired structure as, for example, a pneumatic tire. The rubber will be compounded in the manner set forth above. The reinforcing fabric may be used without any previous treatment, and under these conditions the fabric is known as grey cord

indicating that no treatment in the form of an adhesive composition has been applied to the surface of the cord. Thus, the present invention may be used in the manufacture of a pneumatic tire of conventional present day design as shown, for example, in such United States Patents as 3,157,218; 3,160,191; 3,160,192; 3,217,778; 3,225,810; 3,225,812; 3,244,215; 3,253,633 and 3,253,638 all of which show a vulcanized rubberized fabric carcass of generally toroidal shape having a tread portion superimposed and bonded to the carbon area of the carcass and plies of rubberized fabric forming sidewalls extending from the tread over the carcass to the bead portion.

WHAT WE CLAIM IS:—

1. A modified polyester reinforcing element for a rubber structure, made from a polyester fiber melt spun from a mixture of a polyester with (a) 0.01 part to 2 parts of an isocyanate, (b) 0.1 part to 2 parts of a polycarbonate, (c) 0.001 part to 0.1 part of a metal complex in which the metal ion has an incompletely satisfied 'd' orbital and whose ammonia and amine complexes have a log K stability constant between 5 and 25, or (d) any combinations thereof, the parts being by weight per 100 parts of polyester.

2. A reinforcing element according to claim 1, in which the polyester in the mixture is a thermoplastic linear high molecular weight polyethylene terephthalate.

3. A reinforcing element according to claim 1 or claim 2, in which the isocyanate in the mixture is a blocked isocyanate.

4. A reinforcing element according to claim 3, in which the blocked isocyanate is 4,4'-diphenylmethane diisocyanate blocked with the product resulting from the reaction of ethylene glycol, adipic acid and 1,4-butanediol.

5. A reinforcing element according to claim 3, in which the isocyanate is blocked with a blocking agent selected from primary and secondary alcohols, monohydric and polyhydric phenols, amines, amides, lactams and resinous compositions, all of which have an active hydrogen.

6. A reinforcing element according to any preceding claim, in which the polycarbonate in the mixture is a polyester derived from a 4,4'-dihydroxy-di(mononuclear aryl)-alkane.

7. A reinforcing element according to claim 6, in which the polycarbonate is a polyester of carbonic acid and bis(4-hydroxyphenyl)2,2-propane.

8. A reinforcing element according to any preceding claim, in which the polycarbonate in the mixture has a degree of polymerization between 10 and 400.

9. A reinforcing element according to any preceding claim, in which the metal complex in the mixture is a complex of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Hf, Ta, W, Re, Os, Ir, Pt, Au, Th or Pa.

10. A reinforcing element according to claim 9, in which the metal complex is copper dimethyldithiocarbamate.

11. A reinforcing element according to any preceding claim, in the form of a tire cord.

12. A reinforced rubber structure, comprising a reinforcing element according to any preceding claim bonded to rubber.

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2. A reinforcing element according to claim 1, in which the polyester in the mixture is a thermoplastic linear high molecular weight polyethylene terephthalate.

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