PROCESS FOR BONDING RUBBER TO YARN AND THE RESULTING PRODUCT

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No Drawing. Filed Jan. 8, 1962, Ser. No. 165,002
Claims priority, application Netherlands, Jan. 23, 1961, 260,385
3 Claims. (Cl. 161—227)

The present invention relates to the manufacture of yarn, cord, or fabric from macromolecular polyalkylene terephthalate which adheres satisfactorily to rubber, and to yarn, cord, or fabric thus treated, and to rubber articles reinforced therewith.

Various processes for the improvement of adhesion of textile structures such as yarns, cords or fabrics to rubber have been proposed previously. According to one of these processes, yarn, cord or fabric is first wetted with water and subsequently treated with a latex dispersion of a copolymer of a vinyl pyridine with a diene in an aqueous solution of a pre-condensation product of resorcinal and formaldehyde. If thus-treated yarn, cord, or fabric of macromolecular polyalkylene terephthalate is used as a reinforcement in rubber, the adhesion of said products to rubber is not satisfactory.

It has therefore been suggested to first subject textile structures selected from the group consisting of yarns, cords, or fabrics of macromolecular polyalkylene terephthalate to a pre-treatment with a solution or emulsion of a homo- or copolymer of a vinyl or and a vinylidene halide, subsequently to dry them, and thereafter to treat them with the aforementioned latex dispersion of a copolymer of a vinyl pyridine with a diene in a solution of a reaction product of a phenol and an aldehyde.

Textile structure such as yarn, cord, or fabric comprising a macromolecular polyalkylene terephthalate thus treated adheres satisfactorily to rubber.

It was also suggested that the improved adhesion provided by the foregoing treatment can be improved further by adding amines to the solutions or emulsions of homo- or copolymers of vinyl or and vinylidene halides.

This prior art treatment has the disadvantage that it causes the yarn, cords, or fabrics to lose a great deal of their resilience, which renders them very stiff. As a result, they are less suitable to be used for reinforcing rubber articles.

The present invention provides a process for the manufacture of yarn, cord, or fabric of a macromolecular polyalkylene terephthalate which yarn, cord, or fabric retains substantially the resiliency of the untreated material while adhering well to rubber.

It is one of the principal objects of the present invention to provide yarn, cord, and fabric comprising macromolecular polyalkylene terephthalate having good adherence to rubber while retaining substantially their initial resiliency. It is another object of the present invention to provide a method of treating yarn, cord, or fabric comprising macromolecular polyalkylene terephthalate to provide articles of the aforementioned classes having satisfactory adherence to rubber while retaining the resiliency of the untreated material. It is a further object of the present invention to provide rubber articles reinforced with yarn, cord, or fabric comprising macromolecular polyalkylene terephthalate in which the yarn, cord or fabric adheres satisfactorily to the rubber while retaining substantially the resiliency of the macromolecular polyalkylene terephthalate.

The process of the present invention, for the manufacture of yarn, cord, or fabric comprising macromolecular polyalkylene terephthalate having satisfactory adhesion to rubber while retaining substantially its resiliency, comprises in a first step treating the yarn, cord, or fabric with an aqueous solution of polyethylene imine and thereafter drying the treated material, and in a second step treating the so pre-treated yarn, cord, or fabric in a per se known manner with a latex dispersion of a copolymer of a vinyl pyridine with a diene in an aqueous solution of a pre-condensation product of a phenol with an aldehyde, and finally drying the treated material under tension.

As those skilled in the art know, the class of macromolecular polyalkylene terephthalates includes all polymeric esters containing a large proportion of esters which may be obtained by subjecting glycols of the series HO(CH_2)_nOH, where _n_ is an integer which may vary from 2 to 10, together with terephthalic acid or a mixture of terephthalic acid and isophthalic acid, to a heat treatment under conditions yielding high-polymeric esters. Instead of employing the terephthalic or the isophthalic acid or both, an ester forming derivative thereof, for instance an aliphatic (including a cycloaliphatic) or an aromatic ester or a semi-ester, an acid halide or an ammonium or amino salt can be used. The aliphatic glycol can be replaced with a cyclo aliphatic glycol.

Those skilled in the art know that yarns include both threads made up of continuous filaments and threads spun from staple fibres. The terms "cord" and "fabric" as used herein are intended to refer respectively to "tire cord" and "tire cord fabric."

The rubber can be any natural rubber, including gutta-percha, balata, compound rubber, modified rubber, for instance hydroxylated rubbers, condensation derivatives of rubber and cyclized rubber. The rubber also can be synthetic rubber, for instance synthetic rubber-like diene-polymers and diene-copolymers, such as neoprene, butadiene-styrene-interpolymers, butadiene-acrylic acid nitrile-interpolymers, poly-sulphide rubbers and rubber-like copolymers of an alkyl acrylate and a chloralkylvinyl ether.

The treatment according to the present invention comprises in the first step, contacting threads, cords, or fabrics with a solution of polyethylene imine, the threads, cords and fabrics being relaxed or under tension. For example yarns or cords may be treated while they are in skein form. Or, with the aid of rollers, they may be continuously passed through a bath containing a polyethylene imine solution. If necessary, excess amounts of solution are removed in any suitable manner by centrifuging or squeezing.

The temperature in the first process step is not critical but below the softening point of the polymer. For economy, the treatment is carried out at room temperature.

Illustrative of the polyethylene imines suitable for use in the method of the present invention is the product commercially available under the trademark, "Polymin P," which has a degree of polymerization of the order of
about 160 and a composition corresponding to the formula: $H_2N(CH_2CHNH)_nH$, where $n$ is about 160. The concentration of the polyethylene imine solution may vary from 0.1 to 3% by weight. Although a concentration below 0.1% by weight is effective to some extent, the effect is reduced considerably at lower concentrations. Preferably, solutions having a concentration higher than 0.5% by weight are used in the method of the present invention. Concentrations higher than 3% by weight yield good results, but from the point of view of economy they are not necessary. The drying process following the treatment of the first step can be carried out while the yarn, the cord, or the fabric is under tension. However, the yarn, the cord, or the fabric also may be subjected to the drying process while relaxed.

In the process of the present invention, the yarn can be treated in the second step with the latex dispersion while the yarn, the cord or the fabric is kept under tension. However, the yarn, the cord, or the fabric can be under substantially no tension during this treatment.

As mentioned before, in the second step of the process of the present invention the pre-treated yarn, cord, or fabric is contacted with a latex dispersion of copolymers of vinyl pyridines with dienes in aqueous solutions of pre-condensation products of phenols with aldehydes which latter as such are known in the prior art.

Vinyl pyridines, known to those skilled in the art, are used together with dienes for the preparation of copolymers thereof. Illustrative of the vinyl pyridines are $\alpha$-vinyl pyridine, $\beta$-vinyl pyridines or $\gamma$-vinyl pyridines, or homologues thereof, for example: 5-ethyl-2-vinyl pyridine, 5-propyl-2-vinyl pyridine, 5-butyl-vinyl pyridine, 5-hexyl-vinyl pyridine, 5-heptyl-vinyl pyridine, 6-methyl-2-vinyl pyridine, 4,6-dimethyl-2-vinyl pyridine, 2-methyl-4-vinyl pyridine, 2-ethyl-5-vinyl pyridine and 2-methyl-6-vinyl pyridine.

Illustrative of dienes which can be used with vinyl pyridines for the preparation of copolymers are: 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 1,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 2,4-pentadiene, 3-methyl-2,4-pentadiene and 3,4-dimethyl-2,4-pentadiene.

The latex dispersions of the second step can contain natural rubber as well as the copolymers of vinyl pyridines with dienes.

Furthermore, other substances may be added, for example styrene, filling agents, vulcanization accelerators and plasticizers.

The phenols employed for the preparation of the dispersions of the second steps are mono- or polyhydric phenols.

However, mixtures thereof can also be used. Suitable monohydric phenols are, for instance, phenol, cresol, xyleneols, and naphthols.

Examples of suitable polyhydric phenols are: resorcinol, catechol, phloroglucinol, orcinol and hydroquinone.

The aldehydes used for the preparation of the dispersions of the second step are preferably: paraformaldehyde, acetaldehyde, butyraldehyde, chloral, furfural and salicylaldehyde.

When necessary or desirable, the excess amount of dispersion employed in the second step can be removed in any suitable way, as by centrifuging, or squeezing with rollers.

Preferably, however, the excess amount is removed by high pressure air jets or scrapers.

The yarns, cords, or fabrics treated in the second step are dried, while under tension, at a temperature of at least 100°C, but below the softening temperature of the material.

According to the invention, good results are obtained using a latex dispersion comprising a dispersion of a copolymer of 2-vinyl pyridine and butadiene in a solution of the pre-condensation product of resorcinol and formaldehyde.

Adhesion can be improved even further using as a latex dispersion a copolymer of 2-vinyl pyridine, butadiene and styrene in an aqueous solution of the pre-condensation product of resorcinol and formaldehyde.

Natural rubber can be dispersed in the latex dispersion employed in the process of the present invention.

In treating yarn, cord, or cord fabric of polyethylene terephthalate such as those available under the trade names Terylene, Dacron or Terlenka in the first step of the process of the present invention, the yarn, cord or fabric can be treated under substantially no tension with an approximately 1.5% by weight aqueous solution of polyethylene imine and subsequently be dried, while relaxed, or under no substantial tension at a temperature below 100°C.

In order that those skilled in the art may have a better understanding of the present invention, the following illustrative example is provided.

Example

A tire cord comprising polyethylene terephthalate in the form of a skein was immersed for 10 minutes in a 1.5% by weight aqueous solution of “Polynyl P” (polyethylene imine) and subsequently centrifuged. The pretreated tire cord was then wound on a bobbin, from which it was continuously passed by means of rollers through a bath at 23°C prepared from 438 parts by weight of “Gen Tae” (a commercially available latex, which is an aqueous dispersion of a copolymer of a mixture of butadiene, 2-vinyl pyridine and styrene. The mixture contains about 5 to 30% of 2-vinyl pyridine or 10 to 35% of a mixture of 2-vinyl pyridine and styrene), 11 parts by weight of formaldehyde, 19 parts by weight of resorcinol, and 42% parts by weight of water.

The tire cord treated in this manner was dried under tension for 20 seconds at 210°C. The tire cord was very resilient and not stiff. After the tire cord had been embedded in GR-S rubber or natural rubber, and cured, adhesion between cord and rubber was very satisfactory.

A tire cord subjected to the same treatment, but not to a pre-treatment with polyethylene imine showed poor adhesion to rubber.

A tire cord subjected to the same treatment, after pre-treatment with polyvinyl chloride instead of polyethylene imine showed good adhesion to rubber, but was very stiff.

What is claimed is:

1. A process for treating a textile structure selected from the group consisting of yarn, cord, and fabric comprising macromolecular polyalkylene terephthalate which adheres satisfactorily to rubber whilst retaining substantially the resiliency of the untreated textile structure, which comprises contacting said textile structure comprising macromolecular polyalkylene terephthalate with an aqueous solution of polymerized ethylene imine, drying the so pretreated structure, contacting the dried, pretreated structure with latex dispersion comprising a copolymer of a vinyl pyridine with a diene in an aqueous solution of a precondensation product of a phenol and an aldehyde, and drying and curing the resultant structure while under tension.

2. The process according to claim 1, wherein an approximately 0.1% to about 3% by weight solution of polymerized ethylene imine is used.

3. A rubber article reinforced with polyethylene terephthalate formed structure, said polyethylene terephthalate formed structure having been treated with polyethylene imine and latex dispersion comprising a copolymer of a vinyl pyridine with a diene in an aqueous solution of a precondensation product of a phenol and an aldehyde and cured before embedding in the rubber selected from the group consisting of natural rubber, gutta-percha, balata,
compound rubber, modified rubber, condensation derivatives of rubber and cyclized rubber, synthetic rubber-like diene-polymers, diene-copolymer, butadiene-styrene-interpolymers, butadiene-acrylic acid nitrile-interpolymers, polysulphide rubbers, and rubber-like copolymers of an alkylacrylate and a chloroalkylvinyl ether of said rubber article.

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