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PROCESS FOR MAKING ELASTIC VINYL COPOLYMER RESIN TEXTILE ARTICLES

Theophilus A. Feild, Jr., Charleston, W. Va., assignor to Carbide and Carbon Chemicals Corporation, a corporation of New York

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This invention relates to elastic rubber-like textile articles formed from synthetic resinous compositions. It has especial utility in connection with the production from certain vinyl resins of textile articles such as filaments, fibers, threads, yarns, and textile materials fabricated therefrom, possessing rubber-like properties of elasticity and resilience in conjunction with suitable tensile strength, resistance to mineral and organic acids, to alkalies, to mineral oils in general, and to solvents such as gasoline, benzene, and the like.

Among the more important objects of the invention are the production from readily-available raw materials of novel filaments, threads, yarns and other textile articles having the more important physical properties of rubber, such as elasticity, resiliency, etc., without its chemical instability; and the production of water-insoluble vinyl resin compositions of relatively low softening point in the shape of filaments, fibers and yarns of excellent flexibility, and fabrics and other articles made therefrom.

Processes already are known for the production of filaments, fibers and yarns from vinyl resins produced by the conjoint polymerization of a vinyl halide such as vinyl chloride with a vinyl ester of an aliphatic acid, such as vinyl acetate, wherein the resultant resin contains between around 80% and around 95% by weight of the halide in the polymer, and has an average macromolecular weight of at least 7500, and preferably of 15,000 or more. The production of textile articles from these vinyl resins is described in United States Patents Nos. 2,161,766 and 2,278,895 of E. W. Rugeley, T. A. Feild, Jr., and J. F. Conlon. The textile articles thereby produced have high tensile strengths both in the wet and dry states, high true elasticity, are resistant to water, alkalies, mineral acids, and to attack by microorganisms. Such articles are not inflammable; and they possess excellent electrical insulating qualities.

According to one modification of this invention, filaments, fibers, yarns and woven, knitted, braided, felted or other fabrics made from such fibers and yarns are treated with an elasticizer for the vinyl resin in a manner to impart thereto rubber-like elasticity and excellent resilience, while retaining the shape of such article and the foregoing desirable properties of the vinyl resin from which the article is fabricated. Alternatively, similar results are obtained by incorporating the elasticizer in the spinning dope or resin dispersion, from which the filaments or other articles are produced; or both methods may be combined.

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In the practice of one preferred modification of the invention, a yarn or fabric or other article made from the aforesaid vinyl resin is coated with a selected amount of an elasticizer or plasticizer for the resin, after which the elasticizer is fixed in the yarn or fabric by suitable means, usually by the application of heat within a temperature range between 40° C. and 110° C. In instances where large amounts of from 60% to 70% or more of the elasticizer are incorporated in the resin yarn or fiber, the maximum temperature for the fixation of the elasticizer is around 70° C. to insure against the bonding together of adjacent elasticized fibers or yarns. The fixation of the elasticizer within the yarn or other article may also be accomplished at normal room temperature and slightly above by prolonged ageing of the yarn for upwards of a week or more after the yarn has been coated with the plasticizer, or with a solution or emulsion of the plasticizer in a suitable volatile solvent for the resin. The yarns and filaments, or articles made therefrom, may be treated with the elasticizer, or with suitable solutions thereof in a low or medium boiling solvent, or in the form of an aqueous emulsion; and the treatment may be applied to the filaments or yarns either in the stretched or in the unstretched state.

The elasticizer content of the resultant yarns or other textile article may be varied within the range between around 1% and around 110%, based on the weight of dry resin, depending upon the properties desired in the final article. When fibers or yarns of the resin are to be provided with a plasticizer content of around 20% to 50% or more, this is generally effected by immersing the same, in substantially untensioned condition, in an emulsion of the elasticizer, or by passing the fibers or yarns over rolls or wicks commonly used in standard textile practice for applying liquids to textiles. The resultant product, after fixing the elasticizer thereon, possesses a rubber-like elasticity and resilience. The use of elasticizer in amounts around 5% by weight of the yarn serves to lower the softening point of the resin yarn by about 20° C., without substantial reduction in the tensile strength in the case of unstretched yarn. The use of still smaller amounts of the elasticizer lowers the softening point of the yarn in somewhat lesser degree.

This lowering of the softening point has especial merit in instances where the resultant spun filaments, or yarns made therefrom, are to be composited with textile fibers or yarns made of such materials as cotton, wool, silk, glass, etc., for

the production of composite yarns and/or of fabrics made from such yarns under conditions whereby, as in the process described in the aforesaid United States Patent No. 2,278,895, the vinyl resin fibers or yarns function in the finished products as thermoplastic bonding agents.

The elasticizers preferred for use in the process are resistant to humidity and weathering, and impart good pliability and plasticity to the resin yarns without tackiness. Among suitable elasticizers may be mentioned the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, such as dibutyl phthalate, dioctyl phthalate, methoxy glycol phthalate, dioctyl tetrahydro phthalate, dibutyl sebacate, dioctyl maleate and dioctyl succinate; alkyl and aryl phosphates such as tributyl phosphate and tricresyl phosphate; and polyglycol esters of carboxylic acids, which acids have from six to eight carbon atoms in the molecule, such as triglycol di-2-ethylbutyrate and triglycol di-2-ethylhexoate.

The following examples are intended merely to illustrate the invention.

Example I

A skein of unstretched yarn was immersed for ten minutes at room temperature (about 25° C.) in a body of dibutyl sebacate. The yarn was formed from a vinyl resin made by the conjoint polymerization of vinyl chloride and vinyl acetate in the manner described in the aforesaid United States Patent 2,161,766, excepting that the yarn was unstretched. The resin from which the yarn was made contained between 80% and 95% of the chloride in the polymer, and had a macromolecular weight of over 15,000. The yarn was removed from the dibutyl sebacate and centrifuged to eliminate excess elasticizer. The yarn then was immersed, untensioned, in water at 50° C., containing a few per cent of a water-soluble soap. The temperature of the water was slowly raised to 81° C. over a period of 30 minutes. The yarn remained in the water for 10 minutes to complete fixation of the elasticizer. The yarn was then removed from the heating bath and was well washed in water containing a few per cent of a water-soluble soap to remove excess elasticizer. The resultant yarn contained around 34% of the elasticizer, and was quite elastic. It shrunk slightly during the heat treatment.

The amount of elasticizer taken up by the yarn may be controlled by dilution of the elasticizer with a medium- or low-boiling solvent. A solvent or partial solvent for the resin, when mixed with the elasticizer, accelerates the pick-up of elasticizer by the yarn. A solvent for the elasticizer which is a non-solvent for the resin, when mixed with the elasticizer, may retard the pick-up of elasticizer by the yarn. Control of the elasticizer content of the yarn may also be realized by regulation of the temperature and the time of treatment of the yarn with the elasticizer or emulsion of the elasticizer.

Although the preferred operation is to subject the yarn, after treatment with the elasticizer or the emulsion of the elasticizer, to a fixation treatment at elevated temperatures followed by scouring, these after-treatments are not essential to secure the desired effect of rubber-like elasticity in the vinyl resin yarn. Similar results may be realized on proper ageing of the treated yarns under conditions precluding the development of tackiness in plasticized yarn.

By substituting in the operation described in

Example I, stretched yarns of the said vinyl resin, a similar product having rubber-like elasticity was secured. The shrinkage in this case was greater than for the unstretched yarn.

A woven fabric made by weaving stretched yarns of the vinyl resin described in Example I was treated in the general manner described in that example. The resultant fabric was very elastic.

Example II

An unstretched yarn of a vinyl resin of the type described in Example I was passed continuously over an emulsion roll on a standard winding machine, thereby being surface-coated with a selected amount of dibutyl sebacate.

Two methods were used for fixing the elasticizer on the yarn: In the first method, the yarn, on a collapsible bobbin, was placed in water at 50° C., containing a water-soluble soap, and the temperature was raised to 70° C. over a period of 30 minutes. The yarn then remained in the water for 10 minutes to complete the fixation of the elasticizer. The yarn then was wound from the package.

In the second method, the yarn was continuously passed through a steam cell 15 inches long, heated to 107° C., at such a rate that it was exposed to such heat for a brief period around 0.25 second. The yarn was then oiled and coned without further treatment. The finished yarn contained about 40% of the elasticizer, and had rubber-like elasticity with a quick recovery after the stretching tension was released.

Similar results were secured by substituting in the process of Example II stretched yarns made of the aforesaid resin. In this case, the second method for fixing the elasticizer in the yarn is particularly advantageous.

Example III

Knitted fabric was made from stretched yarn formed of a vinyl resin produced by the conjoint polymerization of vinyl chloride and vinyl acetate and having around 90% of the chloride in the polymer and a macromolecular weight of at least 15,000. Such stretched yarn was produced in accordance with the invention described in the aforesaid United States Patent 2,161,766. The knitted fabric was immersed in an aqueous emulsion containing 50% of dibutyl sebacate and 5.9% by weight of an emulsifying agent comprising an alkali metal salt of a sulfuric acid ester derived from a higher fatty alcohol. The fabric was centrifuged to remove excess elasticizer, and was then immersed in water at 50° C. containing 0.5% by weight of a water-soluble soap. The temperature was then raised to 90° C. and the fabric left in the water for 30 minutes. The final product contained about 45% of the elasticizer, and had rubbery elastic properties. It was suitable for those uses where elastic textile articles are desired which have the high resistance to acids, alkalies, etc., possessed by vinyl resins.

Example IV

Untensioned threads of a vinyl resin of the type described in Example I were immersed for 15 minutes in a bath of dibutyl sebacate containing about 10% by weight of methyl isobutyl ketone, maintained at a temperature around 40° C. After draining excess dibutyl sebacate from the threads, the latter were scoured in water containing a water-soluble soap. The resultant products possessed rubber-like elasticity.

Example V

Lustrous, stretched 1.5 inch staple fibers of a vinyl resin of the type described in Example I were immersed in a bath of dibutyl sebacate for 10 minutes. The excess of the latter was removed by squeezing. The fiber mass was then immersed in a water bath, and the temperature thereof raised to 75° C. After about 10 minutes at this temperature, the fiber mass was removed and scoured in soapy water. The resultant fibrous mass was very elastic and springy.

Example VI

Staple fibers of the type described in Example V were coated with triglycol di-2-ethylhexoate by immersion of the fibers in a bath of the latter at room temperature for about 15 minutes. The excess elasticizer was drained off and the coated fibers were heated for 30 minutes in a water bath maintained at 65° C. The resultant fibers, after scouring with water containing a water-soluble soap, possessed excellent elastic properties, together with other valuable properties normally possessed by fibers made from the aforesaid vinyl resins.

Under similar conditions to those mentioned in Example VI, excepting that the methoxy glycol phthalate was substituted for the elasticizer mentioned, similar elastic fibers were produced somewhat more readily.

Woven fabrics made from vinyl resin fibers described as starting materials in Example V were treated in the manner described in Example VI. The resultant fabrics were quite elastic, while retaining important properties of the unelasticized vinyl resin fabrics, such as resistance to moisture, mineral acids and alkalies.

The following data are based upon comparative tests conducted to illustrate the degree of elasticity and resilience imparted to yarns made from vinyl resins by the process of the invention. Each of the yarns mentioned in the following tables, excepting the cellulose acetate yarn mentioned in Table 4, was prepared from filaments of a vinyl resin produced by the conjoint polymerization of vinyl chloride and vinyl acetate, which resin contained between 70% and 95% of the halide in the polymer and had a macromolecular weight of at least 15,000. The yarns were elasticized in the manner described in Example I.

The yarns were tested at room temperature on a Suter single strand serimeter. The yarns were in the machine and elongated the amount indicated in the tables. Tension on the yarn was immediately released. Other yarns were elongated a selected amount, and were held in the elongated state for one minute before releasing the tension.

Table 1

(For comparison)

Unstretched 600 denier 150 filament bright yarn

A. Elongated with Immediate Tension Release		B. Elongated with Tension Held for One Minute and then Released	
Elongated	Recovery	Elongated	Recovery
Per cent		*Per cent*	
10	50% Complete in 60 Seconds.	10	40% Complete in 60 Seconds.
20	40% Complete in 60 Seconds.	20	33% Complete in 60 Seconds.
40	27.5% Complete in 60 Seconds.	40	20% Complete in 60 Seconds.

Table 2

The same yarn, containing 34.2% of dibutyl sebacate

A. Elongated with Immediate Tension Release		B. Elongated with Tension Held for One Minute and then Released	
Elongated	Recovery	Elongated	Recovery
Per cent		*Per cent*	
20	Complete in 20 Seconds.	20	90% Complete in 60 Seconds.
40	Complete in 30 seconds.	40	90% Complete in 60 Seconds.
80	87.5% Complete in 60 Seconds.	80	89% Complete in 60 Seconds.
100	90.0% Complete in 60 Seconds.		

Table 3

The same yarn, containing 59.5 of dibutyl sebacate

A. Elongated with Immediate Tension Release		B. Elongated with Tension Held for One Minute and then Released	
Elongated	Recovery	Elongated	Recovery
Per cent		*Per cent*	
20	Complete	20	Complete in 20 Seconds.
40	do	40	Complete in 21 Seconds.
80	Complete in 25 Seconds.	60	98% Complete in 60 Seconds.
100	98% Complete in 60 Seconds.	80	98% Complete in 60 Seconds.

Table 4

(For comparison)

Cellulose acetate 100 denier 28 filament yarn containing 19.2% of dibutyl sebacate

A. Elongated with Immediate Tension Release		B. Elongated with Tension Held for One Minute and then Released	
Elongated	Recovery	Elongated	Recovery
Per cent		*Per cent*	
10	50% Complete in 60 Seconds.	10	30% Complete in 60 Seconds.
20	Broke		

The elasticizers preferably employed in the practice of this invention are non-solvents for these vinyl resins at ordinary temperatures. The resins are not substantially dissolved by such elasticizers at temperatures below around 25–30° C. However, sufficient of the resin forming, or contained in, the shaped filaments, fibers, yarns, fabrics and other shaped articles, is dissolved or modified by the elasticizers at elevated temperatures such as herein described, to impart to the articles rubber-like elasticity, and excellent resilience.

The elasticized vinyl resin filaments and yarns, and the woven, knitted, braided, felted and other fabrics of the invention, may be effectively used for the production of shoes, belts, suspenders, garters, bathing suits and other articles of clothing, or in general where rubber threads are used. The elasticized filaments and fibers may be composited with those of other synthetic thermoplastic materials such as the various polyamide

resins, cellulose esters and ethers, and/or with fibers of silk, cotton, wool, glass, asbestos and the like, for the production of composite yarns.

The invention is susceptible of modification within the scope of the appended claims.

I claim:

1. Process for making highly elastic resilient filaments, threads, yarns and other textile articles, which comprises applying to a textile article, made of a water-insoluble vinyl resin formed by the conjoint polymerization of a vinyl halide with a vinyl ester of an aliphatic acid, an elasticizer for said vinyl resin in which the resin is substantially insoluble at temperatures around 25° C. and below, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and said resin having between 80% and 95% of the halide in the polymer and having a macromolecular weight of at least 15,000, and subjecting the coated article to a temperature within the range between around 40° C. and around 110° C. for a time sufficient to fix the elasticizer within the article and provide such article with an elasticizer content within the range between about 20% and about 50%, thereby converting the article to a highly elastic state, and thereafter discontinuing the application of heat and scouring the article to remove excess plasticizer from the surface thereof.

2. Process as defined in claim 1, wherein the elasticizer is an alkyl ester of a dicarboxylic acid wherein each alkyl group contains at least four carbon atoms.

3. Process as defined in claim 1, wherein the elasticizer is a polyglycol ester of a carboxylic acid, which acid has from six to eight carbon atoms in the molecule.

4. Process as defined in claim 1, wherein the elasticizer is a dialkyl phthalate wherein each alkyl group contains at least four carbon atoms.

5. Process as defined in claim 1, wherein the elasticizer is a dialkyl sebecate, wherein each alkyl group contains at least four carbon atoms.

6. Process for making elastic resilient filaments, threads, and yarns, which comprises continuously passing successive portions of a preformed filament, thread, or yarn of a vinyl resin in contact with an elasticizer for said resin which is a nonsolvent for the latter at temperatures below around 30° C., thereby coating the surface of such a filamentary material with elasticizer, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and said resin being formed by the conjoint polymerization of a vinyl halide with a vinyl ester of an aliphatic acid, and having between about 80% and about 95% of the halide in the polymer and an average macromolecular weight of at least 15,000, winding the coated filamentary material to form a package, and heating said material in the package to a temperature within the range between around 40° C. and around 110° C. for a period of time sufficient to incorporate within such filamentary material between about 20% and about 50% of the elasticizer, based on the dry weight of said material, thereby converting the filamentary material to a highly elastic state, and thereafter discontinuing the heating of said material, and removing excess unfixed elasticizer from contact with the filamentary material.

7. Process for making elastic resilient filaments, threads and yarns, which comprises continuously passing successive portions of a preformed filament, thread, or yarn of a vinyl resin in contact with an elasticizer for said resin which is a nonsolvent for the latter at temperatures below around 30° C., thereby coating the surface of said resin with the elasticizer, said elasticizer being selected from the class consisting of the higher alkyl esters of discarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and said resin being formed by the conjoint polymerization of a vinyl halide with a vinyl ester of an aliphatic acid, and having between about 80% and about 95% of the halide in the polymer and an average macromolecular weight of at least 15,000, continuously and rapidly passing each successive portion of the thus coated filament, thread or yarn through a heating zone maintained at an elevated temperature near but below 110° C. in the presence of steam, and withdrawing the resultant elastic filament or yarn from said heating zone after a brief exposure to heat therein.

8. Process for making an elastic textile fabric from a textile fabric made of or containing stretched yarns of an unplasticized vinyl resin produced by the conjoint polymerization of a vinyl halide and a vinyl ester of an aliphatic acid, and having between around 80% and about 95% of the halide in the polymer and a macromolecular weight of at least 15,000, which process comprises subjecting said textile fabric of unplasticized resin to an aqueous emulsion containing an elasticizer for said resin and an emulsifying agent, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, removing excess elasticizer from said fabric, heating the coated fabric in the presence of moisture to a temperature within the range between around 40° C. and around 110° C. for a period of time sufficient to provide said vinyl resin yarns with an elasticizer content within the range between about 20% and about 50%, thereby imparting to the fabric rubber-like elasticity and excellent resilience, and thereafter discontinuing the heating of the resultant elastic fabric.

9. Process for making elastic resilient yarn, which comprises applying to a stretched yarn made of a vinyl resin formed by the conjoint polymerization of vinyl chloride and vinyl acetate, an elasticizer for said resin, in which the resin is substantially insoluble at temperatures around 25° C., said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and said resin having between 80% and 95% of the chloride in the polymer and having a macromolecular weight of at least 15,000, and heating the coated yarn to an elevated temperature within the range between around 40° C. and 70° C. for a brief period sufficient to fix within the yarn between about 20% and about 70% of the elasticizer,

and immediately thereafter removing excess unfixed elasticizer from said yarn.

10. Process for making highly elastic resilient filaments, threads, yarns and other shaped textile articles, which comprises applying to the surface of such a shaped textile article made from a vinyl resin formed by the conjoint polymerization of vinyl chloride and vinyl acetate and containing between 80% and 95% of the chloride in the polymer, an aqueous emulsion of an elasticizer for said resin, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and heating the coated textile article while in the untensioned state to a temperature within the range between 40° C. and 110° C., thereby fixing in the article from 20% to 50% of the elasticizer and providing a textile article possessing rubber-like elasticity and resilience and which, when stretched 100% of its length at room temperature, loses the major portion of its stretch within sixty seconds after release of the stretching tension.

11. Process for making highly elastic resilient filaments, threads, yarns and other shaped textile articles, which comprises applying to the surface of such a shaped textile article made from a vinyl resin formed by the conjoint polymerization of vinyl chloride and vinyl acetate and containing between 80% and 95% of the chloride in the polymer, an aqueous emulsion of an elasticizer for said resin containing a water-soluble emulsifying agent, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, and heating the coated article to a temperature within the range between around 40° and 70° C. while in the untensioned state in water, thereby fixing in the article between 20% and 70% of the elasticizer, based upon the weight of the dry resin, and providing a textile article possessing rubber-like elasticity and resilience and which, when stretched 100% of its length at room temperature, loses the major portion of its stretch within sixty seconds after the stretching tension is released.

12. Process for making highly elastic resilient filaments, threads, yarns and other textile articles, which comprises applying to a relatively non-elastic textile article made from a water-insoluble vinyl resin formed by the conjoint polymerization of vinyl chloride with vinyl acetate an elasticizer for said resin in which the resin is insoluble at temperatures around 25° C. and below, said elasticizer being selected from the class consisting of the higher alkyl esters of dicarboxylic acids wherein each alkyl group contains at least four carbon atoms, and the polyglycol esters of carboxylic acids which acids have from six to eight carbon atoms in the molecule, said resin having between around 80% and around 95% of the chloride in the polymer and having a macromolecular weight of at least 15,000, heating the thus coated article to a temperature within the range between around 40° C. and around 110° C. for a period sufficient to fix the elasticizer within the article and provide such article with an elasticizer content within the range between about 20% and about 50%, thereby converting such article to one capable of being stretched at least 100% at room temperature and, when stretched 40% being capable of recovering its original length within thirty seconds after release of the stretching force, and thereafter scouring the elastic article to remove therefrom excess unfixed elasticizer.

THEOPHILUS A. FEILD, JR.

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